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Coal Liquefaction

A Research Needs Assessment Technical Background

February 1989

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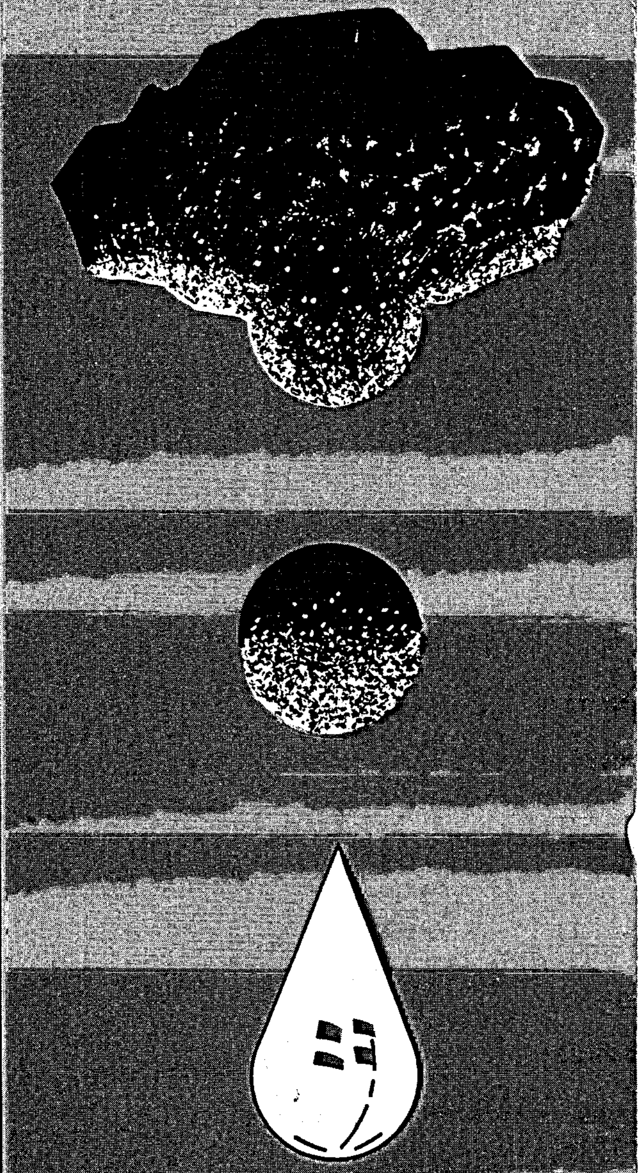

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COAL LIQUEFACTION

- A RESEARCH & DEVELOPMENT NEEDS ASSESSMENT

by the

DOE COAL LIQUEFACTION RESEARCH NEEDS
(COLIRN) PANEL ASSESSMENT

Final Report

Volume II

March 1989

Prepared By:

H.D. Schindler, Chairman of COLIRN
Science Applications International Corporation
1710 Goodridge Drive
McLean, VA 22102

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Coal Liquefaction

- A Research & Development Needs Assessment

Dr. Harvey D. Schindler*, Dr. Francis P. Burke[a], Dr. K. C. Chao[b], Dr. Burtron H. Davis[c], Dr. Martin L. Gorbaty[d], Dr. Kamil Klier[e], Dr. Carl W. Kruse[f], Dr. John W. Larsen[g], Dr. Robert E. Lumpkin[h], Dr. Michael E. McIlwain[i], Dr. Irving Wender[j], Mr. Norman Stewart[k].

* Energy Technology and Engineering, Science Applications International Corporation, 1710 Goodridge Drive, McLean, VA 22102.

a. Consolidation Coal Company R&D, 4000 Brownsville Road, Library, PA 15129.

b. School of Chemical Engineering, Chemical and Metallurgical Engineering Building, Purdue University, West Lafayette, IN 47907.

c. Kentucky Energy Cabinet Laboratory, P.O. Box 13015, Lexington, KY 40512-3015.

d. Exxon R&D, Clinton Township, Route 22 East, Annandale, NJ 08801.

e. Department of Chemistry, Lehigh University, Bethlehem, PA 18015.

f. Illinois State Geological Survey, 615 East Peabody Drive, Champaign, IL 61820.

g. Department of Chemistry, Lehigh University, Bethlehem, PA 18015.

h. AMOCO Corporation, 200 East Randolph Drive, Chicago, IL 60601.

i. Idaho National Engineering Laboratory, 2151 North Blvd., Idaho Falls, ID 83415.

j. Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261.

k. Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, CA 94303.

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The following people, who were not members of the COLIRN panel group, contributed to this publication and are appropriately identified as authors or coauthors of specific chapters or sections.

1. Dr. Christine Curtis, Auburn University
2. Dr. David Gray, MITRE Corporation
3. Mr. Harry Frumkin, Chevron Research Company
4. Dr. Ripudaman Malhotra, SRI International
5. Dr. George Marcelin, University of Pittsburgh
6. Dr. Donald F. McMillen, SRI International
7. Dr. Richard F. Sullivan, Chevron Research Company
8. Mr. Glen Tomlinson, MITRE Corporation
9. Dr. Bary Wilson, Battelle Pacific Northwest Laboratory
10. Mr. Richard A. Winschel, Consolidation Coal Company

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INTRODUCTION TO VOLUME II

Volume II of this report on an assessment of research needs for coal liquefaction contains reviews of the five liquefaction technologies--direct, indirect, pyrolysis, coprocessing, and bioconversion -- in Chapters 4 through 8, respectively. These reviews are not meant to be encyclopedic; several outstanding reviews of liquefaction have appeared in recent years and the reader is referred to these whenever applicable. Instead, these chapters contain reviews of selected topics that serve to support the panel's recommendations or to illustrate recent accomplishments, work in progress, or areas of major research interest. At the beginning of each of these chapters is a brief introduction and a summary of the most important research recommendations brought out during the panel discussions and supported by the material presented in the review.

Chapter 9, which follows these technology reviews, is a review of liquefaction developments outside the U.S.

This volume also contains the appendices for this report. Appendix A is a summary of recommendations contained in the FERWG-II report published in 1980. This appendix also includes a discussion of the current viability of the recommendations in the FERWG-II report. The reader will thus obtain an understanding of the recent evolution of coal liquefaction technologies, the problems that have been resolved, and those that have not.

Appendix B is a review of Oxidative Coupling of Methane, which is a method of converting methane directly to higher-molecular-weight hydrocarbons. Although the COLIRN panel received three presentations on direct methane conversion, it did not consider this technology to be appropriate for a coal liquefaction program. Consequently, this review is not included in the body of Volume II.

Appendix C contains brief descriptions of the qualifications and experience of the panel members.

Appendix D is a review of the two meetings of the full panel; the first in Pittsburgh in January 5-6, 1988, and the second in McLean, VA, on July 13-14, 1988. Between these meetings were seven full-day site visits by panel members. These site visits were to the Pittsburgh Energy Technology Center; the Morgantown Energy Technology Center; the Wilsonville, AL, PDU; ARCO Research Center; Amoco Research Center; Electric Power Research Institute; and the SAIC office in Paramus, NJ.

Appendix E contains the complete list of research recommendations proposed by the panel or received by the panel during site visits. Each of these recommendations is considered important by at least one researcher or research organization currently working in coal liquefaction. This list is, therefore, of great importance and is worthy of careful study.

Appendix F contains peer reviewers' comments and opinions regarding this report and research needs in coal liquefaction in general.

A Glossary of Symbols and Abbreviations completes the appendices.

CHAPTER 4

REVIEW OF DIRECT LIQUEFACTION[1]

4.1 INTRODUCTION AND SUMMARY

4.1.1 Introduction

Direct liquefaction is defined here to mean hydroliquefaction, to distinguish it from pyrolysis and coprocessing, which are reviewed in Chapters 6 and 7, respectively.

In the eight years since the FERWG-II Report, direct liquefaction appears to have undergone significant changes. Processes that were ready for demonstration or commercialization, such as H-Coal, SRC-I, SRC-II, and EDS, have been replaced by ITSL, CC-ITSL, and CTSL. As reviewed in Section 4.3.1, this change in technologies has been the result of an evolutionary process development, starting with H-Coal, but the current procedures are not as far different from their predecessors as might be assumed by the change in acronyms.

The new processes are based on the concept of two-stage liquefaction (see Section 4.3.1), in which coal dissolution and coal resid conversion are carried out in different reactors to optimize the conditions for each. This concept has been adopted in large-scale developments in Japan, Australia, and Great Britain, although reaction conditions differ. The two-stage approach has led to significantly improved liquefaction economics, as described in Section 4.3.4. These improvements stem from

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[1] This chapter was written by Martin L. Gorbaty, Exxon Research and Engineering Company (contributed materials); Donald F. McMillen and Ripudaman Malhotra, SRI International; Burtron H. Davis, Kentucky Energy Cabinet Laboratory; Francis Burke, Consolidation Coal Company; Harvey D. Schindler, Science Applications International Corporation; Richard F. Sullivan and Harry Frumkin, Chevron Research Company; David Gray and Glen Tomlinson, MITRE Corporation; and Bary Wilson, Battelle Pacific Northwest Laboratory.

higher yields and improved product quality, which more than offset the higher capital and operating costs associated with a two-stage process.

When plans were being made in the 1970's to produce large quantities of synfuels from coal, considerable doubt existed regarding the ability of refineries to process coal liquids. Another anticipated problem was the carcinogenic properties of heavy aromatic coal liquids, which would be used either as a refining feed or as an end product, such as a boiler fuel. Significant progress has been made in resolving both of these issues, as reviewed in Sections 4.3.3 and 4.3.5. The Chevron refining work showed that coal liquids with an end point of 650-750°F constitute no processing problem; the Battelle Northwest toxicity work showed that coal liquids with an end point of about 650°F are no more carcinogenic than petroleum streams of the same boiling range.

Their findings encouraged process developers to modify their processes to make 650°F-end-point coal liquids, and this lighter product slate is a major objective in current direct liquefaction programs. This sequence of events, leading to an improved process, illustrates the benefits that are derived from DOE-coordinated research by several organizations, each contributing information in its area of expertise. The obvious conclusion from such an example is that a successful process development program requires a broad range of support research programs to increase the probability of success. Unfortunately, reductions in funding over the last several years have forced DOE to eliminate many of these important supporting programs.

Major advances in coal liquefaction are coming from research in coal chemistry. This work has focused on the breaking of coal bonds, hydrogen transfer, physical interaction of solvent and coal, roles played by mineral matter and catalysts, and research aimed at a better understanding of what happens to the coal before it enters the liquefaction reactor ("preconversion chemistry"). In concert with the increased understanding of coal structure (Section 4.2.1) and the improved analytical tools (Section 4.2.4) that have monitored the physical and chemical changes occurring in liquefaction, this fundamental work is laying the ground work for completely new and more efficient liquefaction processes. None of these findings, however, has found its way into current process development. There seems to be a gap between fundamental research and process development contractors, which must be bridged if we are to test and apply the fundamental work in the context of a liquefaction process.

Rather than try to summarize all the important work on coal reactivity that has been carried out recently, we have selected one investigation as illustrative of the work going on in this area. Section 4.2.2 is a review of work on hydrogen transfer which may alter our thinking on how coal bonds are broken in the presence of hydrogen - donor solvents.

Section 4.2.3 reviews the status of catalysis in direct liquefaction. This section reflects the emphasis in recent years on hydrotreating catalysts to accommodate current process developments. The focus seems to have narrowed from earlier investigations, which studied acid catalysts as well. The recent work with titanate catalysts may be ushering in renewed interest in catalysts with different properties. Catalyst innovations will certainly be necessary if processes are to emerge that operate at conditions significantly different from those now being used in two-stage liquefaction.

Section 4.2.4 reviews analytical techniques in liquefaction research. The chemical and physical properties of coal liquefaction process streams and products are of obvious importance in the development of coal liquefaction technology. Products must be shown to meet end-use and environmental specifications. Physical property data are necessary for engineering design and process scale-up. More importantly, and on a more fundamental level, the conversion of coal to liquids involves a complex sequence of physical changes and chemical reactions. The ability to control and optimize process performance or devise new processes depends on an understanding of these reactions. This understanding depends, in turn, on the ability to analyze the chemical composition and the physical attributes of the feed materials and the reaction mixtures. Therefore, the methods of quantitative and qualitative analytical chemistry are of central importance to coal liquefaction process development.

The review of direct liquefaction in this chapter is meant to provide an understanding of the current state of the art. This technology is moving ahead rapidly in all areas of research and development.

4.1.2 Summary

Research in direct liquefaction has been active in many disciplines, beginning with fundamental coal structure and coal chemistry. In particular, the conventional view of the chemistry and the mechanisms of direct liquefaction -- that the initial reactions of liquefaction involve thermal homolytic bond cleavage with stabilization of the free radicals formed -- is being challenged by recent work being done to develop a deeper understanding of bond-breaking and bond-forming processes via hydrogen transfer. This new model of coal dissolution may explain the cleavage of bonds which are thought to be too strong to be broken thermally at liquefaction conditions. The COLIRN panel agreed that these new understandings of structure and mechanisms are developing rapidly and are expected to lead to more efficient liquefaction processes.

The panel also agreed that more efficient processes are necessary before coal liquefaction can be commercialized. In particular, the panel placed the highest priority on identifying the coal structures responsible for retrograde reactions (Recommendation No. D1[2]). If the mechanisms and the kinetics of these reactions can be determined, then processing strategies can be developed to control these reactions and increase liquid yields. In keeping with this emphasis on conversion

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[2] High-priority recommendation listed in Table 3-1.

chemistry, the panel also placed high priority on testing chemical and low-temperature pretreatments to enhance coal reactivity (No. D3). Other high-priority recommendations involving coal structure and coal chemistry made by the panel were to develop a coal structure-reactivity relationship (No. D5), develop kinetic models of liquefaction (No. D7), develop chemical techniques to solubilize coal based on new information on coal chemistry (No. D8), determine the role of mineral matter on coal reactivity (No. D9), and develop intrinsic quantitative rate expressions as a basis for understanding initial reaction paths during coal dissolution (No. D10).

Process developments have greatly improved direct liquefaction technology, resulting in substantial improvements in liquefaction economics. For example, yields of distillates have increased from 41 percent to 78 percent, resulting in equivalent liquid yields of about 5 bbl/ton of feed coal. The quality of liquid products has also improved substantially, being comparable to or better than No. 2 fuel oil. The work at the Wilsonville PDU has been the focal point of this development. However, significant improvements in CTSL are still possible, and the programs at Wilsonville and Trenton should continue to produce further improvements. Additionally, the new findings in coal chemistry will eventually lead to new process flow configurations.

Whatever developments emerge will ultimately have to be tested at the POC scale, which is provided by the Wilsonville PDU. The importance of this POC unit in the development of new process concepts cannot be overstated; without Wilsonville no direct liquefaction process can be brought to technical readiness for large-scale demonstration. The COLIRN panel underscored this discussion of the importance of Wilsonville by making the operation of a large-scale pilot plant to test engineering and new process concepts the second highest-priority recommendation in direct liquefaction (No. D2).

The economics of direct liquefaction have always been seen as dependent upon hydrogen usage in many ways. Significant progress has been made to make hydrogen utilization more efficient by decreasing the amount of gases made and the amount of hydrogen needed per barrel of primary product. However, significant amounts of hydrogen are, and will always be, required for product upgrading; product quality is directly proportional to the amount of hydrogen added to the distillate liquid products. It is therefore imperative that studies be carried out to achieve more efficient and less costly methods to produce and use hydrogen, and the panel decided to make this a high-priority recommendation (No. D4).

Catalytic reactions are an integral part of any current liquefaction process, and catalysis of hydroliquefaction has received much attention. However, more research is seen to be needed, for example, to develop catalysts which will affect the initial coal conversion in a positive manner. If a catalyst could be found which could influence the product distribution of the primary products as they are formed, entirely different types and quantities of products might be formed. In particular, the COLIRN panel thought that homogeneous catalysts for liquefaction should be investigated (No. D6). Such catalysts were seen to have potential for effecting hydrogen addition at significantly lower temperatures, possibly leading to completely new processes.

In addition, in the same area of research, similar potential was seen by the panel for developing new supported catalysts. Unconventional or novel catalysts and supports should be considered in fundamental and model-compound studies (No. D11). New catalytic approaches will probably be required if the new process concepts to be developed are to deviate significantly from the current CTSL process.

Finally, there are important areas within the current liquefaction technology that require additional study, such as mechanisms of important catalytic and thermal reactions (No. D12).

A review of these recommendations shows that research in areas of coal chemistry received higher priority than process developments. This stems from a consensus of the COLIRN panel that significant improvements are needed before direct liquefaction can be commercially viable. These improvements may require new liquefaction chemistry that has as yet not been discovered or developed.

4.2 FUNDAMENTAL AND APPLIED RESEARCH

4.2.1 Coal Structure Related to Liquefaction[3]

4.2.1.1 Introduction

More fundamental knowledge of coal--its structure and its chemical reactivity--is essential for generating the new technologies necessary for its efficient use in the future as a feedstock for liquefaction. Technologies are available today for the liquefaction of coal, but these generally involve severe processing conditions of high temperatures and high pressures. These severe conditions lead to conversions, thermal efficiencies, and hydrogen utilization well below those theoretically possible. Newer, milder, and more selective process chemistries are needed to help overcome limitations of current processes.

These newer chemistries will develop from a better understanding of the chemical and physical structures of coal and of the reactivities of its various constituents. Major opportunities exist today to provide this new knowledge. Significant advances are providing tools which may be used to obtain answers to critical structure and reactivity questions. Coal is a complex heterogeneous organic rock, made up of fossilized remnants of primordial plant matter and incorporated inorganic materials (4). As such, it has an organic and an inorganic structure. It is also a porous rock and has an associated physical structure. Unraveling the basic chemistry of coal requires a more detailed knowledge of these structures. However, because of coal's inherent heterogeneity, systematic studies of these structures have been limited. With today's modern characterization tools and techniques, a clearer, more precise, and in-depth understanding of each of these structures, the extent to which they interact, and the ways they affect reactivity becomes possible.

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[3] This section is based on articles (1, 2, 3) and materials supplied by Martin L. Gorbaty, Exxon Research and Engineering.

The purpose of this section is to review the state of the art and to suggest specific basic research opportunities and challenges in the areas of coal characterization as related to coal liquefaction. Critical science needs are assessed which could provide the base for improvements to current conversion processes and for entirely new and better ones.

4.2.1.2 Coal Classification

The diverse nature of the deposited plant and mineral matter and burial conditions make it clear that coal is not one substance but a wide range of heterogeneous materials, each with considerably different chemical and physical properties from the others. The heterogeneity of coals can be seen on both the macroscopic and microscopic levels.

On the microscopic level coal layers are seen to be composites made up of discrete entities called macerals. Optically differentiated by microscopic examination of coals under reflected light or by the study of thin sections of coal using transmitted light, macerals are classified into three major groups: vitrinite, liptinite (often termed exinite), and inertinite. The vitrinite class appears orange-red in transmitted light and is derived from fossilized lignin. Liptinites appear yellow and are the remains of spores, waxy exines of leaves, resin bodies, and waxes. Inertinites appear black and are believed to be the remnants of carbonized wood and unspecified detrital matter. Chemically, the liptinites are richest in hydrogen, followed by the vitrinites. Both the liptinites and the vitrinites are reactive and give off a significant amount of volatiles when pyrolyzed, while the inertinites are relatively less reactive. It is not possible to generalize with accuracy the proportional maceral composition of all coals; however, it is fair to say that most bituminous coals contain about 70 percent vitrinite, 20 percent liptinite, and 10 percent inertinite.

It is generally believed that maceral composition ultimately determines a coal's reactivity in a particular process. Today new techniques are available to separate a coal into its component macerals much more easily, and this has renewed interest in maceral characterization and reactivity. It may even be possible one day to tailor coal feedstocks for specific processes such as pyrolysis, gasification, or liquefaction by separation and blending of macerals.

Another method of classifying coals is by the degree of metamorphism they have undergone, or their rank. Since metamorphism is a deoxygenation-aromatization process, rank correlates generally with carbon content and heat content of the coal. Lignites and sub-bituminous coals are generally considered to be low rank, while bituminous coals and anthracite are considered to be high rank.

In general, carbon content, aromaticity (i.e., the percentage of carbon that is aromatic), number and size of condensed rings, and calorific content increase with increasing rank, while volatile matter, oxygen content, oxidizability, and solubility in aqueous caustic decrease with increasing rank. Hardness and plastic properties increase to a maximum, then decrease with increasing rank, while porosity (i.e., moisture-holding capacity) and density decrease to a minimum, then increase with increasing rank. Typical values are shown in Table 4-1. Within each rank classification, a range of values is found.

Physical properties are an important consideration in all uses of coals. Most vary with rank and coal type.

4.2.1.3 Physical Structure

A. Pore Structure

Coals are highly porous materials, many having void volumes as high as 20 percent of their total volume. To describe the pore structure knowledge is needed about the size distribution of the pores, the size ranges of the pores, and the population of each range. The shape of the pores is also important as is the total surface area of the coal. The size and the shape of the pores determine whether a molecule can enter and contact the surface. Most information about pores comes from gas adsorption measurements and mercury porosimetry.

Table 4-1. Properties of Coals of Different Rank

Property*	Lignite	Subbituminous	Bituminous	Anthracite
Moisture capacity, wt. %	40	25	10	<5
Carbon, wt. % DMMF	69	75	83	94
Hydrogen, wt. % DMMF	5.0	5.1	5.5	3.0
Oxygen, wt. % DMMF	24	19	10	2.5
Volatile Matter, wt. % DMMF	53	48	38	6
Aromatic Carbon, mol fraction	0.7	0.78	0.84	0.98
Density (helium), g/cm^3	1.43	1.39	1.30	1.5
Grindability, hardgrove	48	51	61	40
Heat Content, btu/lb DMMF	11,600	12,700	14,700	15,200

*DMMF, Dry, mineral-matter-free.

Source: Ref. 1.

As-mined coal contains significant amounts of water, decreasing with increasing rank (5). Surface areas and pore-size distributions for dried coals of various ranks have been reported, using a number of techniques. However, coal drying, either inadvertently or purposefully, can affect physical structure. It is known that subbituminous coals contract and crack on drying, and this is attributed to gel collapse (6). Using ion exchange as the probe, it was shown that a dried subbituminous coal adsorbed about a third less of the exchange ion when compared with the undried coal (7). If coal has a rigid pore network similar to porous ceramics, it would be expected that all the water removed by drying could be replaced by vapor sorption. In fact, only about 60 percent of the water removed from subbituminous coal and 35 percent removed from lignite can be replaced. Clearly, drying alters the physical structure of lower-rank coals.

Extensive studies have shown that heat-capacity measurements can be used to determine the state of the absorbed water molecules and to study the surface area and the pore network of the coal itself. By studying raw coals containing their natural water and dried coals containing reabsorbed water, the changes to physical structure caused by drying can also be determined. For example, by comparing the heat-capacity behavior of the natural and re-absorbed water in coal samples, it is evident that the effects caused by drying are markedly different for coals of different rank. Dried Illinois bituminous coal re-absorbs almost exactly the amount of water that the raw coal lost, and there is little difference at equilibrium between the samples dried at room temperature versus those dried at 100°C. The re-absorbed water apparently occupies locations in the porous network similar to those occupied by the original water. On the other hand, both dried subbituminous coal and dried lignite do not re-absorb the amounts of water that the original coals lost, and coals dried at 100°C do not re-absorb as much water as those dried at room temperature. The shapes of the heat-capacity peaks suggest that the re-absorbed water does not return to the same locations.

These observations suggest that the structure of the bituminous coal is akin to a "rock with holes in it." Water removed by drying can easily be replaced, and re-absorbed water occupies very similar locations as the water that was removed. The lignite porous network, however, has some of the features of a "gel" (6), in which water is an intimate part of the structure and cannot be removed without marked change to the original material.

It should be kept in mind that conventional surface area and pore size distribution analysis techniques are applied on dried coals, and cannot be used reliably to describe the natural surface areas of low-rank coals. Also, there is no experimental evidence for the structural models assumed either explicitly or implicitly to determine pore-size distributions. These models usually assume interconnected voids having a well-defined pore geometry (spherical or ellipsoidal) with the volume of the interconnections being less that the volume of the voids.

Recently, both x-ray (8, 9-11) and neutron-scattering (12) have been used to probe the pore structure of coal. These techniques are insensitive to the surface adsorption and void penetrability of the probe molecules employed by the more traditional approaches, and provide some information about pore structure which is independent of any particular pore-structure model.

In summary, coal in its natural state is a porous rock, but the pore structure of subbituminous and lower-rank coals is not stable and is changed by removing water. The void volume is best described by a random arrangement of voids of arbitrary size and shape. Pore-size distributions for (bituminous) coal seem to be continuous. The consequences of such a description on the rates of mass and thermal transport through coal have yet to be evaluated. It is clear that any aqueous pretreatments should be carried out on naturally wet coals, and care should be taken to ensure that the coals to be treated do not dry out significantly between mining and shipping to the utilization site. Knowledge of surface areas and pore volumes are needed to help establish correlations between surface areas and chemical reactivity, particularly regarding access of gases and liquids to the interior. However, recently developed mathematical theories and computer simulation routines should allow the effect of including complex geometrical and topological structures to be evaluated (13).

B. Macromolecular Nature of Coals

Coals are believed to be three-dimensionally cross-linked macromolecular networks containing dissolved organic material that can be removed by extraction. This model offers the most detailed and complete explanation of the chemical and mechanical behavior of coals. It is a relatively recent model and somewhat controversial. Although this macromolecular structure is believed to control many important coal properties, it has been relatively little studied.

In this model the insoluble portion of the coal comprises the cross-linked network, which is one extraordinarily large molecule linked in a three-dimensional array. This network is held together by covalent bonds and hydrogen bonds. The extractable portion of the coal is simply dissolved in this solid, insoluble framework. A solvent like pyridine, which forms strong hydrogen bonds, breaks the weaker hydrogen bonds within the coal structure. In the presence of pyridine, the network is less tightly held together, and the coal expands or swells.

Swelling plays a role in slurry processes for the direct liquefaction of coal. For any non-aqueous coal impregnation or pretreatment technique, swelling may play a part since it expands the coal structure, thereby enabling faster or more complete penetration of the coal by liquids or by substances dissolved in liquids. In addition, a swollen coal structure allows more complete or more rapid diffusion of reaction products out of the coal structure. Solvent swelling can be used to obtain information about physical structure through measurement of macromolecular parameters of coals. These can be related to physical characteristics such as hardness, dissipation of mechanical energy, solubility, extractability, and mass transport.

In summary, solvent swelling is accompanied by reorientation and stretching of macromolecular chains driven in part by the entropy change resulting when the swelling liquid is mixed with the coal structure (14). In this view, coal has a gel-like structure containing cross-linkages between the various macromolecular subunits. In the presence of good swelling agents, the gel structure swells, but the covalent cross-linkages prevent dissolution. The high degree of swelling, which is often more double the original volume, indicates that there are a number of flexible molecular subunits in the average chain. In the non-swollen state coals behave like plastics and are likely in a glassy state; significant secondary forces contribute to maintaining the rigid structure.

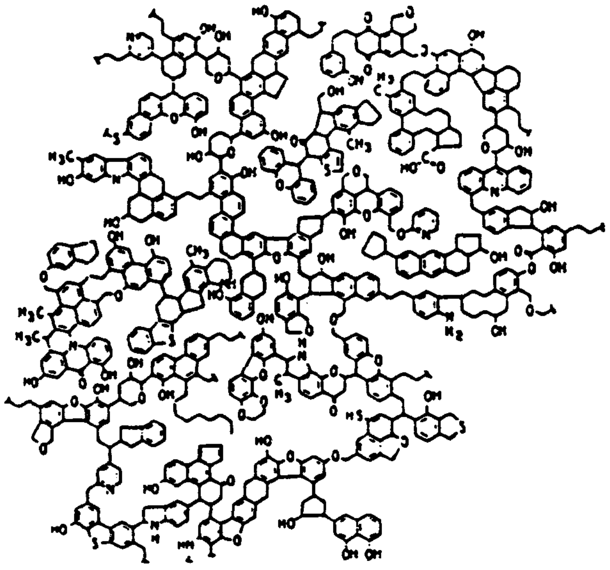
From this viewpoint opportunities exist for characterizing coal physical structure as a polymer by applying modern polymer science techniques in general, and thermodynamic analysis in particular (12). Ways to determine swelling and modulus properties could lead to definition of coal structure in terms of M_c, the average molecular weight between cross-links. This vital parameter could be used to define how many of which bonds need to be cleaved to reduce the "molecular weight" of coal from a solid macromolecular network to desired liquids. Future research opportunities in this area include the thin section swelling and M_c determinations of sub-bituminous coals and lignites. The M_c determination should be extended to coals treated at various temperatures. Ultimately a useful correlation between M_c and reactivity could emerge.

4.2.1.4. Chemical Structure

A. Structure Models

Many average molecular structures representative of the organic material in coal have been and continue to be proposed (15-17) and, as expected, become more refined as new information is obtained. An excellent review of this area is available (18). A recent molecular model typical of proposed structures for bituminous coals is shown in

Figure 4-1. These models are useful to guide thinking, but it must be remembered that they are <u>average</u> structures meant to represent functional group distributions and are not absolutely accurate. Since coals are very heterogeneous, it may never be possible to know the "real" structure. Nevertheless it is possible to refine these structures by more accurate determinations of key structural features which affect utility and reactivity.



Source: Ref. 19.

Figure 4-1. Molecular Structure for a Bituminous Coal

B. Elemental Composition

Nitrogen

Nitrogen is a minor constituent of most coals, being less than 2 percent by weight. Little is known with certainty about the forms and the amounts of each form of organic nitrogen in coal because it is present in such small amounts and the necessary analyses are very difficult. Analysis of coal extracts shows a decreasing amount of basic nitrogen as the coal rank increases. This may be due to the conversion of basic amino ($-NH_2$) groups to nitrogen incorporated in ring structures (heterocyclic nitrogen). It is necessary to know how nitrogen is incorporated in the organic matrix, since it is becoming apparent that nitrogen compounds play a key role in coal asphaltene behavior (20), and it is likely this heteroatom plays a role in coal conversion chemistry (21).

Sulfur

Coals contain a mixture of organic and inorganic sulfur. The amount and the form of sulfur in coals depend much more on the coal's depositional environment than on its age or rank. The inorganic is chiefly pyrite. Much of the pyrite can often be removed by grinding the coal and carrying out a physical separation, usually based on the difference in density between the organic portion of the coal and the more dense mineral matter. The organic sulfur in coals, that is, the sulfur bonded to carbon, is very difficult to remove.

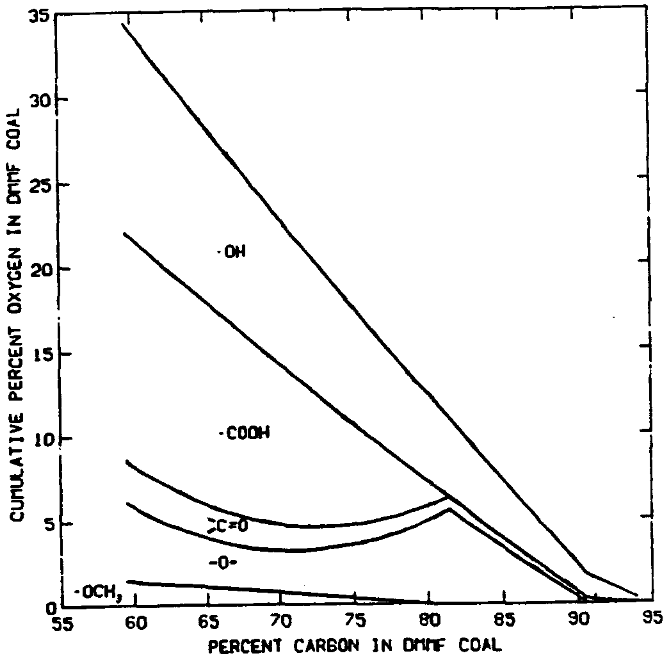
Knowledge of the forms of organic sulfur present in coals is surprisingly small and uncertain, given the importance of this element. There is evidence that both aliphatic and aromatic-SH groups are present. Also, thiophenes are present, probably in large amounts, and present serious problems for organic sulfur removal. Thio ethers are present. Easily reduced forms of sulfur such as disulfide (-S-S-) and thiocarbonyl are probably not present. There are not enough data to allow speculation as to how the distribution of sulfur functional groups changes with coal rank.

While adequate methods are available to determine total sulfur and inorganic sulfur, organic sulfur is determined by difference. An independent method for determining organic sulfur directly is essential. The forms in which organic sulfur exists in coal have been proposed based on analyses of coal liquids (4). Methods to qualitatively and quantitatively characterize forms of organic sulfur as they exist in the native structure are required. Some progress has been made recently using EXAFS AND XANES (222, 223). Ultimately, knowledge of the forms of organic sulfur will support the development of the proper organic chemistry required to remove it from a coal or char.

Oxygen

After carbon and hydrogen, oxygen is the most abundant element in coals, and its content decreases steadily as the rank of the coals increases. Oxygen is present both in organic functional groups and inorganics. Good analytical techniques exist to differentiate and quantify these functional groups (22) so that their populations as a function of rank are known (Figure 4-2). This knowledge makes possible the determination of the role of oxygen functionalities in coal structure and reactivity. For example, the effect of hydroxyl group hydrogen bonding on caking properties of bituminous coals has been demonstrated (23).

Lignites contain water and can be considered to be hydrous gels. Removing the water causes irreversible changes in their structure. The water is an integral part of the native structure of the lignites, not just something complexed to the surface or present in pores. The nature of the water in the structure is unknown. Its presence is undoubtedly due to the presence of a large number of polar oxygen functional groups in the coal.



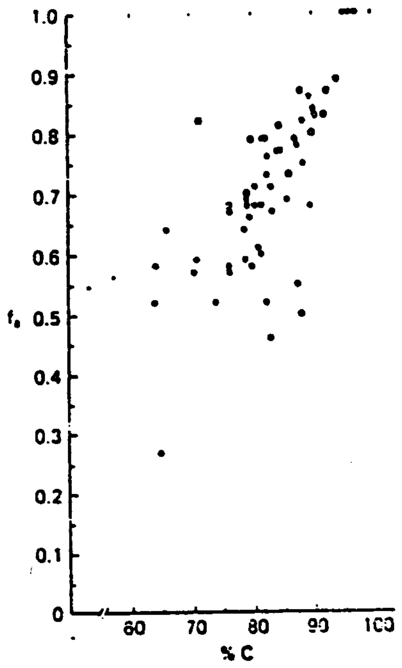
Source: Ref. 24.

Figure 4-2. Distribution of Oxygen Functionality in Coals DMMF, Dry, mineral-matter-free

Carbon

Coal contains both aliphatic carbon and aromatic carbon. Many techniques have been used to estimate the relative amounts of the two types of carbon in coals, but only recently has the direct measurement of the two been possible. Their variation with rank is illustrated in Figure 4-3.

The carbon in coals is predominantly aromatic and is found in aromatic ring structures. It is very desirable to know the frequency of the occurrence of these ring systems in coals, and many techniques have been applied to this problem. Most of the techniques involve rather



Source: Ref. 25.

Figure 4-3. Plot of Fraction of Aromatic Carbon (f_a) Versus Percent Carbon for 63 Coals and Coal Macerals

vigorous degradation chemistry, advanced instrumental techniques, and many assumptions. The distribution of ring systems in any coal remains unknown. For a number of coals, reasonable estimates of the average number of rings per system have been made. Roughly, for coals below 80 percent carbon, the average number of rings per structure is two. Between 80 and 90 percent carbon it is three, and it increases rapidly above 90 percent carbon.

Knowledge of the aliphatic structure in coals is also inadequate. In many low-rank coals there is a significant amount of long-chain aliphatic material. There is a debate as to whether this material is bound to the coal macromolecular structure or whether it is simply tangled up with it and thus trapped. Much of the aliphatic carbon is present in ring systems adjacent to aromatic rings. Some is bonded to oxygen and in short chains of $-CH_2-$ groups linking together aromatic ring systems. No accurate distribution of aliphatic carbon for any coal is known.

Magnetic resonance studies continue to provide valuable information about coal structure (26). In particular, solid-state ^{13}C nuclear magnetic resonance allows determination of how carbon is distributed in coals (27). With the increasing resolution available today through the coupling of ultra-high fields using super conducting magnets with pulse sequencing and "magic angle" spinning (28), it may be possible to define more precisely how the carbons are bound to one another and to the various oxygen, sulfur and nitrogen heteroatoms. Some high-temperature ESR work has been reported on model (29) and real coal systems (30). Similar experiments using ^{13}C-NMR must be carried out. They could provide critical information needed to determine the mechanisms of many coal conversion reactions.

Given the detailed knowledge of the functional groups and their distributions, appropriate model systems can be chosen to study the chemistry of converting coal to liquids either by pyrolysis or hydroliquefaction. In particular, it would be important to determine which bonds break first under a given set of conditions and to quantify the kinetics of these reactions.

C. Maceral Chemical Structure

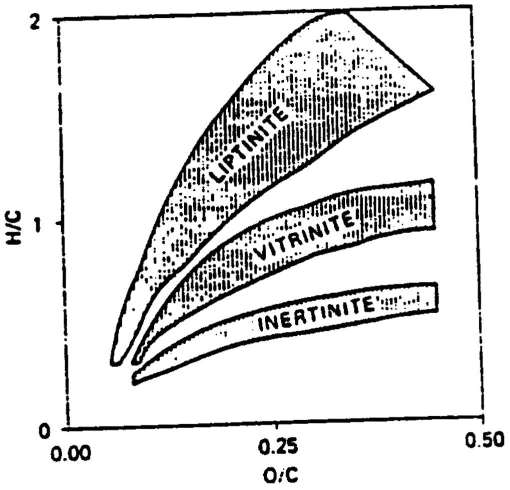
There are four principal maceral groups. The vitrinite macerals are most important in North American coals, comprising 50-90 percent of the organic material. They are derived primarily from woody plant tissue. Since they are the principal component of most coals, vitrinite maceral chemistry usually dominates the chemistry of the whole coal. Inertinite maceral family members comprise between 5 and 40 percent of North American coals. These materials are not at all chemically inert, as the name implies. They are usually less reactive than the other macerals, but their chemical reactivity can still be quite high. They are thought to be derived from degraded woody tissue. The liptinite maceral group makes up 5-20 percent of the coals in question. Its origin is plant resins, spores, and pollens -- resinous and waxy materials that give rise to macerals rich in hydrogen and aliphatic structures. Terpenes and plant lipid resins give rise to the varied group of resinite macerals.

The rank dependence of the elemental composition of the maceral groups is shown in Figure 4-4. The inertinites are the most aromatic followed by the vitrinites and then the liptinites. Their oxygen contents decrease in the order vitrinite >liptinite >inertinite. The reactivity of macerals as substrates for direct liquefaction and their reactivity as hydrogen donors are parallel and in the order liptinite >vitrinite >inertinite >resinite.

D. Mineral Matter

All coals contain minor amounts of inorganic material or mineral matter, ranging from 2 to 30 percent and averaging about 10 percent by weight. This mineral matter was deposited before, during or after coalification of partially decayed biomass. The major components of mineral matter include aluminosilicate clays, silica (quartz), carbonates (usually of calcium, magnesium, or iron), and sulfides (usually as pyrite and/or marcasite). Many other inorganics are present, but only in trace quantities of the order of parts per million.

This mineral matter is not necessarily inert during coal conversion processes, and has been reported to act beneficially in some cases as a catalyst for liquefaction (32). Identification of the chemical species responsible could lead to ways of enhancing its catalytic behavior. Therefore it is important to know the structure of the minerals and their effects on reactivity. Methods are available to remove carbon (33) (Low Temperature Plasma Asher) and to study the residue. Techniques more sensitive than X-ray diffraction and Fourier-Transform Infrared Spectroscopy are required to characterize this mixture.



Source: Ref. 31.

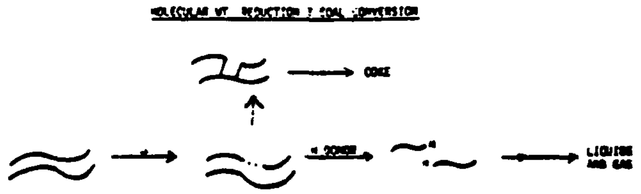
Figure 4-4. Elemental Composition of the Three Main Maceral Groups

4.2.1.5. Coal Chemistry Related to Liquefaction

The basic chemical problem in converting coal to liquid products is to manipulate the hydrogen-to-carbon atomic ratio (H/C). Coal has an H/C ratio of less than one. To make desired liquid fuels with atomic H/C ratios of 1.5-2, either hydrogen must be added or carbon must be removed. The former process is called hydroliquefaction, and the latter is termed pyrolysis.

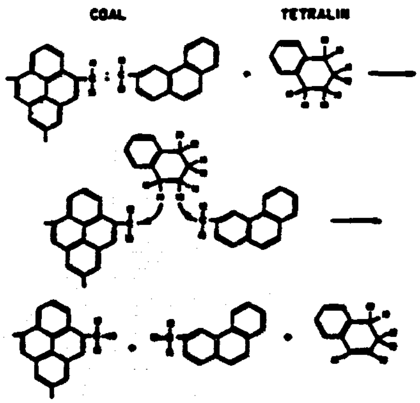
In general, both pyrolysis and hydroliquefaction reactions begin with the same step, thermal homolytic bond cleavage to produce free radicals, effecting a molecular weight reduction of the parent macromolecule (Figure 4-5). If the radicals are stabilized, smaller neutral molecules result leading to liquid and gaseous products. Those radicals that are not stabilized recombine to form products of the same or higher molecular weight than the parent, leading eventually to a highly cross-linked carbonaceous network called coke (if the material passed through a plastic phase) or char. In pyrolysis radicals are stabilized by whatever hydrogen is present in the starting coal. In addition, recent work on dry catalytic liquefaction raises the question of whether these bonds can be cleaved catalytically (224). In hydroliquefaction excess hydrogen is usually added as molecular hydrogen and/or as molecules (such as 1,2,3,4-tetrahydronaphthalene) that are able to donate hydrogen to the system (Figure 4-6). Thus, hydroliquefaction produces larger amounts of liquid and gaseous products than pyrolysis at the expense of additional hydrogen consumption. Conventional pyrolysis takes place at temperatures higher than those of hydroliquefaction, but hydroliquefaction requires much higher pressures.

Many techniques have been used in hydroliquefaction. They all share the same thermal initiation step but differ in how hydrogen is provided: from molecular hydrogen, either catalytically or noncatalytically, or from organic donor molecules. Obviously, rank and type determine a particular coal's response to pyrolysis and hydroliquefaction, and the severity of the processing conditions determines the conversion, and



Source: Ref. 3.

Figure 4-5. Coal Conversion to Liquids Begins with a Thermolysis Capping radicals with hydrogen leads to liquids; Recombination leads to coke.



Source: Ref. 3.

Figure 4-6. Proposed Chemistry of Hydrogen Donation product selectivity and quality. The various processes also differ in whether and what kind of solvent is used. Thus, study of the physical solution properties of macromolecules from coal in various solvents as well as the colloidal nature of the solutions would be helpful. The phase behavior at high temperatures and under high hydrogen pressures should also be determined to help understand liquefaction processes.

A better understanding of the kinetics and the mechanism of the first step -- thermal cleavage of bonds -- is critical to improving liquefaction processes. It is known that these initial reactions are rapid, as coals can be rendered soluble in a few minutes at temperatures of 400°C (34). Questions such as which bonds break first, the effect of the solvent on bond breaking, and how can these reactions be controlled need to be answered.

Catalysis of hydroliquefaction has received much attention. More research is needed to develop catalysts which will positively affect the initial coal conversion and these needs have been documented recently (225). It may be relatively easy to affect the course of reactions after the primary products are out of the coal particle. However, by this time the product distribution may already be determined. If a catalyst could be found which could influence the product distribution of the primary products as they are formed, entirely different types and quantities of products might be formed.

The question of catalysis by inherent mineral matter is still open. There have been reports of catalysis by the sulfur-containing minerals pyrite and pyrrhotite (35). However, there is other evidence (36, 37) to indicate that H_2S derived from these minerals is acting as the catalyst. Obvious processing consequences could result by resolution of this question.

4.2.2 Chemistry and Mechanisms of Direct Liquefaction Reactions

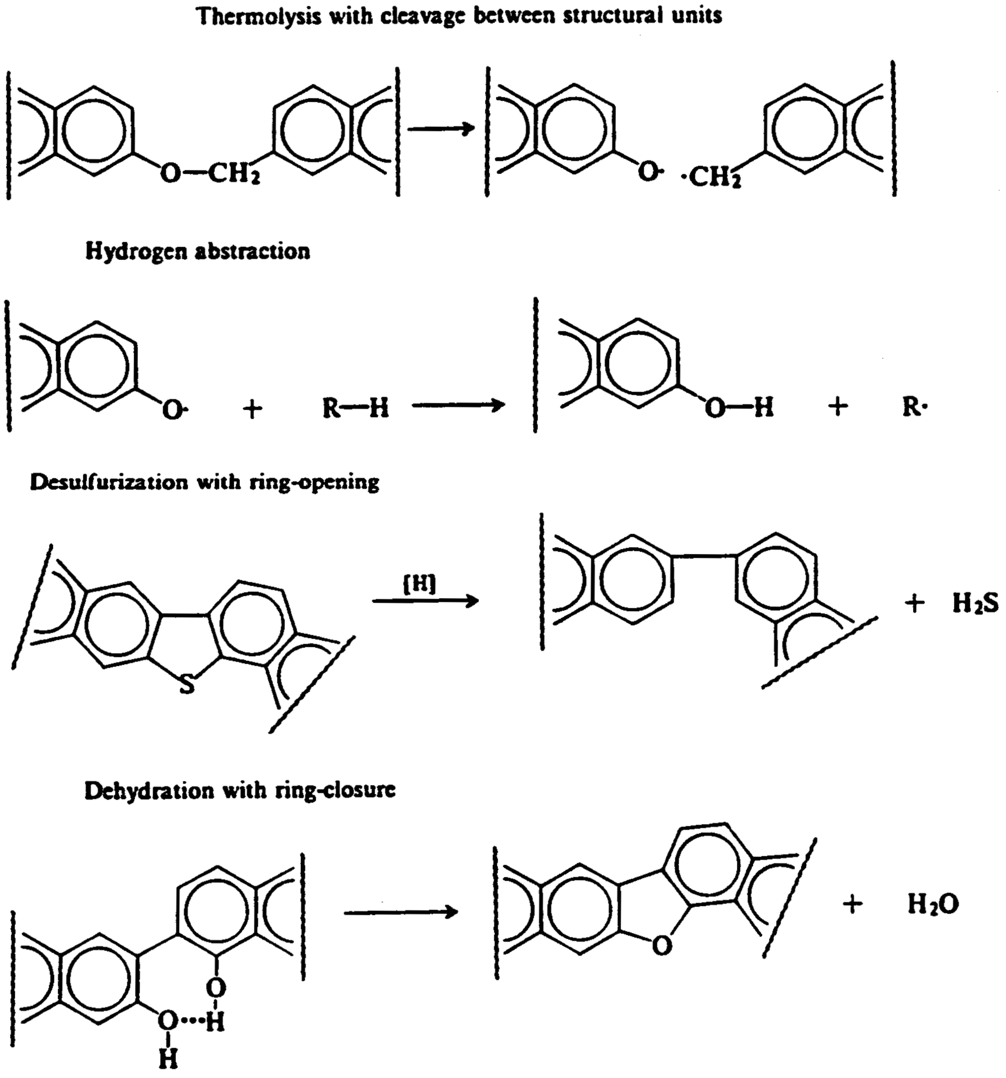
4.2.2.1. Conventional View of Liquefaction Chemistry and Mechanisms

The direct liquefaction of coal has been a very widely studied process. Most of the current processes for the liquefaction of coal have features in common and are largely extensions of the early work by Bergius. In the majority of these processes, the coal is dried and pulverized, and then slurried with a coal-derived recycle oil. The slurry is then pumped into a high-pressure reactor, wherein the coal is liquefied by hydrogenation at high temperature and pressure. The operating temperature and pressure are similar for most liquefaction processes.

Under mild conditions (low temperature, low pressure, and short reaction times) or in the absence of a catalyst, the liquefaction product is usually a heavy oil suitable for boiler fuel applications. Under more severe conditions the heavy oil is further converted into distillable products. In either case, the products generally require further upgrading before they are suitable for use as fuels.

The operating temperature (approximately 450°C) tends to determine the mechanism most likely involved in the coal liquefaction process. It has been reasonably well established that above 400°C the pyrolytic breakup of the coal matrix begins. A large number of concurrent and competitive chemical reactions occur during the liquefaction process, such as thermolysis, hydrogen abstraction, dealkylation, cleavage of bridges between structural units, desulfurization, dehydration, and ring opening. Four of the possible reactions are illustrated in Figure 4-7.

Once one or more of these weaker bonds has been cleaved, the free radicals generated are thought to be stabilized by the addition of hydrogen. The hydrogen may be added either from molecular hydrogen or from a hydrogen-donor solvent, especially when a good donor solvent (such as tetralin or a tetralin-like species) is present. Tetralin or tetralin-like molecules are good donors due to the fact that the free



Thermolysis with cleavage between structural units

Hydrogen abstraction

Desulfurization with ring-opening

Dehydration with ring-closure

Source: Ref. 38.

Figure 4-7. Some Possible Reactions During Hydroliquefaction radical intermediate is a relatively stable benzylic-type free radical and the product after the loss of four hydrogen atoms is a stable aromatic compound (naphthalene). In the absence of a good hydrogen source, the free radicals may couple to form coke or char.

The hydrogen-transfer reactions appear to be purely thermal processes. Attempts to accelerate the reaction by the use of contact catalysts have been largely unsuccessful. The coal itself is, of course, not in solution during the initial phase of the liquefaction process. This fact would seem to preclude the possibility of catalysis in the initial phase of coal liquefaction. It is much more likely that the donor solvent (or molecular hydrogen) rapidly diffuses into or dissolves in the coal particle and that the hydrogen-transfer reaction takes place between the solvent (or hydrogen) and the radical species within the coal particle itself. The function of a donor solvent, then, appears to be to enter the coal particle and provide a source of hydrogen for the free radicals generated thermally within the matrix. The rate of hydrogen transfer with the more active donors appears to be roughly the same regardless of the structure of the donor. Thus the rate of thermal decomposition of the coal matrix appears to determine the extent of hydrogen transfer once a sufficiently reactive donor is available.

Studies of the hydrogenation of coal using both molecular hydrogen and donor solvents indicate that hydrogenation by molecular hydrogen and by the solvent are both important. In fact, it appears that both are roughly equal in their ability to hydrogenate the free radicals formed in the thermolysis of the coal matrix. These results support the view that the conversion process is free radical in nature, with liquefaction ultimately achieved by stabilization of the coal fragments by the addition of hydrogen from either molecular hydrogen or donor solvent. In addition, experiments indicate that different product distributions can result depending on whether molecular hydrogen or a donor solvent is used to quench the thermally generated free radicals. The products derived via direct liquefaction of coal may, therefore, depend to some extent on the kind of hydrogen source employed in the specific process.

This conventional view of the chemistry and the mechanisms of direct liquefaction is, however, being challenged by recent work (226) being done to develop a deeper understanding of bond-breaking and bond-forming processes via hydrogen transfer. Briefly, the authors claim that bond cleavage is initiated by hydrogen transfer from solvent to coal, and that the role of a good solvent is to transfer hydrogen before bond cleavage. This model of coal dissolution may explain the cleavage of bonds that are thought to be too strong to be broken thermally at liquefaction conditions. This recent work, described in the next section, poses a number of questions which should be addressed via long-range research needs. Obviously, new understandings of structure and mechanism are developing rapidly and are expected to lead to more efficient liquefaction processes.

4.2.2.2. The Role of Hydrogen Transfer in Bond-Cleavage and Bond-Forming Processes During Coal Conversion[4]

A. Introduction

As a result of work over the last six years, researchers at SRI International have found that hydrogen transfer (H-transfer) plays a critical role both in bond scission and in bond formation. Specifically, they have found that H-transfer includes not only abstraction of hydrogen by free radicals from donor solvent components, but also H-transfer from free radicals to closed-shell alkyl-aromatic structures. Secondly, this latter type of H-transfer is apparently required for the cleavage and the formation of strong bonds during coal conversion. It is evident that much more is going on in primary liquefaction reactions besides weak-bond cleavage. H-transfer is a double-edged sword, making possible in some cases what is desired -- bond cleavage -- and in other cases bringing about what is definitely not desired -- C-C and C-O bond formation. In summary, this research has accomplished the following:

- Highlighted the inadequacy of the traditional mechanism for liquefaction.

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[4] This section was written by Donald F. McMillen and Ripudaman Malhotra, SRI International.

- Observed the cleavage of strong bonds under coal liquefaction conditions.
- Demonstrated the existence of a new H-transfer mechanism, radical hydrogen-transfer (RHT) that engenders scission of strong bonds.
- Showed that RHT helps explain liquefaction solvent effectiveness.
- Showed that changes in selectivity and efficiency reflect shifts in competition between cleavage by free H-atoms and RHT (experiments and numerical modeling).

As a result of this research, the following aspects of H-transfer deserve particular attention in further work:

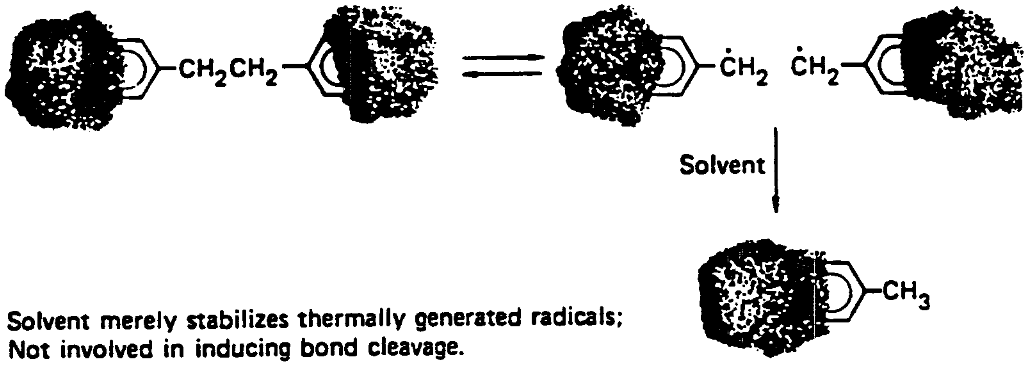
1. Identification of the structures responsible for retrograde reactions, and determination of the kinetics of these reactions.
2. Extraction of the process implications of competing H-transfer reactions for bond cleavage and retrogression during coal conversion.
3. Exploration of the role of electron transfer reactions and their facilitation by oxygen functional groups in coal liquefaction.
4. Characterization of the factors controlling the nature and the kinetics of catalyst fouling.

In the discussion below the findings are summarized which show how the details of H-transfer have led to a recently improved understanding of coal liquefaction phenomena. The basis is also shown for the key role played by H-transfer in the four areas listed above.

B. H-Transfer in Bond Cleavage

As a result of this work, researchers at SRI have been forced to conclude that the conventional weak-bond-scission/radical-capping liquefaction model is inadequate to explain the phenomenology of coal liquefaction. In the traditional picture, depicted in Figure 4-8a, the solvent serves merely to stabilize, or scavenge, radicals generated in

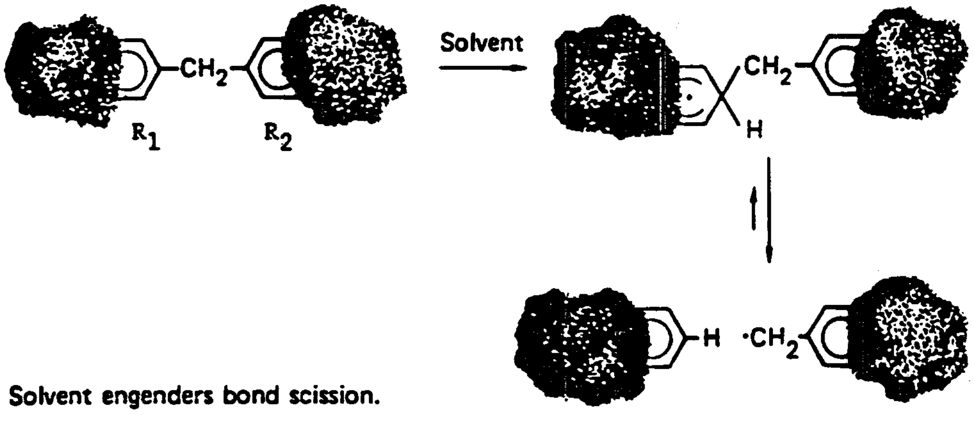
a) CONVENTIONAL MECHANISM:



Solvent merely stabilizes thermally generated radicals;
Not involved in inducing bond cleavage.

JA-7744-4

b) SOLVENT MEDIATED HYDROGENOLYSIS:



Solvent engenders bond scission.

JA-7744-5

R_1 = naphthyl, R_2 = phenyl

$t_{1/2}(PhCH_2\cdot \text{ loss}) = 10^{-10}s$
$t_{1/2}(H\cdot \text{ loss}) = 10^{-5}s$

Figure 4-8. Liquefaction Mechanisms

the spontaneous thermal scission of inherently weak links in the coal structure. Careful scrutiny of conversion data reveals that the measured scavenging abilities of various solvents, when compared on an all-other-things-being-equal basis, definitely do not correlate with their liquefaction effectiveness (39, 40). Some other factor besides radical capping ability clearly must distinguish between better and poorer liquefaction solvents.

Evidence is available to support the suggestion that the better solvents are those that more effectively mediate the transfer of hydrogen to positions on aromatic clusters bearing linkages (39-44). It is well known from the technology of high-temperature hydropyrolysis that formation of cyclohexadienyl intermediates, such as the one shown in Figure 4-8b, will lead extremely rapidly at 400°C to cleavage of virtually any except di-aryl linkages.

Vernon showed some years ago (45) that such intermediates were formed under rather severe liquefaction conditions, namely 450°C and high hydrogen pressures, leading to the unsymmetrical cleavage of bibenzyl. He correctly attributed this to the addition of free H-atoms. However, his data showed that increasing levels of donor solvent actually decreased the amount of hydrogenolysis; donor solvents generally improve coal conversion. Since strong-bond hydrogenolysis has been observed in model-compound/donor-solvent mixtures with no H_2 pressure (41), it can be speculated that methods of formation of the intermediate other than free H-atom addition must be important.

It is now known that the principal alternate means of cyclohexadienyl radical formation is the reaction depicted in Figure 4-9. This is an example of the bimolecular H-transfer process that we call "radical hydrogen-transfer" (RHT). It leads directly to the formation of the cleavage intermediates without the intervention of free H-atoms. This reaction was without precedent in the chemical literature when SRI's work was begun, but has since also been shown to occur by other workers

H- TRANSFER INDUCES SCISSION OF STRONG BONDS

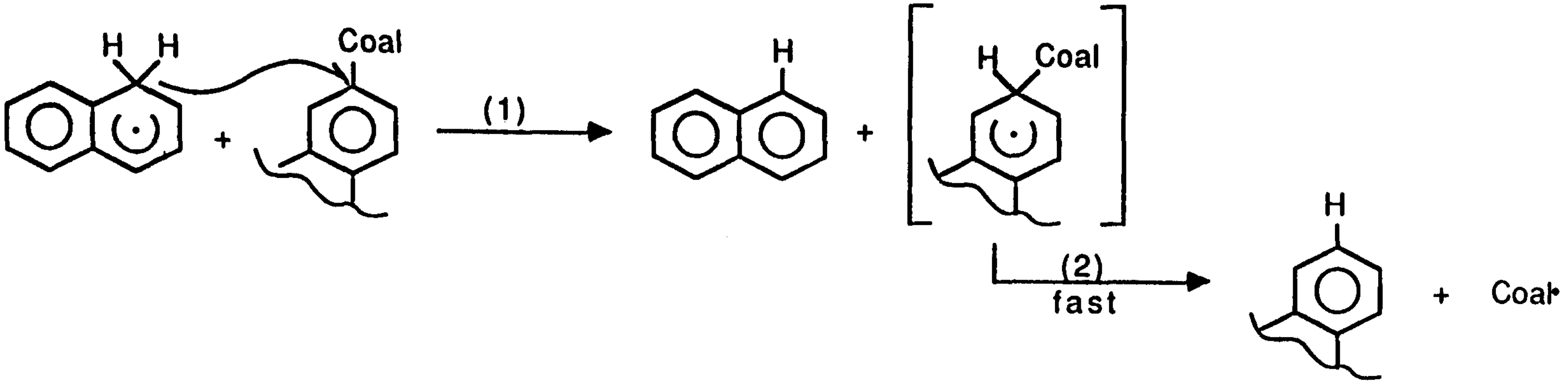


Figure 4-9. Scission of Strong Bonds Via H-Transfer

(46, 47), most notably by Stein and coworkers. Various aspects of the evidence for, and implications of, the RHT process are discussed in References 39-44.

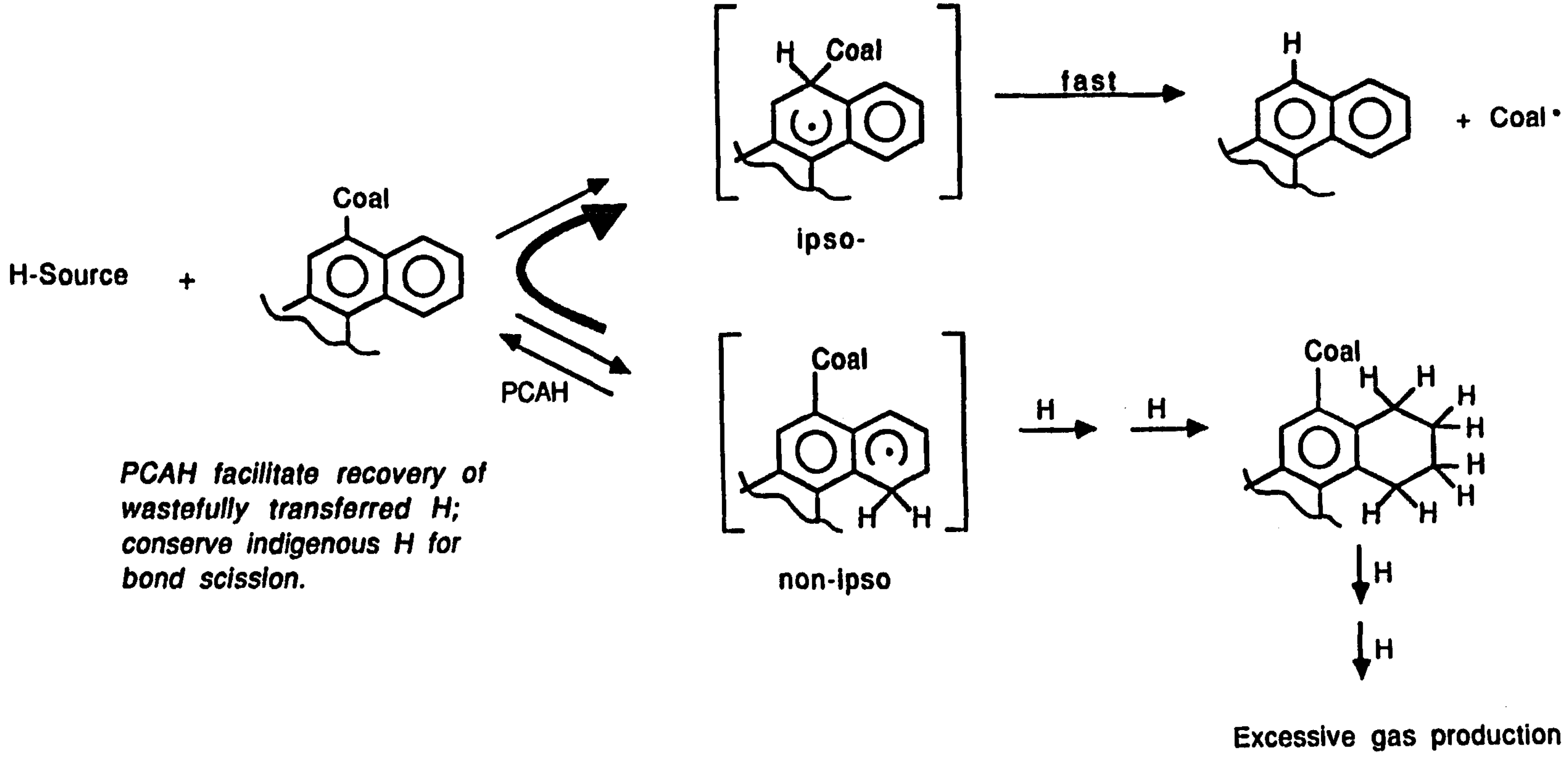
The RHT process is not under all liquefaction conditions dominant, but competes with free H-atoms in the H-transfer process. H-atoms are highly reactive and highly unselective, tending to bring about large amounts of aromatic ring reduction. H-atoms also abstract H (e.g., hydroaromatic H from the donor solvent) to make H_2. RHT is much more selective, tending to result in H-transfer to larger ring systems and selectively to position bearing linkages (see Figure 4-10). RHT also does not result in the formation of any H_2. Thus when there is a shift in the competition between free H-atoms and RHT, there will be a corresponding shift in the efficiency with which hydroaromatic hydrogen (from the donor solvent or the coal structure) is used to bring about linkage cleavage. If efficiency is important, it clearly is important to control such shifts in competition.

The general trend in the free H-atom/RHT competition is illustrated by the computed bond cleavage rates shown in Figure 4-11. These are the rates of H-transfer to one of the ipso positions of 1,2'-dinaphthylmethane, a compound used extensively for mechanistic studies and as a "surrogate" for the linkages in coals that are too strong to break by simple thermolysis. The rates are computed with a mechanistic numerical model consisting of all the initiation, termination, and competing H-transfer processes. The rates are shown in this figure for the anthracene/dihydroanthracene solvent system, at constant dihydroanthracene concentration and as a function of increasing anthracene content (40). The trend common to all aromatic/hydroaromatic solvent systems becomes clear upon consideration of just the upper three lines, indicating transfer to the ipso positions (i.e., cleavage) due to free H-atoms, RHT, and the sum of all H-transfer processes. The total rate changes relatively little as anthracene concentration changes; however, the free H-atom and RHT components change quite markedly as the

Figure 4-10. Rationale for Using Additives Rich in Polycyclic Aromatic Hydrocarbons (PCAH)

Premises:

1. **Significant contribution of induced bond cleavage.**
2. **Factors enhancing induced bond cleavage also tend to minimize retrogressive reactions.**



PCAH facilitate recovery of wastefully transferred H; conserve indigenous H for bond scission.

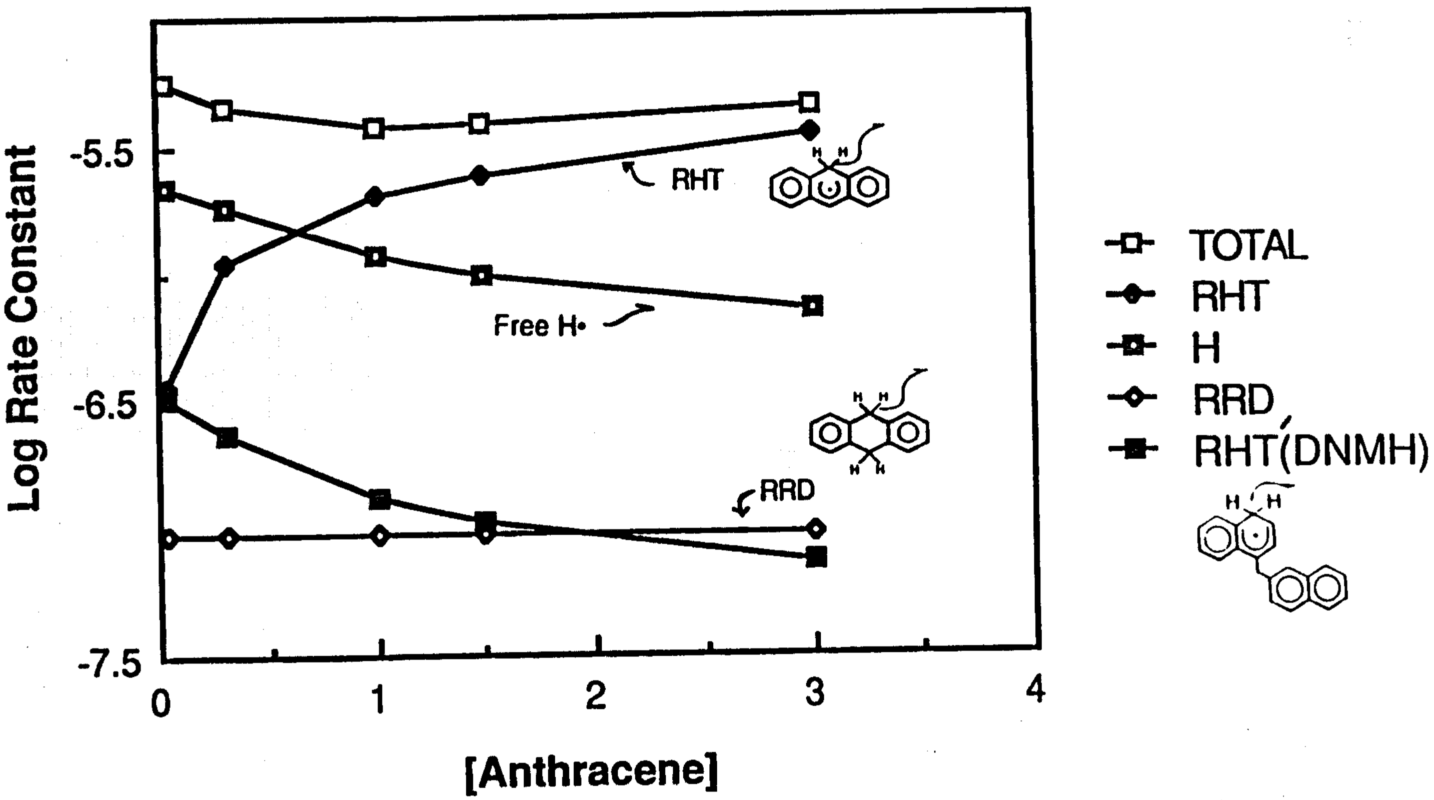


Figure 4-11. Computed Rates for Cleavage by Different Modes

aromatic content increases. At low anthracene concentrations the free H-atom contribution is most important, but it decreases markedly as the aromatic concentration approaches that of the hydroaromatic. The general character of these curves is the same in other solvent systems, so that the trend will always be toward increasing selectivity and efficiency of hydroaromatic hydrogen utilization as the aromatic component increases.

Recently, Mochida and coworkers have published (48) results of subbituminous and brown coal liquefaction that appear to bear out the predictions made on the basis of numerical modeling results like those shown above, i.e., increasing efficiencies with increasing aromatic contents. Figure 4-12 shows the product yields at the time of maximum oil yield for liquefaction of an Australian brown coal in 100 percent tetrahydrofluoranthene (THFL), a very good donor, and in 75 percent THFL/25 percent fluoranthene (FL). The oil yield (measured at the time of maximum oil yield in each case) increased when the amount of donor was decreased, and there was a 30-percent decrease in the gas yield. Even more marked was the 60-percent increase in H-utilization efficiency, as defined by oil yield per THFL consumed.

Other examples of this behavior can be found. Whitehurst and coworkers (49) had earlier reported modest improvements, and Cassidy et al. (50) have recently reported very striking improvements resulting from partial replacement of tetralin with pyrene. Presumably, the literature contains numerous other examples, some clearer than others.

The rate and efficiency factors discussed above are not limited to purely "thermal" conversion processes, but also have implications for catalytic systems. Figure 4-13 suggests that in multiphase systems such as coal liquefaction, the reaction medium plays a very important role in getting the H-atom activity generated at the catalyst surface to the coal-structure site where it is needed for hydrogenolysis. The ability to form these carrier radicals is presumably what enables heterogenous catalysts to function reasonably well in liquid-solid or in liquid-liquid

Figure 4-12. Replacing Part of Tetrahydrofluoranthene (H-Donor) by Fluoranthene (Non-Donor) Increases Efficiency of H-Utilization and Selectivity to Oils

	PRODUCT YIELD*	
THFL Content	100%	75%
Gas	18	13
Oil	63	68
Asph.	13	14
PA + Res.	6	5
$\frac{\text{Oil Yield}}{\text{THFL Consumption}}$	1.1	1.7

* Optimal yield for coal
conversion at 450°C/N_2
Solvent:Coal 3:1

Data from Mochida, 1988 (Ref. 48).

HYDROGEN SHUTTLING MAY ALSO BE IMPORTANT IN CATALYTIC LIQUEFACTION

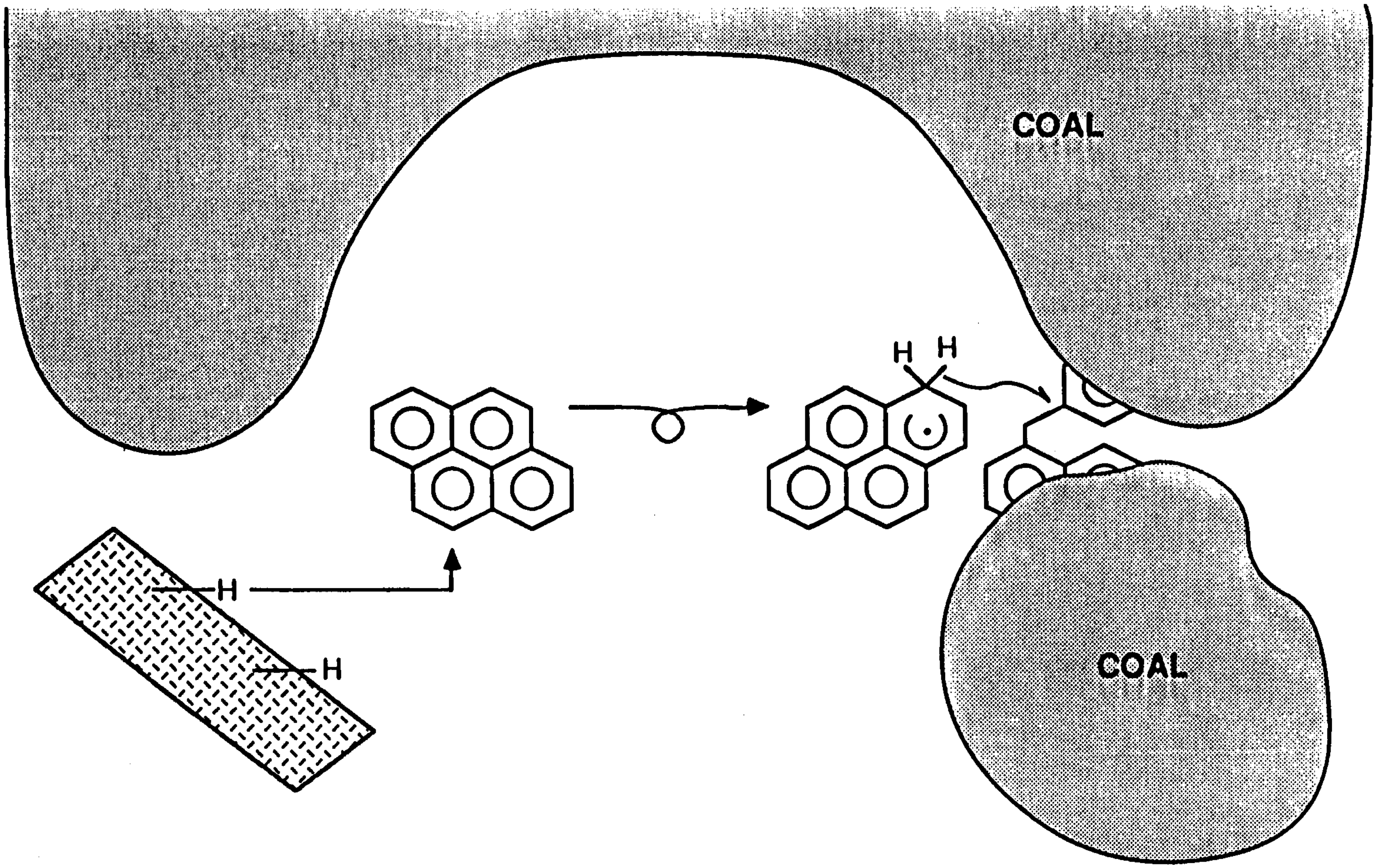


Figure 4-13. Importance of Hydrogen Shuttling in Catalytic Liquefaction

multiphase systems. Whether the rate of this H-atom transport is rate limiting depends of course on the particular circumstances. This is clearly illustrated by the recent study by Curtis and coworkers (51) of the interactions of catalysts, solvent, and coal in the context of coprocessing, where the solvent (i.e., petroleum resid) is normally terrible. Their results clearly illustrated that for the "homogeneous" catalyst molybdenum naphthenate, the nature of the solvent had relatively little impact, but for supported catalysts, the character of the solvent was quite important.

C. H-Transfer in Bond Formation

Radical recombination is often cited as the bond-forming mode in retrogressive reactions. While radical recombination undoubtedly occurs, and is presumably often significant, recombination of the dominant (i.e., resonance-stabilized) radicals generally only produces weak bonds. Radical recombination thus slows conversion but does not provide a route to unconvertible retrograde products. (Ring coupling of phenoxy radicals can produce moderately refractory linkages, such as the methylene linkage in benzylphenol.)

One presumably important route to truly refractory products involves radical addition to aromatic ring systems. Since the radicals most available for addition will again be resonance-stabilized radicals, the addition intermediates will be exactly the same class as the cleavage intermediates shown in Figure 4-9. The greater detail in Figure 4-14 shows that this intermediate can be formed either by hydrogen transfer to a position bearing a pre-existing linkage, or by addition of a coal radical to an aromatic system to generate a potential new linkage. In the conversion direction the critical step is H-transfer to the position bearing the linkage; in the retrograde direction the critical step is H-transfer from the intermediate to "lock" the new linkage into place.

As already alluded to, any intermediates except those where the linkage is bi-aryl react extremely rapidly at 400°C and show an

WHEN TEMPERATURE IS:
TOO LOW -- RETROGRESSION IS FAVORED
TOO HIGH -- HYDROGEN WASTE IS FAVORED

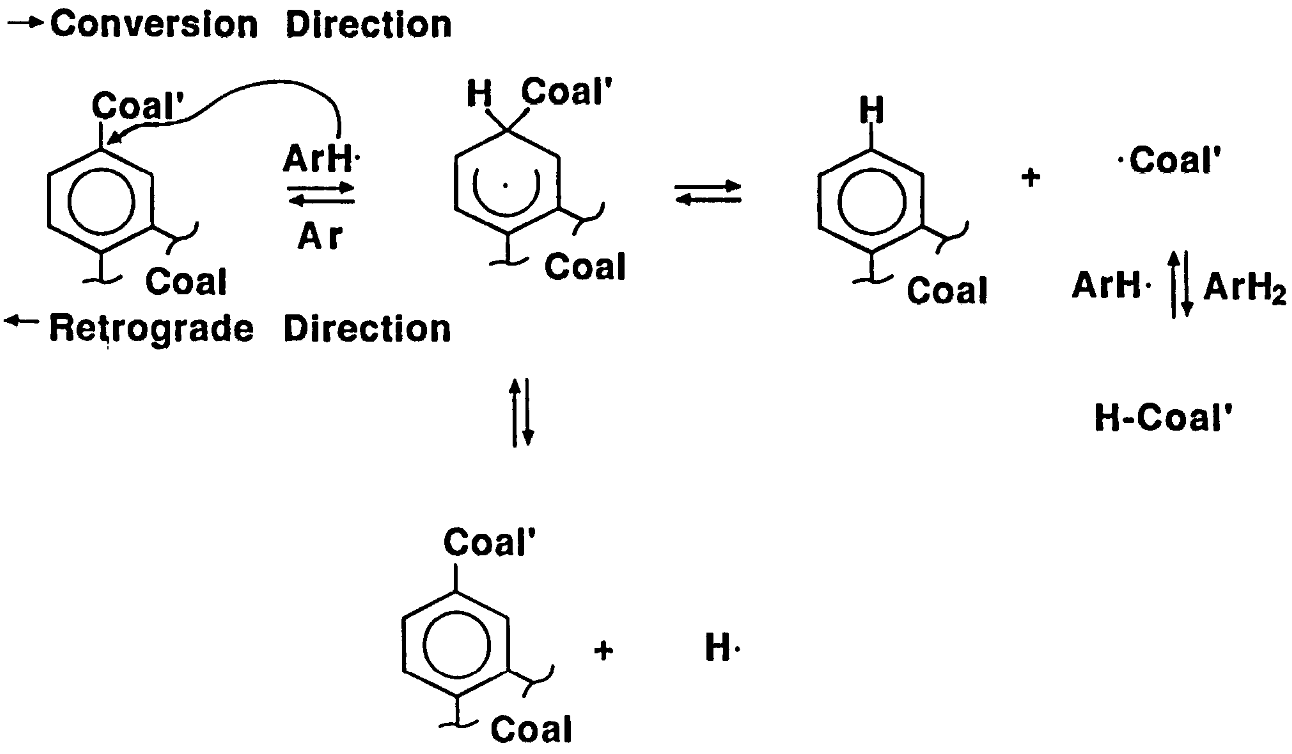


Figure 4-14. Intermediates in Liquefaction Reactions

overwhelming (> 10^4) preference for unimolecular elimination of the linkage, rather than of an H-atom. Thus, the chances that any individual addition intermediate will, under liquefaction conditions, be stabilized rather than revert to its component pieces are extremely small. This analysis if pertinent is heartening, since it means that retrograde reactions (which coal liquefaction phenomenology clearly show to be important) result from special circumstances that counteract the inherent tendency of the addition intermediates to preferentially lose the potential new linkage. This suggests in turn that an understanding of the special factors that sometimes permit H-removal to compete could lead to ways to substantially mitigate retrograde reactions.

Some of the factors that are known or expected to facilitate H-atom removal and stabilization of the intermediates are:

- Multiple opportunity for H-atom transfer
  - intramolecular
  - intermolecular (e.g., phase separation)
- Good H-atom acceptors
- Easily oxidizable substrate (ET followed by H+ loss)

It is useful to consider potential examples of several of these factors using the reaction sequence in Figure 4-14. If ·Coal' is an alkyl radical but is generated (e.g., by decarboxylation) at temperatures below the normal liquefaction range (i.e., where the concentration of carrier radicals ArH· is low), then the chances for moving the intermediate in the retrograde direction are increased: [Ar] is of course not lowered by the low temperature, but [ArH·] will be dramatically lowered.

At higher temperatures the situation becomes more complicated. When [ArH·] or [H·] is substantial, then the tendency of the intermediate to preferentially eliminate the linkage and move in the conversion direction can be counteracted by having multiple opportunities for stabilization of the addition intermediate. This can be provided in an intramolecular sense as for example by biaryl-type structures that hold the two retrograde candidates continually in close proximity, or in an intermolecular sense as for example by separation of a separate phase on a pre-heater or other surface. Hydrogen removal is also perhaps possible as proton loss, which could be extremely rapid following a one-electron oxidation. Hydroxy groups in the proper location could provide the key for this (52), as they stabilize the development of positive charge. The importance of multiple opportunity for coupling and of structures that may facilitate electron loss followed by proton transfer is illustrated in Figures 4-15 and 4-16.

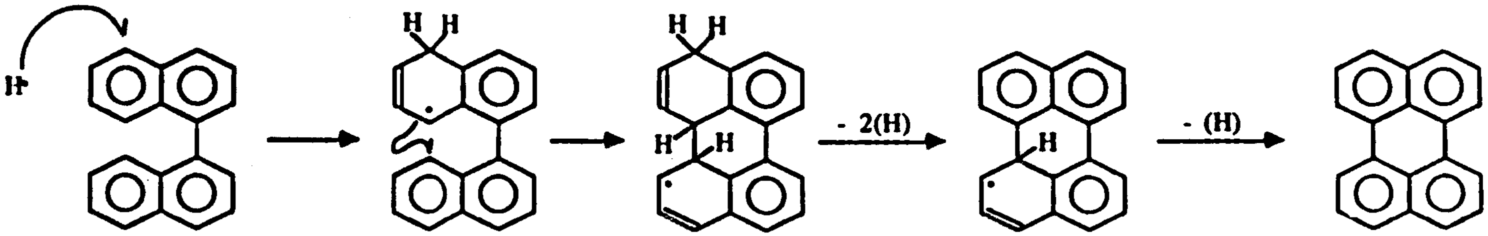
The presence of good H-atom acceptors does make it possible to remove H-atoms even without oxidation. In considering this factor the complexity of the issue suddenly becomes more evident: as discussed in the first part of this section, a high ArH· activity is preferred for high rates of bond cleavage, and a high reactivity of Ar as an H-acceptor is desired to increase H-utilization efficiency. However, the same capability of Ar for acting as an acceptor to increase efficiency by recovering wastefully transferred hydrogen also permits the Ar to stabilize retrograde intermediates.

This situation may indicate why the anthracene/dihydroanthracene system, which is slightly better at strong-bond hydrogenolysis, is generally found to be somewhat inferior to the phenanthrene/dihydrophenanthrene solvent system in actual coal liquefaction. The two solvent systems produce similar net reactivities from their respective pools of ArH· (as shown by measured cleavage rates under conditions where there is no retrogression of the surrogate structure), but anthracene is a far better H-acceptor than phenanthrene (53). When retrogressive reactions come into play, they could well make anthracene a poorer liquefaction system.

An example of the importance of this latter factor is given by the measured ring-closure and cleavage rates (54) shown in Figure 4-15. Whereas both of the measured cleavage rates are similar in the two

Figure 4-15. Ring Closure and Cleavage Rates of 1,1'-Binaphthyl and 1,2'-Dinaphthylmethane

	Rate constant/10^{-6} s^{-1}		
Solvent	BN Ring Closure	BN Cleavage	DNM Cleavage
An/ANH_2	2.1	0.3	6.9
Phen/$PhenH_2$	<0.2	0.5	3.4



The presence of hydroxy groups may facilitate one-electron oxidation and subsequent proton loss.

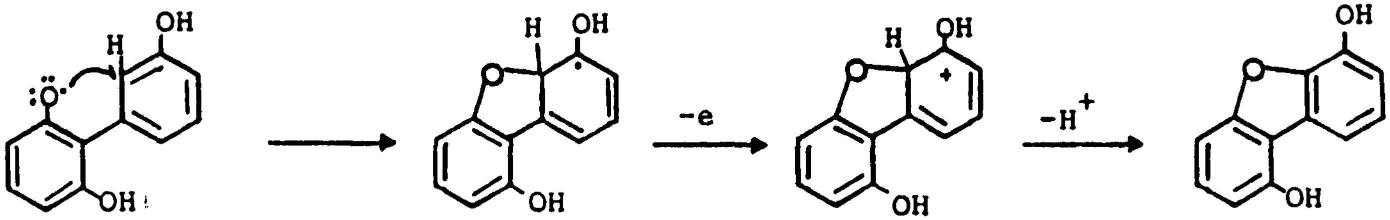


Figure 4-16. Electron Loss and Proton Transfer

solvent systems, ring closure is about 10 times faster in the anthracene system. Since the cleavage of DNM shows that the rates of H-transfer to the naphthalene system are about the same, H-transfer of one or more of the hydrogens away from the intermediates is clearly an important rate controlling step in perylene formation.

Once again, the relevance of H-transfer and retrogressive reactions is not limited to non-catalytic systems. Catalyst fouling because of carbon buildup is an important factor in the use of catalyst-intensive processes. While an important aspect of this fouling has been shown to involve adsorption of nitrogen-containing aromatics on the supported catalyst, facilitated removal of H-atoms (or protons) from retrograde intermediates could be responsible for the synthesis of some of these aza-aromatics (or their condensation to larger PCAH) directly on the catalyst (or reactor) surfaces.

D. Conclusions and Recommendations

The foregoing examples and discussion illustrate the double-edged-sword nature of hydrogen transfer and the important role that it plays in coal liquefaction. Without H-transfer strong bonds will not be broken, nor will refractory bonds, by and large, be formed. This fact makes a strong argument that optimum balancing of the various factors may well require an improved understanding of the chemical details that control this balance.

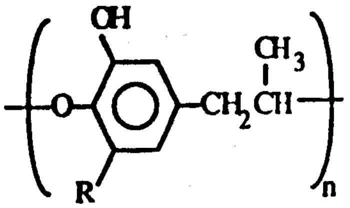
The recent work that has added solvent-mediated hydrogenolysis of strong bonds to the picture of coal liquefaction constitutes a substantial step in this direction. It has provided the ability to understand, and even predict, some surprising trends in complex liquefaction phenomena. This picture needs to be improved, extended to larger PCAH solvent components, and integrated with a picture of the impact of H-transfer reactions on retrograde processes. Successful pursuit of the four areas listed above in the introduction would, be a significant additional step in obtaining a useful understanding of the many-faceted nature of H-transfer in coal conversion.

A study of the reactions of structures such as those shown in Figure 4-17, under various conversion conditions, would substantially enhance the current understanding of retrograde processes in coal conversion. These structures are intended to be most relevant to low-rank coals, which tend to be most susceptible to retrograde reactions. Low-rank coals contain hydroxy groups that facilitate hydrogen, electron, and proton transfer; they contain carboxyl groups which provide probable cross-link sites via low-temperature decarboxylation; and they contain the three-atom chains commonly associated with lignin remnants.

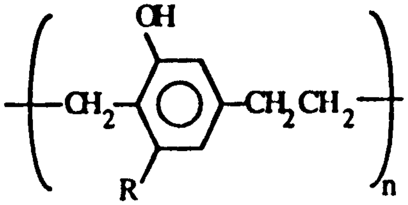
While it should be realized that such surrogate structures cannot be expected to mimic real coals in all aspects, definitive information about the factors affecting chemical transformations cannot be obtained unless the structures are known. The structures shown here are more closely related to real coals than the model compounds typically studied, and are at the same time simple enough that judicious choice of experimental conditions and analytical techniques will still make it possible to obtain definitive information about their bond-cleavage and cross-linking reactions.

In addition, wherever possible, further advantage should be taken of the hybrid studies approach to bridge the gap between the "definitive" information obtained from model compound studies and the more "relevant" but more vague data obtained with real coals. Hybrid studies can be done with physical mixtures of coals and surrogate structures, with coals that have had known structures covalently bonded to them, and with organic or inorganic polymeric matrices that have model structures bonded to them.

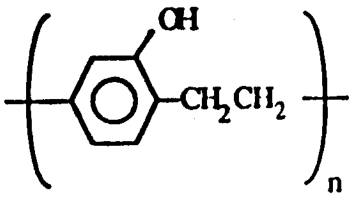
Figure 4-17. Candidate Structures for Study of Retrogressive Reactions



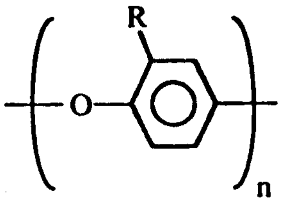
type IV R = H
COOH
OCH_3



type V R = H
COOH
OCH_3



type VI



type VII R = H
OH
OCH_3

4.2.3 Catalysis of Direct Liquefaction[5]

4.2.3.1. Introduction

Since coal was first converted to liquids and gases (55), efforts have been made to improve the process of bond rupture to make small molecules, and to transfer hydrogen to stabilize these molecules and prevent polymerization reactions. A major component of these efforts has been the use of various materials as catalysts. Hundreds of compounds and combinations have been tested and many used for coal conversion processing. The selection of the catalytic materials has been sometimes accidental, sometimes based on past experience. However, because of the complexities of both the material involved -- coal -- and the reactions to be catalyzed or controlled, no simple rules have been found to guide the catalyst selection process.

A short history of catalysis has recently been presented by one of the pioneers in this area (56). Trial-and-error studies requiring mammoth efforts by numerous research groups led investigators to settle upon molybdenum, iron or tungsten sulfides as the active component of the catalyst (57).

Two operating philosophies have evolved: one employs a cheap, low-activity catalyst with a high partial pressure of hydrogen and the other utilizes lower hydrogen pressure and compensates with a more active, more expensive catalyst. European technology usually followed the cheap-catalyst, high-pressure approach while U.S. industries have usually opted for the lower-pressure, higher-catalyst-cost process. Thus, European processes have generally utilized iron (e.g., low-area red mud) or unsupported MoS_2 or WS_2 as the catalyst while U.S. processes normally employ high-area supported catalysts. Consequently, the typical European process is more amenable to once-through throw-away catalysts.

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[5] This section was written by Burtron H. Davis, Kentucky Energy Cabinet Laboratory.

The FERWG-II report (58) identified important process development and exploratory work on catalytic liquefaction in 1980, and provided a list of references through about 1978. A listing of this work and the current status is provided in Table 4-2. It is apparent that those works in Table 4-2 which attained their objectives utilized well-known catalysts and/or catalytic processing. Thus, at best, only incremental advances have occurred in catalyst developments in liquefaction. For example, Ruhrkohle was able to reduce the operating pressure from 700 to 300 bar by process advances; they utilized the same catalyst at both pressures (59). The H-Coal and EDS processes utilized catalysts that were similar to petroleum hydrotreating catalysts. Included in Table 4-2 is the SRC process. With time the pilot plant for the SRC-I process at Wilsonville has evolved to incorporate several processing schemes that utilize multiple reactors. Incorporated into these studies have been tests with several catalysts, including those with bimodal catalyst supports.

4.2.3.2 Primary Liquefaction Catalysis

A. Diffusion Constraints

The hydroliquefaction of coal using heterogeneous catalysts may be strongly influenced by the diffusion of coal components into the pores of the catalysts, and the problem is compounded when the catalyst is in pellet form. This is not surprising, when the size of the molecules and/or micellar-type structures is considered. For example, a range of 15 to 50 A diameter has been estimated for a moiety of molecular weight of 1000 amu (60), with the actual size depending on configuration. Catalyst pore structure is an important variable in the optimization of three important catalyst performance parameters: conversion, selectivity, and deactivation. These parameters are related to one another from the viewpoint of the chemical reaction(s) which occur in the catalyst and thus share a common dependence upon pore diffusion effects. In view of the extent of research on this problem during the past 8 years, this topic will be considered in some detail.

Table 4-2. Important Process Development and Exploratory Work

Name	Catalyst	Process	Status Today
H-Coal	$CoMo/Al_2O_3$	Ebullated Bed	200-600 ton/day plant operated for 11 runs; met design criterion; standby for commercialization
EDS	$CoMo/Al_2O_3$	External Hydrogenation Reactor	Successfully demonstrated to operate on Illinois #6, Wyoming subbituminous, and Texas lignite; design for liquefaction section of 20-30,000 ton/day plant
Dow	MoS_2	Colloidal, unsupported	
SRC	None	-------	Dormant; commercial plant design completed?
Synthoil	$CoMo/Al_2O_3$	Fixed Bed	Development ceased in early 1980s
Consol	$ZnCl_2$	Molten Salt	Development ceased in early 1980s
University of Utah	$ZnCl_2$	Molten Salt	Development ceased in early 1980s
Ruhrkohle/ Bergbauforshung	Iron	------	Reduced operating pressure from 700 to 300 bars decreased conversion costs.

Source: Ref. 56.

B. Relationship Between Conversion and Selectivity

One of the most demanding tasks of the coal liquefaction research scientist is to define conversion. Today, this is usually done on the basis of physical properties: (1) separation by solubility classes (oils, asphaltenes, preasphaltenes, and residue) or (2) separation by boiling point fractions up to 950°F. In practice the distillate fraction is equal to oils as determined by heptane solubility. Conversion and hence catalytic activity and selectivity are then determined from these broad kinetic lumps (61).

Unfortunately, the above lumps do not provide chemical information upon which to develop a scientific basis to provide mechanistic approaches to coal liquefaction catalysis. The lack of definition of the products severely limits advances in our understanding of coal liquefaction catalysis.

C. Impact of Pore Size of Support

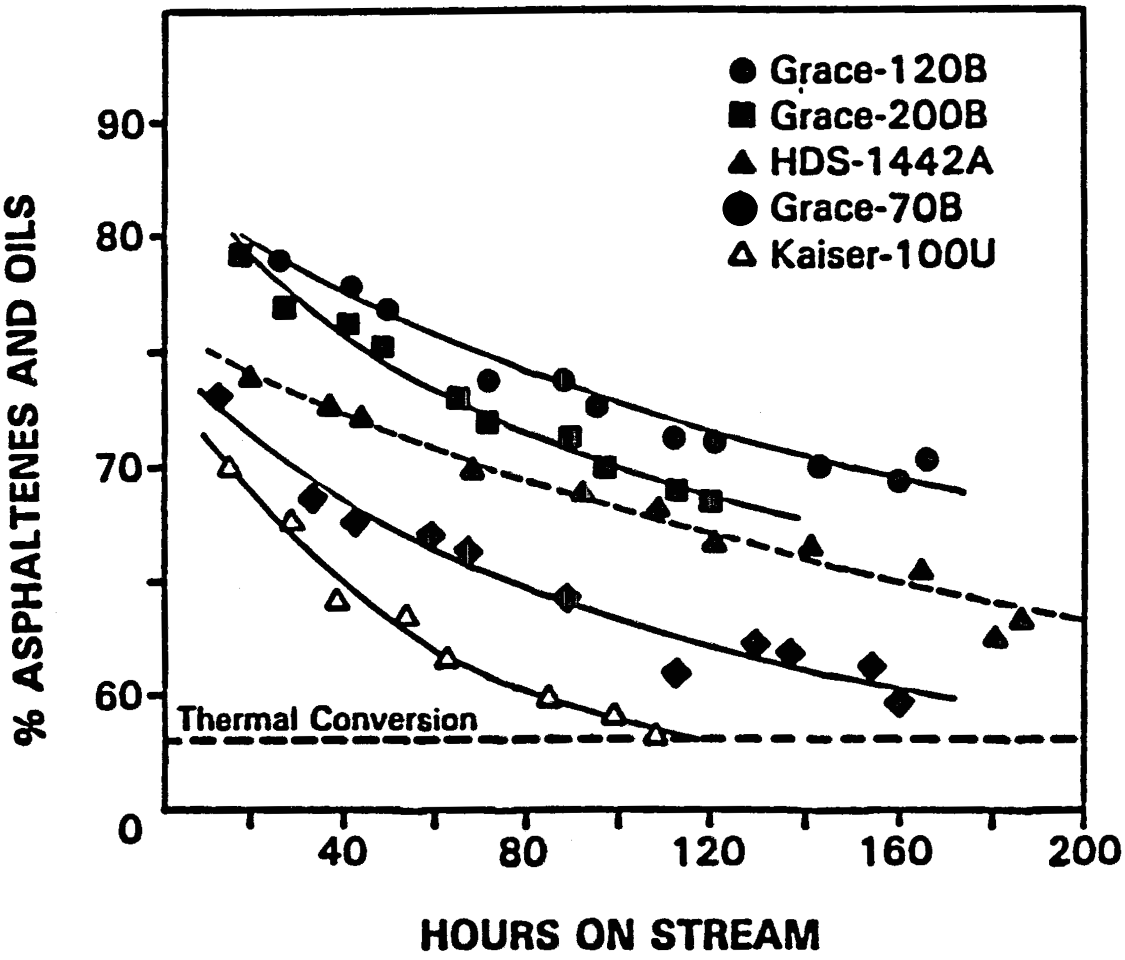
One of the earliest studies aimed specifically at the pore diffusion effect was reported by Yen et al. (62) in 1976. They compared coal conversion in the presence of identical masses of catalysts having unimodel pore size distributions with peak pore diameters of 220 A and 120 A. Their results showed that the large-pore (220 A) catalyst gave better overall conversion of the coal; this occurred even though the small-pore (120 A) catalyst had a larger specific surface area than the large-pore catalyst.

Bertolacini et al. (63) investigated a number of catalysts of Co or Ni with either Mo or W on a variety of aluminas, all but one with a bimodal pore-size distribution. Production of asphaltenes and oils increased as the mean mesopore size increased and the unimodal catalyst was least active; this trend continued for the life of the catalyst (Figure 4-18). Even in this careful study, probably the best effort reported to date to define this problem, the investigators recognized several complications:

- a constant catalyst mass, not constant surface area, was present in the reactor
- the catalyst pore volume in the reactor varied from one catalyst to another
- Co(Ni) and Mo(W) levels were not adjusted to maintain constant coverage
- only one residence time was used.

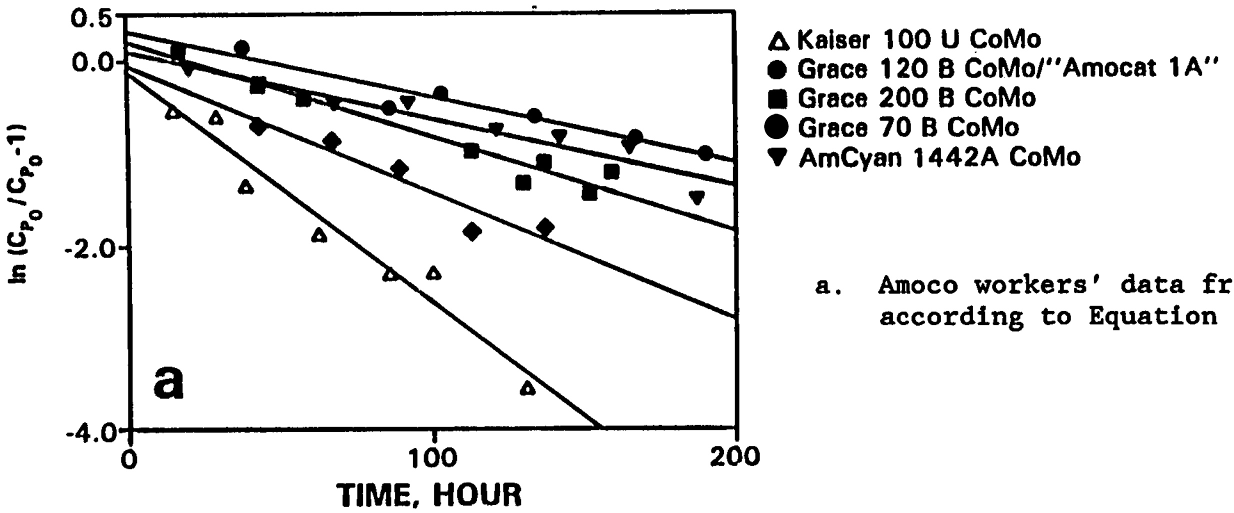
One conclusion derived from the data in Figure 4-18 is that a bimodal pore size distribution is beneficial. However, these data can be correlated equally well with a model that requires only that: (1) activity is proportional to the total surface area in the reactor, (2) deactivation resistance depends mainly upon the pore volume available for storing contaminants and (3) the rate of contaminant accumulation depends only upon the extent of deactivation (Figure 4-19). This latter analysis points out the difficulties inherent in assigning the results of kinetic measurements to pore diffusion effects when other variables are present, especially deactivating catalysts.

The comparison of catalysts under conditions of constant surface area in the reactor and constant dispersion of active ingredient was carried out in a study published in 1981 by Ho and Weller (60). Ho and Weller performed hydroliquefaction in the presence of unimodal-pore CoMo catalysts with mean pore diameters of 90 A, 180 A, 530 A and 850 A. The Mo loading was maintained at 3g MoO_3 per square meter of alumina surface area, and the catalyst-to-coal mass ratio was based on the amount of MoO_3 and CoO, rather than total catalyst. The most significant results were a trend showing total coal conversion increasing with catalyst pore size. Asphaltene concentration in the product increased even more than total conversion as the pore size increased; oil concentration either decreased or remained constant. Ho and Weller suggested that the production of asphaltenes is diffusion-limited in the small-pore (90 A and 180 A diameter) catalysts. Apparently, the production of oils is not diffusion

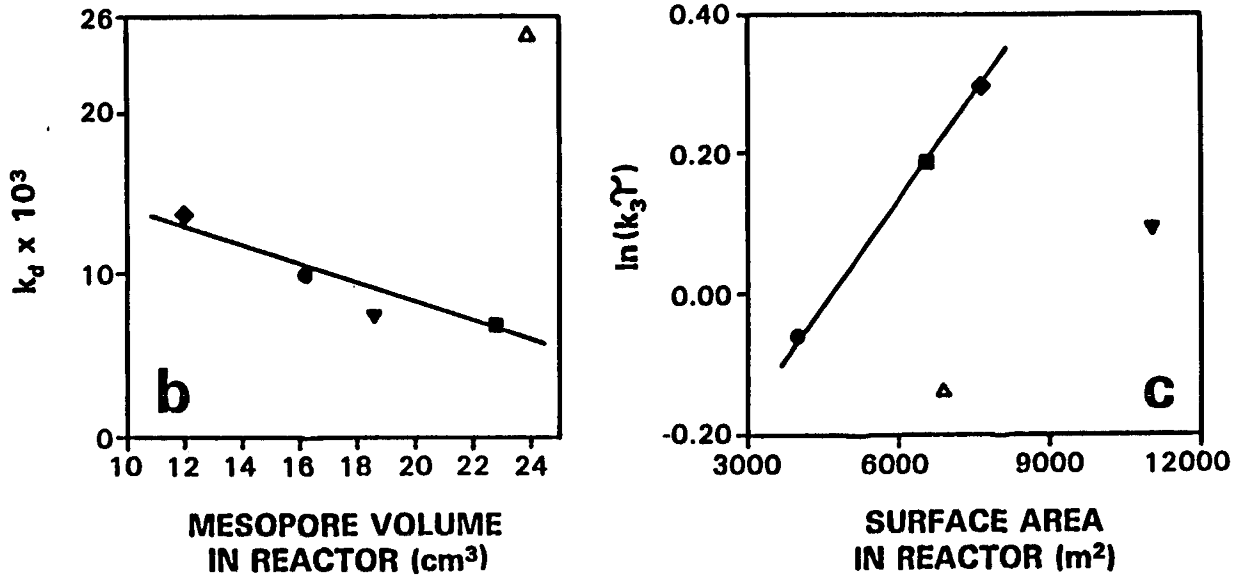


Amoco Oil Co. data showing relative yields of asphaltenes and oils from coal, employing five different Co-Mo catalysts with different pore structures reproduced from 1979 Electric Power Research Institute (EPRI) Report AF-1084, "Catalyst Development for Coal Liquefaction".

Figure 4-18. Asphaltene and Oil Production as a Function of Catalyst Type



a. Amoco workers' data from Fig. 4-18 plotted according to Equation 14 of Ref. 63.



b&c. Deactivation rate constant (k_d), and initial rate activity (ln k_3) from (a).

Figure 4-19. Pore Diffusion Effects in Catalysts limited to the same extent, so that as pore size increases, the net result is an apparent enhanced selectivity to asphaltenes.

Perhaps the most quantitative attempt to examine the role of pore diffusion in coal liquefaction was recently published by workers at Auburn University (64, 65). In this study the authors obtained catalyst effectiveness factors with a model having parallel thermal and catalytic kinetics and a non-deactivating catalyst. The effectiveness factor for the conversion of preasphaltenes to asphaltenes was essentially zero; hence, diffusion prevents the catalyst from participating in this reaction. The factor for converting asphaltenes to oils is 0.66 rather than 1.0 for no diffusion limitations.

The Gollakota et al. (65) model has not been used at this writing to compare catalysts of different pore sizes. Such a comparison would provide additional credibility to the conclusions concerning effectiveness factors; nevertheless, it is probably the best model yet published for pore diffusion effects in coal liquefaction.

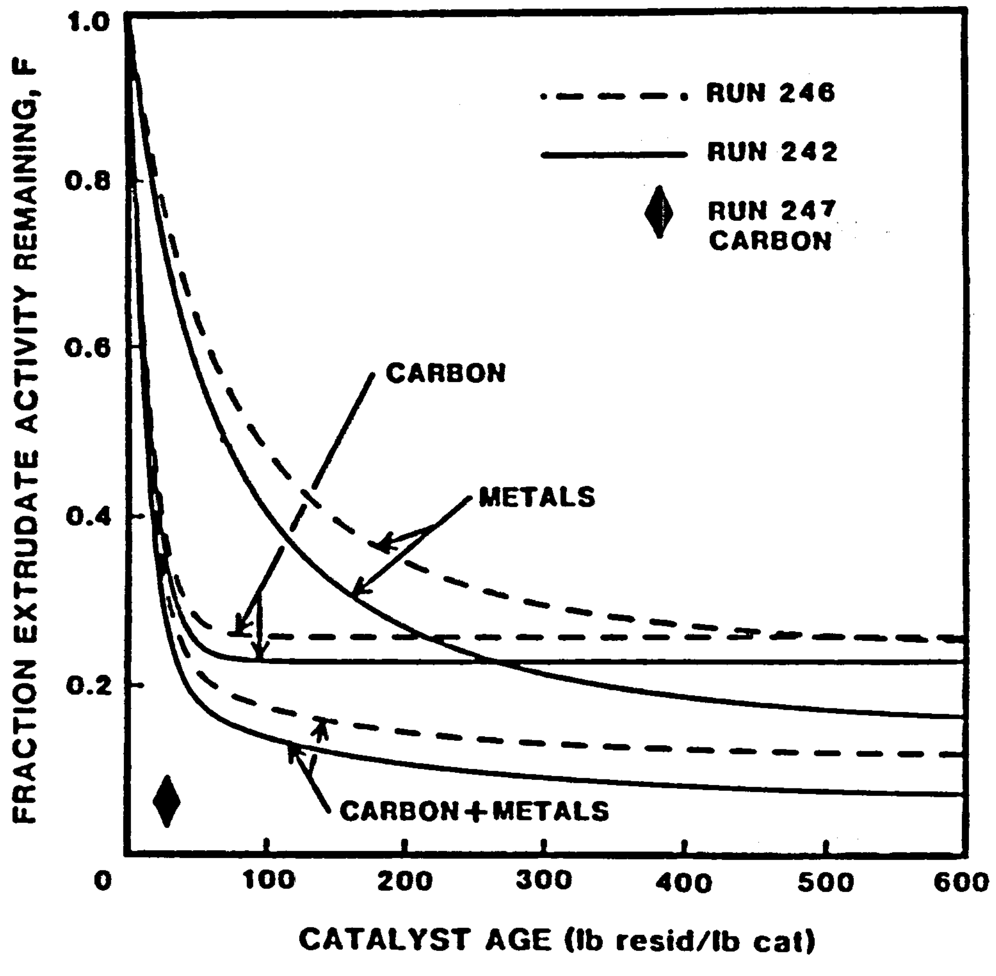
4.2.3.3 Deactivation of Coal Liquefaction Catalysts

A. Carbon Accumulation

In nearly all cases catalysts used in converting heavy resids undergo a very rapid deactivation over a period of hours or days, and residual activity then persists for many months. Thus, the industrial process does not take advantage of the high initial activity but utilizes the period of relatively slow deactivation (Figure 4-20).

Contaminant accumulation is presumably an important aging factor since careful regeneration of a supported catalyst usually returns the original surface area. Three major types of contaminants accumulate in coal liquefaction catalysts: coke, trace metals, and alkali. The nature of these contaminants is a major research concern, as is the complex interaction between these contaminants and the process. Much research has been concerned with specific contaminants in coal liquefaction catalysts; examples include basic nitrogen compounds as poisons (66-71),

Initial extrudate activity losses range from 80% with DITSL processing to 95% with RITSL processing.



Source: Ref. 82

Figure 4-20. Catalyst Activity Versus Catalyst Age the nature of Fe and Ti contaminants (72-77), and the adsorption of alkali metals (69, 72, 78).

Numerous investigators have used extensive electron microprobe analysis and reported coke deposition profiles which are uniform or appear mildly diffusion limited (63, 67, 68, 72, 79-81) while few measurements of severely diffusion limited coke profiles have been reported. However, the predicted major pore sizes do not agree with measured data obtained using mercury porosimetry.

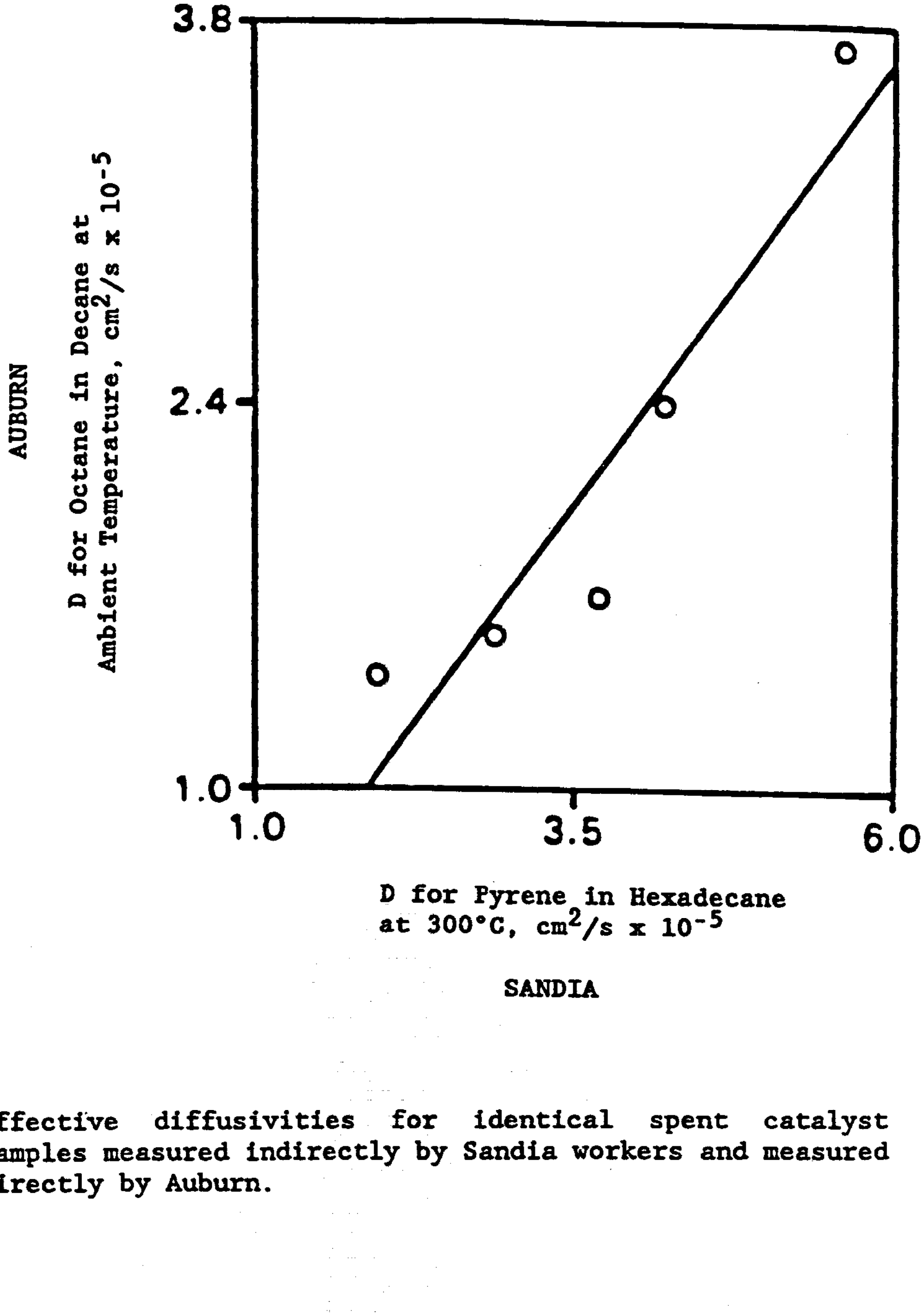
Attempts to precisely model accumulation kinetics must make the best possible use of experimental data. Otherwise, there is no advantage gained in constructing detailed models; less detailed, more empirical models are equally verifiable. Along this line of reasoning, a model was constructed by Sandia Laboratory investigators (82, 83). The combined effects of carbon and metals contamination in a mixed-contamination type model incorporated three additional characterization features: (1) coke, measured by microprobe analysis, is often distributed uniformly in the catalyst pellet, (2) metal deposits often tend to approximate the "shell-progressive" pattern, and (3) the pore volume losses due to carbon are much greater than those due to metals because the metals accumulate in much lower amounts and are denser deposits. The Sandia workers compared activity for pyrene hydrogenation for a series of aged catalysts, both in the pellet and finely ground form. They concluded that for catalysts withdrawn early in a Wilsonville run, the dominant deactivation of Ni-Mo-alumina catalysts was uniform poisoning due to carbonaceous deposits.

Workers at Auburn University (84) attempted to measure the loss of effective diffusivity in spent catalysts from the Wilsonville process using a more fundamental approach. Their method was to measure the rate of uptake of octane from an octane-decane solution in fresh and aged catalysts. The model used to calculate the effective diffusivity was similar to that derived by Ma and Evans (85) and assumes, like the Sandia model, that the effective diffusivity does not change with position in the catalyst pellet. It is interesting that the effective diffusivities measured for catalysts from the same Wilsonville run using the two methods, the Sandia reaction model and the Auburn diffusion model, compare favorably with one another, as shown in Figure 4-21. Both sets of measurements indicate that the greatest loss in effective diffusivity occurs early in the run when carbon accumulation is rapid.

Finally, a very different type of study of coke deposition kinetics in coal liquefaction catalysts has been published by Adkins et al. (81). This model is based entirely on the pore-size distributions calculated from gas adsorption isotherms. The concept is based in part upon previous work by Prasher et al. (86) and is similar to recent work applied to the problem of carbon combustion from porous catalysts by Chang and Perlmutter (87). In this model the rate of deposition of carbon in a pore under steady-state conditions is equal to the rate of diffusion. The results were consistent with the diffusion term in the model not varying with pore size: an apparent combination of a rapidly saturating uniform poisoning from the "start-up" and a slow poisoning due to the resid associated species.

B. Combined Effects of Carbon and Metals

Currently, the Sandia model is the most detailed attempt to combine the effects of carbon and metals in deactivating coal liquefaction catalysts, including losses in diffusivity due to early fouling. With the exception of considering metals deposition to be a shell progressive mechanism instead of a combination of uniform and intermediate poisoning mechanisms, the Sandia model is in good agreement with most of the characterization and detailed modeling efforts. It also has the advantage of comprising straightforward algebraic equations instead of differential equations. It does not, however, predict the kinetics of the coking or metals deposition processes and must be combined with other models in order to be used in, for example, reactor optimization studies.



Effective diffusivities for identical spent catalyst samples measured indirectly by Sandia workers and measured directly by Auburn.

Figure 4-21. Effective Diffusivities for Spent Catalyst Samples

Pore diffusion effects have been demonstrated conclusively, and some tentative conclusions can be made. These include (61):

- For "typical" coal liquefaction catalysts, coal dissolution is rapidly achieved thermally, under appropriate conditions, and the only likely role of the catalyst is indirect, through the donor solvent hydrogenation. Oil production almost certainly occurs at a higher effectiveness factor than preasphaltene conversion (production of asphaltenes and oils).
- Pore structure bimodality has an effect on catalyst performance and catalyst deactivation resistance. There is, however, no single explanation for the observed effects. Both activity and deactivation resistance are improved in many cases by bimodal pore structures.
- Mesopore size has been demonstrated to affect catalyst performance. For the most part, the observed effects are associated with diffusional restrictions combined with trade-offs involving catalyst surface area and catalyst pore volume.
- Coke formation in coal liquefaction catalysts is more likely associated with oil production or upgrading than with preasphaltene conversion. Adsorption phenomena may play an important role in coke formation; strongly adsorbed compounds such as basic nitrogen compounds are especially suspect. In keeping with the link to oil production, coke formation is probably not diffusion limited in the majority of cases.
- Conversely, metals accumulation is subject to diffusion limits ranging from intermediate (for example, corresponding to a Thiele modulus of 3) to very strong. Metals can often be correlated with process streams concentrated in preasphaltenes, but ash components may also be involved. Not surprisingly, catalysts with bimodal pore structures often show significantly higher rates of metals adsorption.
- Currently no adequate simple model exists for incorporating carbon and metals accumulation into predictions of catalyst deactivation.

It is clear that there are many unanswered questions involving the engineering implications of pore diffusion effects. The area most in need of research is not the development of more sophisticated mathematical models, but rather applied research which can provide shortcuts and all-important model verification.

In most of these studies, the accumulation of carbon has been considered without regard to composition. Recently, it has been reported that most of the carbon on aged Wilsonville plant catalysts is present as distinct nitrogen compounds (88). Furthermore, these nitrogen compounds are in dynamic equilibrium, exposing a fraction of the total acid sites at any instance. In addition, sodium can irreversibly displace this "coke" over a period of days or weeks so that 50-80 percent of the "coke" is removed.

C. Metals Accumulation

Fe and Ti are frequently reported to be the major metals deposited on coal liquefaction catalysts, although alkali metals are often observed at similar levels. Numerous investigators have measured penetration profiles for Fe and Ti in coal liquefaction catalysts and found them to be indicative of intermediate to strong diffusion limitations (63, 71, 72, 82, 83, 89-91). Equally debated is the source of these contaminants, i.e., whether they are associated with organometallics (e.g. porphyrins) or inorganic particles. For Ti, as an example, some authors argue for organometallics (72, 73, 74, 78, 83) while others argue for inorganic origins (74, 75); neither viewpoint has been proven conclusively. Based upon metal profiles for more than 50 catalyst withdrawal periods of the Wilsonville plant, it was concluded that the Thiele modulus for the deposition of Fe and Ti was somewhere between 3 and 7; this corresponds to a shell-progressive poisoning (92).

4.2.3.4. Research Leading to Revolutionary Advances

The above illustrates evolutionary research results in a well established area. The period since the FERWG-II report also includes much activity in a search for new catalytic materials with the potential for providing revolutionary advances in coal liquefaction. In general, the goal of this research has been to obtain catalysts that will operate at significantly lower temperature or pressure, or both.

Considerable effort has been expended, especially internationally, to apply superacids or other superactive catalysts to activate and cleave chemical bonds at low temperatures. For example, Olah, et al. have investigated a number of superacids for bond cleavage of both model compounds and coal (93). While some success has been attained, the breakthrough is not in hand.

Probably the most active research topic in the area in the U.S. is the activation of CH bonds. The current excitement comes from recent discoveries that some transition-metal complexes can catalyze reactions in alkanes with considerable selectivity and do this at ambient conditions! Currently, most of the publicized findings are from academe; few industrial researchers have disseminated their results. Much of the work in this area to date has been directed more to specialty chemicals than directly to coal liquefaction, but the scientific advances in understanding should be applicable to this area.

Much of the research to develop newer catalyst supports has focused upon the use of novel, complex metal oxides. For example, Tanabe and coworkers (94) utilized a variety of supports in an effort to obtain a balance of acidity and hydrogenation; it appears that the balance needed varies from coal to coal. Sandia workers (95) have developed a promising catalyst that utilizes alkoxide-derived hydrous metal oxides, and have reported special success with palladium on titanium oxide catalyst. This latter catalyst has shown sufficient promise that large-scale pilot-plant testing has been described.

While the use of colloidal catalysts is not new to coal liquefaction, novel approaches to unsupported and even supported materials are being developed. A novel variation of this is the utilization of an encapsulated catalyst as a means of attaining a controlled catalyst size (96).

Anderson and Miin (97) tested more than 80 catalysts for the conversion of bituminous coals at mild (300°C or lower) conditions. They found only one property that directly correlated with the yield of products; this property was the electronic softness of the Lewis acid.

The authors believed that the most effective catalysts combined with functional groups of the coal to produce more stable ion pairs to react with hydrogen.

Bergius first attempted to directly hydrogenate coal in the presence of a catalyst but without an added solvent. The inability to prevent thermal excursions producing severe overheating caused this approach to be abandoned, and the use of a process solvent was introduced. Recently, renewed interest in this mode of operation has developed, primarily as a result of studies by Derbyshire and coworkers (98) as well as in low solvent-to-coal operations (99).

4.2.3.5. Upgrading

Coal liquids upgrading has not received as much attention as coal liquefaction. Nearly all of the studies in this area have concentrated on modifications of the catalytic upgrading of petroleum. Sullivan and his associates at Chevron (100) have shown that, while products from various liquefaction processes vary, conventional catalysts can be employed. In general, it is only when heavier resids are included that upgrading becomes a problem. With respect to this, it is anticipated that the current emphasis upon catalytic upgrading of heavy petroleum resids, such as the Engelhard ARC process, will provide many advances in both catalytic materials and process configurations.

Another area that cannot be viewed as new is the use of a molten metal as a catalyst. Included is the continued use of tin and zinc; at the same time this is being expanded to other elements. One of the problems associated with preventing retrograde reactions at high temperatures has been limitations on "copying" the radicals formed. Another approach may be to inhibit the rapid formation of radicals during the initial rapid heat-up period so that the demand for catalytically generated hydrogen donors may be significantly decreased. Metals like tin may be able to serve this purpose (101).

It is not possible to cover all topics, nor to cover in depth any of the topics, in this space. The reviews and references in the FERWG-II report are equally valid today. For reviews of a more recent vintage, reference can be made to 56, 61, 82, 88, 102-109.

4.2.3.6. Areas of Research Needs

One of the important research areas is to continue to make the evolutionary advances in catalyst systems currently utilized: Co or Ni with Mo or W. These studies should emphasize the slow-aging region that is utilized by industry rather than the initial rapid-aging period. The role of porosity and surface acidity should be defined in studies where support coverage remains constant, and comparisons made where the pore volume or surface area in the reactor is held constant from catalyst to catalyst.

Catalyst stability studies should be conducted with the view of defining how contaminant deposition varies with time and how these depositions affect both physical (mass transport, heat transfer, further contamination, etc.) and chemical (HDN, hydrogenation, HDS, etc.) properties.

While not normally viewed as catalyst research, special emphasis should be paid to developing improved methods for characterizing coal liquefaction feed and product streams. Catalyst activity should be measured in terms of chemically significant parameters in addition to product yields based upon boiling point or solubility fractions.

Special efforts should be made to test catalytic materials under conditions that include, as well as exclude, equilibrium limited conversions. For example, typical hydroprocessing involves an olefin intermediate. Thus, studies should be made at conditions where hydrogenation-dehydrogenation is at the equilibrium value as well as removed from this point. Investigators should be encouraged to show, by analysis of products, those steps of the reaction network that are at equilibrium for the various catalytic selectivities.

The search for new, novel catalyst systems should be emphasized. Included in this should be an effort to learn whether the formation of the large coal radicals from coal can be inhibited so that the demands of hydrogen transfer during the initial introduction of a coal particle into the reactor could be made less severe.

Catalyst characterization results were described in some of the examples in this brief discussion. During the past 20 years the increase in the number of surface and bulk instrumental techniques, and the increasing sensitivity of these instruments, has been astounding. These instruments provide the means to elucidate a number of surface and bulk properties: chemical valence,coordinating elements, deposition profiles, surface and bulk concentration, crystal phase, etc. Clearly these techniques should be utilized extensively in developing understanding of coal liquefaction catalysts. The major emphasis should be on real catalysts, both fresh and aged.

4.2.4 Methods for Characterizing Coal Liquids from Direct Liquefaction[6]

4.2.4.1. Introduction

The materials produced by direct coal liquefaction are complex mixtures which span a significant range in composition. Describing the composition of a coal liquid requires the use of a variety of tools to separate, identify, and quantify individual components or component classes, and to measure other important parameters, such as elemental composition. This information can be used to make various statements about the liquefaction process which are useful in process development.

There are various reasons for performing analyses of coal liquids. It is important to determine the compositions of liquid products relative

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[6] This section was written by Francis P. Burke, Consolidation Coal Company.

to end-use specifications. The environmental impact of liquid products must be assessed, and data on their physical properties must be obtained for engineering design.

Within the process itself, analytical data are used to follow the chemical transformation of coal to residual liquids, and of the residual liquids to distillate products. Since both distillate and residual liquids commonly are recycled in the process, their composition has an impact on process performance in both roles of reactants and recycle solvent. The interactive nature of recycle solvent composition, process conditions, and process performance makes the characterization of the recycle stream particularly useful in assessing a variety of process performance factors.

Analytical tools can be divided on the basis of use into routine and non-routine. The development of non-routine analyses is the more fruitful ground for analytical research. However, an assessment of research needs for direct liquefaction should also recognize the need to promote application of the routine methods, if these existing methods are not being fully utilized in fundamental and applied research.

4.2.4.2 Routine Analysis

The most commonly employed analytical techniques provide information about the yields and the characteristics of the liquefaction products. The information provided includes boiling point distribution, elemental composition, viscosity, specific gravity, and analysis of the heteroatoms and light hydrocarbon gases. Information of this type usually is obtained using the methods of quantitative analytical chemistry and therefore is subject to data quality control procedures. The data frequently are used to establish the validity of process performance measurements through the calculation of mass and elemental balances. The routine analytical data also provide some idea of product acceptability for end use, or as a feedstock for further upgrading. These data are required to perform a process engineering and economic analysis.

Therefore, the routine analyses should always be performed in any program of process development.

There are several common deficiencies in the current application of routine analytical methods that should be considered in assessing research needs. First, some of the analytical methods are not standard. For example, laboratory vacuum distillations are performed to measure total liquid yield, usually reported as C_4 x 975°F, C_4 x 850°F, C_5 x 975°F, etc. However, the actual vacuum distillation conditions used to produce these atmospheric equivalent endpoints are not standard (110), and may be so specific as to depend on a given piece of home-made laboratory apparatus and a yellowing Cox chart taped to the side of a fume hood. This lack of standardization can make it difficult or impossible to compare results from different sources, requiring some estimated adjustment of reported yield structure to put different processes on a comparable basis (111).

A second problem with application of routine analyses is the frequent lack of information on product characteristics as they relate to end use or upgradeability. For example, parameters such as pour point, smoke point, and aniline point and analyses such as PONA are rarely reported in coal liquefaction process development. An exception is the work done by Sullivan (112), who obtained products from various liquefaction processes and assessed product characteristics and upgradeability as refinery feedstocks.

A third problem with the application of routine analyses is the lack of data provided by some investigators who conduct more fundamental or exploratory research. There are two excellent reasons for obtaining routine analytical data even in basic research. First, it allows one to calculate mass and elemental balances, which can reveal experimental problems, such as product contamination, which are often encountered in small-scale research. Second, it allows some assessment to be made of the experimental product characteristics. Although these may be viewed as initial reaction products and not end products, some characterization by standard methods should be performed.

4.2.4.3. Non-Routine Analysis and Characterization

There are many non-routine analytical and characterization techniques available for application to coal liquids. Particularly in the 1970's and early 1980's, there was an upsurge of interest in the development of analytical methodology and its application to coal liquids. This interest was stimulated, in part, by the wide availability of new and sophisticated analytical instrumentation incorporating more powerful data-processing systems. Coal liquids provided interesting grist for this mill.

Some techniques such as gas chromatography and mass spectrometry, which had been developed originally for petroleum analysis, were directly applicable to those coal liquids which resembled their petroleum counterparts, particularly the lighter distillates.

However, the more difficult analysis problem for coal liquids is posed by the heavier distillable liquids and by the non-distillable, or residual, material. These higher-boiling liquids and the resid of coal liquefaction differ considerably from their petroleum counterparts, primarily in their lower H/C ratio, greater aromaticity, and other differences in molecular weight and heteroatom content. An important contribution to the characterization of coal-derived resids was the EPRI-funded study of "The Nature and Origin of Asphaltenes in Processed Coals" conducted by Mobil R&D (113). This work included the development of a liquid chromatographic compound class fractionation method specific to heavy distillate residual coal liquids. Although these methods did not come into general use, the Mobil work stimulated renewed interest in the development of analytical techniques specific to coal liquids.

A. Separations

A number of methods have been developed to separate coal liquids on the basis of chemical functionality, molecular size, or solubility (113-

121, 129). Although some attempts have been made to compare different separation techniques (122), no standard methods have emerged. However, when individual methods are used intramurally for relative comparisons, most appear to give reasonable results.

Higher-resolution techniques, including GC, HPLC, and SCF-GC (128), have been employed as analytical methods (121, 123) and as preparative separations for additional characterization (122-126). Generally, the problem with high-resolution separation as an analytical method is the difficulty in quantitative reproducibility and identification of separated components. Therefore, although the resulting data can be of interest as a qualitative characterization, the separations are difficult to use as routine analytical methods.

B. Functional Group Analyses

An alternative approach is to select a parameter of interest and develop a reliable analytical method to quantitatively measure that specific parameter. Of particular interest here is quantitation of the functional groups (N,S,O) in coal liquids. Various methods have been reported for determining nitrogen compounds (119, 130, 133, 137, 138),phenols (116, 125, 130, 131, 133-135, 139, 140, 144) and sulfur compounds (132, 136). Dadey et al. (131) provide a good comparison of several methods for determining phenolic OH, which illustrates the point that these analytical methods are amenable to verification, and that several methods may be used to determine a particular, well-defined compositional parameter. What is often lacking in reports of analytical methods is a validation of the utility of the method through sufficiently extensive application.

C. Spectroscopic Techniques

The development of analytical methods for coal liquids has also involved exploitation of the capabilities of specific types of analytical instrumentation. Since spectroscopic methods can often be applied to a wide range of samples without the need for extensive sample preparation, these methods have found general use. For example, carbon and proton nuclear magnetic resonance spectroscopy have been used by a number of investigators (115, 119, 141-143, 145-147). Proton NMR has been broadly useful for the analysis of soluble liquids because it is quantitative, analyzes for an important property (hydrogen distribution), and is analytically simple. Carbon NMR has not been as broadly applied, in part because of problems with quantitation of internal carbons in fused ring systems.

Infrared spectroscopy has found less general use, probably because of difficulties in both quantitation and qualitative analysis, except when it is used as a determination step in a specific analysis, such as phenol determination (139). However, infrared analysis has occasionally been used in conjunction with other characterization techniques such as ^{13}C-NMR (115, 125, 127). The use of UV-visible spectroscopy has also been limited, although some potential applications have been advanced (148).

Mass spectrometry has offered considerable promise as a general analytical technique for coal liquids. Methods and applications involving Field Ionization Mass Spectrometry (FIMS) (113, 125, 149-152), low voltage ionization (153-155), GC/MS (121, 123, 124) and tandem mass spectrometry (156) have been reported. A problem with mass spectrometry is that low-resolution techniques cannot distinguish nominal mass isomers, and high-resolution techniques tend to produce a great deal of data, making practical use of the data difficult. There are also concerns about ionization cross sections of dissimilar components which complicate quantitation, and the lack of sensitivity to higher-molecular-weight components. For coal liquids which are similar to their petroleum counterparts, MS techniques developed in the refining industry can probably be applied with little modification.

D. Hydrogen Donor Solvent Characterization

A particularly interesting problem in coal liquefaction is the role of the recycle oil in the liquefaction reaction. The importance of recycle solvent as a physical medium and a hydrogen donor has been the subject of extensive work, and has inspired the use of a variety of techniques for analytical or empirical evaluation of solvent quality. Because of the interactive nature of recycle oil characteristics and liquefaction process conditions, it is desirable, and probably necessary, to simultaneously assess both process performance and recycle oil composition. A number of published works in this area used ^{13}C-NMR (115, 141, 143, 157, 159, 160) spectroscopy. However, ^{1}H-NMR spectroscopy may be better suited to measure hydrogen donor properties, alone or combined with ^{13}C-NMR analysis (142, 145, 155, 157, 158, 160).

Various empirical methods have been proposed to measure hydrogen donation ability through reaction of the donor solvent with coal (147) or a model compound (159, 163). One limitation of some previous studies has been a failure to relate measured solvent composition parameters to some meaningful facet of process performance. Another problem is the frequent failure to use authentic coal liquids or to document sample sources.

A systematic evaluation of recycle oil composition in relation to coal liquefaction process performance has been conducted by Consol R&D since 1976, under DOE sponsorship since 1978. In this program frequent (often daily) samples of recycle and process oils from major coal liquefaction process development efforts were collected and characterized in context to process operating conditions and performance. Reported data include characterization of recycle oils from CSF (161), SRC (146, 151, 162, 164, 165), H-Coal (166-168), Lummus ITSL (169, 171-175), HRI-CTSL (170, 176), and Wilsonville Two-Stage Liquefaction (170, 177, 178). Analytical techniques used include ^{1}H-NMR, FTIR, HPLC, solubility fractionation, and empirical techniques.

E. Environmental

Assessments of the toxicological properties of coal liquids are required to determine their acceptability in conventional product markets and to determine steps necessary to produce acceptable products. A systematic study of this kind was conducted by Battelle PNL (123), and data have been reported by others (124). These studies clearly point to the need for continued evaluation as different synthetic liquids are produced in new exploratory and process development efforts.

4.2.4.4. Summary and Research Needs Assessment

The foregoing discussion is not intended as a detailed review, but is presented to highlight some important advances in the development of tools and methods for the analysis and characterization of coal liquids. Application of these tools has provided new insight into the chemical composition of coal liquids. However, the greater promise of analysis and characterization is to improve the understanding of coal liquefaction, so that processes can be devised and developed on the basis of fundamental chemical reactions, rather than empirical observations. That this is the promise of coal liquids analysis can be read in any of a number of proposals for funding in this research area. However, this objective has not been fully realized. To understand why, it is useful to identify three categories of analytical research -- instrument development, methods development, and applications -- and consider how they have progressed.

Instrument development can proceed almost without reference to the end use of the instrumentation. Fundamental physical and chemical phenomena, which form the basis of new analytical techniques, are properly investigated without an immediate need to demonstrate a practical application. When the analytical instrumentation is developed, it is important to show a broad range of potential applications, but satisfactory to leave the development of methods and the actual application of those methods to others. Therefore, instrument development, per se, is responsible for much of the promise but little of the actual end benefits of coal liquids analysis.

Research in methods development can be stimulated by the availability of a particular type of instrumentation, but does require a target analytical application. For example, a number of methods were developed to use NMR, FTIR, HPLC, and chemical derivation to analyze phenols in coal liquids. These methods and others cited above clearly are pertinent to characterization needs. However, despite considerable work in methods development, this effort is far from complete. Much advanced research concentrates on the method and not on applications. Methods development frequently lacks the extensive work in application of the method necessary to demonstrate its practicality and usefulness. As a result, instruments and methods are applied to too few of the wrong samples for the results to clearly demonstrate the usefulness of the method to the process researcher or developer.

Applications have been largely ignored in the recent development of novel analytical and characterization techniques for coal liquids. Most process development efforts are routinely supported by the same analytical techniques that were in use 15 years ago: elemental analysis, boiling-point determination of distillates, solubility fractionation of resids. Exploratory research is often supported by nothing more than solvent insolubles determinations on reaction products. New methods have not made the transition from development to practical application and general acceptance.

In summary, the literature contains numerous reports of potentially useful techniques for coal liquid analysis. (The list provided here is the iceberg's tip.) These include methods of qualitative and quantitative analysis, and empirical characterization. However, few, if any, of these promising techniques have gained general acceptance in either exploratory research or process development. It does not appear that new instrumentation or methods are needed as much as an evaluation of existing resources through extensive application in both exploratory research and process development.

4.3 DIRECT LIQUEFACTION PROCESS DEVELOPMENT

4.3.1 Overview of Technology Development Status

During the 1970's direct coal liquefaction processes depended on high temperatures and high pressures. Among the disadvantages of such an approach are high hydrocarbon gas yield, inefficient hydrogen utilization, low-quality recycle solvents, and low-quality products. Between 1975 and 1982 four direct liquefaction processes became contenders for commercialization: H-Coal, Exxon Donor Solvent (EDS), SRC-I, and SRC-II. These processes all were based on the same high-severity philosophy of liquefaction.

In the 1980's two-stage liquefaction (TSL) processes have emerged and displaced the preceding processes. TSL separates coal liquefaction and coal upgrading, thereby allowing each to be performed at its optimum conditions. The result has been greater distillate yield, lower gas yield, and higher-quality product -- even though the reaction severity has been reduced. The temperature of the second stage is relatively low, resulting in a good hydrogen donor solvent. This improved solvent is a major cause of the process improvements.

In general, coal liquids made by current processes differ from products of the preceding processes by having no residuum, lower heteroatom content, and a higher H/C ratio. Consequently, these liquids are more easily refined, i.e., with lower reaction temperatures, slower catalyst deactivation, and lower hydrogen consumption.

Two preferred refining plans are being developed for upgrading coal liquids. In the first refining plan the targets are gasoline and middle distillates. No cracking conversion is needed. The whole oil is hydrotreated at high severity to produce jet fuel or diesel fuel, and the naphtha is catalytically reformed to high-octane gasoline. In the second plan the target is all gasoline. The whole oil is hydrotreated as before, but the required severity is lower because the purpose is to remove heteroatoms rather than to make finished products. The hydrotreated oil is then hydrocracked to convert the high-boiling fraction to naphtha, which, in turn, is reformed to gasoline.

4.3.2 Evolution of Direct Liquefaction Technology[7]

4.3.2.1. Introduction

During the 1970's, with expectations of a continuing rise in oil prices and the possibility of a shortage in crude oil, several single-stage direct liquefaction processes were in advanced states of development by 1980 poised for rapid commercialization. However, since 1980, these development plans have been deferred in response to the ready availability of cheap foreign crude oil. As a result, the coal liquefaction R&D community has had the opportunity to perform additional process development, which has resulted in processes superior to those of the 1970's. This new generation of direct liquefaction technology is based on low-severity two-stage liquefaction, which separates hydroliquefaction and the upgrading reactions, so that both stages can be optimized separately to increase distillate yield and improve hydrogen efficiency.

Two-Stage Liquefaction (TSL) has been under development in the U.S. since 1980. During this time the process has continuously evolved to the present configuration, which produces the highest liquid yield and product quality of any process worldwide. TSL has been successfully applied to bituminous and subbituminous coals. Development programs at Wilsonville, Alabama, and Trenton, New Jersey, continue to improve the process.

4.3.2.2. Development of Single-Stage Processes

The two-stage approach is built upon the experience in direct liquefaction that has been accumulated in the U.S. for close to thirty

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[7] This section was written by Harvey D. Schindler, Science Applications International Corporation.

years of development of single-stage processes. To understand the evolution of the Two-Stage Liquefaction (TSL) technology to its current state, the contributions of the major single-stage processes will be briefly discussed in the following sections.

A. H-Coal

H-Coal is a direct catalytic coal hydroliquefaction process invented in 1963 by Hydrocarbon Research, Inc. (HRI). Development of the H-Coal process proceeded through conceptual stages to bench-scale (25 lb/day) and Process Development Unit (PDU) (3 tons/day) studies. The work culminated in the construction and operation of the H-Coal Pilot Plant, a 200-600 ton per day facility in Catlettsburg, Kentucky. This was a $300 million project funded by DOE, the Commonwealth of Kentucky, EPRI, Mobile, Amoco, Conoco, Ruhrkohle, Ashland Oil, Sun, Shell, and Arco. The project started in 1973 with preliminary design and laboratory studies and continued through a 36-month operating period, which ended in January 1983. During operation of this pilot plant, data necessary for the design, environmental permitting, construction, and operation of a pioneer commercial H-Coal facility were obtained.

The key component in the H-Coal process is the ebullated-bed reactor (see Figure 4-22). Pulverized coal, recycle liquids, hydrogen and a catalyst are brought together in the reactor to convert the coal into hydrocarbon liquids and gaseous products. The catalyst particles in the H-Coal reactor are 0.8- to 1.5-mm diameter extrudates, which are fluidized by the upward flow of liquid and gas. This fluidization enables the hydrogenation exotherm to be distributed uniformly over the entire reactor volume and allows the ash and unconverted coal to flow through the reactor without causing interparticle plugging of the catalyst. In addition, catalyst addition and withdrawal is performed in a manner similar to fluid catalyst so that a constant catalyst activity is maintained and temperature staging is not required to compensate for deactivation.

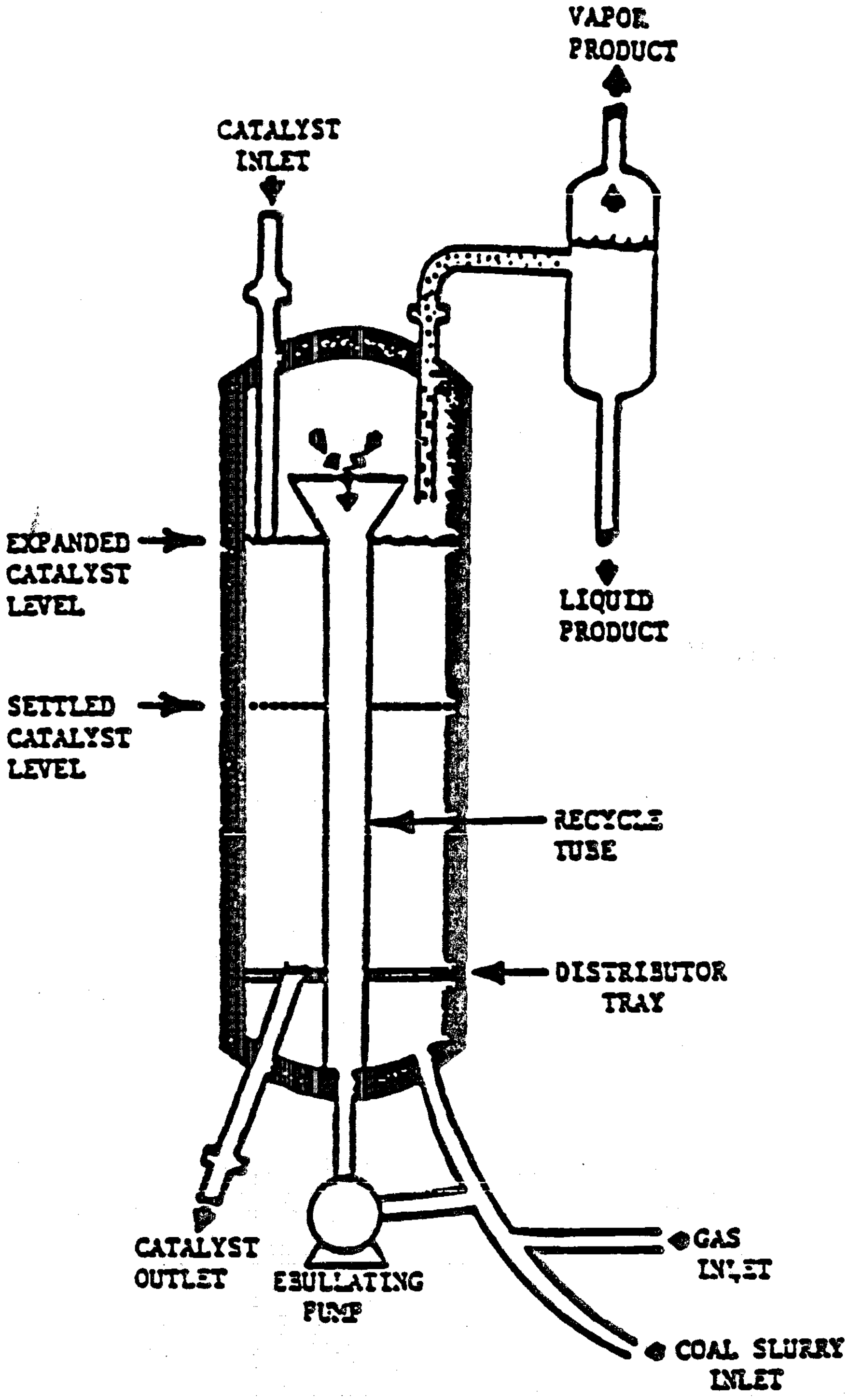

Figure 4-22. H-Coal Ebullated-Bed Reactor

The H-Coal process embodies several unique features and advantages:

- Coal dissolution and upgrading to distillate products are accomplished in one reactor;
- Products have a high H/C ratio and low heteroatom content as the result of catalytic hydrogenation;
- A high throughput of coal is achieved due to the rapid catalytic hydrogenation rates;
- Ash is removed by vacuum distillation, followed by gasification of the vacuum tower bottoms to generate the hydrogen requirement of the process.

H-Coal, however, has several shortcomings:

- The high reaction temperature 833 to 851°F (445-455°C) results in excessive thermal cracking and consequently high (12-15 percent) hydrocarbon gas yields.
- The hydrogen consumption is high relative to the liquid yield. Some distillate product, in addition to the vacuum tower bottoms, is gasified to satisfy the hydrogen production requirements of the process.
- The product includes considerable vacuum gas oil (650-975°F b.p.). Subsequent tests by Chevron showed that coal liquids in this boiling range are difficult to upgrade by standard refinery processes. It, therefore, has utility solely as a boiler fuel.

Like all single-stage processes, H-Coal is best suited for high-volatile bituminous coals. When subbituminous coal was tested in the H-Coal process, the coal throughput had to be reduced, and distillate yield was considerably lower than from bituminous coals.

Although H-Coal development has ceased, the ebullating-bed reactor is an integral part of all TSL flow configurations.

B. Solvent Refined Coal (SRC-I)

In 1962 the Spencer Chemical Company began to develop a process which was later taken up by Gulf, who in 1967 designed a 50-ton-per-day

SRC pilot plant at Fort Lewis, Washington. The plant was operated in the SRC-I mode from 1974 until late 1976.

In 1972 Southern Company Services, Inc. (SCS) and Edison Electric Institute designed and constructed a six ton per day SRC-I pilot plant at Wilsonville, Alabama. This plant is still in operation, generating valuable design data and providing large samples of product for test purposes, but it no longer operates in the original SRC-I (solids product) mode.

The primary product in the original SRC-I process was a solid boiler fuel with a melting point of about 300°F and a heating value of 16,000 Btu/lb. In the interest of enhancing commercial viability, during the early stages of the Demonstration Project, the product slate was expanded to include liquids that were products of a Coker/Calciner, an Expanded-Bed Hydrocracker, and a Naphtha Hydrotreater.

SRC-I is a thermal liquefaction process wherein solvent, coal, and hydrogen are reacted in a "dissolver" reactor to produce a non-distillable resid (or extract), which upon deashing can be used as a clean boiler fuel. Reaction conditions are only slightly less severe than in H-Coal. However, the absence of a catalyst diminishes hydrogenation rates, so that the product is a 842°F+ (450°C+) resid. This resid has a H/C ratio about the same as the coal feed; all of the net hydrogen reacted goes into hydrocarbon gases and heterogases. The solvent is a heavy distillate that is recovered by vacuum distillation. In addition, some of the bottoms feed to the deasher may also be recycled.

The process is most successful with bituminous coals, especially those that contain high concentrations of pyrite. The pyrite is considered to be the liquefaction "catalyst." In the absence of pyrite-laden ash, as is the case for all subbituminous coals, additional pyrite is required as a disposable catalyst in the slurry feed in order to maintain conversion and good operability.

The process had technical and economic drawbacks. The all-distillate solvent was often of poor quality, i.e., its ability to shuttle hydrogen from the gas to coal was insufficient to prevent coking or precipitation of heavy product, usually within the preheater to the dissolver. Solvent was often incorporated into the resid product, so that solvent balance could not be maintained. When reaction conditions were moderated, production of toluene-insolubles increased and precipitation ensued in equipment downstream of the reactor.

The non-distillable SRC-I resid product cannot be recovered and deashed by vacuum distillation. Instead, extraction-type separation processes were developed specifically for this process. Typical of these is Kerr-McGee's Critical Solvent Deashing (CSD), which uses a light aromatic solvent to precipitate the heaviest (toluene insoluble) fraction of the resid and, with it, all of the ash and unconverted coal. This deashing procedure has been retained in TSL processing as the means to recover a heavy, but solids-free recycle solvent.

C. Exxon Donor Solvent (EDS)

This process development was a joint venture of DOE and private industry participants. The early phases of the program were carried out in the period from 1966 to 1975 and were financed entirely by the Exxon Research and Engineering Company. The process development work progressed from bench-scale research to small-scale pilot units (100 lb/day and 1 ton/day) and culminated in the construction and operation of a large-scale Exxon Coal Liquefaction Plant (ECLP) with a capacity of 250 tons/day at Baytown, Texas. Mechanical completion of ECLP and start of operations took place in April 1980. This pilot plant continued in operation until it was shut down and dismantled in late 1982.

The EDS process utilizes a non-catalytic hydroprocessing step for the liquefaction of coal to produce liquid hydrocarbons. Its salient feature is the hydrogenation of the recycle solvent, which is used as a donor of hydrogen to the slurried coal in a high-pressure reactor. The

EDS process is considered single stage because coal dissolution and resid upgrading to distillate products take place in one thermal reactor. The recycle solvent, however, is catalytically hydrogenated in a separate fixed-bed reactor. This solvent then transfers hydrogen to the coal in the liquefaction reactor.

Reaction conditions are similar to those of SRC-I and H-Coal. The recycle solvent "donates" hydrogen to effect rapid hydrogenation of the primary liquefaction products; thermal hydrogenation and cracking follow to produce distillates. The product distribution is close to that of H-Coal, although product quality is poorer due to the absence of a hydrotreating catalyst. The hydrogenated solvent is mostly distillate, and the resid that is separated by vacuum distillation is gasified to provide the hydrogen requirement. The distillate solvent is hydrogenated in a fixed-bed reactor.

The process performed well with bituminous coal. Subbituminous coal precipitated calcium salts in the thermal reactor and its preheater. This problem was later solved by adding resid, including ash, to the recycle solvent. It was believed that the ash particles acted as sites for deposition of the calcium salts.

EDS solvent had to be well hydrogenated to be an effective hydrogen donor. This highly hydrogenated distillate solvent may, therefore, have been a relatively poor physical solvent, which could account for process operability problems. Bottoms recycle (non-hydrogenated resid) was used near the end of the process development, with improved operability and liquid yields. The improvement may have been due to the better physical solvent properties of the resid.

Distillate yields were not as high as for the H-Coal process. Therefore, process economics were about the same despite the less expensive thermal reactor and the simple solids removal procedure.

The EDS process contains features that have been incorporated into TSL. First, the donor solvent concept showed that hydrogenation of the coal could be effectively and quickly accomplished without a catalyst. Second, bottoms recycle dramatically improved process operability, even though the bottoms (resid) were not hydrogenated. Finally, the use of ashy recycle enabled subbituminous coal to be processed effectively in a thermal reactor and without the need of a disposable catalyst.

D. SRC-II

The SRC-II process employs direct hydrogenation of coal in a reactor at high pressure and temperature to produce liquid hydrocarbon products instead of the solid products in SRC-I. In 1975 a process development unit (P-99), with a one-half ton per stream day capacity was used to provide accurate process and design information data. The 50-ton-per-day pilot plant at Fort Lewis, Washington, which operated from 1974 to late 1976 in the SRC-I mode, was modified to run in the SRC-II mode, producing liquid products for testing. The pilot plant was operated from 1978 until it was shut down in 1981.

The SRC-II process is thermal; the mineral matter in the coal is the only "catalyst" used. Its concentration in the reactor is kept high by recycle of the heavy oil slurry. The use of recycled mineral matter and the more severe reaction conditions distinguish the SRC-II operation from SRC-I and account for the lighter products. The net product is -1000°F distillate, which is recovered by vacuum distillation. The vacuum bottoms, including the ash, are sent to gasification to generate process hydrogen.

The SRC-II process is limited to coals that contain "catalytic" mineral matter, which excludes all lower-rank coals and some bituminous coals. The high-temperature thermal liquefaction reaction results in high yields of hydrocarbon gases and poor liquid product quality, relative to those produced by the H-Coal process.

E. Summary of Technical and Economic Characteristics of Single-Stage Processes

These and other single-stage processes have several features in common:

- Reaction severity is high, with temperatures of 820-860°F and liquid residence times of 20-60 minutes. These severe conditions were considered necessary to achieve coal conversions of over 90 percent (to THF- or quinoline-solubles).
- Distillate yields are low--about 50 percent of MAF coal with bituminous coals and even lower from subbituminous coal.
- Hydrogen efficiency is low due to high yields of hydrocarbon gases.

Although the processes are technically sound, process economics suffer for the reasons stated above. In 1980, about the time that the H-Coal and EDS processes were ready to be tested at a scale of 200 tons per day, coal liquefaction began to take a new direction toward conditions that were more efficient and could produce more liquid, of higher quality.

4.3.2.3. Non-Integrated Two-Stage Liquefaction (NTSL)

By the late 1970s it was apparent that the costs associated with the SRC-I process could not be justified to produce a boiler fuel. A coal liquefaction process is best applied to make higher value-added products, such as transportation fuels. To do this with the SRC-I process, the resid must first be hydrocracked to distillate liquids. Attempts at fixed-bed hydrocracking by Chevron and Mobil were unsuccessful because (1) the resid contained small quantities of ash that plugged the fixed bed and (2) the hydrogenation exotherm coked the large aromatic molecules in the feed and rapidly deactivated the catalyst (179).

The SRC-I resid was, however, successfully upgraded, or hydrotreated, by LC-Fining, a variation of ebullated-bed technology (180). Eventually, hydrocracking was added to the SRC-I process to form

Non-Integrated Two-Stage Liquefaction (NTSL), so called because the hydrocracking did not contribute solvent to the SRC-I part (Figure 4-23). The NTSL process was, in fact, two separate processes, coal liquefaction (SRC-I) and resid upgrading, combined in series.

NTSL was an inefficient process even though the hydrocracking section had been added to maximize conversion of resid to distillates. The SRC-I section still contained the shortcomings discussed above. In addition, SRC-I product is an unreactive feed to hydrocracking, and complete conversion to distillates requires high (over 800°F) temperature and extremely low space velocity. To keep the reactor at a reasonable size and temperature, and to prevent rapid catalyst deactivation, resid conversion was held below 80 percent, so that considerable unconverted resid goes with the product distillates (Table 4-3). As a result, in the NTSL configuration, recycling resid to extinction to produce an all-distillate liquid product slate was not possible. Yields were nevertheless higher than for H-Coal, but hydrogen consumption was still high because of the extensive thermal hydrogenation in the SRC-I dissolver, which was renamed the Thermal Liquefaction Unit (TLU).

The NTSL development was short-lived. Soon, it was to be supplanted by a staged integrated approach, which has been the basis for all subsequent developments.

4.3.2.4. Development of Thermal Integrated Two-Stage Liquefaction

A. Early Development

Thermal coal dissolution investigations by Consol, Mobil, Wilsonville, and others in the late 1970's had shown that coal conversion to THF- (or quinoline-) solubles is essentially complete in an extremely short time, 1-5 minutes. Longer dissolution times increase conversion slightly, but the incremental increase in yield goes principally to gases. Within this short dissolution period, hydrogenation from the gas phase is negligible, and almost all hydrogen comes from the solvent in

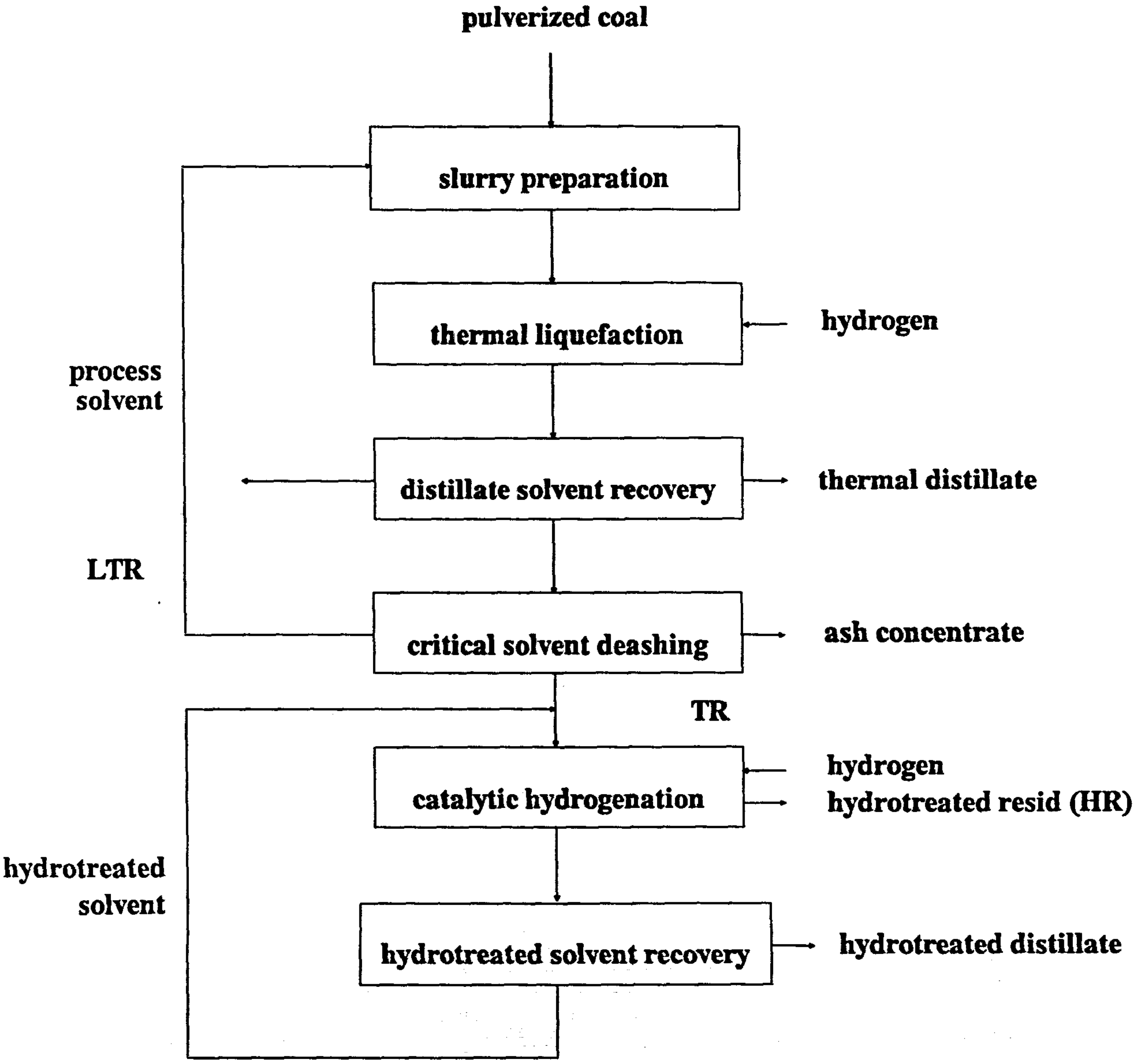

Figure 4-23. Block Flow Diagram of NTSL Operation

Table 4-3. **Wilsonville Facility - NTSL (Illinois No. 6 Coal)**

OPERATING CONDITIONS	
Run No.	241CD
Configuration	NTSL
Catalyst	Armak
Thermal Stage	
Average Reactor Temperature, °F	805
Coal Space Velocity, lb/hr ft^3 > 700°F	20
Pressure, psig	2170
Catalytic Stage	
Average Reactor Temperature, °F	780
Space Velocity, lb Feed/hr lb Catalyst	1.7
Catalyst Age, lb Resid/lb Catalyst	260-387
YIELDS, WEIGHT PERCENT MAF COAL	
C_1-C_3 Gas	7
C_4+ Distillate	40
Resid	23
Hydrogen Consumption	4.2
Hydrogen Efficiency	
lb C_4+ Distillate/lb H_2 Consumed	9.5
Distillate Selectivity,	
lb C_1-C_3/lb C_4+ Distillate	0.18
Energy Content of Feed Coal Rejected to Ash Concentrate, percent	20

Source: Ref. 185.

the liquid phase. If hydrogen transfer from the solvent is insufficient to satisfy the liquefaction needs, the product will have a high concentration of toluene insolubles, causing precipitation within the reactor or in downstream equipment. With a well-hydrogenated solvent, however, the Short-Contact-Time (SCT) liquefaction is the preferred thermal dissolution procedure because it eliminates the inefficient thermal hydrogenation inherent in SRC-I.

Meanwhile, Cities Service Research and Development was successfully hydrocracking SRC-I resid via LC-Fining at relatively low temperatures, 750-780°F (179). Gas yield was low and hydrogen efficiency high. A combination of these two reaction stages, wherein the second stage, (i.e., the low-temperature LC-Fining) provides the liquefaction solvent to the SCT first stage, was seen to have the potential to liquefy coal to distillate products in a more efficient process than any of the single-stage processes.

B. Lummus ITSL (1980-1984)

The features described above were combined by Lummus in the ITSL process (181). Operation of a 500-pound-per-day Process Development Unit (PDU) with the ITSL process started in 1980. This operation departed significantly from earlier developments and was the forerunner of all subsequent TSL developments. The important features of the Lummus program are reviewed below.

Process Features

The Lummus ITSL process consists of an SCT coal dissolution first stage and an LC-Fining catalytic upgrading second stage (Figure 4-24). Coal is slurried with recycled solvent from LC-Fining and is converted to quinoline solubles in the SCT reactor; the resid is hydrogenated/hydrocracked to distillates in the LC-Fining stage, where recycle solvent is also generated. The ash is removed by the Lummus Antisolvent Deashing (ASDA) process, which is similar to deasphalting operations with petroleum. The net liquid product is either -650°F or-850°F distillate. The recycle solvent is hydrogenated +650°F atmospheric

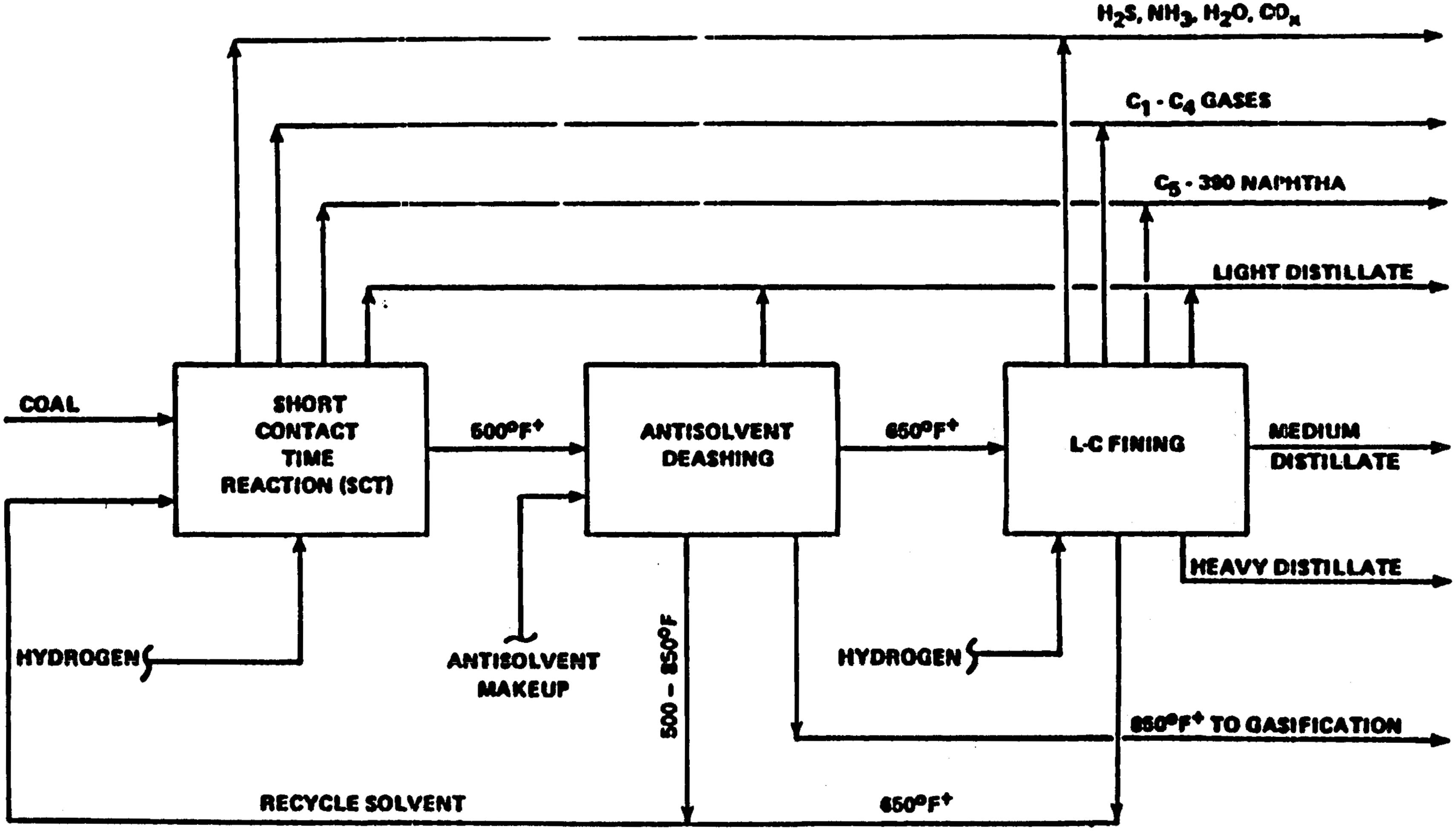

Figure 4-24. Process Flow Diagram of Integrated Two-Stage Liquefaction

bottoms. It is the recycle of this full-range bottoms, including resid, that couples the two reaction stages and results in high yields of all-distillate product.

Features of SCT

The SCT reactor is actually the preheater for the dissolver in the SRC-I process. ITSL therefore eliminates a long-residence-time high-pressure thermal dissolution reactor. The coal slurry and gas feeds flow through the SCT reactor in plug flow, exiting at a maximum temperature of 810-860°F. The kinetic average temperature is about 810°F, which is lower than the dissolver temperature in SRC-I. Liquid residence time is 2-3 minutes for bituminous coal and 8-12 minutes for subbituminous coal. Initial tests were made at 2400 psi pressure. But, as it became apparent that essentially no molecular hydrogen was being reacted, the pressure was lowered to 1000 psi and then to 500 psi in later tests, with no detrimental effects. Coal conversions were 92 percent of MAF coal for bituminous coals and 90 percent for subbituminous coal.

Molecular hydrogen gas consumption was essentially zero, and the hydrogen transferred from the solvent was equivalent to 1.2 - 2.0 percent of the coal weight (see Table 4-4). The hydrocarbon gas yield was thereby reduced to about one percent for bituminous coal and to 5-6 percent for subbituminous coal. Heteroatom removal was about the same as by the SRC-I process.

The SCT resid was more reactive to hydrocracking than SRC-I resid. It was also more stable, being able to withstand days, and even weeks, in heated holding tanks without loss of activity or the formation of solids (retrograde reactions). In summary, the most noteworthy advantage of SCT over SRC-I was that it was able to achieve the same coal conversion with very little consumption of hydrogen and did so at milder conditions, which resulted in a more reactive resid.

Table 4-4. Integrated Two-Stage Liquefaction Process Yields (Lummus SCT Only)

	Run 2 SCT 10	Run 3 SCT 2
	Illinois #6	Wyodak
Components	Net Yields (lb/100 lb MAF Coal)	
H_2-S, NH_3, H_2O, CO_x	6.4	19.6
C_1-C_4 Gases	0.6	6.0
C_5 - 500°F Distillate	1.6	6.9
500-850°F Distillate	0.5	3.4
Solids Free 850°F+	83.2	52.8
Unconverted Coal	8.0	11.2
	100.3	100.0
Hydrogen From Recycle Solvent	1.4	2.0
Hydrogen From Gas	0.3	---

Features of the Second-Stage Hydrotreater (HTR)

The LC-Fining second reactor stage had two tasks: (1) to make essentially all of the distillate product and (2) to generate recycle solvent capable of supplying the hydrogen required by the SCT first stage. These tasks are in contrast to the second stage of NITSL, which was required only to convert resid to product. In ITSL all the unconverted resid was recycled to the first stage, resulting in recycle to extinction. Thus, an all-distillate product was achieved. Although bottoms recycle had been used in preceding processes, this was the first time that resid had been hydrotreated prior to recycle, so that it was more than a physical solvent, but also a donor of hydrogen and a product precursor, capable of cracking to lighter oils at SCT conditions.

The second task, to hydrogenate the recycle solvent, dictated the reaction conditions. Hydrogenation equilibrium becomes less favorable at higher temperatures, and in fact, above 800°F the second-stage product is more aromatic than the feed (182). On the other hand, conversion kinetics suffer at low temperatures, and solvent quality suffers because of accumulation of alkylated species that would otherwise crack to light oil at higher temperature. A second-stage HTR temperature of 750°F provides sufficient hydrogenation and cracking activity to accomplish both tasks. The low HTR temperature kept hydrocarbon gas yields to only 5-6 percent for bituminous coal and under one percent for subbituminous coal.

Catalyst deactivation was much slower than at the higher temperatures used by other processes. As a result, the hydrogen-transfer quality of the recycle solvent remained undiminished over the life of the catalyst. Ages of 3500-5500 pounds of resid per pound of catalyst were achieved without catalyst failure.

As stated earlier, the SCT resid was reactive, not only for conversion to distillate, but also for heteroatom removal. Product quality surpassed any achieved by the preceding processes. Chevron subsequently refined the ITSL products in a small-scale simulation of conventional refinery operations (183). As expected, ITSL products were easily upgraded, requiring relatively low temperatures and high space velocities. The low heteroatoms content contributed to the ease of refining, enabling Chevron to achieve specification transportation fuels with a hydrogen consumption that was lower than for liquids made from the same coals by other processes.

Antisolvent Deashing (ASDA)

The ash was removed by ASDA, which used a process-derived naphtha as antisolvent to precipitate the heaviest components of the resid and the solids. Initially, the ASDA unit was placed between the two reactors, so that SCT product was deashed. Eventually, the best TSL yields and deasher operation were achieved when the second stage liquid product was deashed. In addition, the conversion of subbituminous coal was increased to 90 percent and the operability of both stages was improved when part of the deasher feed was recycled to the first stage as solvent.

The ash-reject stream from ASDA is pumpable in order to maximize gasification efficiency. This stream therefore could contain no more than 55 percent solids, leading to relatively high rejection of organics with the ash. Since the process was kept in hydrogen balance and hydrogen consumption was low, the ASDA method of ash removal was acceptable. It had the advantages of low pressure (100-1000 psi), low temperature (500-540°F), and it required no external antisolvent. If, however, the liquid yield was to be increased, it could be done only by converting more resid in the second stage. This would have made the ash-reject stream from ASDA high in solids concentration (>55 percent) and too heavy to pump. It was this limitation on ASDA that limited the distillate yield to 60 percent of MAF coal.

Overall Results of ITSL

ITSL incorporated two features that were significant improvements over those developed in the past and tested them with new processing concepts that combined to produce the highest liquid yield yet attained, and at the highest hydrogen efficiency (see Table 4-5).

Table 4-5. Lummus ITSL Product Yields

	lbs/100 lbs MAF Coal Illinois No. 6	 Wyodak
H_2S_1, H_2O, NH_3, CO_x	15.08	23.08
C_1-C_4	4.16	7.30
TOTAL GAS	19.24	30.38
C_5/390°F	6.92	1.25
390/500°F	11.46	8.49
500/650°F	17.26	22.46
650/850°F	23.87	21.36
TOTAL DISTILLATE PRODUCT	59.51	53.56
Organics Rejected with Ash	26.09	20.22
GRAND TOTAL	104.84	104.16
Chemical Hydrogen Consumption	4.84	4.16
Hydrogen Efficiency lb dist./lb H_2	12.28	12.86
Distillate Yield, Bbl/Ton MAF	3.52	3.08

First, unconverted resid was hydrotreated and recycled as part of the liquefaction solvent. Thus, resid was recycled to extinction, and an all-distillate product (-650°F or -850°F) was made. This recycle also allayed the fears that resid contained coke precursors that would foul reactors if recycled. Instead, the hydrotreated resid is now well recognized as an excellent physical and hydrogen-donor solvent, whose full contribution to coal dissolution has not yet been fully appreciated.

Second, the SCT coal dissolution reactor accomplished all that SRC-I did, but more efficiently in a smaller volume reactor. Hydrocarbon gas yields were reduced to about one percent (much smaller than the 10-20 percent experienced with other processes), and heteroatom removal was comparable. Of even greater importance, the SCT resid was a more reactive second- stage feed and caused slower catalyst deactivation.

Additionally, ITSL showed that ashy recycle (including toluene-insolubles) is not detrimental to catalyst activity; that subbituminous coal is an attractive feed for direct liquefaction, with some advantages over bituminous coal; and that a lighter product (-650°F) can be made with little loss in hydrogen efficiency. The last point is of special importance for commercialization because the -650°F liquid poses no environmental problems (184). The product quality, including heteroatoms content, is excellent (see Table 4-6) and is easily refined to marketable products by standard refinery operations.

The maximum distillate yield from ITSL was 60 percent of MAF bituminous coal and 53 percent of MAF subbituminous coal (see Table 4-5). These were obtained in "hydrogen-balanced" operation and constituted significant improvement over H-Coal and other single-stage processes. Hydrocarbon gas yields were held to about 7 percent, so that the hydrogen consumption efficiency was the highest of any process, with 10-12 pounds of distillate produced per pound of hydrogen reacted.

Table 4-6. Lummus ITSL Distillate Product Quality (Illinois No. 6)

	°API	C	H	O	N	S	HHV Btu/lb
NAPHTHA							
NTSL	36.8	86.79	11.15	1.72	0.18	0.16	19,411
ITSL	45.4	86.01	13.16	0.62	0.12	0.09	20,628
LIGHT DISTILLATE (390 - 500°F)							
NTSL	15.5	88.62	9.51	1.50	0.28	0.09	18,673
ITSL	22.9	87.75	11.31	0.73	0.13	0.08	19,724
MEDIUM DISTILLATE (500 - 650°F)							
NTSL	7.5	90.69	8.76	0.27	0.25	0.03	18,604
ITSL	12.9	89.29	10.26	0.28	0.12	0.05	19,331
HEAVY DISTILLATE (650 - 850°F)							
NTSL	-1.5	91.47	7.72	0.26	0.50	0.05	18,074
ITSL	1.8	90.77	8.47	0.45	0.23	0.08	18,424

The distillate yield was limited by the philosophy of a "hydrogen-balanced" process; one that gasified the ash-reject stream to produce all of its hydrogen requirements. If distillate yield were to be increased, less resid would have to be rejected with the ash. The next step in the evolution of TSL, therefore, was to operate in a "non-hydrogen-balanced" mode, in order to maximize distillate yield. This was accomplished in subsequent developments at HRI and Wilsonville.

C. Wilsonville ITSL (1982-1985)

The Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama, is sponsored by the U.S. Department of Energy, the Electric Power Research Institute, and Amoco Corporation. The facility is operated by Catalytic, Inc., under the management of Southern Company Services, Inc. Kerr-McGee has participated by supplying deashing technology at Wilsonville. The technology for the design of the hydrotreater was provided by Hydrocarbon Research, Inc.

The Wilsonville facility began operation as a 6-ton/day single-stage plant for the production of solvent-refined coal (SRC-I) in early 1974 and has continued over the intervening fourteen years. Over this period the plant has evolved into the current advanced coal liquefaction facility by developments made possible by three major additions to the facility. In 1978 a Kerr-McGee Critical Solvent Deashing (CSD) unit replaced the filtration equipment that had been used for solids removal from the SRC product. In 1981 an H-Oil ebullated-bed hydrotreater was installed for upgrading of the recycle solvent and product. The hydrotreater increased the flexibility of the facility and allowed the investigation of two-stage liquefaction configurations. In 1985 a second ebullated-bed reactor was added in the hydrotreater area to allow operation with close-coupled reactors. The results of the ITSL runs at Wilsonville are summarized in a recent report (185).

Scale-Up of Lummus ITSL

The Lummus ITSL results had demonstrated significant advantages over single-stage processes. Scale-up appeared to be warranted, which was done at Wilsonville. In late 1982 modifications were made to Wilsonville that included piping changes needed for integrated operation and to bypass the TLU. Run 242 was the first ITSL scale-up run; it was operated at 3 tons of coal per day. The Integrated Two-Stage Liquefaction (ITSL) configuration that was used at Wilsonville for the bituminous runs is shown schematically in Figure 4-25. In this configuration the deashed thermal resid is fed to the hydrotreater, along with the heavier cuts of the thermal distillate. The process solvent that is recycled to the thermal stage is obtained from the hydrotreater product.

A distillate yield of 54 percent of MAF coal was confirmed (see Table 4-7). This yield was less than anticipated because of (1) retrograde reactions in the CSD unit that lowered coal conversion from 92 to 88 percent (Table 4-7), and (2) high organic rejection with the ash-concentrate stream because of a high concentration of toluene-insolubles in the SCT product. Nevertheless, the distillate yields were higher than had been achieved by NITSL, and the advantages of the integrated process were proven.

Modifications to ITSL

During most of Run 242, the second-stage HTR was operated at a low temperature, with most of the liquid product being made by thermal cracking in the first stage. Thereupon, Wilsonville decided that it was preferable to shift more of the conversion to the first reactor in subsequent runs and use the second stage primarily as a solvent hydrogenation unit. An advantage of such an arrangement is that the concentration of toluene-insolubles in the first-stage liquid is reduced, leading to lower organic rejection by CSD. Consequently, the TLU was reinstalled starting with Run 243, and first-stage reactors of relatively long residence time were used in all subsequent ITSL runs.

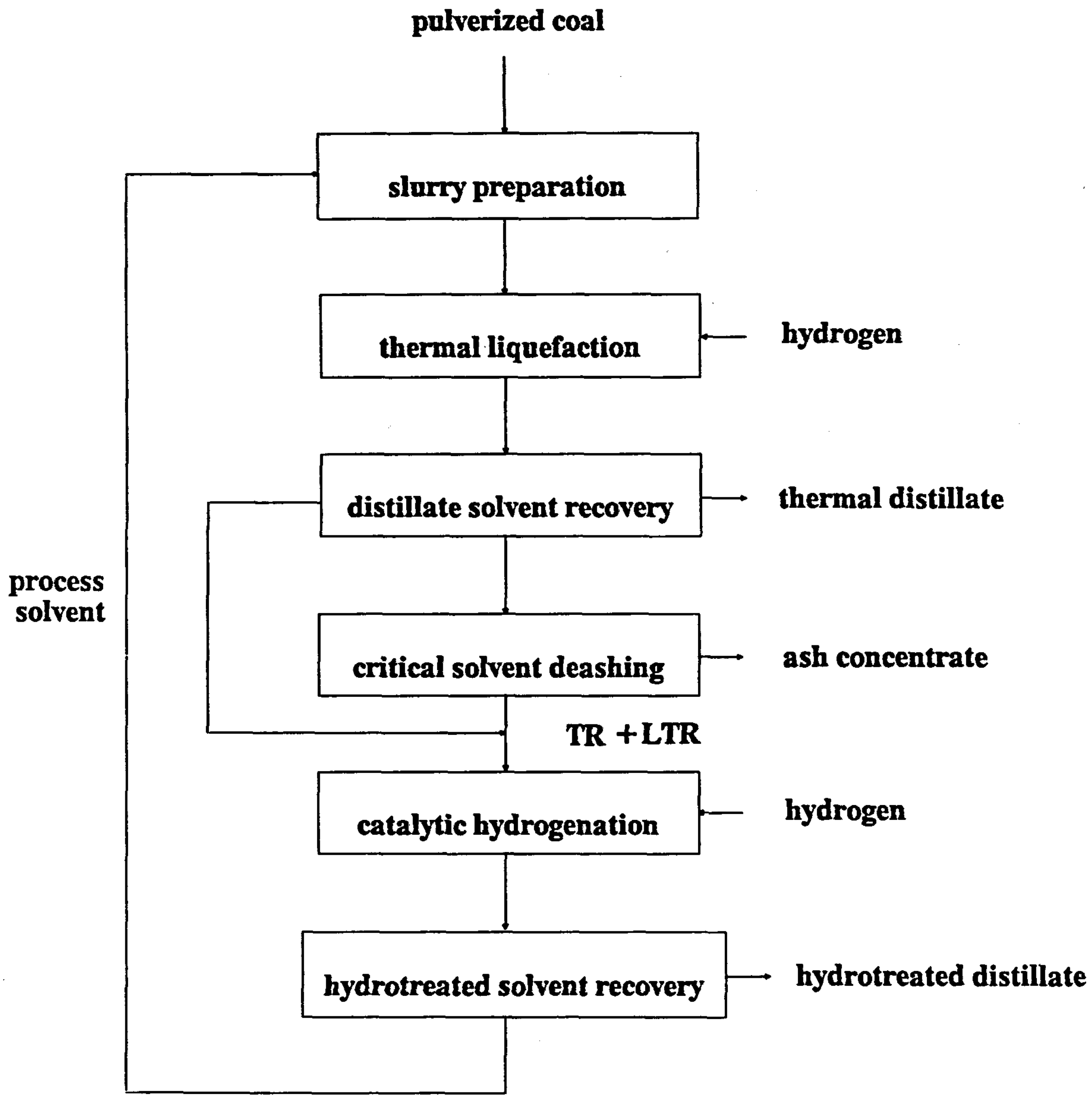

Figure 4-25. Block Flow Diagram of Integrated Two-Stage Liquefaction (ITSL)

Table 4-7. Wilsonville Facility ITSL (Illinois No. 6 Coal)

OPERATING CONDITIONS						
Run No.	241CD	7242BC	243JK/244B	247D	250D	250G(a)
Configuration	NTSL	ITSL	ITSL	RITSL	CC-ITSL	CC-ITSL
Catalyst	Armak	Shell 324M	Shell 324M	Shell 324M	Amocat IC	Amocat IC
Thermal Stage						
Average Reactor Temperature, °F	805	860	810	810	824	829
Coal Space Velocity, lb/hr ft^3 > 700°F	20	43	28	27	20	20
Pressure, psig	2170	2400	1500-2400	2400	2500	2500
Catalytic Stage						
Average Reactor Temperature, °F	780	720	720	711	750	750
Space Velocity, lb Feed/hr lb Catalyst	1.7	1.0	1.0	0.9	2.08	2.23
Catalyst Age, lb Resid/lb Catalyst	260-387	278-441	380-850	446-671	697-786	346-439
YIELDS, WEIGHT PERCENT MAF COAL						
C_1-C_3 Gas	7	4	6	6	7	8
C_4 + Distillate	40	54	59	62	64	63
Resid	23	8	6	3	2	5
Hydrogen consumption	4.2	4.9	5.1	6.1	6.1	6.4
Hydrogen Efficiency, lb C_4 + Distillate/lb H_2 Consumed	9.5	11	11.5	10.2	10.5	9.8
Distillate Selectivity, lb C_1-C_3/lb C_4+ Distillate	0.18	0.07	0.10	0.10	0.11	0.12
Energy Content of Feed Coal Reject to Ash Concentrate, percent	20	24	20-23	22	23	16

Source: Ref. 185.

Reconfigured Two-Stage Liquefaction (RITSL)

Lummus, in further development of the ITSL process, had increased distillate yield by placing the deasher after the second stage, with no detrimental effect of ashy feed on catalyst activity. This was confirmed at Wilsonville in RITSL Run 247. The RITSL configuration is illustrated in Figure 4-26. The slurry preparation, thermal liquefaction, and fractionation steps are the same as in the ITSL mode (Figure 4-25). However, the vacuum bottoms containing the thermal resid, unconverted coal, and ash are fed directly to the ebullated bed hydrotreater. The vacuum flashed bottoms from the hydrotreater is the feed to the CSD unit. The recycle solvent is composed of the deashed resid from the CSD unit and hydrotreated distillate.

A primary objective of Run 247 was to demonstrate unit operability in the RITSL mode. Because the hydrotreater feed was not deashed, it contained all the coal ash along with unconverted coal and heavy organics that would normally be removed in the deashing step in the ITSL mode (Figure 4-25). Thus, there was concern that catalyst deactivation would increase. Another operability question regarded the effect that this mode would have on deashing. Since the feed to the CSD unit would be the vacuum flashed bottoms from the hydrotreater, the CSD feed properties were expected to be considerably different than had previously been experienced.

Good operability with the RITSL configuration in Run 247 was demonstrated. On-stream times of each unit were 95 percent or better. The hydrotreater catalyst performed well in the RITSL mode. The catalyst used was presulfided Shell 324-M, and throughout the run, activity was higher than in previous runs in the ITSL configuration.

Retrograde reactions were essentially eliminated, increasing the potential distillate yield to 70 percent. Wilsonville then successfully tested ashy recycle. The main benefit of this ashy recycle with bituminous coal was to reduce the feed to CSD by over 50 percent, and

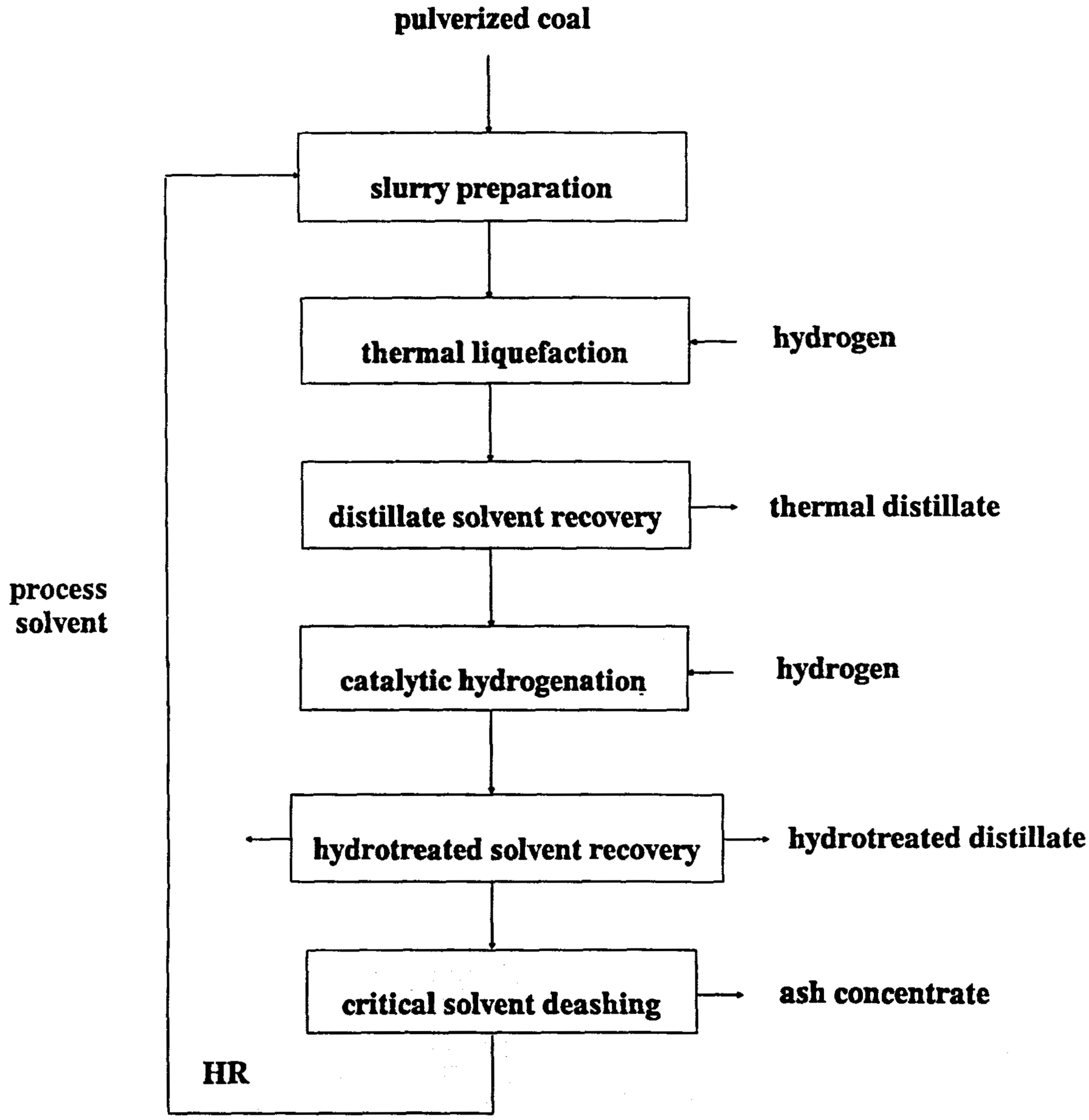

Figure 4-26. Block Flow Diagram of RITSL Operation

thereby reduce organic rejection in the ash-concentrate stream (see Run 250G in Table 4-7).

Close-Coupled ITSL (CC-ITSL)

With the deasher placed after the second stage reactor and the two stages operating at about the same pressure, the two reactors were close-coupled to minimize holding time between the reactors and eliminate pressure letdown and re-pressuring between stages (Figure 4-27). All the first-stage gases and light oil included with the second-stage feed did not affect the activity of the catalyst (Table 4-7). This close-coupling of the reactors removed several additional product letdown and separation operations between the two stages.

Operations with Subbituminous Coal

All single-stage processes had found subbituminous coal more difficult to convert to soluble liquids than bituminous coal. At first, ITSL experienced the same difficulty. Two changes in the ITSL process resulted in conversions of over 95 percent with Wyodak subbituminous coal (see Table 4-8). First, iron oxide and a sulfiding liquid, dimethyl disulfide, were added to the coal slurry to provide the beneficial effects for which iron sulfide is well known. This raised coal conversion to about 90 percent. Then, ashy recycle in Run 249 raised conversion to above 95 percent (see Table 4-8). The energy rejection, which had been high (30 percent or higher) in low-conversion runs, was reduced to 13 percent in Run 251 (Table 4-8), lower than the 16 percent achieved for bituminous coal (Run 250 in Table 4-8).

Additionally, the TSL approach in Runs 246-251 showed that subbituminous coal had a significant advantage over bituminous coal due to the high reactivity of its resid, which was apparent in the second stage. Wilsonville PDU was therefore able to produce an all-distillate product and make a high-quality solvent with a second-stage temperature below 700°F, which is lower than the temperature utilized for bituminous coal. Subbituminous coal also produced a -650°F product with greater ease (lower temperature) than does bituminous coal. These runs verified

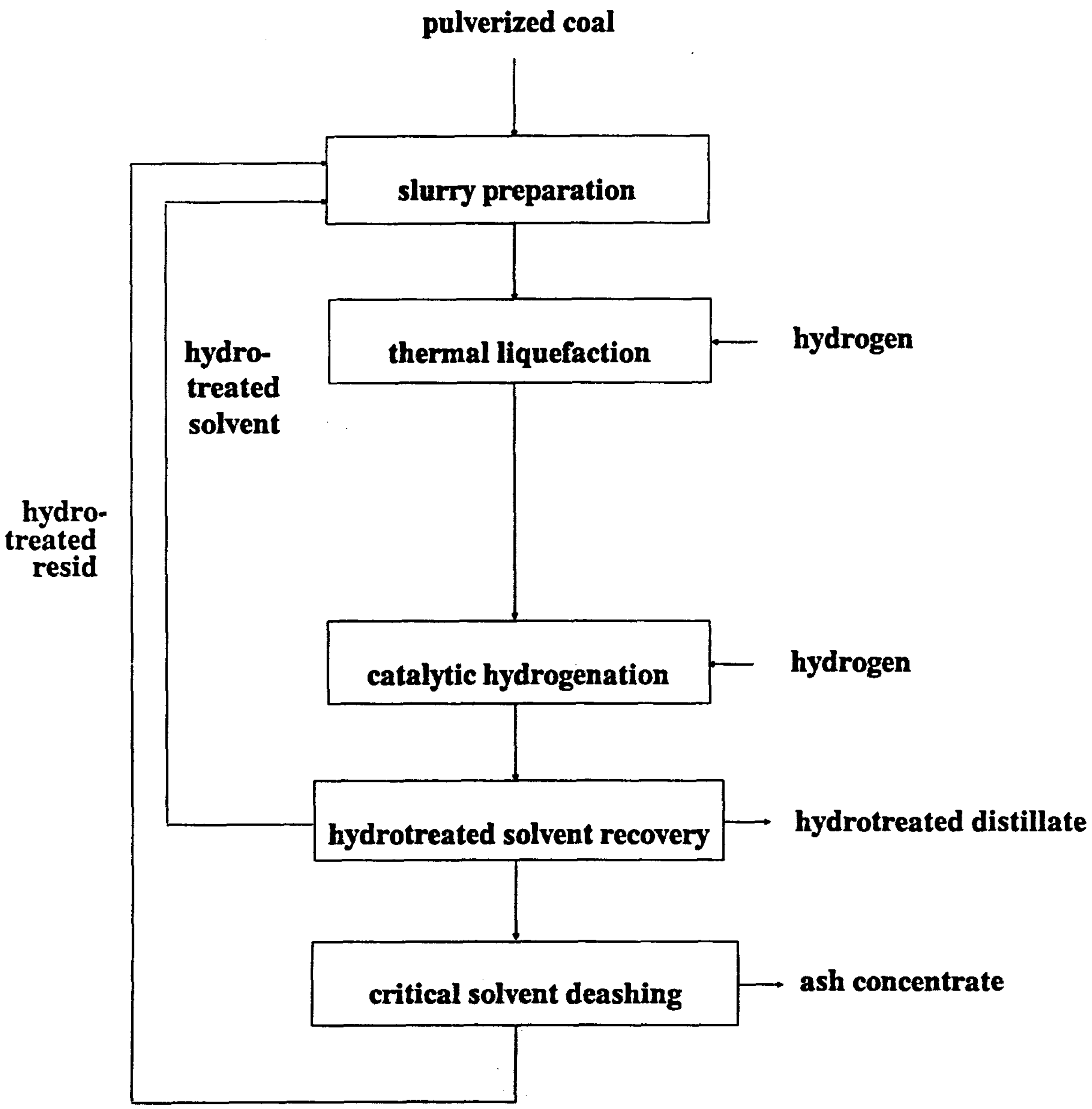

Figure 4-27. Block Flow Diagram of CC-ITSL Operation at Wilsonville

Table 4-8. Wilsonville Facility ITSL (Wyodak Subbituminous Coal)

Run No.	246G	249H	251-IIB
Thermal Stage			
Average Reactor Temperature, °F	813	802	819
Inlet Hydrogen Partial Pressure, psi	2,040	2,170	2,510
Coal Space Velocity, lb/hr-ft^3 > 700°F	17	17	25
Solvent-to-Coal Ratio	1.8	2.0	2.0
Solvent Resid Content, wt%	30	22	25
Catalytic Stage			
Reactor Temperature, °F	623	700	743
Space Velocity, lb Feed/hr lb Catalyst	1.0	1.6	2.8
Feed Resid Content, wt %	34	27	31
Catalyst Age, (lb Resid/lb Catalyst)	496	1683-1703	915-968
YIELD* (% MAF COAL)			
C_1-C_3 Gas	9	7	8
C_4+ Distillate	53	57	61
Resid	1	5	4
Hydrogen consumption	5.4	6.3	6.3
Hydrogen Efficiency, lb C_4+ Distillate/H_2 Consumed	9.8	8.9	9.7
Distillate Selectivity, lb C_1-C_3/lb C_4+ Distillate	0.18	0.12	0.13
Energy Content of Feed Coal Rejected to Ash Concentrate, %	20-24	18	13

* Elemental balanced yield structures
246G SO_3-free ash

Source: Ref. 185.

the earlier results at smaller scale that subbituminous coal is an attractive feed for direct liquefaction.

4.3.2.5 Development of Catalytic Two-Stage Liquefaction (CTSL)

Beginning in 1985 all PDU programs have used two catalyst stages. The following section reviews this process and its economics.

A. HRI CTSL (1982-Present)

Background

The limitations of the H-Coal process were discussed earlier. H-Coal is inherently a high temperature (830-845°F) catalytic process, in which extensive thermal cracking produces excessive hydrocarbon gases at the expense of additional hydrogen consumption. The higher temperature is favorable for liquefaction and upgrading reaction rates but is unfavorable for making a hydrogen-donor solvent. To control the relative rates of cracking and hydrogenation and to improve the solvent quality, a two-stage process was developed.

Features of CTSL Process

In 1982 HRI initiated the development of a catalytic two-stage concept, in which the first-stage temperature was lowered to 750°F to more closely balance hydrogenation and cracking rates, and to allow the recycle solvent to be hydrogenated in situ to facilitate hydrogen transfer to coal dissolution. The second stage was operated at higher temperature (815-825°F) to promote resid hydrocracking and generate an aromatic solvent, which is then hydrogenated in the first stage (see Figure 4-28). The lower first-stage temperature provides better overall management of hydrogen consumption, with hydrocarbon gas yields reduced by about 50 percent compared to H-Coal (186).

CTSL development also incorporated new thinking regarding deashing. The product from the second stage has undergone catalytic hydrogenation twice and is a much lighter deasher feed than the SRC-I resid for which deashers were designed. Its flow characteristics are more amenable to standard liquid-solid separation techniques, such as filtration. HRI

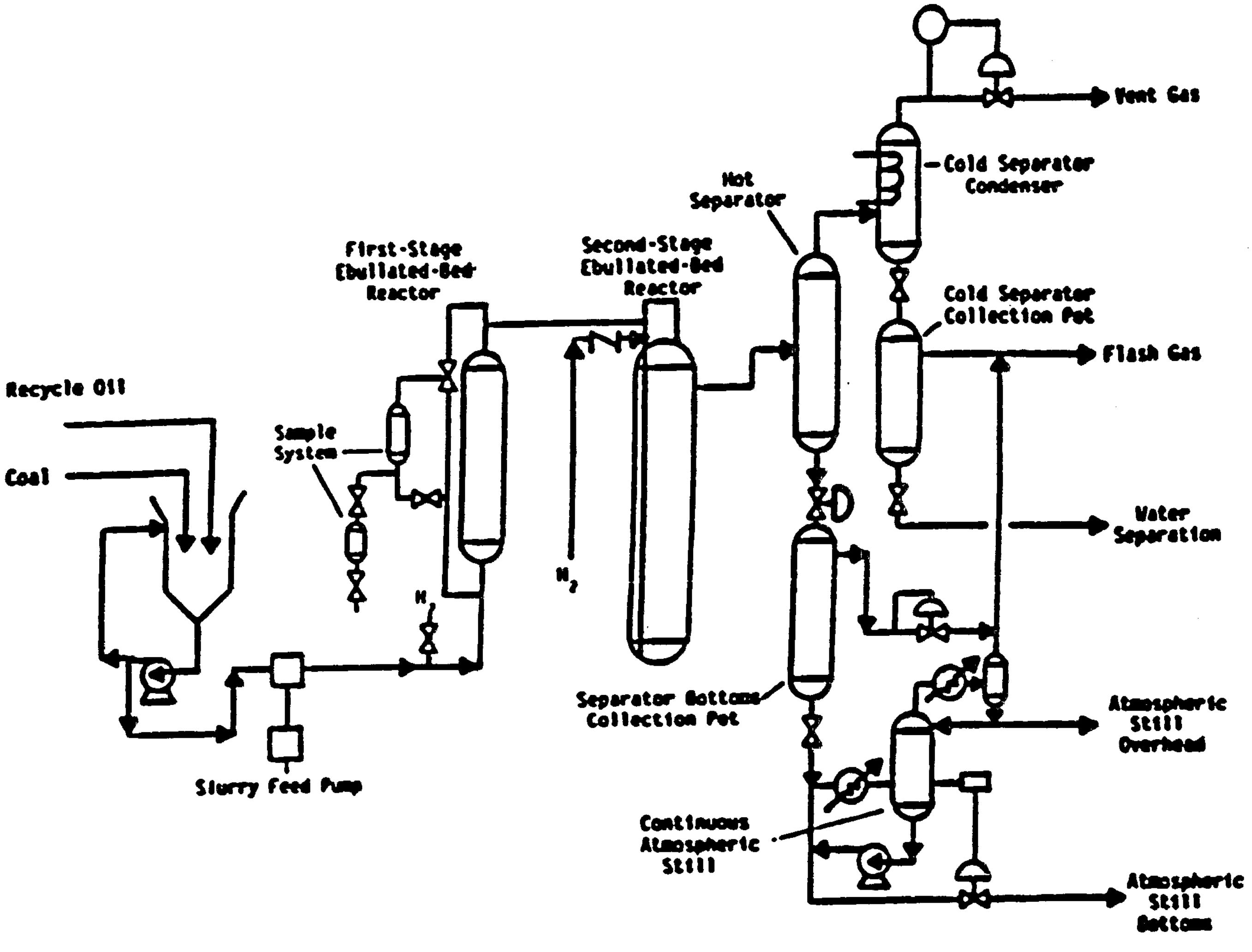

Figure 4-28. HRI Catalytic Two-Stage Unit

realized that higher distillate yields could be attained by the reduction of resid that is rejected in the ash-concentrated stream and the subsequent conversion of that recovered resid to distillate. Their CTSL process, therefore, successfully incorporates a pressure filter to reduce resid concentration in the reject stream (filter cake) below the 45-50 percent in the vacuum tower bottoms of the H-Coal process and even lower than had been achieved at that time by CSD. This change in deashing philosophy was in response to economic studies, which showed that overall liquefaction economics improve if the process maximizes distillate yield and produces hydrogen by natural gas reforming or by coal gasification. These studies signalled the end of the "hydrogen balanced" processes; no longer would a vacuum tower be suitable as the final step in ash removal.

A third change by HRI was in the catalyst. The H-Coal process had used a cobalt-molybdenum (CoMo)-on-alumina catalyst, American Cyanamid 1442B, that had been successful in hydrocracking petroleum resids. In petroleum applications, however, thermal cracking occurs first, followed by catalytic hydrogenation of the cracked products. In coal liquefaction hydrogenation must occur first, before the hydroaromatic molecules can thermally crack. The catalyst must hydrogenate large molecules, and this hydrogenation capability determines the rate at which resid is converted. The H-Coal catalyst was not well suited for this task because its porosity distribution was designed for smaller molecules. For CTSL the H-Coal catalyst was replaced by a nickel-molybdenum (NiMo) catalyst of a bimodel pore distribution with larger micropores, 115-125°A as opposed to 60-70°A for H-Coal catalyst. The nickel promoter is also more active for hydrogenation than cobalt.

These three changes constitute the major advances of CTSL over H-Coal. Their combined effect on liquid yields has been dramatic.

<u>Overall Results of HRI CTSL</u>

The latest reported results with Illinois No. 6 coal show a 76-percent distillate yield (<u>187</u>). Gas oil recycle to extinction has produced only slightly lower yield of -650°F distillate (see Table 4-9

Table 4-9. CTSL Demonstration Run Comparison with H-Coal (Illinois No. 6 Coal)

Process	H-Coal PDU-5	CTSL Run No. (227-20)	CTSL Run No. (227-47)
C_1-C_3	11.3	6.6	8.6
C_4-390°F	22.3	18.2	19.7
390-650°F	20.5	32.6	36.0
650-975°F	8.2	16.4	22.2[1]
975°F+ Oil	20.8	12.6	2.7[1]
HYDROGEN CONSUMPTION	6.1	6.3	7.3
COAL CONVERSION, Wt % MAF	93.7	94.8	96.8
975°F+ CONVERSION, Wt % MAF	72.9	82.2	94.1[1]
C_4-975°F, Wt % MAF	51.0	67.2	77.9[1,2]
HYDROGEN EFFICIENCY	8.4	10.7	10.7
C_4+ DISTILLATE PRODUCT QUALITY			
EP, °F	975.0	975.0	750.0
°API	26.4	23.5	27.6
% Hydrogen	10.63	11.19	11.73
% Nitrogen	0.49	0.33	0.25
% Sulfur	0.02	0.05	0.01
bbl/Ton	3.3	4.1	5.0

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1 750°F Distillate end point.
2 Coal contained 5.8% ash.

Note: All data at catalyst age representative of typical commercial replacement rates.

CTSL and H-Coal yields). Hydrogen efficiency is over 10 pounds of distillate per pound of hydrogen reacted. In addition, the two catalytic reaction stages produce a liquid with low heteroatom concentrations and a high H/C ratio, making this liquid closer in properties to petroleum than any coal liquids made by earlier processes.

B. Wilsonville CTSL (1985-Present)

At the Wilsonville Advanced Coal Liquefaction Facility a second ebullated-bed reactor was installed in 1985, and the plant has since operated in the CTSL mode. However, Wilsonville has made substantial modifications to the process operating conditions, the most significant being the reactor temperatures. As in ITSL, Wilsonville prefers to have most of the thermal cracking take place in the first reactor and solvent hydrogenation in the second reactor. Therefore, the first reactor is at the higher temperature (800-820°F), while the second reactor is kept lower at 760-795°F. Other reaction conditions are similar, including the catalyst type (see process flow diagram Figure 4-29).

Wilsonville, unlike HRI, continues to deash by CSD, and steady improvement in operation has reduced organic rejection to 8-15 percent, about the same as HRI achieves by filtration. This has enabled Wilsonville to operate CTSL at over four tons of coal per day during Run 254G and obtain distillate yields of up to 78 percent (Table 4-10). Yields with subbituminous coal are 62 percent. However, Wilsonville has still to test gas oil recycle to extinction.

4.3.2.6. Evolution of Liquefaction Technology

Since the early 1970's, after the oil embargo, substantial improvement in liquefaction processes and catalysts associated with these processes have taken place. The yields of liquids have increased, and simultaneously, their quality have also improved substantially. This history of process development improvements in the form of yields and quality of distillates is shown in Table 4-11 (188).

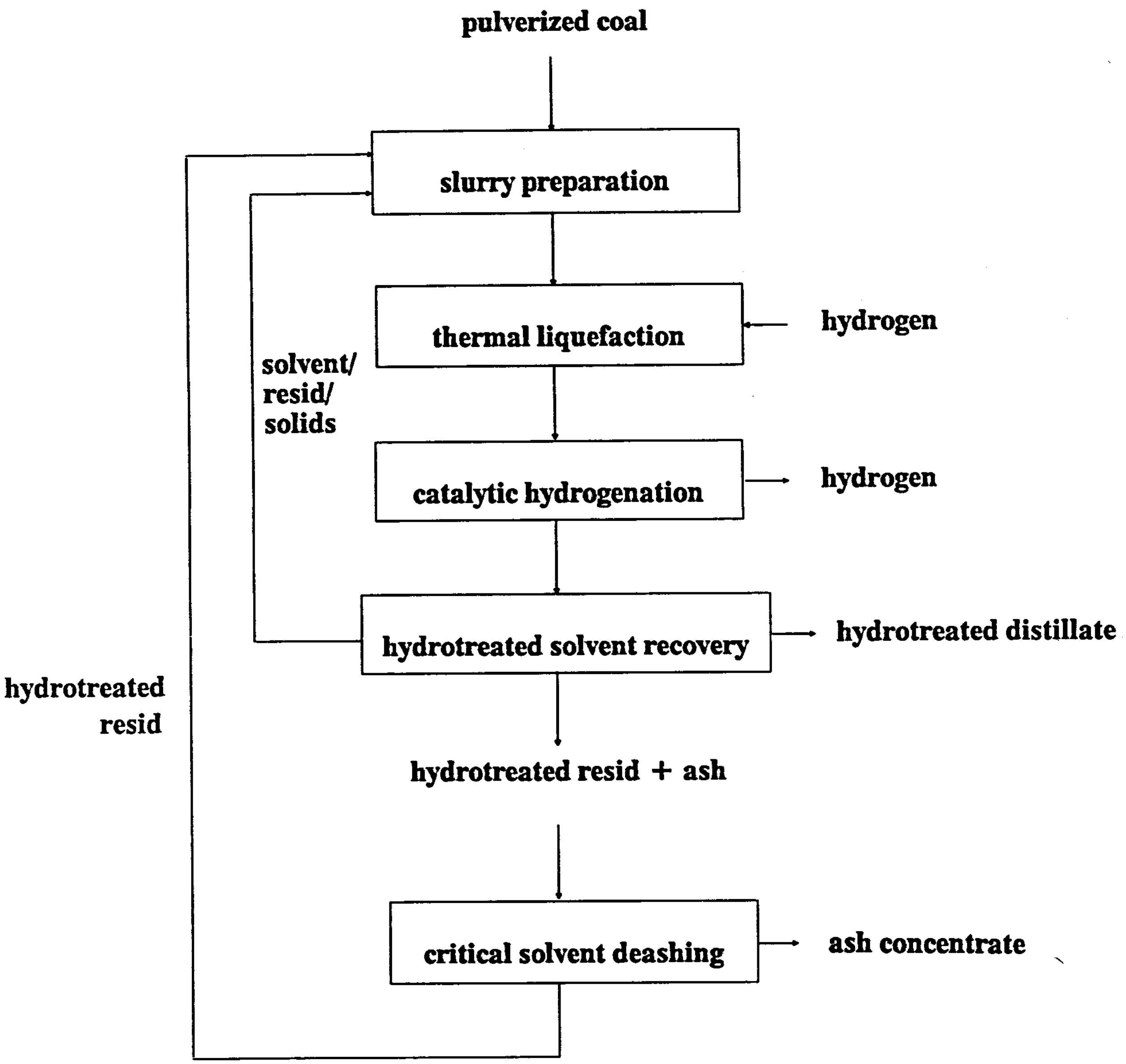

Figure 4-29. Block Flow Diagram of CTSL Operation with Solids Recycle at Wilsonville

Table 4-10. Wilsonville Facility - CTSL

OPERATING CONDITIONS

Run No.	253A	254G	251-IIIB
Coal	Illinois #6	Ohio 6[1]	Wyodak
Catalyst	Shell 317	Shell 317	Shell 324
First Stage			
Average Reactor Temperature, °F	810	811	826
Inlet Hydrogen Partial Pressure, psi	2,040	2,170	2,510
Feed Space Velocity, lb/hr/lb Catalyst	4.8	4.3	3.5
Pressure, psig	2600	2730	2600
Catalyst Age, lb Resid/lb Catalyst	150-350	1003-1124	760-1040
Second Stage			
Average Reactor Temperature, °F	760	790	719
Space Velocity, lb Feed/hr lb Catalyst	4.3	4.2	2.3
Catalyst Age (lb resid/lb catalyst)	100-250	1166-1334	371-510
Yield, Weight Percent MAF Coal			
C_1-C_3 Gas	6	8	11
C_4+ Distillate	70	78	60
Resid	-1	-1	+2
Hydrogen Consumption	6.8	6.9	7.7
Hydrogen Efficiency lb C_4+ Distillate/H_2 Consumed	10.3	11.3	7.8
Distillate Selectivity, lb C_1-C_3/lb C_4+ Distillate	0.08	0.11	0.18
Energy Content of Feed Coal Rejected to Ash Concentrate, %	20	10	15

---

[1] Approximately 6% Ash.

Table 4-11. History of Process Development and Performance for Bituminous Coal Liquefaction

Process	Configuration	Distillate wt % MAF coal	Yield bbl/t MAF coal	Distillate Qty gravity °API)	Nonhydrocarbon (wt %) S	O	N
SRC II (1982)	One-stage, noncatalytic	41	2.4	12.3	0.33	2.33	1.0
H-Coal (1982)	One-stage catalytic	52	3.3	20.2[#]	0.20	1.0	0.50
Wilsonville (1985), RITSL	Integrated two-stage, thermal-catalytic	62	3.8	20.2[##]	0.23	1.9	0.25
Wilsonville (1986), CTSL	Integrated close-coupled two-stage catalytic-catalytic	70	4.5	26.8[##]	0.11	<1	0.16
Wilsonville (1987), CTSL	Integrated close-coupled two-stage low-ash coal	78	5.0	+	+	+	+
HRI, CTSL (1987)	Catalytic-catalytic	78	5.0	27.6	0.01	-	0.25

[#] Light product distribution, with over 30% of product in gasoline boiling range; less than heavy turbine fuel.

[##] Higher boiling point distribution, with 20% of product in gasoline fraction and over 40% turbine fuel range.

+API and elemental analysis data unavailable at this time.

Source: Ref. 188.

Yields of distillates have increased from 41 percent to 78 percent, resulting in equivalent liquid yields of about 5 barrels/ton of MAF bituminous coal (such as Illinois No. 6 and Ohio No. 6). Quality is comparable or better than No. 2 Fuel Oil with good hydrogen content and low heteroatom content.

Several economic studies have charted the progress of TSL, all of which show the same trend of reduced cost per barrel of liquid product. A following section in this chapter discusses the dramatic improvement in liquefaction economics that have resulted from the technical advances of the last few years. The development programs at Wilsonville and Trenton should continue to produce further improvements.

4.3.2.7. Research Needs in Direct Liquefaction Process Development

Although developments have greatly improved direct liquefaction technology, significant improvements in CTSL are still possible. These include:

- More active catalyst or reduced rate of catalyst deactivation
- Gas oil recycle to extinction (-650°F product) with bituminous coals
- The use of deep-cleaned (<< 10% mineral matter) coal to improve distillate yield and reduce energy rejection
- Reduction of hydrogen consumption

Additionally, the new findings in coal chemistry will eventually lead to completely new process flow configurations. Whatever developments emerge will ultimately be tested at the proof-of-concepts (POC) scale, which is provided by the Wilsonville PDU. The DOE development program could actually be made more efficient if it had a smaller (50-200 pounds of coal per day) unit that could be an intermediate screening unit between Wilsonville and the research laboratories. Currently, the only unit of such size is the 50-pounds/day bench unit of HRI's, which has been used exclusively to test HRI's proprietary technology. A similar, or slightly larger, fully integrated continuous-operation process unit is needed to screen and develop emerging process concepts and thereby allow

Wilsonville to continue to do what it does best -- demonstrate POC of processes that have been developed at smaller scale.

4.3.3 Refining Coal Liquids[8]

4.3.3.1. Introduction

The name "syncrude" or "synthetic crude" is used rather loosely to describe hydrocarbon oils derived from sources other than petroleum. The name implies that they can serve as substitutes for petroleum crude. However, liquids produced from coal in direct liquefaction processes are quite different from petroleum. Can they really take the place of petroleum? Can we make products from coal syncrudes that meet petroleum specifications using conventional refining technology? If so, are there differences between products from petroleum and those from coal-derived oils? Are fuels from coal better or worse than conventional petroleum-derived fuels? How much will it cost to refine coal syncrudes?

From 1978 to 1985, Chevron under a contract with the U.S. Department of Energy studied the refining of coal liquids. Detailed results are given in a series of DOE Interim Reports (189). This work is the most extensive study of the refining of coal liquids. The results are briefly reviewed here. Also, the above questions will be addressed and areas identified in which further research is needed. For a more extensive overview of the state of the art in coal liquids upgrading, the reader is referred to a recent comprehensive study by Oak Ridge National Laboratory (190).

DOE supplied to Chevron the "net whole-liquid process product" from each of a group of liquefaction processes for which they have supported research and development. These processes are Solvent-Refined Coal (SRC-II), H-Coal, Exxon Donor Solvent (EDS), and Integrated Two-Stage Liquefaction (ITSL).

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[8] This section was written by Richard F. Sullivan and Harry A. Frumkin, Chevron Research Company.

In Chevron's program conceptual refining schemes were developed for processing each of the syncrudes in a "grass-roots" refinery (that is, a completely new stand-alone refinery) to produce fuels meeting current specifications. Then, pilot-plant tests were conducted for the key upgrading steps to make reasonable estimates of commercial catalyst performance. Finally, detailed engineering studies were made to determine stock balances and estimate refining costs.

4.3.3.2. Properties of Coal-Derived Oils

Table 4-12 summarizes some of the key properties of the coal-derived oils that served as feedstocks for these upgrading studies. For comparison Arabian Light crude is also included. Each of the coal oils was selected by DOE to represent, as nearly as possible, the net whole-liquid product from the liquefaction process at the time the oil was chosen. However, it should be recognized that an oil's properties may not be representative of the oil that an optimized commercial process would produce. All of the processes have only operated on a pilot-plant scale, and none is yet fully optimized. Furthermore, each process can operate in various modes, generating products with different properties.

These oils differ from typical petroleum crudes in a number of ways: (1) They are generally much lower boiling than typical petroleum crude. (2) They contain no residuum. (3) They contain mostly condensed cyclic compounds and few paraffins. (4) Most have relatively high heteroatom contents, particularly nitrogen and oxygen. (5) Most have a relatively low hydrogen content compared to petroleum.

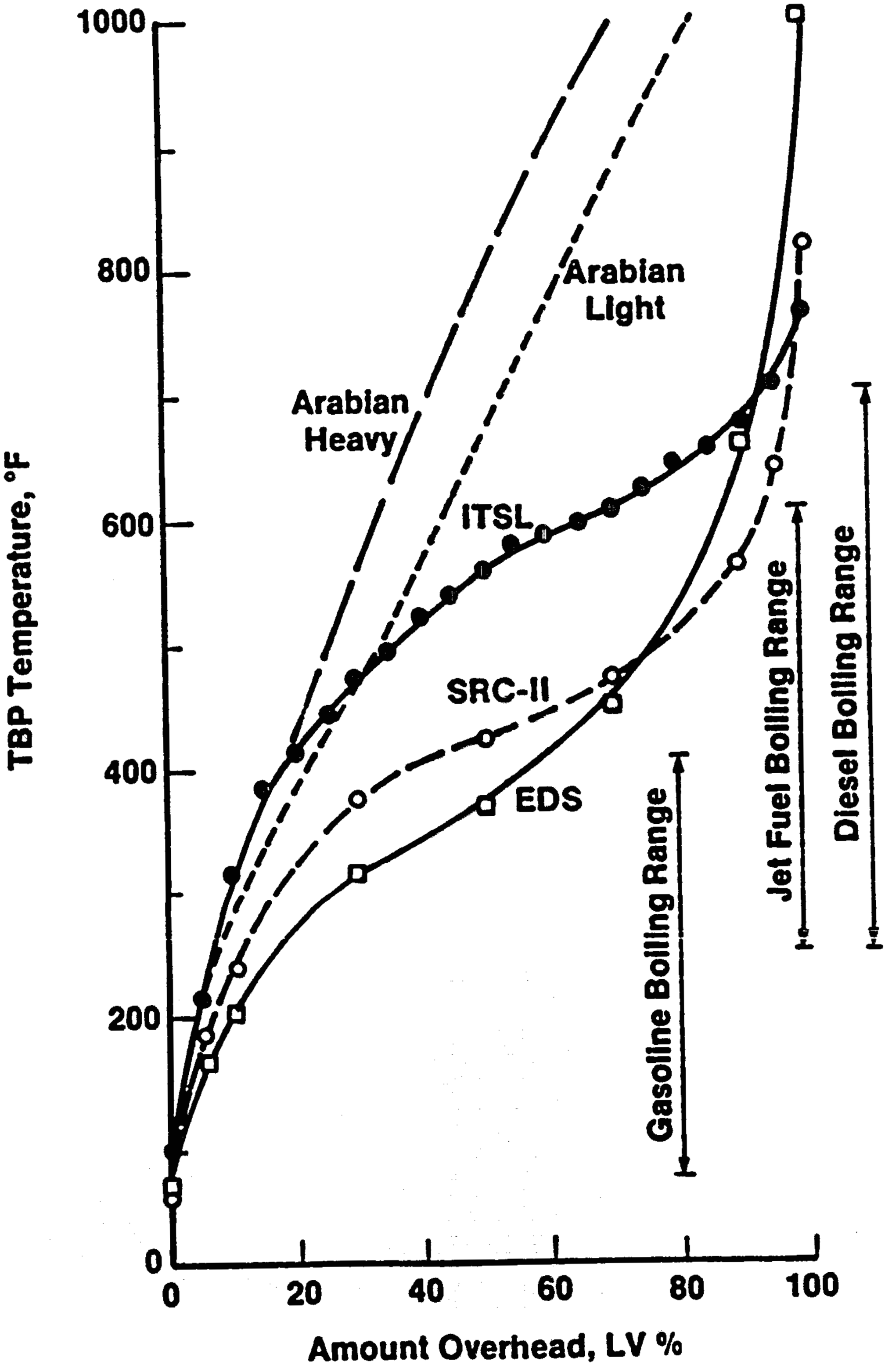
Figure 4-30 shows typical distillation curves of several coal-derived oils compared to typical Middle-East petroleum crudes. (The curves for the H-Coal oils are not shown in the figure, but fall into the envelope included by the other coal oils.) The coal oils contain little high-boiling material compared to petroleum because most of the higher-boiling oil is typically used as a recycle solvent in the liquefaction process and ultimately converted to lower-boiling products. The boiling range of the oil used as solvent can vary, however, depending on how the

Table 4-12. Coal - Derived Pilot Plant Feeds: Comparison of Properties

	<------- Whole Liquid (as Received) ------->					<------ Redistilled* ------>			
Liquefaction Process	ITSL	H-Coal	H-Coal	SRC-II	EDS	H-Coal	H-Coal	EDS	ARABIAN LIGHT CRUDE
Type of Coal	Illinois No. 6	Illinois No. 6	Wyodak	Pittsburgh Seam	Texas Lignite	Illinois No. 6	Wyodak	Texas Lignite	
Inspections									
Gravity, deg API	17.6	25.8	35.1	18.6	29.0	28.1	35.1	33.4	33.4
Sulfur, ppm	700	2000	410	2900	1180	1400	250	1000	17000
Nitrogen, ppm	730	4600	1700	8500	3000	3300	1500	1600	1000
Oxygen, ppm	1800	18000	8500	37900	19200	19600	6700	23400	1000
Hydrogen, Wt%	10.68	11.29	12.74	10.46	11.25	11.44	12.97	11.63	13.10
Carbon, Wt%	88.99	86.25	86.20	84.61	86.41	86.18	86.18	85.77	85.00
Hot Heptane Insolubles ppm	290	3500	680	469	1300	54	< 10	264	4400
Ramsbottom Carbon, Wt%	0.30	0.29	0.23	0.70	0.57	0.30	0.15	0.18	2.6
TBP Distillation, deg F@ St/5	97/214	56/177	56/156	56/189	53/164	56/170	52/165	47/142	112/219
10/30	314/471	213/333	173/261	241/379	203/317	200/310	178/269	171/296	287/472
50	560	404	354	424	370	380	356	342	655
70/90	609/676	476/588	429/535	473/562	452/662	440/508	424/509	404/512	875/ -
95/99 LV%	703/763	654/765	602/785	642/820	799/950	538/589	542/603	547/627	- / -
Boiling Range, LV%									
St - 400 deg F	18	49	60	37	57	57	63	69	31
400 - 700 deg F	76	48	38	60	35	43	37	30	16
700 deg F+	6	3	2	3	8	0	0	1	16

*	Illinois H-Coal	Wyodak H-Coal	EDS
Overhead, LV% of As-received Oil:	87	96	87

Figure 4-30. Distillations of Arabian Crudes and Coal-Derived Oils



liquefaction process is operated. Therefore, the boiling range of the net product can also vary, and upgrading studies can help guide the selection of the best operating mode for the liquefaction facility.

There are some significant differences among the different coal liquids, particularly between the two-stage liquefaction product -- ITSL oil -- and the others. The ITSL oil contains a much larger middle distillate fraction (76 LV percent boils between 400°F and 700°F) and less naphtha. It is also lower in heteroatom content and (except for SRC-II) lower in hydrogen content.

Some of the as-received oils, in particular the EDS and H-Coal oils shown in Table 4-12, have appreciable quantities of a high-endpoint "tail", which makes these stocks relatively hard to hydrotreat. These oils were distilled to remove the highest-boiling fraction, and the distillates were hydrotreated as well as the whole oils. Properties of the re-distilled oils are also given in Table 4-12.

In addition to the oils shown in Table 4-12, Chevron also studied the upgrading of several higher-boiling coal oils. Results are given in DOE reports (189) and a recent paper (191). The heavy fractions of these oils could either be used as recycle solvent or be part of the net liquid product, depending on how the liquefaction process is operated.

4.3.3.3. Conceptual Refining Plans

Chevron considered a variety of conceptual refining plans for orienting and guiding the pilot-plant work. The discussion here will be limited to two basic plants which will be used later as a framework for comparisons between the different coal-derived oils that were processed. Simplified flow schemes for these refineries are shown in Figures 4-31 and 4-32. Each scheme represents the main hydrocarbon flow in a refining module, excluding the many supporting plants necessary in a full-scale "grass-roots" refinery, such as byproduct recovery, waste treatment and hydrogen supply. Considering hydrocarbon flow alone, these coal-liquid processing schemes are less complex than those required for a modern

Figure 4-31. Refining of Coal Syncrude to Transportation Fuels

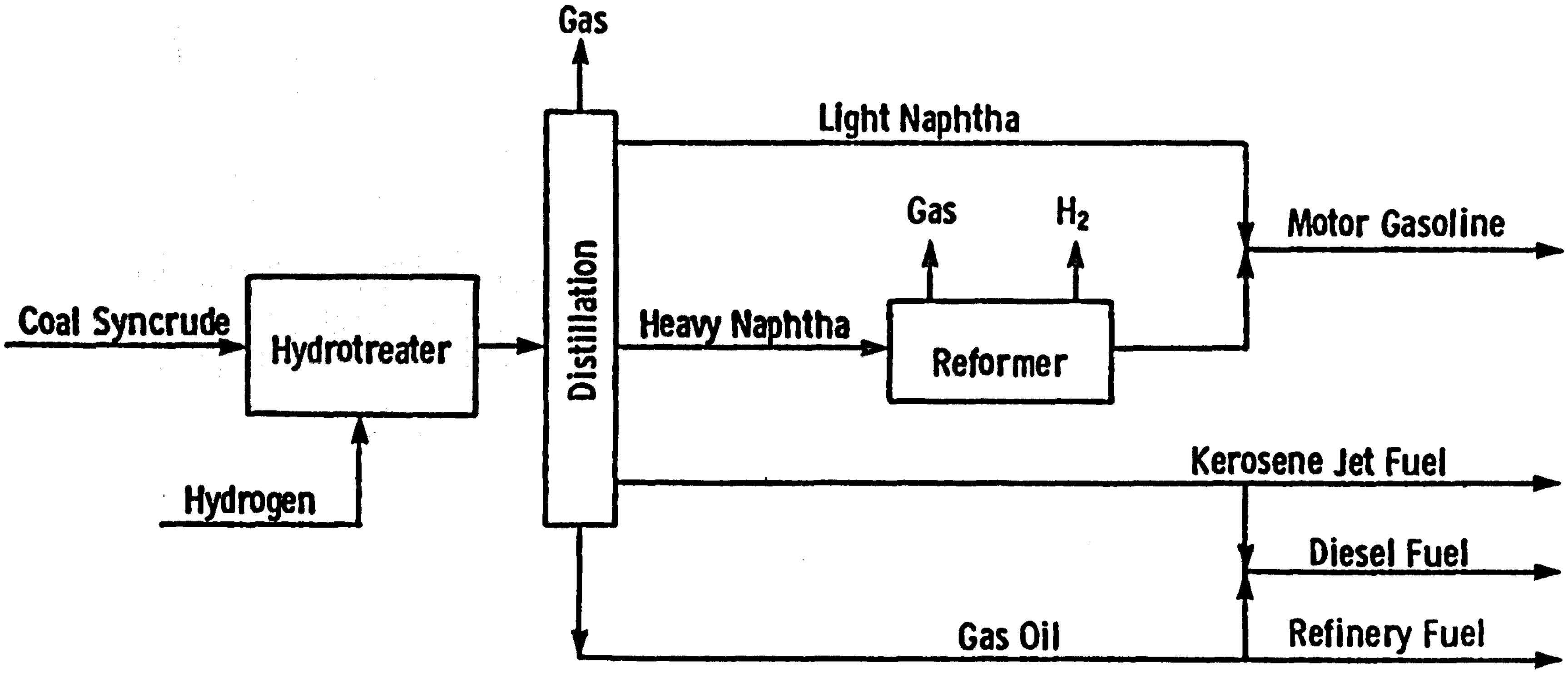
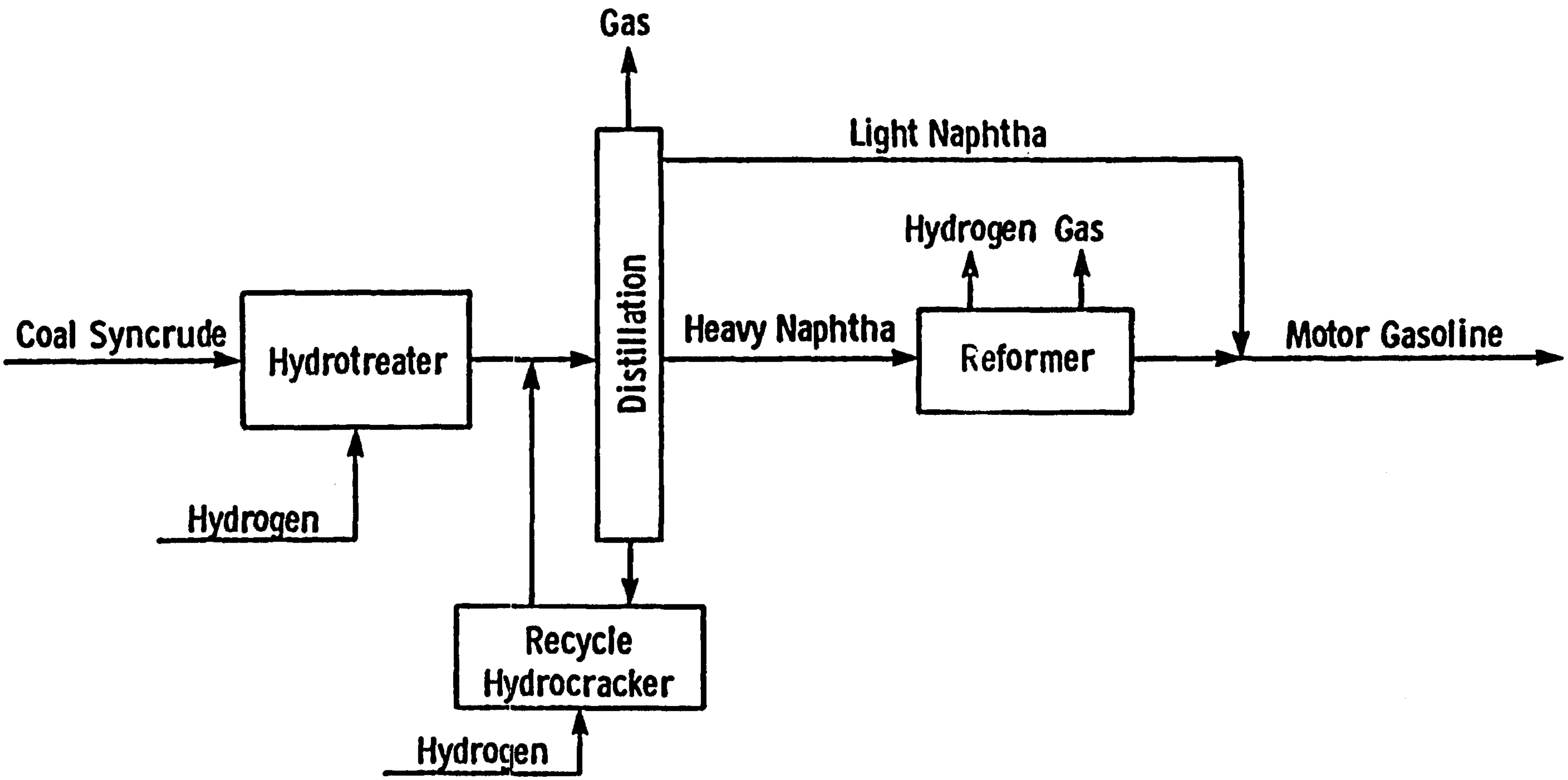


Figure 4-32. Refining of Coal Syncrude to Gasoline



large petroleum refinery processing heavy crudes. These schemes are less complex because these coal liquids contain no residuum. But, whereas the flow scheme would be simpler than for petroleum, the processing would be at least as severe.

In the first refining plan (Figure 4-31) the target products are gasoline and middle distillates (diesel and/or jet fuel). Because most of the feed already boils in the range of the desired products, no cracking conversion process is required. The whole oil is hydrotreated at a high severity to produce specification jet fuel or diesel, and the naphtha is catalytically reformed to high-octane gasoline. (This refinery could also produce No. 2 heating oil as the middle distillate product rather than jet/diesel. In that case, the hydrotreater could be operated at a lower severity than required for specification jet or diesel.)

In the second refining plan (Figure 4-32), as shown, the target product is all gasoline. In this case, as in the first refining scheme, the oil is first hydrotreated. However, the severity can be somewhat lower than in the first case, because the purpose is to remove heteroatoms rather than to make finished products. Then the hydrotreated oil is hydrocracked to convert the high-boiling fraction into naphtha, and the naphtha is catalytically reformed to gasoline.

4.3.3.4. Hydrotreating Runs

As indicated earlier, full-boiling-range coal oils require relatively high hydrotreating severities to remove the heteroatoms and increase the hydrogen contents. The hydrotreating studies have been described in detail elsewhere (189). Table 4-13 briefly compares results obtained with the feeds listed in Table 4-12 at comparable conditions with a single commercial hydrotreating catalyst, Chevron's ICR 106. The tests were made at 750°F average catalyst temperature, two hydrogen partial pressures (2300 and 1800 psia), and three different liquid hourly space velocities (LHSV): 0.5, 1.0, and 1.5 volumes of feed per volume of catalyst per hour.

Table 4-13. Hydrotreating Pilot Plant Tests for Coal-Derived Oils 750°F Catalyst Temperature; Fresh ICR 106 Catalyst

Liquid Hourly space Velocity Hydrogen Pressure, p.s.i.a. (approximate)	0.5 2300	1.0 2300	1.5 2300	1.5 1800
Re-distilled Illinois H-Coal				
Hydrogen consumption, SCF/bbl		2000	1950	
Product nitrogen, ppm		< 0.3	< 0.3	
Product aromatics, LV%		2	5	
Re-distilled Lignite EDS				
Hydrogen consumption, SCF/bbl			1600	1500
Product nitrogen, ppm			< 0.3	< 0.3
Product aromatics, LV%			6	10
Wyodak H-Coal				
Hydrogen consumption, SCF/bbl		1225	950	
Product nitrogen, ppm		< 0.3	< 0.3	
Product aromatics, LV%		3	13	
Illinois ITSL				
Hydrogen consumption, SCF/bbl	*	*	950	600
Product nitrogen, ppm			0.4	6
Product aromatics, LV%			38	58
Illinois H-Coal				
Hydrogen consumption, SCF/bbl	2150	1600	1275	825
Product nitrogen, ppm	< 0.3	0.3	10	50
Product aromatics, LV%	2	20	35	45
SRC - II				
Hydrogen consumption, SCF/bbl	3100	2500	2000	1725
Product nitrogen, ppm	< 0.3	0.4	20	150
Product aromatics, LV%	4	20	40	47
Lignite EDS				
Hydrogen consumption, SCF/bbl	1550		825	725
Product nitrogen, ppm	< 0.3		170	350
Product aromatics, LV%	16		38	40

*The Illinois ITSL was tested at lower temperature. The results:

L H S V	0.5	1.0
Temperature, deg F	710	730
H2 Consumption, SCF/bbl	1600	1400
Product nitrogen, ppm	< 0.2	< 0.2
Product aromatics, ppm	10	26

The best direct comparison is at 1.5 LHSV and 2300 psia because all the feeds were tested at these conditions and the results show major differences. In Table 4-13 the feeds are listed in order of ease of hydrotreating. The easiest feeds to upgrade are the redistilled Illinois H-Coal and lignite EDS, as indicated by the low product nitrogen and aromatic contents. Of the full-boiling-range oils, the Wyodak H-Coal is easiest, probably because of its high hydrogen content and low average boiling range.

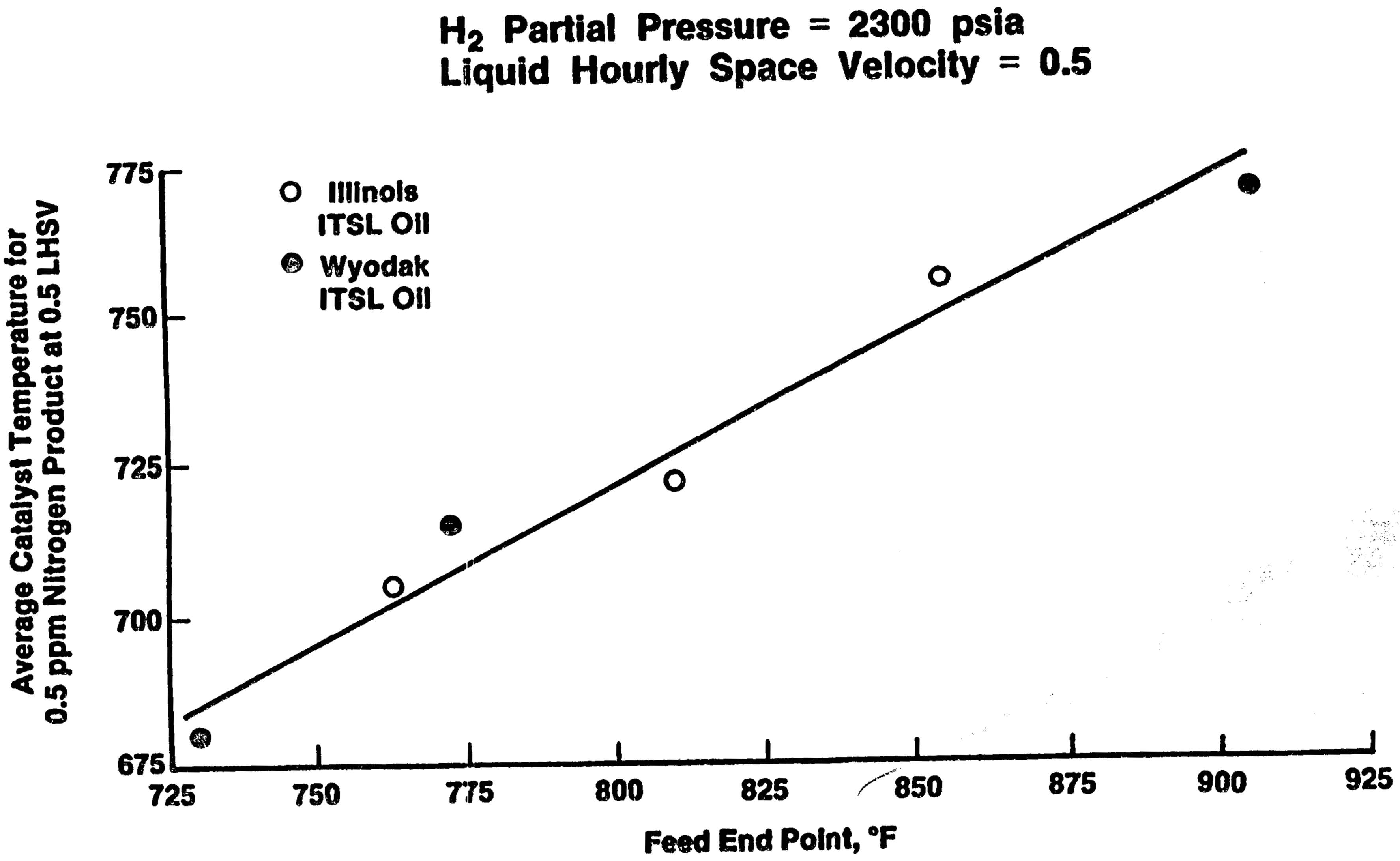
ICR 106 catalyst was quite stable at 2300 psia for hydroprocessing all the feeds, except for the full-boiling-range lignite EDS oil. With the EDS oil there was measurable decrease in hydrogenation activity with time on stream, even at 0.5 LHSV. It is believed that this result was due to coke-precursors in the high-endpoint "tail" of the EDS oil (Figure 4-30). When the high-boiling fraction was removed by distillation, the catalyst was very stable at these conditions.

At a lower pressure (1800 psia) and 1.5 LHSV, the catalyst was stable for both redistilled oils, and two of the full-boiling-range oils: Wyodak H-Coal and Illinois ITSL. However, in addition to the EDS oil, the Illinois H-Coal and the SRC-II oils also caused measurable catalyst deactivation at these conditions.

The hydrogen consumption needed for a given product quality from these coal liquids depends on their hydrogen content and heteroatom contents. The hydrogen consumption is higher than that usually needed in petroleum hydrotreating. Still, in spite of the relatively severe hydroprocessing conditions, there was little cracking to light gases, and liquid-volume yields were typically higher than those obtained when hydrotreating petroleum (because of the higher hydrogen input).

Chevron compared a series of oils produced in the ITSL process from two different coals -- Illinois and Wyodak. These oils have different endpoints, and are not all full-boiling-range oils. However, Figure 4-33 shows a fairly good correlation between the required catalyst temperature

Figure 4-33. Effect of Feed End Point on Catalyst Temperature for Hydrodenitrogenation of ITSL Oils with Fresh ICR 106 Catalyst



for 0.5 ppm nitrogen product and the feed endpoint, regardless of coal source. With the oils with endpoints of 750°F or below, the catalyst is very stable, and catalyst lives of several years can be predicted at the test conditions. The higher temperatures required for hydrotreating the higher-boiling feeds would significantly shorten the catalyst lives.

4.3.3.5. Hydrocracking Runs

In a paper (192), Chevron discussed in detail the hydrocracking of a representative coal oil, hydrotreated ITSL oil. Hydrocracking is a flexible process that can be varied to make only naphtha (as shown in Figure 4-33) or a combination of gasoline and middle distillate if the recycle cut point is increased. The products from hydrocracking coal oils are similar to those obtained from hydrotreating; the relative quantities of the products can be varied depending upon the demand.

4.3.3.6. Product Properties

A. General Comments

After being hydrotreated, products of similar boiling ranges from the different liquefaction processes and different coals are actually quite similar. After removal of the heteroatom-containing compounds, the products consist mainly of cyclic hydrocarbons. The severity of hydrotreating determines the amount of hydrogenation of aromatics to naphthenes. There are, however, some differences. Products from subbituminous coals contain more paraffins than those from bituminous coals, but fewer paraffins than products from lignites. Even so, the paraffin contents of lignite products are lower than those of petroleum products. For a given coal ITSL-process products contain fewer paraffins than those from the other processes. (Probably less ring opening occurs because of the lower severities required in two-stage liquefaction.)

B. Naphtha

Hydrotreated and hydrocracked naphthas from coal liquids are excellent feeds for catalytic reformers because of the high content of cyclic compounds. The naphthenes can be converted to high-octane aromatics by reforming at relatively mild conditions. Also, because they are easy to reform, such naphthas can be reformed at higher severities to an extremely high-octane product, which makes a superb gasoline blending stock or which could be used for the production of benzene, toluene, and xylene as chemicals. Because of the mild conditions required to produce a given octane product compared to petroleum, much of the hydrogen previously consumed can be recovered (193).

C. Jet Fuel

To make jet fuel from these coal liquids, most of the aromatics must be saturated. To meet the smoke-point specification of 20 mm or higher, the aromatic content for a full-boiling-range kerosene would typically be no higher than about 10 LV percent.

Jet fuels prepared from coal liquids offer some unique advantages over those prepared from petroleum. They have unusually low freezing points (because of the low paraffin content). Also, because they contain high concentrations of naphthenes, they are very dense and have high heating values by volume. Therefore, they could have specialized uses such as for military fuels.

Franck et al. (194) compared different hydrocarbon types to determine which had properties best suited for jet fuel. They showed that naphthenic hydrocarbons with two or three rings (molecular weight between 120 and 200) were the only ones to have all the following properties simultaneously: (1) high volumetric heat of combustion, (2) satisfactory mass heat of combustion, (3) acceptable thermal stability, (4) very low freezing point, (5) acceptable low-temperature viscosity, (6) low volatility, and (7) acceptable flame characteristics. Because coal liquids are extremely rich in these compounds, they make high-quality jet fuels.

D. Diesel Fuel

Diesel products from coal-derived oils also meet typical specifications including cetane number. As with jet fuel, most of the aromatics have to be hydrogenated before the specification for a cetane number of 40 is met. With all the oils studied except ITSL oil, the aromatics content has to be about 10 LV percent to meet this specification. With ITSL oils the specification could be met with about 20 LV percent aromatics present. The ITSL diesel had a somewhat higher average boiling range than the diesels from the other oils, and this may account for the difference.

Coal-derived liquids respond well to certain cetane improvers. Because of the high cost of hydrogen, it may be cost effective to substitute cetane improvers for hydrotreating severity to some extent. For example, adding 0.3 LV percent octyl nitrate (a commercial cetane improver) to diesel fuels from hydrotreated Wyodak H-Coal oil was shown to increase the cetane number by 6-8 numbers (195).

As with jet fuel, the diesel fuels also have excellent cold-weather properties, and high volumetric energy contents.

E. Heating Fuel

Although the primary purpose of Chevron's studies was to make transportation fuels, No. 2 heating oil was also evaluated as a possible product. Generally, it is possible to make heating oil by hydrotreating coal liquids less severely than is necessary to produce jet and diesel fuels. All specifications can be met, except gravity. The gravity specification could probably be waived in some applications. (Usually, the gravity specification also can be met by hydrotreating at higher severity to make a diesel-quality product.)

4.3.3.7. Detailed Refining Plans and Stock Balances

Based closely on the results of the pilot-plant work and conceptual refining plans, Chevron developed detailed refining plans and stock balances for each coal-derived feedstock. The primary basis for the detailed plans and stock balances was to produce 50,000 barrels per calendar day of the desired products in a complete new refinery. This refinery would include all necessary supporting facilities such as utility plants, tankage, and required environmental control equipment.

The refinery would be self-sufficient in fuel and hydrogen plant feed. It would produce finished distillate fuels meeting current specifications along with environmentally acceptable byproducts, e.g., sulfur and ammonia.

Stock balances have two kinds of results: (1) individual plant capacities and (2) feed and product flow rates. Interested readers will find detailed comparisons of the stock balance results in the Tenth Interim Report listed in Reference 189; only a brief summary is presented here. The stock balance plant capacities were used as part of the basis for the refining cost estimates. Stock balance flow rates are summarized as product yields along with the costs.

4.3.3.8. Refining Yields and Cost Estimates

Table 4-14 summarizes these results for the coal-derived oils studied. The costs are all given on a common basis, first-quarter 1984 dollars. (Cost studies of ITSL oil upgrading were not completed.) The oils are of two general classes: the "net whole-liquid process product" as received from DOE, and the stock as re-distilled at Chevron Research. There are three general refining modes as discussed above: two-stage hydrocracking to produce only motor gasoline, severe hydrotreating to produce motor gasoline and kerosene jet fuel or diesel, and less severe hydrotreating to produce motor gasoline and heating oil.

Because Chevron assumed "grass-roots", self-sufficient refineries for the comparison, the net yields allow for using part of the coal-derived feeds and/or refined products for hydrogen production and refinery fuel. If refining of coal liquids were integrated with an existing refinery, a less expensive stream would be the source of hydrogen and fuel.

The investment costs are estimated from correlations of costs of actual petroleum processing plants built by Chevron over the last twenty years, adjusted for the many factors which have changed or could change if and when a synfuels refinery is constructed. The synfuels-specific

Table 4-14. Summary of Yields and Refining Costs for Coal-Derived Oils

Feed		Yield of Desired Products, Liquid Volume Percent			Total[1] Investment, Millions of Dollars	Refining[2] Cost, $/bbl of Desired Products
		motor gasoline	kerojet/ diesel	heating oil		
SRC-II	as received	21	66	--	1160	23.5
	as received	92	--	--	1030	20.5
	as received	25	--	63	870	17.5
Illinois H-Coal	as received	18	73	--	960	19.5
	re-distilled	20	72	--	850	17
	as received	96	--	--	950	18.5
	as received	20	--	75	660	13.5
Wyodak H-Coal	as received	28	65	--	750	14
	re-distilled	30	64	--	720	14
	as received	96	--	--	840	16
	as received	23	--	72	560	10.5
Lignite EDS	re-distilled	24	67	--	740	15
	as received	97	--	--	960	19.5
	re-distilled	88	--	--	820	15.5
	re-distilled	23	--	66	710	14.5

(1) On-plot + off-plot + initial catalyst for capacity to produce 50,000 barrels per calendar day of desired products; first quarter, 1984. Excludes all costs for coal resources, mining, handling, liquefaction, and transportation.

(2) Calculated rigorously by discounted cash flow analysis using 15% after-tax constant dollar rate of return, 6% background inflation rate, 100% equity financing, 48% income tax, 10% investment tax credit, depreciation according to 1982 Tax Equity and Fiscal Responsibility Act, 5-year tax life, 20-year project life.

plants (the hydrotreaters and hydrocrackers) are estimated in further detail; design conditions are based directly on the pilot-plant data.

The histories of large, first-of-their-kind engineering projects show that the refining cost estimates will almost certainly change as synfuels development moves closer to commercialization. Therefore, the main value of these estimates is not for predicting ultimate synfuels costs, but rather for comparing one set of results versus another--different feeds, different processing schemes, and different product mixes. The results then can guide future research and development. For this reason a strong effort was made to keep the estimates consistent with each other.

From these refining costs some qualitative conclusions were reached. For example, the feeds rank differently depending on the product slate. To make all gasoline from the as-received stocks, the cost ranking is Pitt Seam SRC-II > lignite EDS > Illinois H-Coal > Wyodak H-Coal. But the EDS stock would be the most expensive from which to make a combination of gasoline and jet fuel or diesel. Also, re-distilling affects the refining cost of each feed differently: $4/bbl reduction for Lignite EDS, $2.50/bbl for Illinois H-Coal, and no reduction for Wyodak H-Coal.

The refining yield and the cost differences can be rationalized by considering the boiling range and the composition of each feed: (1) higher-boiling stocks are more expensive to refine but lend themselves to higher-boiling products; (2) heteroatom content can influence refining cost, although it usually trends with boiling range; and (3) the cost difference between refining to gasoline and refining to jet and/or diesel fuel increases as the hydrogen content of the feedstock decreases. (For example, with high-hydrogen-content feeds such as Wyodak H-Coal oil, the costs of making all gasoline or a combination of gasoline and jet/diesel are about the same. But with low-hydrogen-content feeds such as SRC-II, it is appreciably less expensive to make all gasoline than the combination.)

4.3.3.9. Relationships Between Coal Liquid and Petroleum Upgrading Costs

Several facts must be kept in mind if one is to judge what these costs mean and how they might be applied in situations other than internal comparisons. First, with the present and quite probably the future excess of petroleum refining capacity in this country, no new "grass-roots" refineries are likely to be constructed for coal-derived oils. Instead, refining facilities either will be integrated with liquefaction plants, or even more likely, coal-derived stocks will be refined along with petroleum in existing refineries. Of course, refining costs will then be entirely different from those presented here.

Second, petroleum refining costs themselves increased 50 to 60 percent between 1980 -- when estimated costs of refining coal-derived oils were first published -- and 1984, the basis for the costs presented here. (They are estimated to have increased an additional 15 percent by the first quarter of 1986.) Correction factors must be applied to earlier cost studies, whether for coal-derived oils or petroleum. Finally, the size of the refinery affects per-barrel cost. For example, product from a 50,000 barrel-per-day refinery costs about 20 percent more than that from a 100,000 barrel-per-day refinery. [(189), Report 10].

As with coal liquids, the costs of refining petroleum vary widely, depending on boiling range, heteroatoms and metals contents, and desired product slate. Most petroleum crudes have the advantage of being relatively hydrogen rich, but the disadvantage that they contain varying amounts of residuum.

There is little question that distillate fuels from coal will be more expensive than those from petroleum, based on the current prices of petroleum and state-of-the-art liquefaction and refining technologies (196). This is largely the result of the high cost of liquefaction, rather than the upgrading costs. Chevron did not attempt to compare the costs reported here with those for upgrading petroleum. However, other studies -- in particular, those of Universal Oil Products, Inc. (UOP) (197, 198, 199) -- serve to put these costs in perspective.

The refining costs shown in Table 4-14 are for a 50,000 barrel-per-day (BPD) grass-roots refinery. Earlier, UOP had made a cost comparison for grass-roots 100,000-BPD refineries, based on feeds of (1) Arab Heavy/Light, (2) Boscan, and (3) H-Coal liquid (198). BRSC/SAIC later escalated those costs to 1984 to form a comparison with Chevron's costs shown in Table 4-14. The results, shown in Table 4-15, indicate good agreement with costs in Table 4-14. The results also indicate that coal liquids cost less to refine than the middle-eastern blend and less than half the refining costs of a heavy Venezuelan crude. The advantages for coal liquids derive from (1) the absence of resid and (2) the relative insensitivity in refining costs to produce a predominantly gasoline product.

In the same report BRSC/SAIC estimated the incremental costs of refining coal liquids in an existing refinery. These costs are shown in Table 4-16. The lowest costs are for the case of liquids from Wyodak coal refined to gasoline, jet fuel, and No. 2 oil. The low end of the cost range for each feed is based on credit taken for backing out the crude oil needed to produce the same product slate. Based on this study BRSC/SAIC reported the conclusions shown in Table 4-17.

4.3.3.10. Conclusions

If the properties of the coal liquids shown in Table 4-12 are indeed representative of the liquefaction products made from an eventual commercial process, there is virtually no doubt that they can be upgraded to specification transportation fuels using modern commercial petroleum-processing technology. Of course, not every refinery could handle them. High-pressure hydrotreating units would be necessary. Still, important questions remain as to how the liquefaction of coal and the refining of coal liquids will interface, and additional research is needed to optimize this relationship.

Table 4-15. Refinery Costs Based on UOP Summary[1]

	65/35% Lt/Hvy Arabian	Boscan	H-Coal Distillate
Feed rate bbl/CD	100,000	100,000	100,000
Products,[2] bbl/CD	87,600	92,900	92,900
Investment, MM dollars	1,119.4	1537.7	853.5
Investment for 50,000 bpd prod.[3]	777	1028	573
Escalated to 4th qtr. 1984	953	1261	703
Total Operating Costs, MM$/yr.[4]	39.5	258.5	39.6
Capital Charges, MM$/yr.[5]	285.9	378.3	210.9
Operating Costs, $/bbl prod.	2.72	13.66	2.65
Capital Charge, $bbl prod.	17.41	23.03	12.84
Total Refining Costs, $/bbl prod.	20.13	36.69	15.49

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[1] Tables 7 and 8 "Processing Requirements and Economic Analysis of Heavy Oil and Syncrude Refining" UOP Process Division, Second World Congress of Chemical Engineering, Montreal, Canada, October 4-9, 1981.

[2] 66.7 volume percent gasoline, 33.3 percent No. 2 fuel oil.

[3] Calculated as follows: (50,000 bbl/CD products) then escalated to fourth quarter 1984.

[4] Labor, catalyst, chemicals and utilities per bbl of product escalated to fourth quarter 1984. Investment-related costs calculated as per (3).

[5] 30 percent of Capital Charges, as per UOP.

Table 4-16. Differential Refining Costs, Dollars per Barrel of Desired Product

Syncrude Feed	Gasoline	Gasoline/ Jet Fuel	Gas/Jet/ No. 2
W. Virginia SRC-II	6.50 - 10.40	4.30 - 8.30	3.50 - 7.40
Illinois H-Coal	4.00 - 7.70	4.70 - 8.70	1.30 - 5.40
(Redist) Illinois H-Coal	— —	3.70 - 7.40	— —
Wyodak H-Coal	2.50 - 6.30	2.10 - 5.70	0.00 - 3.50
(Redist) Wyodak H-Coal	— —	1.80 - 5.40	— —
Texas Lignite EDS	3.50 - 7.90	— —	1.90 - 4.60
(Redist) Texas Lignite EDS	2.90 - 6.50	2.30 - 5.90	1.80 - 5.40

Table 4-17. Conclusions from BRSC/SAIC Economics Study

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1. If coal-derived syncrudes are a substitute for some of the heavy crude oil feed to a refinery, processing costs are $0-5 per barrel of products greater than the cost of refining crude oil in the same process units. A syncrude with a high hydrogen content and low heteroatom concentrations will cost less to process to finished products than a high-sulfur, low-hydrogen heavy crude.

2. If the syncrude is used to add incremental capacity to the refinery, processing costs are $5-10 per barrel of product. This may be lower than the cost of processing additional heavy crude oil to achieve the same products.

3. Wyodak H-Coal Syncrude required the lowest processing costs and West Virginia SRC-II syncrude required the most, but the differentials among the four coal-derived syncrudes that were investigated were only $2.50-4.40 per barrel of products, depending on the product slate. This apparent advantage of Wyodak H-Coal is minor compared to the cost of converting coal to syncrude.

4. Of probably greater significance is that the Chevron report shows that coal-derived syncrudes can be processed to make refined products, using conventional refinery operations, and at reasonable costs. Product selectivity was relatively insensitive to coal or liquefaction process, and was about 100 volume percent for all cases.

5. Hydrogen is the major cost item and the only significant cost differential among the syncrudes processing cost items.

In most liquefaction processes a substantial degree of product-slate adjustment can be achieved within the liquefaction plant itself by changes in the process variables. The relationship between the cost of these changes and the cost of downstream refining must be considered. The most economical combination may require product-slate adjustment in the main process, followed by appropriate downstream units for product upgrading to market specifications (200). For example, MacArthur et al. (201) evaluated the merits of operating the H-Coal process in the mode of extinction recycle of 650°F+ vacuum gas oil, compared to typical H-Coal operating conditions. They concluded that this operating mode improved the selectivity to liquid product and reduced commercial plant investment (including upgrading) by 10 percent and the cost of producing coal liquids by 6 percent compared to typical operation.

In addition to boiling range, another factor that has a large effect on the cost of refining coal liquids is their hydrogen content. Because the finished fuels require a certain hydrogen content, hydrogen either must be added during the liquefaction process or during refining. Downstream hydrotreating makes efficient use of hydrogen, because it produces very little byproduct light gas. Therefore, it may be cost effective to have relatively hydrogen-poor liquefaction product (such as that from the ITSL process shown in Table 4-12), even though this adds to the downstream cost. Also, cheaper sources of hydrogen would significantly reduce costs. Furthermore, if the liquefaction and the refining facilities were integrated, they could share the same hydrogen plant, and additional costs could be saved.

The difficulty and, therefore, the cost of hydrotreating a coal-derived liquid increase rapidly with its boiling range, particularly if the endpoint is increased above 700°F. This is because of the high concentration of condensed aromatic and polar compounds in the high-boiling fractions which tend to cause rapid deactivation of the catalyst by coke deposition. Therefore, if at all possible, the high-boiling fraction should be removed from the 700°F- oil before hydrotreating. Usually, the high-boiling oil can be used to advantage as recycle solvent in the liquefaction process. Clearly, sharp separation between the net liquid product and the heavy oil to be recycled is desirable. None of the oils shown in Table 4-12 contains large amounts of 700°F+, but even the amounts present have a very large deleterious effect. When this material is removed by distillation, the oils become much easier to upgrade.

Coal liquids boiling in the 700-900°F range are relatively hard to upgrade. However, it is technically feasible to hydrotreat coal oils in this boiling range to acceptable products. Almost certainly, the cost will be high, and more research is needed to optimize their upgrading. Clearly, from the viewpoint of the refiner, it is desirable to have them consumed as recycle solvent in the liquefaction process. Also, most of the biologically hazardous material is reported to be in the 700°F+ oil (190), and environmental problems in refining can be minimized if these materials are recycled to extinction at the upstream facility.

Any coal oils boiling above 900°F would be exceedingly hard to upgrade using conventional petroleum technology. New technology would be required to handle these materials.

4.3.4 Economics of Coal Liquids[9]

4.3.4.1. Introduction

Work to review and analyze ongoing research in coal liquefaction, with specific emphasis on the impact of current and projected technical advances on the cost of liquid products from coal, was begun in the early 1980's. The primary emphasis at that time was on the single-stage liquefaction processes which were being demonstrated in pilot plants of about 200 tons per day. The two processes demonstrated at this scale were the Exxon Donor Solvent (203) or EDS process, and the H-Coal (204) process developed by Hydrocarbon Research.

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[9] This section was written by David Gray and Glen Tomlinson, The MITRE Corporation, based upon a presentation made at Alternate Energy '88, Napa, California, April 1988.

There has been considerable technical progress in coal liquefaction since that time. This technical progress is briefly reviewed below, and coal liquefaction economics are addressed.

4.3.4.2. Technical Progress in Direct Coal Liquefaction

There are two parts to the problem of producing quality liquid products from coal. The first requirement is to dissolve the coal in order to produce a liquid product. The second requirement is to upgrade the liquid to a product which can be distilled and treated to produce refined specification products. The early coal liquefaction processes attempted to accomplish both these requirements in a single reactor. It has since been learned that the two steps have different process requirements and are better accomplished in two reaction stages, each operating under different conditions.

Another important development has been the recognition of the important role played by catalysts. It was always feared that the ash and other residue which is necessarily present when coal is processed would reduce catalyst life to unacceptably low levels. The H-Coal experience, and much subsequent experimental evidence, have proven that this is not the case (205).

One of the main byproducts of recent research in coal liquefaction was the discovery that subbituminous coals, which were once thought to be unsuitable for liquefaction, can give surprisingly good yields when properly processed (206).

Figure 4-34 shows the current two-stage processing scheme which has evolved from continued research. Both stages employ ebullating-bed reactors which are derived from H-Oil and LC-Fining (207). These reactors are becoming more common in petroleum resid upgrading. This current two-stage configuration has resulted from several significant modifications since the two-stage concept was originally conceived by Neuworth (208) and demonstrated by Lummus in the early 1980's (209). The

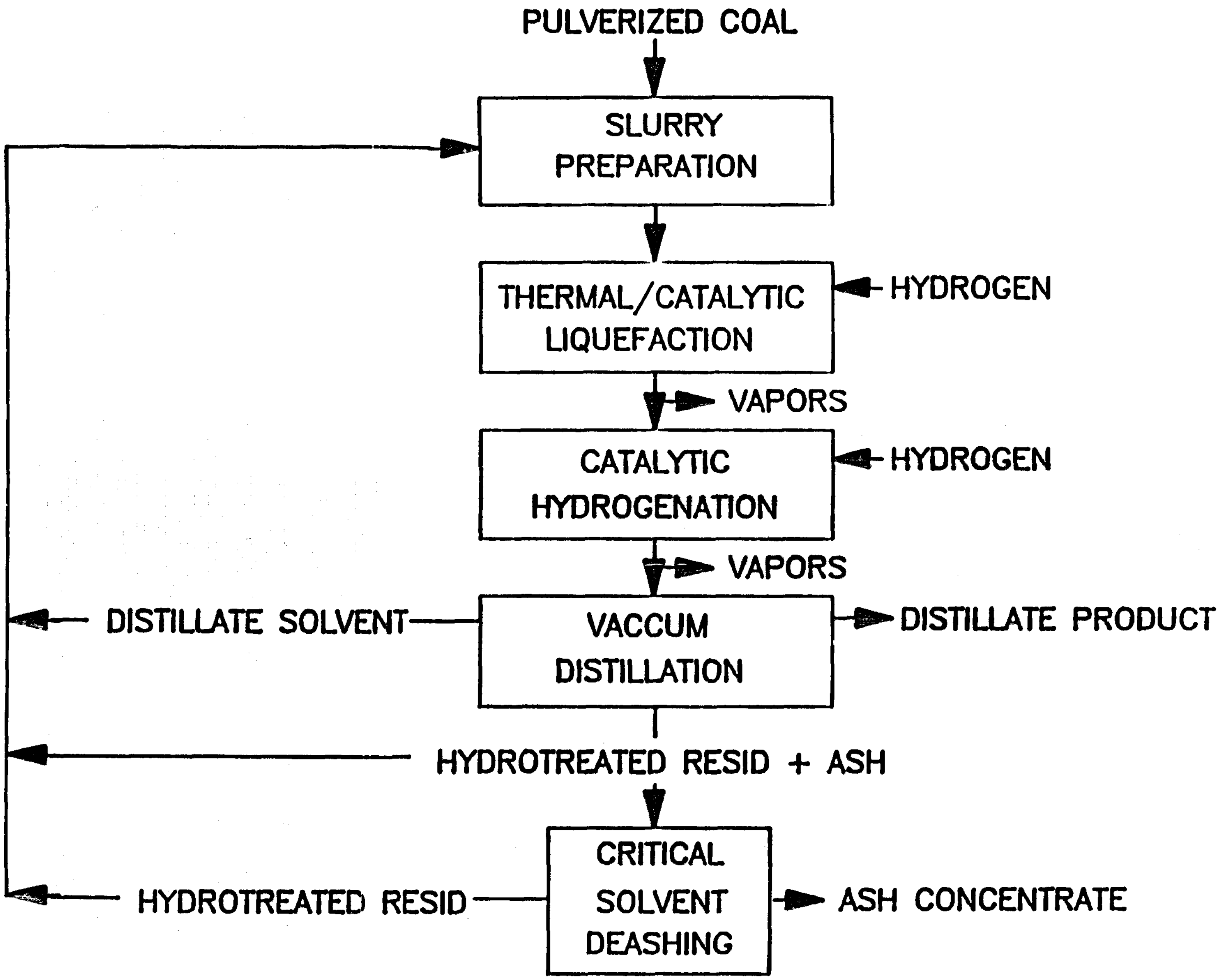

Figure 4-34. Close-Coupled Ash Recycle Configuration

early Lummus concept used a short-contact-time thermal dissolver for the first stage followed by a deashing system. The deashed material was then hydrotreated in an ebullating-bed LC-Finer. The recycled solvent from the second-stage LC-Finer proved to be a potent hydrogen donor, permitting the first-stage thermal reactor to achieve high coal dissolution.

Early work at the Wilsonville coal liquefaction facility in Alabama (3-6 tons per day coal throughput) demonstrated a two-stage configuration that differed from the Lummus configuration in that the first-stage thermal treatment was of longer duration and a different, more efficient deashing system was used. Wilsonville subsequently demonstrated a configuration which deashed the dissolved coal after hydrotreatment. Thus the first-stage effluent was passed directly to the second-stage catalytic reactor with no interstage deashing. The current two-stage configuration shown in Figure 4-34 uses an additional modification wherein a portion of the ash-containing effluent from the second-stage hydrotreater is recycled to the first stage. Sufficient material is deashed to remove the steady-state solids accumulation.

These configurational changes have resulted in some important process improvements. When deashing is accomplished after the second stage, the liquid being separated from the ash and unconverted coal is relatively light and much easier to deash. Thus less coal liquid is rejected, and more is recovered for recycle and ultimate conversion to distillate. Coupling the first and second stages eliminates equipment for interstage product separation and distillation and permits the initial coal solution to be more rapidly stabilized by hydrotreatment. Recycling some of the ash-containing second-stage effluent and deashing only sufficient material to remove the steady-state accumulation of solids greatly reduce the size of the deashing unit. The remaining material in the ash concentrate can be gasified to produce hydrogen for the process. If the residue is insufficient, coal or natural gas can be used to produce additional hydrogen.

Figures 4-35 and 4-36 compare the output of H-Coal and EDS to the Lummus Integrated Two-Stage Liquefaction (ITSL) system, and to the current two-stage system recently demonstrated at Wilsonville (210). The substantial improvement in liquid yield has been the result of reducing both the formation of hydrocarbon gases, and the soluble residue. Both of these improvements also have a very favorable impact on the effective use of hydrogen in the system by incorporating more hydrogen in the liquid product.

Figure 4-37 shows the increase in yields in terms of barrels per ton of coal liquefied. Yields are shown for both Illinois and Wyoming coal feedstocks. The results dramatically illustrate the point made earlier about the suitability of the current process for low-rank coal.

Figure 4-38 compares the quality of the liquid products from the four systems. The current two-stage products are higher in hydrogen, and contain fewer heteroatoms than products from the earlier systems. These characteristics make the current two-stage products easier to upgrade to specification fuels and hence more valuable to refiners.

4.3.4.3. Economic Considerations

There is of course a cost associated with these improvements. Two reactors obviously cost more than one. However, since the reactors themselves make up only a small part of the overall investment, the capital cost increase is small compared to the yield improvement shown earlier.

Table 4-18 summarizes the technical and economic performances of commercial-design coal liquefaction plants for Illinois No. 6 coal based on the yield data discussed above. The estimates of capital required were developed by MITRE on a consistent basis so that the differences between plants are not obscured by differences in estimating procedure. The total overnight capital requirement is about 60 percent greater than the plant construction cost. The major additional capital items are engineering design and project contingency (25 percent), allowance for

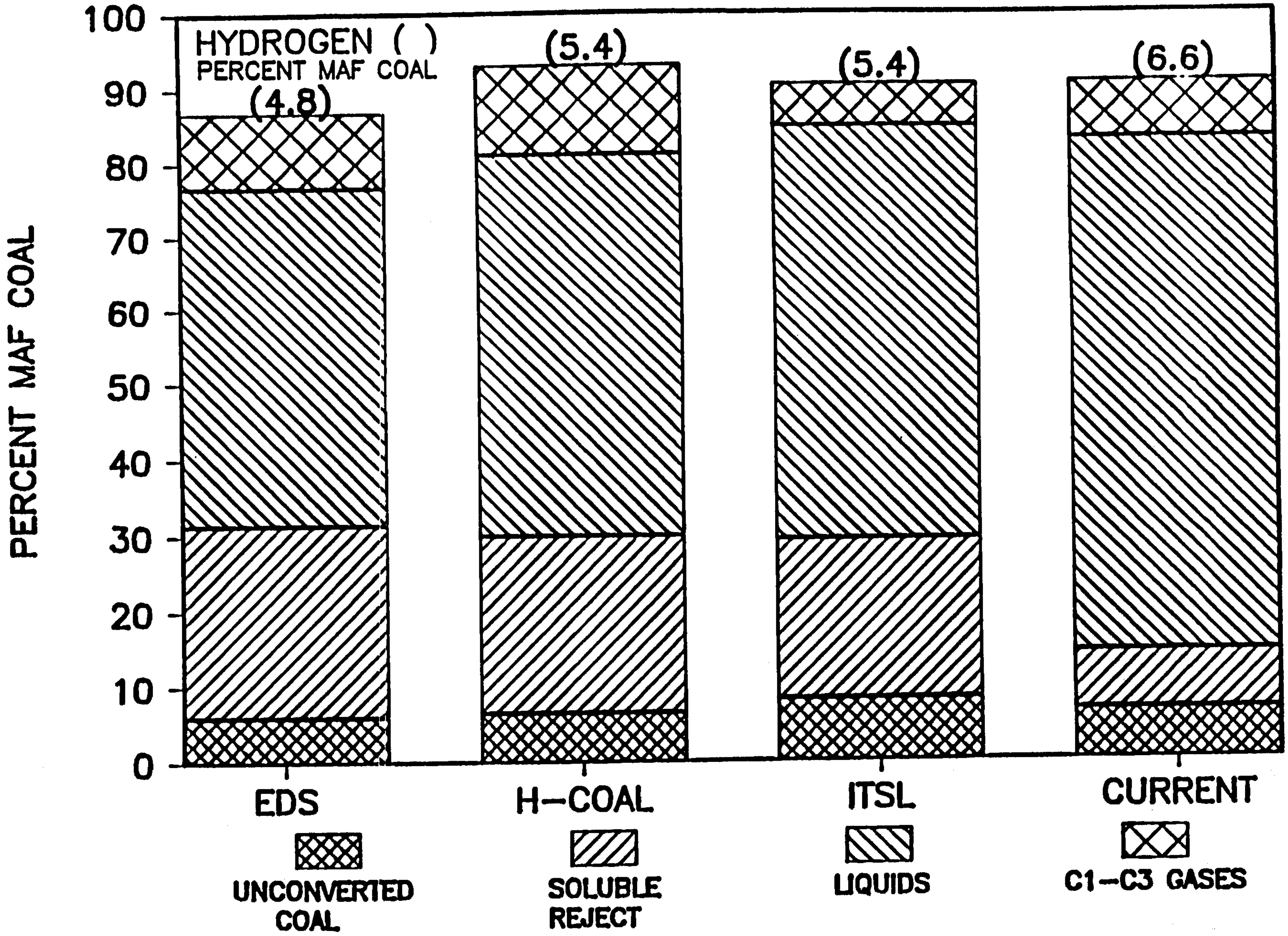

Figure 4-35. Yields from Illinois No. 6 Coal

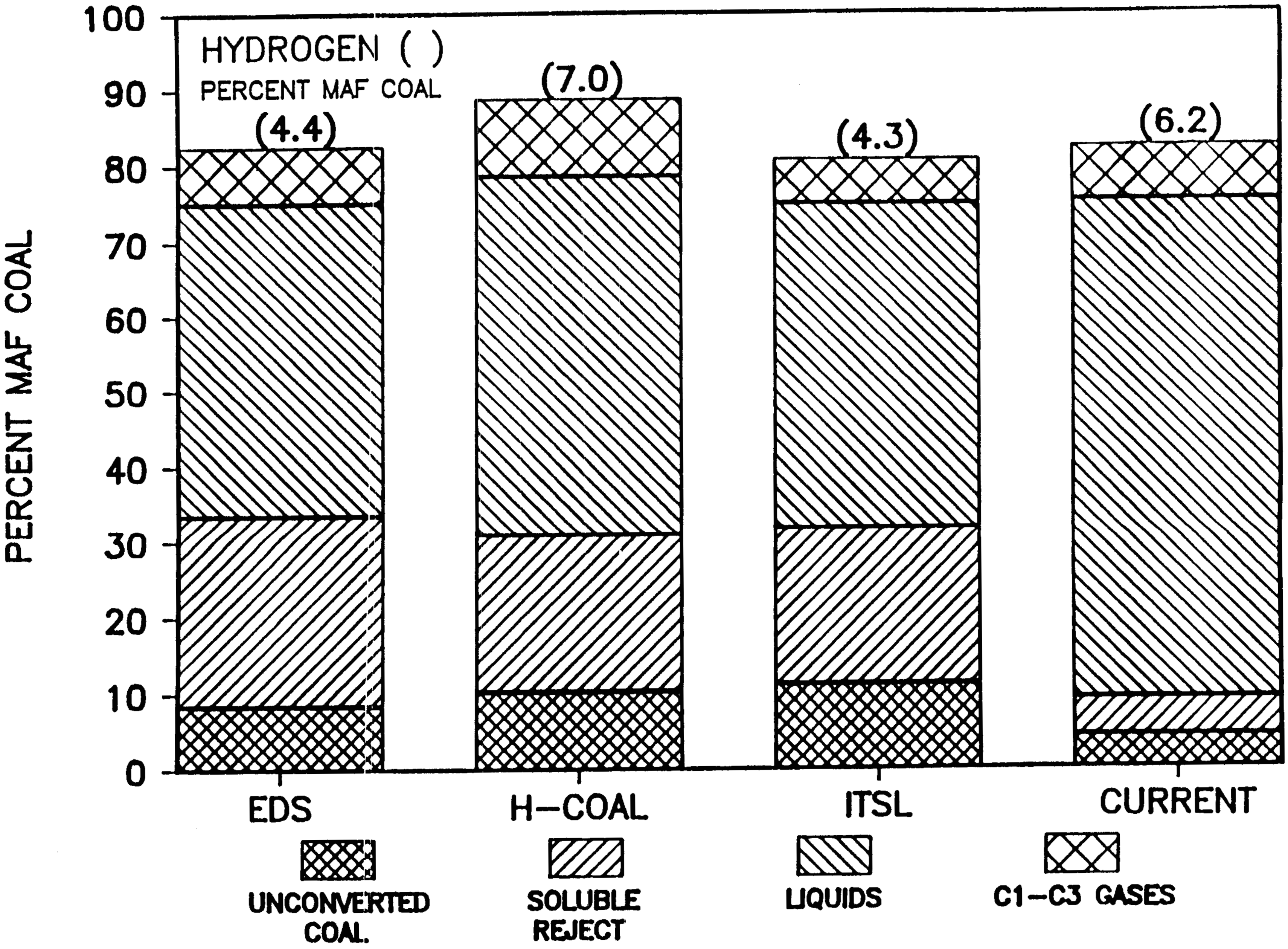

Figure 4-36. Yields from Wyoming Coal

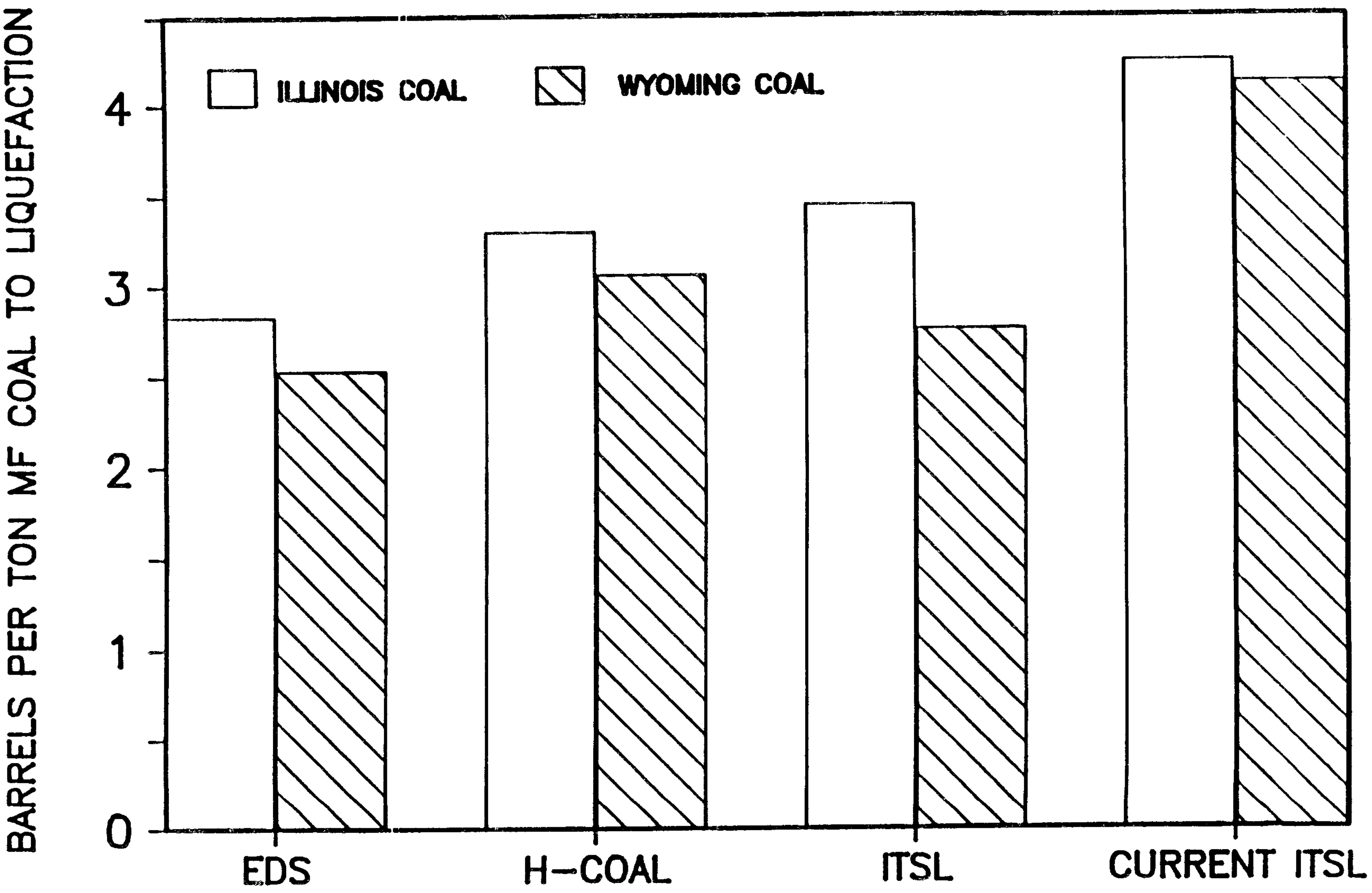

Figure 4-37. Liquefaction Yields Per Ton of Coal

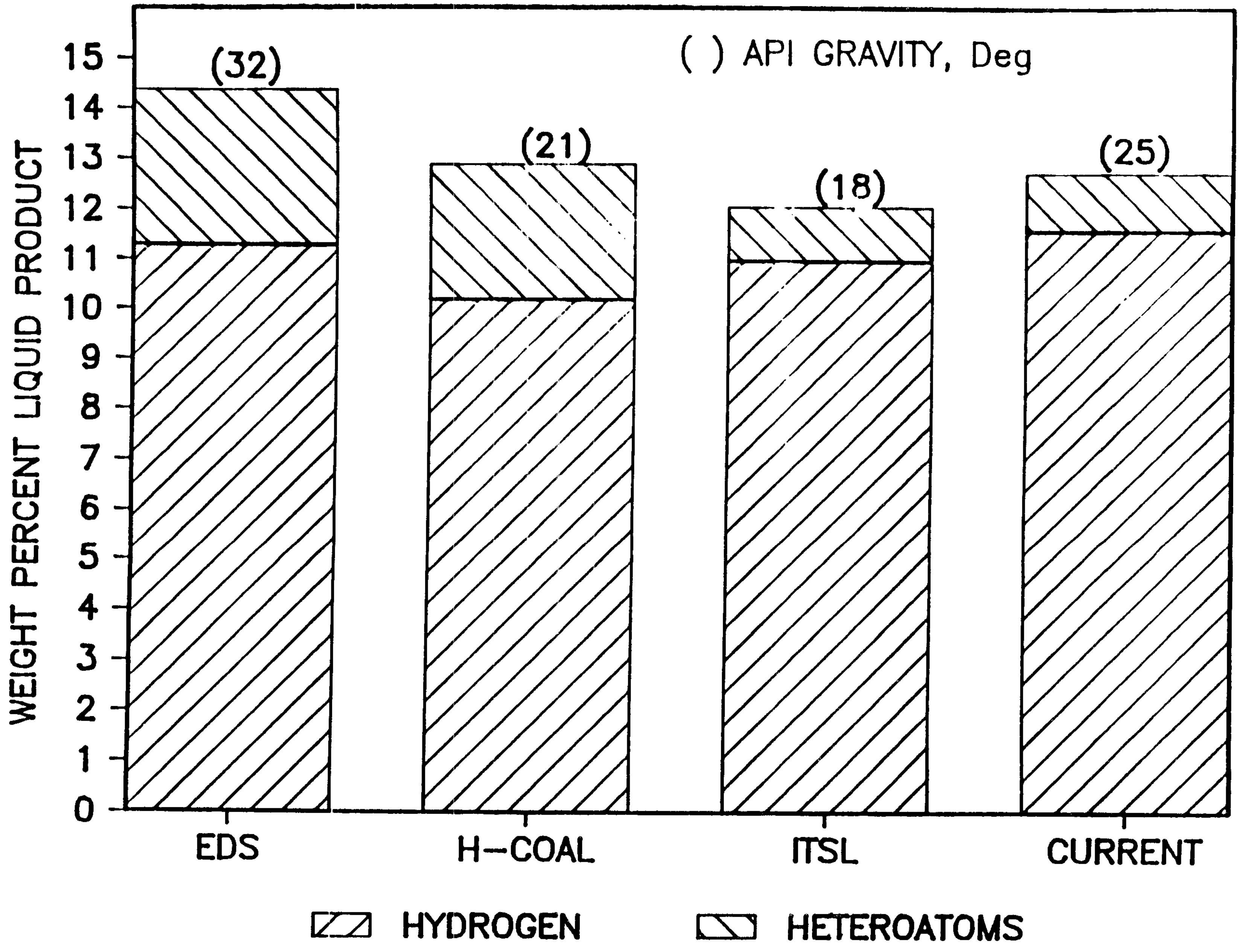

Figure 4-38. Product Quality From Illinois Coal

Table 4-18. Plant Summaries, Illinois No. 6 Coal

($1986)

	EDS	H-COAL	ITSL	CURRENT
MF COAL INPUT, (1000 T/D):				
LIQUEFACTION	30.0	30.0	30.0	30.0
HYDROGEN PRODUCTION	0.0	0.5	0.4	2.4
STEAM	2.5	2.5	2.6	7.2
TOTAL	32.5	33.0	33.0	39.6
OUTPUT, BBLS/DAY (RAW)	79,512	85,117	92,398	116,851
OUTPUT, BBLS/DAY (HYDROTREATED)	79,390	92,316	103,790	127,663
CONSTRUCTION COST ($MILLION)				
LIQUEFACTION	$1,372	$1,490	$1,657	$1,643
HYDROGEN PRODUCTION	$607	$611	$627	$763
BALANCE OF PLANT	$550	$552	$527	$521
TOTAL	$2,530	$2,654	$2,812	$2,928
CAPITAL REQUIRED ($MILLION)	$4,104	$4,291	$4,418	$4,658

funds used during construction (16.9 percent), start-up costs, working capital, and the initial charge for catalyst and chemicals.

As the baseline, a commercial design of a two-stage plant developed by UOP/SDC (211, 212) was used. Since the same process elements are common to all the designs, it was possible to estimate the cost of the other plants by scaling the cost of the individual process units making up the design. A 0.7 scaling factor based on throughput was used. However, the errors introduced by scaling were minimized by keeping the overall size of the plants the same. As Table 4-18 shows, these plants all process 30,000 tons per day of moisture-free coal in the liquefaction unit. The total coal feed to the plant is greater with the current system because the residual material rejected with the ash is reduced, and hence additional coal must be used to meet steam and hydrogen requirements.

The capital cost of the current design is about 12 percent higher than the capital cost of EDS, with the other plants falling in between. It should be noted that there is very little difference in the capital cost of the current design and the original Lummus two-stage configuration. The increases in reactor size and in sophistication are compensated for by the elimination of the interstage let-down system, and the much smaller deasher. The small overall difference is attributable to the increased hydrogen required by the current design. Overall, there is a very substantial improvement in product quality and quantity, with only a nominal increase in capital cost.

Table 4-19 shows operating costs for the four designs based on Illinois No. 6 coal as feedstock. As was noted earlier, the current design requires more coal because less reject material is available for hydrogen production. Other operating costs are dominated by maintenance and thus tend to be proportional to the plant construction cost. Byproduct credits for sulfur and ammonia reflect the quantity of coal sent to liquefaction and gasification. SNG in access of plant fuel needs is assumed to be marketable at $5 per million Btu.

Table 4-19. Annual Operating Costs Illinois No. 6 Coal

Millions ($1986)

	EDS	H-COAL	ITSL	CURRENT
OPERATING COSTS				
COAL COST	$271	$275	$270	$330
OTHER	$329	$337	$337	$374
TOTAL	$601	$612	$607	$704
BYPRODUCT CREDITS				
SULFUR @ $100/TON	$47	$48	$47	$51
AMMONIA @ $150/TON	$22	$22	$22	$24
SNG @ $5/MMBTU	$74	$69	$10	$76
TOTAL	$143	$139	$79	$150
HYDROTREATING COST	$145	$297	$227	$209

The hydrotreating cost shown is an estimate of the cost to bring the raw products to a comparable quality basis. This analysis was performed to get an economic measure of the differences in quality of the products from the plants. The cost estimate is based on the amount of hydrogen that must be added to bring the raw product to a 40 API Gravity, 14 percent hydrogen product. The total cost of hydrotreating is estimated as $1 per pound of hydrogen required to remove the heteroatoms and to hydrogenate the remaining liquid. Assumptions about the hydrotreating response of these new coal liquids were based on the extensive refining studies of these feedstocks undertaken by Chevron (213). The hydrotreatment usually results in a volume gain so that there are usually more barrels of hydrotreated product than raw product. This is not always so, however. The EDS liquids are relatively light products with a high content of oxygen and sulfur. They lose more volume from the removal of heteroatoms than is gained from hydrogen addition so that there is an overall loss in product volume.

Any estimate of the required selling price of products from a liquefaction facility will be very sensitive to the economic assumptions used in the analysis. Table 4-20 shows the consistent economic assumptions used by MITRE in these analyses. It was assumed that the plant is funded with 25 percent equity and 75 percent debt at 8 percent interest. The discount rate, which is the return on the equity investment, is 15 percent, and general inflation 3 percent. No escalation of costs or prices over and above the general inflation rate was assumed.

Table 4-21 shows the computed required selling prices for raw and hydrotreated products from the four conceptual plant designs. The required selling prices for raw and hydrotreated products from the current design are approximately $34 and $36, respectively, in 1986 dollars. A recent independent economic assessment of costs of liquid products from coal liquefaction undertaken by Lumpkin (214) of AMOCO projects similar prices.

Table 4-20. Baseline Economic Assumptions

EQUITY	25 PERCENT
PROJECT LIFE	25 YEARS
TAX LIFE	16 YEARS
INCOME TAX RATE	34 PERCENT
GENERAL INFLATION	3 PERCENT
PRICE ESCALATION*	0
O&M ESCALATION*	0
COAL PRICE ESCALATION*	0
DISCOUNT RATE (DCF)	15 PERCENT
INTEREST ON DEBT	8 PERCENT
CONSTRUCTION PERIOD	5 YEARS

*Relative to general inflation

Table 4-21. Required Selling Prices of Products

ILLINOIS No. 6 COAL
$/BARREL ($1986)

	EDS	H-COAL	ITSL	CURRENT
RAW PRODUCT	$43.58	$42.35	$41.52	$34.52
HYDROTREATED PRODUCT	$49.18	$48.80	$43.61	$36.56

The raw coal liquids currently being produced are 100 percent distillable, and are $2 to $4 per barrel more valuable than a 70 percent distillable sweet crude as a feedstock for gasoline production. Further research is expected to demonstrate additional improvement in product yield and quality which will further improve the economic competitiveness of coal liquids. Improvements permitting synthetic crude to be produced at a price competitive with sweet crude selling for $25 per barrel are expected (215).

4.3.4.4. Coal Liquefaction Economics in Perspective

Twenty-five dollar crude still seems high compared to present prices of $16 or so. However, crude prices were in excess of $30 not so many years ago and were projected to go still higher. The cost of liquids from coal must also be compared with the costs of other domestic sources, including oil from new domestic reserves. Coal liquids may already be competitive with domestic oil from new reserves or enhanced oil recovery.

Finally, the costs presented here can be compared with the estimates of the cost of coal liquefaction products made in the early 1980's. Table 4-22 shows results of earlier studies for EDS (216), H-Coal (204), and the original Lummus two-stage process (211). These early studies cannot be used to make comparisons about the relative technical merit of different processes because of the wide variations in financial assumptions and plant scale used. The H-Coal cost numbers were prepared by Bechtel as part of a solicitation for the Synthetic Fuels Corporation funding of the Breckinridge Project. The results are shown for two sets of assumptions; 100 percent equity financing for a return on investment of 15 percent, and 52/48 debt/equity ratio with a 10.8 percent interest rate. A comparison of these two cases shows dramatically that the required selling price is affected by financial assumptions.

The most significant financial assumptions are shown at the bottom of the figure. Inflation rates were high in the early 1980's, and these analyses assumed a continuation of this trend. This assumption about

Table 4-22. Required Selling Prices from Published Study Designs

$/Barrel

PROCESS DATA SOURCE DEBT/EQUITY RATIO	H-COAL BECHTEL 0/100	H-COAL BECHTEL 52/48	EDS EXXON 0/100	ITSL UOP/SDC 75/25
REQUIRED SELLING PRICE				
1981 DOLLARS	$57	$36	$53	$43
START UP YEAR DOLLARS	$90	$57	$121	$69
(YEAR)	(1988)	(1988)	(1993)	(1986)
FINANCIAL ASSUMPTIONS				
RETURN ON EQUITY	15.0%	15.0%	15.0%	26.0%
INTEREST RATE	NA	10.8%	NA	17.0%
INFLATION RATES				
CONSTRUCTION COSTS	8.5%	8.5%	7.5%	10.0%
OPERATING COSTS	6.0%	6.0%	7.0%	10.0%
PRODUCTION VALUE	6.7%	6.7%	9.0%	10.0%

inflation doesn't greatly affect the required selling price in constant dollars of the year of the analysis, so that these numbers are not greatly different from the results shown previously. However, the cost estimates for coal liquids still remembered by many are the very high current-dollar prices projected for the products when the plants came on stream. These numbers are directly affected by the assumption of continued high inflation; they projected that prices of $80 to $100 would be required before synfuels became competitive.

4.3.4.5. Conclusions

Over the past decade continued research and development in the production of liquid fuels from coal have substantially increased both the quantity and the quality of distillate from a ton of coal. This increase of distillate, which amounts to approximately 35 percent, has resulted in a real significant decrease in the cost of liquid products from coal. With present technology, and with economic assumptions which are reasonable for this time period, high-quality synthetic liquids from coal can be produced for around $35, and they would be competitive with sweet crude oil selling for as low as $30. Continued research in this area is expected to reduce the cost of coal liquids still further.

4.3.5 Environmental Considerations[10]

The chemical compounds contained in coal and coal-derived liquids present direct liquefaction process development with several environmental problems--toxicity, disposal of hazardous waste, and carcinogenic properties. These and other environmental problems posed by process streams, untreated wastewaters, and raw products must be addressed if the technology is to be commercialized.

Table 4-23 summarizes an Oak Ridge National Laboratory assessment of the potential ecological risks faced by the coal liquefaction industry

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[10] This section is based upon material from Bary Wilson, Battelle Pacific Northwest Laboratory, and References 180 and 181.

Table 4-23. Summary of Ecological Impacts for A 1-quad Coal Liquefaction Industry and Research Recommendations

Environmental risk basis	Exposure		Range of quotients or risks[a]	Major sources of uncertainty	Research recommendation to reduce uncertainty
	Agent	Route			
Phytotoxicity	Chromium	Soil	0.5-1.9	Availability of deposited Cr to plants	Improved and standardized methods for assessing phytotoxicity
Phytotoxicity	SO_2	Air	0.001-0.02	Interaction with other pollutants	Interactions between gaseous and heavy metal pollutants
Respiratory toxicity	SO_2	Air	0.02	Significance of respiratory injury to wildlife populations; applicability of mammalian data to other animals	Data on air pollution effects on wildlife, particularly birds
Toxicity to fish	Cadmium	Water	<0.009-0.4	Effects of water quality on availability and uptake; variation in sensitivity among species and life stages	Improved understanding of environmental chemistry; more data on effects of cadmium on ecologically/socially important species
Toxicity to fish	Lead	Water	<0.001-0.1	Effects of water quality on availability and uptake	Improved understanding of environmental chemistry
Toxicity to fish	PNA	Water	<0.001-0.7	Composition of PNA's in waste streams	Characterization of PNA components of waste streams
Toxicity to fish	Mono/diaromatic hydrocarbons	Water	<0.001-0.8	Significance of environmental removal pathways; variations in sensitivity among species	Quantification of volatilization and degradation rates; data on effects on ecologically/socially important species
Toxicity to fish	Aliphatic/alicyclic hydrocarbons	Water	<0.001 -0.01	Composition of waste streams. Variations in sensitivity among species	Characterization of aliphatic components of waste streams; data on effects on ecologically/socially important species
Toxicity to phytoplankton	Chromium Cadmium Lead	Water Water Water	<0.002-1.5 <0.001-0.73 <0.001-0.12	Metal speciation and availability; consistency and ecological relevance of bioassay techniques	Improved understanding of environmental chemistry; improved and standardized bioassay techniques

[a] Ratios of estimated environmental concentrations to toxicological benchmarks.

Source: Ref. 217, p.9.

(217). This risk analysis was directed primarily at the effects of toxic contaminants, because the effluents and products of coal liquefaction technologies are likely to be substantially different in composition from those of conventional petroleum technology. Other environmental impacts of a synfuels industry, notably habitat disturbance due to plant construction and waste disposal, will be similar to impacts accompanying the construction and operation of coal-fired electric power plants.

Only near-field impacts were considered in this assessment (187). Except for contributions to regional/global pollution problems such as acid precipitation and CO_2 accumulation, it is likely that the ecological effects of contaminant releases from a synfuels facility would decrease with increasing distance from the plant site.

Chemical and toxicologic characteristics of direct coal liquefaction materials are highly dependent upon the specific process variables that affect boiling-point range and degree of hydrogen incorporation. These conclusions are based upon analyses of products from many of the process configurations that have been run at the Wilsonville Advanced Coal Liquefaction Unit. This process and product experience includes both non-integrated and integrated two-stage liquefaction (NTSL and ITSL) and materials from close-coupled and reconfigured two-stage liquefaction.

Advances in direct coal liquefaction technology, such as the use of catalytic hydrogenation, reduced liquefaction severity, and lowering the upper temperature cut-point for the distillation of fuels, have resulted in products with higher hydrogen-to-carbon ratios and lower heteroatom content. These higher-quality fuels tend to be less mutagenic and carcinogenic in laboratory assays than earlier coal liquefaction products. It is likely that application of post-production hydrotreatment, as well as restriction of upper distillation temperature, for coal-based fuel products could result in materials that exhibit mutagenic or carcinogenic activity no greater than that of their petroleum-derived counterparts.

Several conclusions can be drawn regarding the toxicologic activity of coal liquefaction materials (219):

- Chemical classes responsible for toxicological activity in coal-conversion materials are qualitatively the same regardless of the coal-conversion process used to produce the material.
- Chemical classes primarily responsible for mutagenic and carcinogenic activity of coal liquids and tars are high-molecular-weight, polycyclic aromatic hydrocarbons (PCAHs). Amino-PCAHs are a major source of mutagenic activity.
- Toxicological activity of coal-conversion materials can be predicted from their 95 percent distillation temperature (the temperature at which 95 percent of the feed material has been distilled) and their aromaticity. Toxicological activity is concentrated in those highly aromatic components boiling above 640°F and having hydrogen/carbon (H/C) ratios below 1.5.
- Selective distillation, heavy-ends process recycle, and catalytic hydrotreating -- singly and in combination-- can effectively reduce toxicological activity through control of product boiling point and aromaticity.

Pacific Northwest Laboratory (PNL) carried out studies described by Wright et al. (220) to compare the chemical composition and the toxicity of coal liquefaction materials with those of coal-derived products in everyday use. These studies showed that many of the mutagens found in materials from the earlier coal liquefaction processes such as SRC-II are also present in consumer products such as creosote.

Pacific Northwest Laboratory also compared the chemical composition and the carcinogenicity of coal-tar-base therapeutic agents to the properties of SRC-II heavy distillate (HD) (221). SRC-II HD is a product of a non-catalytic process and is considered one of the most carcinogenic of the coal liquefaction distillate materials. Chemical composition, microbial mutagenicity, and skin carcinogenicity of the materials for the therapeutic topical agents were similar to those properties of NBS coal tar and SRC-II HD. Coal-tar-based products are routinely used as topical agents by those with certain skin disorders, apparently without statistically significant increase in cancer incidence. Based on its work, PNL has concluded that safe coal liquids can be produced using presently available technology. The main precaution is that adequate specifications on aromatic content, nitrogen content, and upper-boiling-point range must be established and maintained.

Stringent industrial hygiene and worker protection measures, good engineering controls and control technology, and responsible waste disposal practices will be needed for commercialization of the direct liquefaction process to be acceptable both environmentally and from the standpoint of human health and safety. Many questions remain concerning details of the measures that will be necessary to comply with federal and state regulations and concerning what is known about the safe handling of unregulated, but potentially hazardous, emissions or substances. There are also many gaps in our knowledge about health and environmental effects of long-term releases of small amounts of pollutants.

Most of the atmospheric emissions such as TSP, NO_x, and SO_x will result from burning fuel to provide power, process heat, and steam for the direct liquefaction process. The nature and amounts of these emissions will depend on the fuel used. Because the emissions are regulated, their impact on ambient air quality will depend on the ambient background levels in the region of the plant.

Operation of the pilot plants indicates that emissions can be well controlled during periods of stable operation but that during startup, shutdown, process upsets, and, especially, at times of major storm events, the wastewater control system can be overwhelmed; and large amounts of untreated toxic wastewaters may be released. Such releases probably constitute the most acute hazard to the aquatic environment.

Small amounts of organics, including PCAHs and related compounds, will be released continuously to both the atmosphere and the terrestrial and aquatic environments. Small amounts of metals and trace elements will also be released; some of these are toxic and are of considerable concern because of levels already present in the environment. The forms in which these metals and other trace elements will be released are not well understood.

Human exposure and potential health effects differ for the workers in the plants and the general public. Potential exposures are certainly greater for workers. Because the processes involve high temperatures and pressures during certain steps of the operations, there is a risk of fire and explosion. Such accidents could also lead to ruptures and spills of process streams. In the pilot plants acute effects have included eye irritation, respiratory tract irritation, dermatitis, and thermal burns.

Certain areas of the pilot plants have excessive noise and above-compliance levels of TSP or benzene-soluble organics. Workers in these areas, as well as maintenance and process workers, are at risk of inhalation and dermal exposure to PCAH-containing materials that, over time, constitute some level of carcinogenic risk and possibly other hazards. Information and methods either to quantitate actual worker exposures to PCAHs or to calculate quantitatively the potential health risks encountered by workers at a given level of exposure are not available. With good engineering controls and stringent industrial hygiene monitoring and procedures, the health effects of most concern even to workers are probably those of long-term, low-dose exposure to toxicants; the health effects of such chronic exposures are not well understood.

Public health hazards involve long-term, low-dose exposure primarily to PCAHs, aromatic amines, and toxic metals. The necessary information to predict the level of risk associated with such exposures is not available. Public awareness of plant emissions will more likely involve observation of haze if excessive TSPs are emitted and annoyance due to odors from sulfur-bearing gases if sufficient quantities are released to reach populated areas.

Environmental effects of concern result from the long-term release of small amounts of toxic materials to either the aquatic or the terrestrial environment. However, acute effects could result from spills and leaks of products during storage or transport; from releases of untreated wastewaters, especially if the treatment system is inadequate to handle either large amounts of toxicants during process upsets or large volumes of water during storm events; and from cooling tower drift in the immediate plant site. The levels of several toxic heavy metals--such as lead, cadmium, and mercury--are already high enough in the environment that even a small increase in these levels is a matter of concern. Should these or other toxic metals be released in, or converted to, organometallic forms that are readily incorporated into the food chain, there is concern for both environmental effects and human health effects. The release of even small amounts of PCAHs and related compounds to the environment is of concern because of the high toxicity of some of these compounds and because of their long persistence in the biosphere.

There are many gaps in our knowledge of the environmental transport, fate, and effects of many of the substances of concern. There is also uncertainty about the amounts to be released from commercial-scale direct liquefaction plants. Predictions of environmental and health effects are also hindered by a lack of site-specific information.

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CHAPTER 5

REVIEW OF INDIRECT LIQUEFACTION[1]

5.1 INTRODUCTION AND SUMMARY

5.1.1 Introduction

Indirect liquefaction encompasses a wide range of catalytic processes to convert coal-derived synthesis gas to liquid fuels, and can be categorized into two principal areas: (1) conversion of synthesis gas to light hydrocarbon fuels (gasoline and light paraffins) via Fischer-Tropsch synthesis, and (2) conversion of synthesis gas to oxygenates such as methanol, higher alcohols, and ethers.

An excellent in-depth review of the status of indirect liquefaction technologies and their research needs may be found in the 1987 DOE-sponsored COGARN study report entitled "Coal Gasification: Direct Application and Synthesis of Chemicals and Fuels, A Research Needs Assessment" (1). The COGARN report should be consulted for complete descriptions of indirect liquefaction technologies and their backgrounds. This report will be referenced in the current review where appropriate.

Another recent review document by IEA entitled "Catalysts for Fuels from Syngas: New Directions for Research (IEACR/09)," authored by G.A. Mills, should also be consulted (2). In this IEA document, which emphasizes catalysis research, research priorities were divided into three categories: (1) research for near-term, (2) research for mid-term, and (3) research for long-term applications.

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[1] This chapter was written by Irving Wender, University of Pittsburgh, and Kamil Klier, Lehigh University.

In this current review emphasis is placed on the recent advancements in synthesis of oxygenates, since this is a relatively new emerging technology. For the synthesis of light hydrocarbon fuels, a summary of the most significant progress will be presented. An attempt will be made to incorporate or report on developments that have occurred or are undergoing change since the 1987 COGARN report.

5.1.2 Summary

Indirect liquefaction encompasses a variety of catalytic technologies to convert synthesis gas to (1) light hydrocarbon fuels and (2) oxygenates. Commercial technologies exist for both hydrocarbon fuel and oxygenates production, although only the SASOL plant in South Africa uses coal to make the synthesis gas for fuel and chemical production. In the U.S., plants have been built to produce ammonia and other chemicals via coal-derived synthesis gas. The distinguishing features of synthesis gas derived from coal are the low H_2/CO ratio and various catalyst contaminants in coal gas.

Coal-derived synthesis gas with a low H_2/CO ratio often requires shifting via the water gas shift reaction to achieve the higher ratios necessary for F-T or oxygenate syntheses. A sulfur-tolerant shift catalyst would greatly reduce the cost of synthesis gas clean-up and lead to improved process economics for indirect liquefaction processes. The panel made the development of such catalysts a high-priority recommendation (No. I6).

For light hydrocarbon synthesis the oil slurry F-T process has recently been shown to yield high synthesis-gas conversion with the advantages of accepting low-H_2/CO coal-derived synthesis gas. Extensive research on three-phase slurry reactors for optimum performance of catalytic reactors is ongoing.

Another initiative in F-T process research is to maximize the yield of middle distillates and wax, while minimizing the production of light gases. The wax is then cracked to marketable fuel products. Continued work in this area was recommended by the panel with special emphasis on developing catalysts having high selectivity to long-chain hydrocarbons suitable for cracking to naphtha and distillate fuels (No. I5). If this high wax yield is achieved in a slurry reactor, separation of wax products from the catalyst and catalyst recovery and recycle will have to be addressed as part of the overall process.

Continued research is also needed in improving F-T synthesis catalysts to attain high activity with controlled and reproducible properties. Based on its assessment of current F-T catalysts and the potential for developing improved catalysts, the panel recommended that new advances in materials science be applied to catalyst preparation for F-T synthesis reactions (No. I1). These new techniques include production of novel supports and new ways of developing the active surface as well as new methods of catalyst characterization. In general, these new techniques appear to offer major opportunities for the scientific design of greatly improved catalysts -- catalysts which would not be achieved by traditional trial-and-error methods. As related recommendations, the panel also recommended that supported organometallic complexes be analyzed for application to F-T syntheses (No. I2) and that the factors leading to deactivation of F-T catalyst be determined (No. I8).

Technologies to produce oxygenates, with emphasis on new methanol technology, higher-alcohol synthesis, and production of ethers, have received a great deal of attention in recent years. This interest in oxygenates production will continue to increase as these compounds penetrate the transportation fuel market as additives, either neat or as precursors to other clean-burning octane-enhancers. Thus, many of the panel's recommendations were directed toward alcohol or ether production in the areas of new catalysts, new processes, and studies of kinetics and catalysis.

For methanol synthesis, new developments are being made in the liquid-phase methanol process by Air Products and Chemicals and the gas-solid-solid trickle flow reactor by Shell. Progress is continuing on new heterogeneous and homogeneous catalysts for methanol synthesis, although additional studies on reaction kinetics are needed. The low H_2/CO ratio and the catalyst contamination problems associated with impurities in coal-derived gas point to the need for testing an integrated gasification/indirect liquefaction system. Such testing is currently being done at the LaPorte liquid-phase methanol PDU, which is the only unit in the DOE's indirect liquefaction program of sufficient size and integration which can be used to investigate complete system performance. The panel felt that new catalysts are needed having good activity with syngas streams but without requiring the extensive expensive cleanup needed for current catalysts (No. I7).

Progress is being made on developing higher-alcohol synthesis (HAS) processes. These developments include recent work related to (1) the SEHT (MAS) process, (2) the IFP (substifuel) process, (3) the DOW HAS process, (4) the Lurgi OCTAMIX process, and (5) the Lehigh University (LU) HAS process. Review of this work points to the need to develop better synthesis catalysts and new processes. In particular, new routes are needed to produce ethanol from synthesis gas with greater selectivity, minimizing the hydrocarbon yield (Recommendation No. I3).

Improvements must also be made in methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME) technologies. The panel also saw potential for finding new catalyzed paths to produce octane-enhancing ethers and made this a high-priority recommendation (No. I4).

The major focus of the panel's recommendations in indirect liquefaction is catalysts -- new materials, methods of characterization, structure, deactivation, kinetics, and mechanisms. This focus may be somewhat narrow, but it stems from a program in which little process development is being performed. (The Liquid-Phase Methanol program is the notable exception.)

In addition, indirect liquefaction is the second reaction of a two-stage reaction sequence that starts with coal gasification. DOE has placed gasification in a separate program, leaving only syngas reactions as part of the liquefaction program. Since gasification constitutes at least 70 percent of the total cost, improvements in syngas conversion technology may have relatively little impact on overall economics. Furthermore, such improvements may be contingent on process changes upstream of the syngas reactor.

5.2 CONVERSION OF SYNTHESIS GAS TO LIQUID HYDROCARBON FUELS[2]

5.2.1 Fischer-Tropsch Reactions, Chemistry, and Mechanisms

A broad view of the Fischer-Tropsch synthesis (FTS) mechanism is that it is a simple polymerization reaction, the monomer being a C_1 species derived from CO. This polymerization follows a molecular-weight distribution described mathematically by two groups independently: Anderson and the Bureau of Mines groups (3) and Manes (4), and the polymer chemists, Schulz (5) and Flory (6).

The description of the FTS product distribution is usually referred to as the Anderson-Schulz-Flory (ASF) distribution. The ASF equation is now well known and constantly used. This F-T distribution has also been described by Madon (7) and Dry (8). The ASF equation is usually written as:

$$\log \frac{Wn}{n} = n\log x + \log \frac{(1-x)^2}{x}$$

Wn is the mass fraction, n is the carbon number, and x is the probability of chain growth. The equation predicts the highest selectivities attainable by an F-T synthesis with an optimized process and catalyst:

Product	Maximum Selectivity, Wt.%
Methane	100
Ethylene	30
Light Olefins (C_2-C_4)	50
Gasoline (C_5-C_{11})	48

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[2] This section was written by Irving Wender, University of Pittsburgh.

These predictions hold whether the products are hydrocarbons (paraffins and olefins) or hydrocarbons plus alcohols.

A linear plot of log Wn/n indicates that the data are indeed consistent with a chain growth mechanism. The chain growth probability, x, can be calculated either from the slope, log x, or from the intercept, log $[(1-x)^2/x]$.

5.2.2 F-T Synthesis Catalysts

Catalysts with a small value of x produce a high fraction of methane; thus a selective methanation catalyst would have an x value approaching zero. At the other extreme, a high x value indicates the production of heavier components. As will be discussed, the latest FTS work is aimed at producing high-molecular-weight products (and thus very little CH_4) and then cracking these materials to produce lower hydrocarbons.

There have been many attempts to "beat" the ASF prediction so that one could produce gasoline and diesel or middle distillate range products in yields that exceed those allowed by ASF polymerization. While there have been many indications that the particle size of the metal catalyst or the pore structure of the support may cause deviations from the ASF prediction, none of these has proven valid under further scrutiny. Deviation from the ASF distribution, at least on a practical industrial scale, has been the result of the conversion of primary FTS products by secondary reactions.

The only commercial use of the FTS is at SASOL in South Africa. Cheap iron catalysts prepared by fusing iron oxides such as millscale oxides are used. In practice, either an alkali salt or one or more non-reducible oxides are added to the catalyst. The literature on the use of iron catalysts is enormous. However, because of the wide range of experimental differences in catalyst preparation, pretreatment, reaction conditions, and product analysis, it is virtually impossible to make direct comparisons of much of the data.

The SASOL plants furnish more than 40 percent of that country's requirements for fuels and chemicals. Data on the existing SASOL plants are listed below:

Plant	Start Date	Coal t/d	Liquids bbl/d	Cost $Billion
SASOL-1	1935	6,600	6,000	-------
SASOL-2	1981	30,000	40,000	2.9
SASOL-3	1982	30,000	40,000	3.8

An approximate distribution of products from SASOL-2 follows:

Product	Tons/Year
Motor fuels	1,650,000
Ethylene	204,000
Chemicals	94,000
Tar Products	204,000
Ammonia (as N)	110,000
Sulfur	99,000
Total Saleable Products	2,361,000

SASOL is now planning to use its same process to produce synthetic oil from offshore natural gas (9). In May 1988 a government corporation selected a mining corporation to build a gas liquefaction project to explore the newly-discovered Mossal Bay offshore gas field. This project will be broken down into two parts, Mossgas plans to process natural gas and gas liquids directly into gasoline, diesel oil, and other higher-boiling liquids. Mossref -- short for Mossel Bay refinery -- will produce synthetic crude and chemicals from the remaining methane. However, contracts have not as yet been let for the needed bank of SASOL Synthol reactors.

There are thousands of journal publications and patents on investigation of other F-T catalysts, chiefly cobalt, ruthenium, nickel, rhodium, and molybdenum (the last as a sulfide). Researchers have claimed high yields of particular products or types of products, often in differential reactors under particular conditions. Dry (10) (personal communication) has been asked why SASOL cannot reproduce these results. Obviously, since SASOL's process is tied to a cheap throwaway iron catalyst employed in integral reactors, it is not possible for SASOL to reproduce the often desirable products via processes that appear in various publications.

5.2.3 Fischer-Tropsch Processes Not Yet in Commercial Operation

The title for this section is taken directly from the 1987 COGARN report (1). Modern gasifiers make synthesis gases with low (0.6-0.7) H_2/CO ratios. Iron is a good water gas shift (WGS) catalyst while neither cobalt nor ruthenium is active. In the absence of WGS activity, the oxygen in CO is rejected as water so that a synthesis gas with an H_2/CO ratio of two is needed to produce olefins or alcohols; for paraffins an H_2/CO ratio somewhat larger than two is required. With good WGS catalysts the oxygen in CO is mostly rejected as CO_2. When water is formed in the F-T reaction, it can react with CO to form more H_2 so that low-H_2/CO-ratio synthesis gas (SG) can be used with these catalysts.

Attempts to produce C_2-C_4 hydrocarbons in the F-T reaction have not resulted in conversions that exceed those predicted by the ASF equation. This result, coupled with low H_2/CO gas ratios produced by current or developing coal gasification processes, has led to F-T syntheses that produce high-molecular-weight/low-methane products. The long-chain products are then used to produce lower hydrocarbons by cracking, as well as gasoline and diesel fuels (1).

Most of the current work uses slurry F-T reactors. Koelbel and Ralek (11) have published an excellent review of the development of slurry F-T work up to the 1970s. Major developments of slurry F-T processes since 1980 have been done at the Mobil Research and Development Corporation, with some funding from DOE (12, 13). The work was done in association with the concept of upgrading a total vaporous F-T reactor effluent over a ZSM-5 catalyst. This concept is reported in the 1987 COGARN coal gasification research needs report (1), which described two modes of operation: (1) a gasoline or low-wax mode of operation and (2) a gasoline and diesel or high-wax mode of operation.

In 1985, Shell announced its SMDS (Shell Middle-Distillate Synthesis) process for the production of kerosene and gas oil from natural gas (14). It is a two-stage process based on the development of a catalyst which converts synthesis gas into long-chain hydrocarbon waxes, which are hydroconverted and fractionated into naphtha for gasoline, kerosene for jet fuel, and gas oil for diesel. The thermal efficiency from natural gas is 60 percent. The synthesis gas made from natural gas would have a high H_2/CO ratio. Little CO_2 is produced so that the proprietary F-T catalyst has little or no WGS activity. A fixed-bed (Arge-type) reactor will be used for the F-T reaction and a trickle flow reactor for hydrocracking. The catalyst almost certainly is partly or largely cobalt with iron or ruthenium likely present. Product carbon number distributions obtained with these catalysts have x values from 0.7 to over 0.9 (15). The calculated distributions of C_1 - C_{10} and C_{10} - C_{20} products from the SMDS concept are 64 and 36 respectively for $x = 0.8$, and 20 and 80 for $x = 0.95$(2).

In related work UOP (16) characterized F-T wax and its potential for upgrading. Obviously, high wax formation in the FTS will minimize methane formation. Utilization of catalysts designed for high wax/low methane, coupled with new catalyst technology for selective cracking of the wax, is a very promising route to desired products via F-T technology.

The COGARN coal gasification report discusses the Gulf-Badger process for converting natural gas to liquid hydrocarbons via methane steam reforming followed by an F-T reaction. Again, an Arge-type reactor is used. The proprietary catalyst, probably cobalt with some ruthenium, has little or no WGS activity. Typical process conditions of 210°C, 250 psig, $H_2/CO = 1.5-2$, space velocity of 500-1000 1/hr, with a CO conversion of 40-60 mol percent plus product selectivities are listed in the COGARN report. STATOIL of Norway is involved in a similar process.

Dow has developed molybdenum catalysts with a sulfur tolerance up to about 20 ppm. The catalyst system is selective for the synthesis of C_2-C_4 hydrocarbons, especially when promoted with 0.5-4 weight percent potassium.

5.2.4 Fischer-Tropsch Synthesis in the Slurry Phase

Using a precipitated iron catalyst, the slurry F-T reactor, which operates with a finely divided catalyst suspended in an oil reactor medium, has been shown to yield high single-pass syngas conversion with low (0.6) H_2/CO ratios. Koelbel and Ralek (11) and Frohning et al. (17) have reviewed slurry-phase F-T processing more recently. Kikuchi (18) developed ultrafine particles of Fe-Co-Ni or Fe for liquid-phase F-T synthesis. There have been extensive studies of three-phase slurry reactors for optimum performance of catalytic reactors (2, 19).

5.2.5 Conversion of Methanol to Gasoline with Zeolite-Containing Catalysts

This work was discussed in detail in the COGARN report on gasification for the synthesis of fuels and chemicals, and the reader is directed to this report (1).

The Mobil Research and Development Corporation developed the methanol-to-gasoline (MTG) process, one of the very few synthetic fuel technologies that has been commercialized since the 1973 oil embargo. The process is based on the use of zeolites of the ZSM-5 class (20,21) discovered by Argauer and Landolt (22).

The MTG process may be represented as:

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} (CH_3)_2O \xrightarrow{-H_2O} -C_2\text{-}C_5 \text{ olefins}$$

$$C_2\text{-}C_5 \longrightarrow \begin{array}{l}\text{Olefins, Paraffins,}\\ \text{Naphthenes, Aromatics,}\\ C_6\text{+ Olefins}\end{array}$$

The mechanism may involve the formation of ethylene as the primary product, but there is much debate on this subject. Several mechanistic pathways have been proposed.

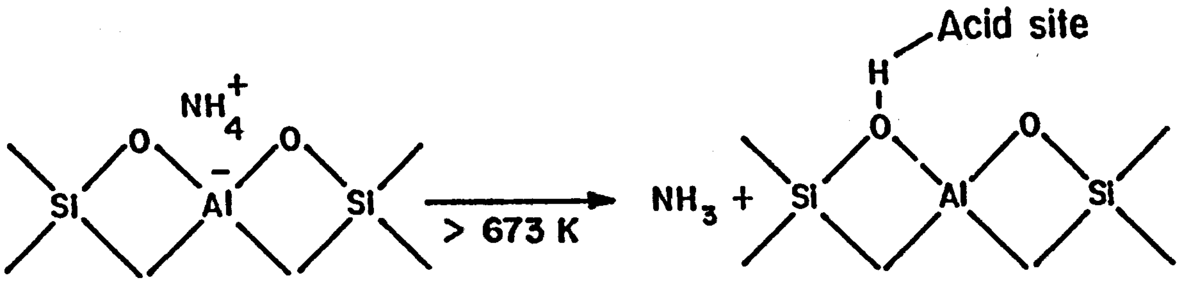
Because of the shape-selective pore structure of the ZSM-5 zeolite, the hydrocarbons produced are predominantly in the gasoline range. The paraffins consist mostly of isoparaffins, and a large yield of aromatics is obtained. The total product is in the C_5-C_{10} range so that it has a high octane number. The aromatics are highly substituted by methyl groups due to the alkylation of the aromatics by methanol and dimethyl ether (DME).

A discussion of zeolites, natural and synthetic, is given in Reference 1. They are porous crystalline solids which have well-defined pore systems and large surface areas. The most common zeolites are tectosilicates (23) (T is usually Si or Al, but other atoms may be present) such that each of the four oxygen atoms is shared with another tetrahedron.

Weisz (24) has discussed the thinking that lead to the synthesis of highly siliceous zeolites such as ZSM-5. This zeolite has high structural stability, thermally and particularly toward hydrolytic attack during chemical processing. The Mobil workers were able to form aluminosilicate frameworks in which both Al and Si were the principal building units. SiO_2 was the main constituent with occasional, almost randomly positioned Al substitutions; this leaves the Al sites available in a dilute, isolated state in the zeolite, a condition which seems to confer high acidity to the Al sites. In amorphous silica-alumina, such as that found in clays, only a small fraction of the Al atoms are sufficiently active.

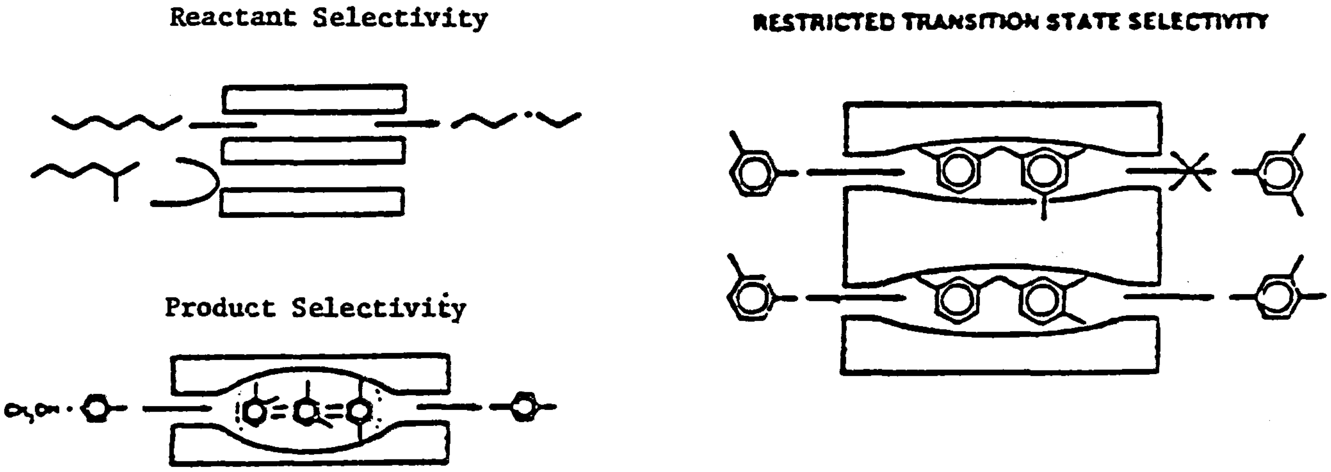
The acidity of zeolites is the fundamental basis of their catalytic activity. This holds for the MTG process for the conversion of methanol to gasoline; the catalyst is used in the HZSM-5 form. Acidity, shape selectivity, and structural stability of the catalyst combine to make the MTG process a success.

Acidity of Zeolites



Csicsery (25) has pointed out three categories of shape-selective catalysts. These are reactant selectivity, product selectivity, and restricted transition state selectivity (Figure 5-1). The interior surface of the zeolite is the principal source of catalytic activity although reactions may take place on the external surface.

The synthesis of ZSM-5 led to the discovery, by Chang and Silvestri (26), of the MTG process. It also led to an enormous amount of research on its use in chemical processing. Because of its molecular shape and size (Figure 5-2), ZSM-5 does not generate appreciable amounts of aromatics larger than C_5-C_{10}, thus avoiding generation of coke precursors which would quickly deactivate the catalyst.


Reactant Selectivity

Product Selectivity

RESTRICTED TRANSITION STATE SELECTIVITY

Figure 5-1. Types of Zeolite Selectivity

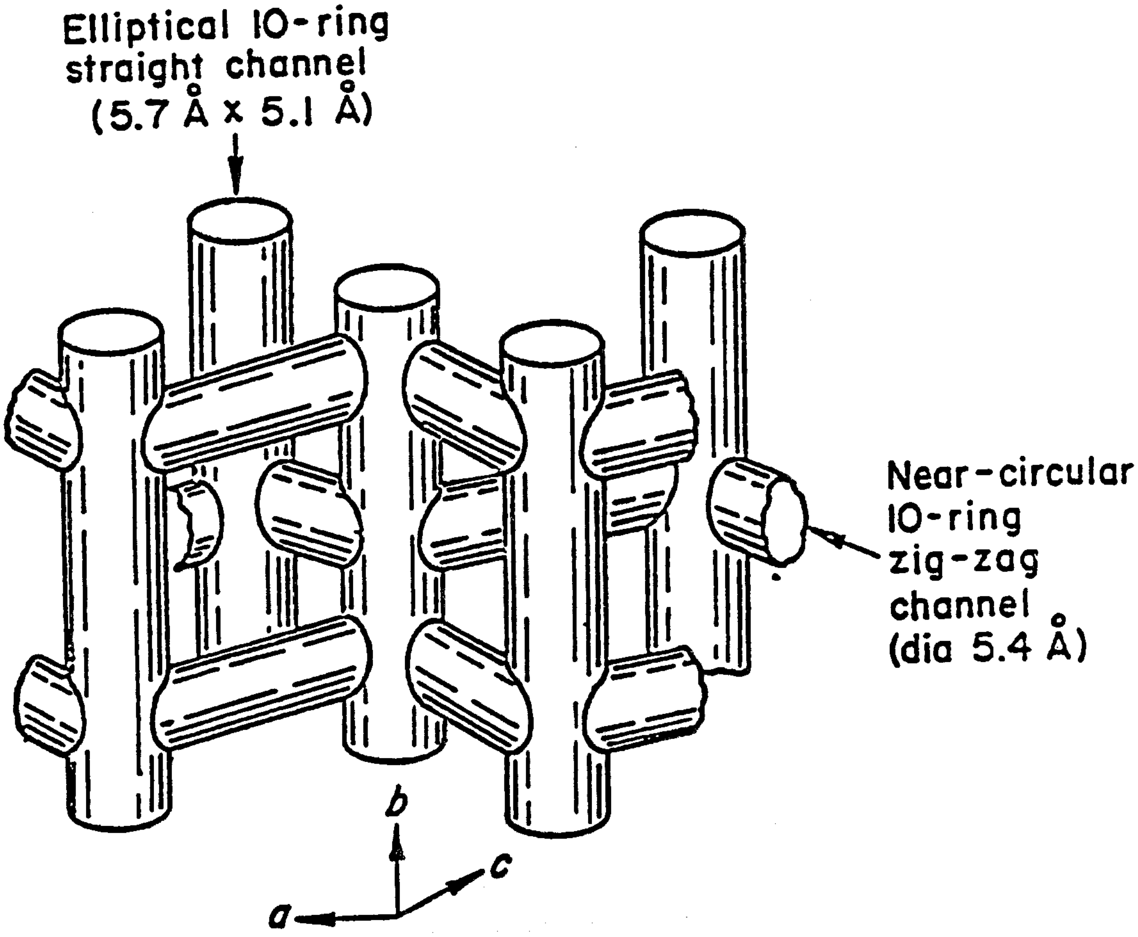


Figure 5-2. Framework Structure of ZSM-5

The MTG process first converts synthesis gas (SG) to methanol; in a second step the alcohol is nearly quantitatively converted to high-octane gasoline over the ZSM-5 molecular sieve. The MTG technology was developed under the joint technical direction and financial sponsorship (30/70) of Mobil and the U.S. DOE (27). The MTG process has been tested in a fixed-bed mode at the Mobil laboratories and in a fluid-bed mode in a 100-BPD unit in West Germany (28). In Table 5-1 Haag et al. (1) have compared process conditions and product yields from the two MTG systems.

New Zealand, desiring to become more self-sufficient in liquid transportation fuels, had the choice of adopting the F-T process or the Mobil MTG process. They chose the fixed-bed version of the MTG process over the fluid-bed, chiefly because of the simpler engineering and easier scale-up. The fixed-bed version had only been tested previously in a four-barrel-a-day unit. The choice of the MTG process over a Fischer-Tropsch route involved thinking along the following lines:

- The selectivity of the MTG process is much greater.
- The MTG process gives little or no CH_4, in contrast to the F-T process.
- The MTG process yielded extensive aromatics formation, conducive to a high-octane rating of the gasoline.
- The MTG catalysts have long lives and may be regenerated in situ. The F-T catalyst, millscale, is cheap and adequate; while its composition changes during its life, it is a throw-away catalyst.
- The MTG route is more efficient (57 percent to SASOL's 48 percent).
- The MTG process has lower investment costs with fewer upgrading steps.

New Zealand now produces about 14,000 BPD of 92-93 octane gasoline via the MTG process; this is one-third of their requirements. The SG needed for the manufacture of methanol is obtained from offshore gas fields. New Zealand has extensive deposits of coal and could eventually use coal as their source of SG.

Table 5-1. Typical Process Conditions and Product Yields for MTG Processes

Conditions	Fixed-bed Reactor	Fluid-bed Reactor
MeOH/Water charge, w/w	83/17	83/17
Dehydration reactor inlet T, °C	316	-
Dehydration reactor outlet T, °C	404	-
Conversion reactor inlet T, °C	360	413
Conversion reactor T, °C	415	413
Pressure, kPa	2170	275
Recycle ratio, mol/mol charge	9.0	-
Space velocity, WHSV	2.0	1.0
Yields (wt% of MeOH charged)		
MeOH + dimethyl ether	0.0	0.2
Hydrocarbons	43.4	43.5
Water	56.0	56.0
CO, CO_2	0.4	0.1
Coke, other	0.2	0.2
	100.0	100.0
Hydrocarbon product (wt%)		
Light gas	1.4	5.6
Propane	5.5	5.9
Propylene	0.2	5.0
Isobutane	8.6	14.5
n-Butane	3.3	1.7
Butenes	1.1	7.3
C_{5+} gasoline	79.9	60.0
	100.0	100.0
Gasoline (including alkylate),		
RVP-62kPa (9psi)	85.0	88.0
LPG	13.6	6.4
Fuel gas	1.4	5.6
	100.0	100.0
Gasoline octane (R+O) (Research octane number, lead-free)	93.0	97.0

Source: Reference 1.

There is now an enormous literature on ZSM-5, a good deal of it on understanding the scientific aspects of the MTG reaction chemistry. There is also much literature on developing improved catalysts to maximize olefin or aromatic production, and using ZSM-5 to upgrade products from the F-T process, and developing a hybrid slurry F-T/MTG process (26). Other ions have been added to replace Al in the ZSM-5 crystal framework.

The Topsoe Integrated Gasoline Synthesis process (TIGAS) (27) uses combined steam reforming and autothermal reforming for SG production with a multifunctional catalyst system to produce an oxygenates mixture rather than only methanol. When the MTG process is integrated into this synthesis of oxygenates, operating conditions are relatively mild.

Lurgi, alternatively, has developed a direct heat exchange MTG reactor (29).

5.3 OXYGENATE SYNTHESIS AND PROCESSES[3]

5.3.1 Methanol Synthesis

5.3.1.1 Introduction and Historic Notes

At an annual rate of approximately three billion kg, methanol is one of the top ten organic chemicals produced in the world. It is catalytically synthesized by the reactions

$$CO + 2H_2 \rightarrow CH_3OH, \quad \Delta H^o_{600K} = -100.46 \text{ kJ/mol and} \quad \Delta G^o_{600K} = +45.36 \text{ kJ/mol} \qquad [1]$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \quad \Delta H^o_{600K} = -61.59 \text{ kJ/mol and} \quad \Delta G^o_{600K} = +61.80 \text{ kJ/mol.} \qquad [2]$$

Simultaneously occurring with methanol synthesis is the water gas shift (WGS) reaction:

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H^o_{600K} = -38.7 \text{ kJ/mol and} \quad \Delta G^o_{600K} = -16.5 \text{ kJ/mol.} \qquad [3]$$

The synthesis gas (SG) from which methanol is produced can be obtained by steam reforming of natural gas or naphtha and by gasification of coal. Depending on the source, SG contains different ratios of $H_2/CO/CO_2/(H_2O)$ and impurities.

The current major uses of methanol are: as raw material for production of formaldehyde, as solvent, and as a basic chemical for organic syntheses. Pure methanol also is a proven high-octane (~130) fuel for internal combustion engines and is used in racing cars. Blends of methanol with cosolvent alcohols are used in variable amounts as

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[3] This section was written by Kamil Klier, Lehigh University.

octane-enhancing additives in gasoline, and methanol can also be converted to other fuel alcohols by processes reviewed in Section 5.3.2. There are known drawbacks of cosolvent-free-methanol/gasoline blends, the most significant being a limited miscibility and phase separation in the presence of water.

The first catalysts used for methanol synthesis were based on the oxides, salts, and metals patented by Patart in 1921 (30). The ZnO/Cr_2O_3 catalysts were commercialized by BASF in the 1920's (31). During the late 1920's systematic studies of binary Cu/ZnO catalysts were carried out by Frolich and coworkers (32), who examined the synthesis of methanol at 20.7 MPa and the decomposition of methanol at 0.10 MPa at temperatures >593°K (320°C) as the Cu/Zn ratio in the catalysts was varied. Methanol synthesis catalysts based on $Cu/ZnO/Al_2O_3$ operating at 15-25 MPa were employed on an industrial scale in Poland in 1952 (33). A new generation of low-pressure (<10 MPa) and low-temperature (220-270°C) $Cu/ZnO/Al_2O_3$ catalysts was introduced by ICI in the late 1960's (34-36). ICI developed a technology with $Cu/ZnO/Al_2O_3$ catalysts which were most active and stable in a synthesis gas containing both carbon monoxide and carbon dioxide, as well as hydrogen.

Other companies such as Lurgi, Topsoe, and BASF also practice low-pressure methanol synthesis using the $Cu/ZnO/M_2O_3$ (M = Cr, Al) catalysts. The basic difference between the ICI and Lurgi engineering is the use of a multi-quench (ICI) and multi-tubular (Lurgi) reactors.

The modern low-pressure methanol synthesis is very selective, >99.5 percent to methanol by reactions [1] - [2]. The high selectivity achieved has to be appreciated in view of the fact that methanol is thermodynamically the least probable product of the SG conversion; i.e., other compounds are formed with a more negative free energy change than methanol. A graphic example is given in Figure 5-3, which shows the standard Gibbs free energy change at 600°K (327°C) in kcal/mol of carbon

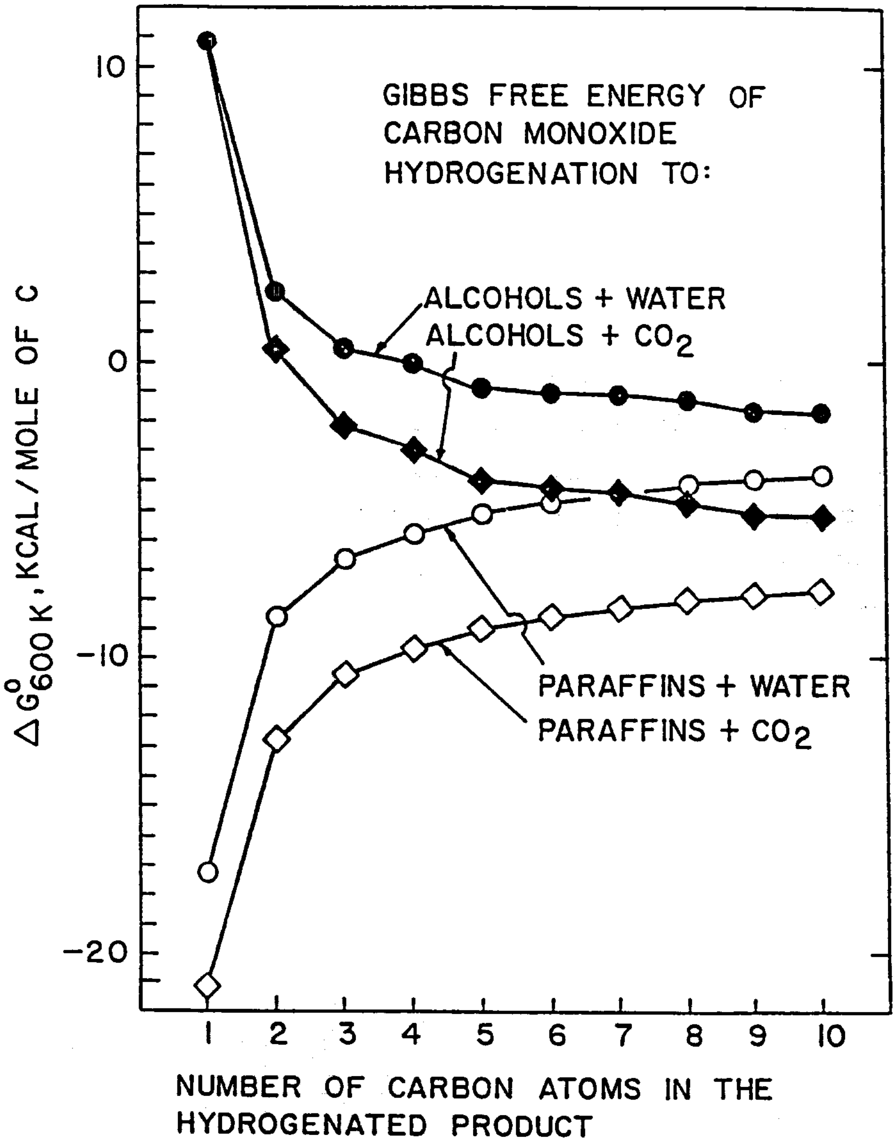


Figure 5-3. **Gibbs Free Energy of Carbon Monoxide Hydrogenation**

as a function of chain length n in the product C_n linear alcohols or paraffins generated by the reactions

$$nCO + 2nH_2 \rightarrow CH_3(CH_2)_{n-1}OH + (n-1)H_2O \quad (\bullet) \tag*{[4]}$$
$$(2n-1)CO + (n+1)H_2 \rightarrow CH_3(CH_2)_{n-1}OH + (n-1)CO_2 \quad (\blacklozenge) \tag*{[5]}$$
$$nCO + (2n+1)H_2 \rightarrow CH_3(CH_2)_{n-2}CH_3 + nH_2O \quad (\bigcirc) \tag*{[6]}$$
$$2nCO + (n+1)H_2 \rightarrow CH_3(CH_2)_{n-2}CH_3 + nCO_2 \quad (\lozenge) \tag*{[7]}$$

For long chains n, alcohols plus water formed by reaction [4] tend to have the same standard free energy as paraffins plus water by reaction [6], and alcohols plus CO_2 by reaction [5] the same standard free energy as paraffins plus CO_2 by reaction [7]. The difference for any single reaction type with water or CO_2 coproduct is given by the standard free energy of the water gas shift reaction [3], some -4 kcal/mol.

For short chains the free energies of formation for alcohols and hydrocarbons from CO/H_2 diverge, with hydrocarbons being significantly more favored. The greatest thermodynamic driving force is for the product methane (hydrocarbon with $n = 1$) plus CO_2 and the least thermodynamic driving force, in fact given by positive Gibbs free energy, is toward methanol (alcohol with $n = 1$). Because of the negative volume change of reactions [1] and [2], methanol synthesis can be thermodynamically driven against positive free energy by high pressures, but the catalyst must kinetically prevent the formation of all thermodynamically more favored products, i.e., hydrocarbons and C_2+ alcohols.

5.3.1.2 Existing Technology

Although methanol is a cheap commodity chemical ($0.72/gal in 1988), new plants (most for the low-pressure process) are being constructed all over the world. A staggering new or revamped annual capacity in excess of four billion kilograms of neat methanol has been completed, engineered, or planned in 1986-88, evidently with confidence in the future world market for fuel methanol (37). The ICI and Lurgi low-pressure technologies for methanol are described in some detail below.

The earlier high-pressure technologies are omitted in the present review because all new methanol plants built after 1967 have utilized the more modern low-pressure process. However, several high-pressure plants have been refurbished for higher-alcohol synthesis, and examples are given in Section 5.3.2.

A. The ICI Low-Pressure Process for Methanol

Although copper-based catalysts were known to be active and selective in methanol synthesis since the 1920's (38), they were not believed to be practical because of their low tolerance to sulfur poisoning and sintering of copper (39). Their practicality was proven when they were introduced in 1952 in a plant in Poland operating at 15-25 MPa (40) and in 1966 in an ICI (Imperial Chemical Industries) 109,500-tons-per-year plant at Billingham, U.K., that operated at pressures below 10 MPa. In 1972 ICI commissioned a 400,000-tons-per-year plant operating at 10 MPa and used a modified version of the original low-pressure methanol synthesis catalysts $Cu/ZnO/Al_2O_3$. The service life of the modern ICI catalysts is 3-4 years of continuous operation. The ICI technology spearheaded a worldwide commercially successful low-pressure (< 10 MPa) methanol technology that is responsible for the low prices of methanol in today's market. Two large ICI methanol plants are a part of the MTG (methanol-to-gasoline) complex at New Plymouth, New Zealand. In the mid-1980's over 75 percent of all new licensed methanol plants were based on the ICI process, accounting for one-third of the world's total methanol capacity. Plants ranging in size from 47,000 to 580,000 tons/year are in operation, and more are being built (37).

The ICI low-pressure methanol process is carried out at industrial sites that consist of a plant for producing the SG (H_2, CO, and CO_2 in various proportions), a low-pressure methanol synthesis plant, and a distillation plant. In most existing plants the source of SG is natural gas which is steam reformed to hydrogen-rich SG ($H_2/(2CO + 3CO_2) > 1$). Alternatively, the naphtha reforming process produces a nearly stoichiometric SG ($H_2/(2CO + 3CO_2) \approx 1$). Coal or heavy fuel oil, another source of SG, can be partially oxidized (gasified) to SG rich in carbon

($H_2/(2CO + 3CO_2) < 1$) that contains considerable quantities of sulfur. Because the copper-based catalysts are extremely sensitive to sulfur poisoning, the coal-derived SG must be purified to bring the sulfur content below 0.1 ppm. This can be achieved by several purification processes which operate by physical or chemical adsorption of acid gases, followed by a catalytic purification stage. The adjustment of hydrogen-to-carbon ratio suitable for methanol synthesis can be achieved by the water gas shift reaction between hydrogen-poor SG and steam. The flow diagram for the ICI low-pressure methanol synthesis from naphtha or natural gas is shown in Figure 5-4.

The synthesis loop contains a circulator, converter, heat exchanger, cooler, and separator. An ICI reactor of the quench gas converter type is shown in Figure 5-5. In this design there is a single catalyst bed with lozenge distributors for the injection of cold quench gas located at optimal depths of the catalyst bed. Good mixing of gases and temperature distribution in the reactor are ensured by this design. The distillation plant consists of a unit that removes volatile impurities such as dimethyl ether, esters, ketones, and iron carbonyl, and a unit which removes water and higher alcohols. After the first Billingham methanol plant was operated at 5 MPa since 1966, the pressure of 10 MPa was selected for the second, larger plant, with the carbon efficiency, defined as 100x(mols of methanol produced)/(mols of CO + CO_2 in the synthesis gas), 17 percent higher than that of the 5-MPa process. Pinto and Rogerson of ICI point out, however, that the above pressure advantage in efficiency holds only for hydrogen-rich SG from natural gas or naphtha and not for coal-derived carbon-rich SG (40).

The coal gasification conditions are usually such that SG with high CO/CO_2 ratio is obtained, which results in high carbon efficiencies over a wide range of pressures in the synthesis loop. Thus methanol synthesis is adaptable, without loss of carbon efficiency, to match a range of output pressures from various coal gasifiers. The general range of operating conditions of ICI low-pressure methanol plants is 5-10 MPa, 220-280°C, GHSV 5,000-60,000, and $H_2/(2CO + 3CO_2)$ ratios ≥ 1 but adaptable

Figure 5-4. ICI Low-Pressure Methanol Synthesis Process

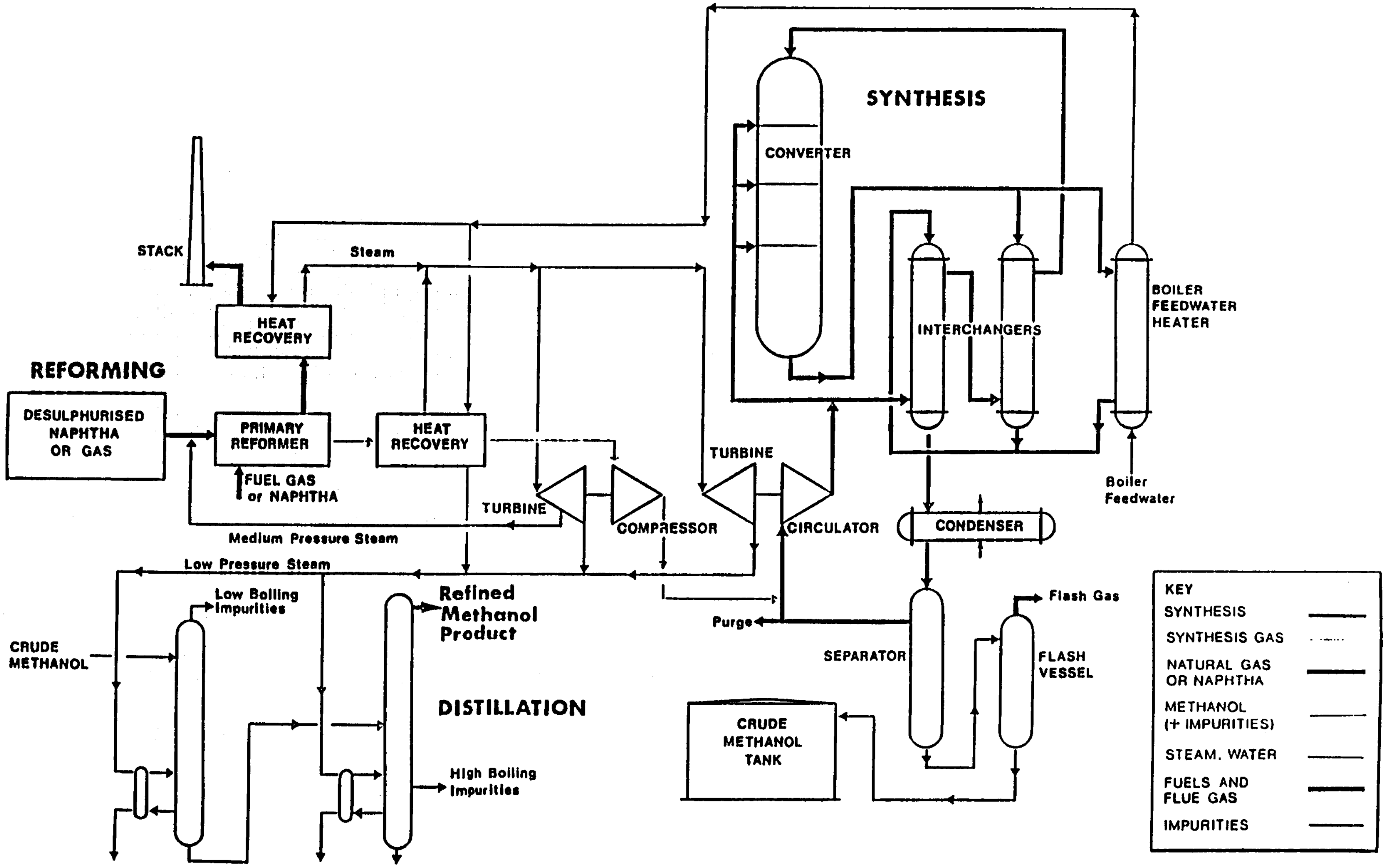
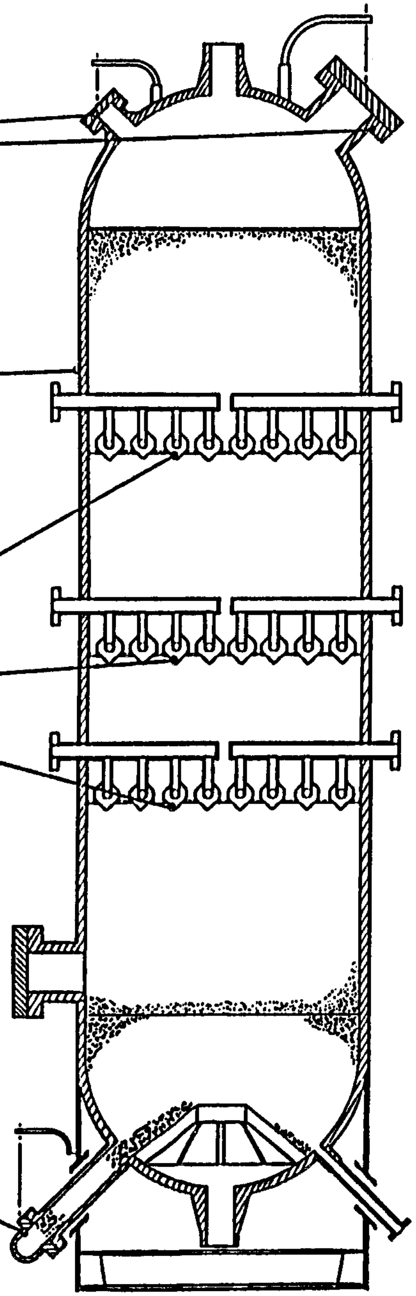


Figure 5-5. ICI Methanol Convertor



Catalyst can be readily charged and inspected through these manholes.

The pressure vessel is of a simple design readily manufactured in most parts of the world.

No internal catalyst basket is required.

The ICI Lozenge quench distributors ensure good gas distribution and allow the free passage of catalyst for charging and discharging.

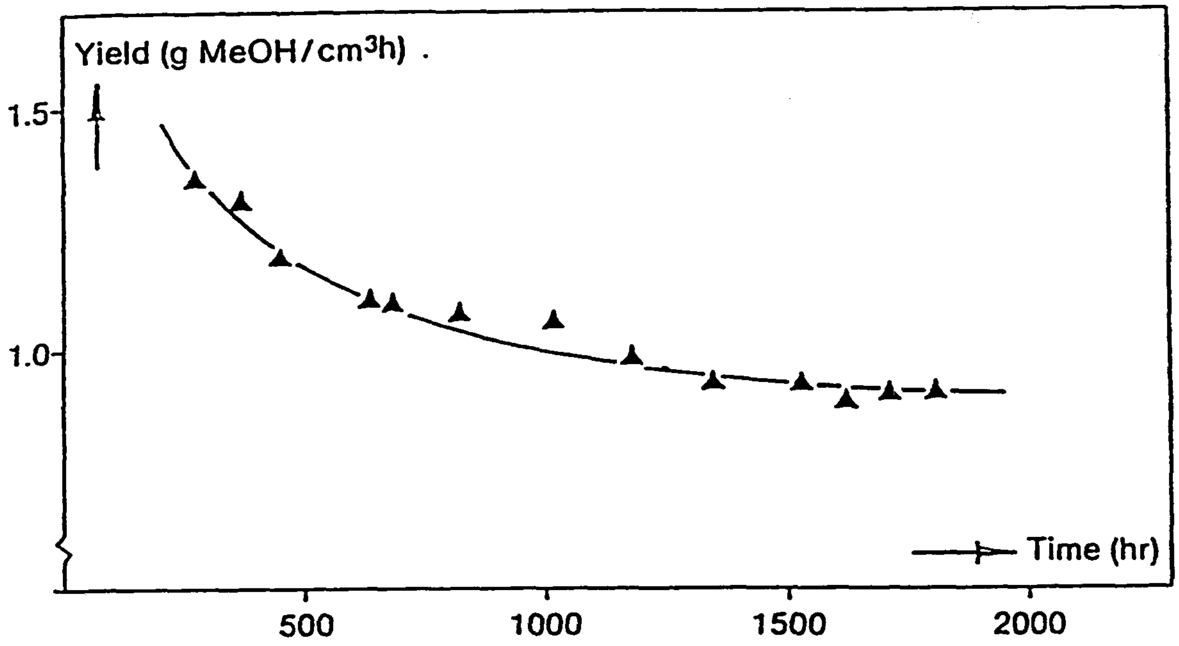
Gravity discharge of catalyst permits rapid preparation for maintenance or recharging.

to <1. Economic considerations have to take into account the energy and capital costs, and the main advantage associated with the use of coal-derived SG is that the SG compression can be avoided without penalty in carbon efficiency.

Although the ICI-type $Cu/ZnO/Al_2O_3$ catalysts have been optimized for maximum selectivity, STY's (space time yields), and long service life, they still deactivate, but no detailed reports on the rate of deactivation exist in the patent or open literature. In the recent review by Bart and Sneeden (41), an unpublished report of C. Boelens is quoted that presents deactivation data for an industrial $Cu/ZnO/Al_2O_3$ catalyst that operated for 2000 hours at 7 MPa and 240°C, as shown in Figure 5-6. In a 700-hour laboratory test of a binary Cu/ZnO catalyst at 7.5 MPa, 180-250°C, and variable SG ($H_2/CO/CO_2/H_2O$) compositions, Vedage et al. (42) detected no deactivation. In view of the results on deactivation of the copper-based catalysts under the more severe higher alcohol synthesis conditions described in Section 5.3.2.2, the main deactivation mechanism probably entails poisoning by chemical impurities, including trace iron carbonyl even in copper-lined reactors with pre-purified gases, rather than physical deactivation by redistribution of the elements in the catalyst and particle growth.

B. The Lurgi Low-pressure Process for Methanol

The Lurgi low-pressure technology also utilizes copper-based catalysts, principally of the composition $Cu/ZnO/Cr_2O_3$, the detailed preparation and additional promoter composition of which are not disclosed. The Lurgi reactor is a multi-tubular type, the tubes being filled with the catalyst and cooled with pressurized boiling water on the outside. The flow diagram of the Lurgi methanol synthesis from natural gas is shown in Figure 5-7. The natural gas is mixed with steam and converted to SG ($H_2/(2CO + 3CO_2)$~1) at 780°C and 4 MPa in the steam reformer 1 and autothermal reformer 2. High-pressure steam is produced in heat exchanger 3, and the SG is compressed to 7-10 MPa, preheated and fed into the reactor 4 together with the recycle gas. The reactor operates at 240-270°C, and good heat transfer to the pressurized boiling



Stability of industrial $Cu/ZnO/Al_2O_3$ catalyst. Reaction conditions: T 240 °C, p = 70 bar, S.V. = 35.000 h^{-1}

Figure 5-6. Stability of Industrial $Cu/ZnO_3/Al_2O_3$ Catalyst

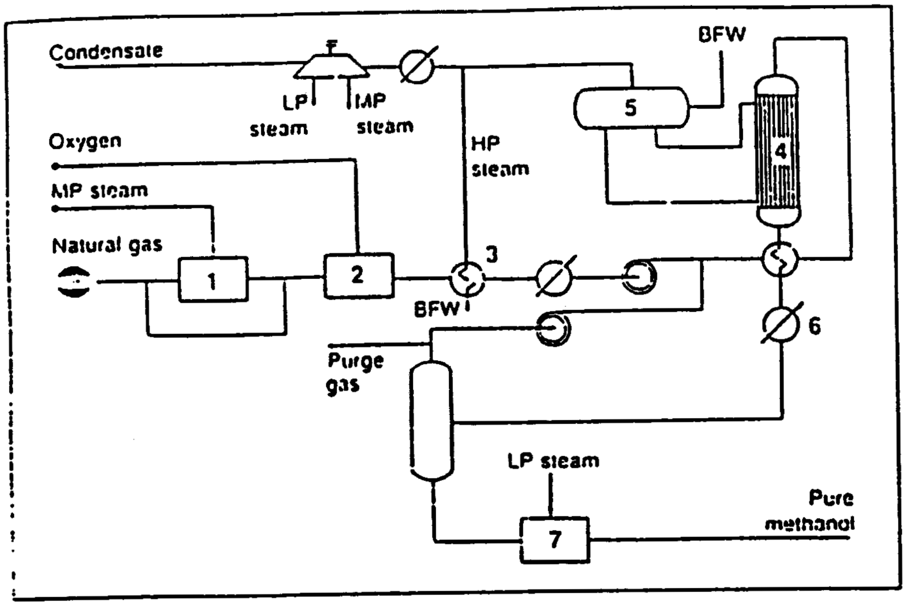


Figure 5-7. Flow Diagram of Lurgi Methanol Synthesis

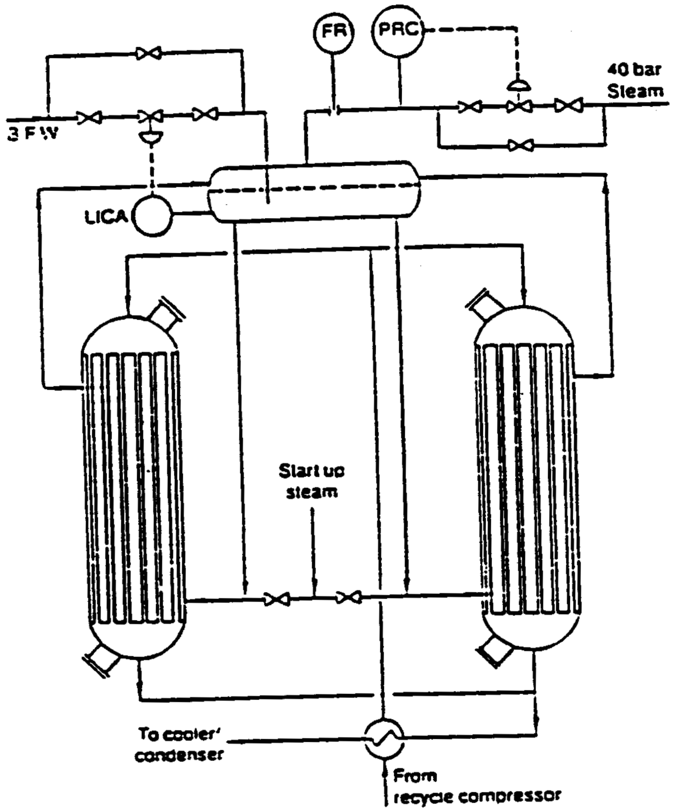


Figure 5-8. Lurgi Boiling-Water Low-Pressure Methanol Reactor

water that yields steam 5 is achieved. Methanol is produced at STY's close to 1 kg MeOH per liter of catalyst per hour. The crude methanol product is condensed 6, cooled, and distilled 7. The Lurgi tubular reactor is shown in greater detail in Figure 5-8.

The reactor has been called "quasi-isothermal" because of the smooth temperature profile along the reactor tubes, with exotherm variations not exceeding 10°C (43). The catalyst life is 3-4 years. The process can be easily adapted to utilize coal-derived SG by replacing the steam and auto-reformers by coal gasifiers and purification plant, mainly to remove sulfur from the SG. In early 1980 Lurgi Corporation was reported to have had almost 40 percent of the market for low-pressure methanol plants (43).

5.3.1.3 New Developments in Methanol Technology

Improvements in methanol technology have been sought by improved engineering and by novel catalyst design. Among the engineering developments are the Air Products and Chemicals (APCI)/Chem Systems liquid-phase methanol process and the gas-solid-solid trickle flow reactor (GSSTFR) developed at Twente University of Technology in the Netherlands and patented by Shell. Among the catalyst designs are some very active new heterogeneous copper-based catalysts that have been invented, but which are less selective and are poisoned by CO_2. Effort in the development of soluble "homogeneous" catalysts led to the two-stage Brookhaven process and to the soluble Cu(I)-sodium methoxide system of Union Carbide, with variable or not-yet-evaluated degree of success.

Another interesting development is the Shell process for direct synthesis of dimethyl ether (DME). Although DME-- CH_3OCH_3 -- contains two carbon atoms, it is often classified as a C_1 chemical because the two carbon atoms are not directly bonded with each other but rather connected via an oxygen bridge. Despite the claims, both in the patent (44) and open (45) literature, that alkali impurities are detrimental to the productivity and the selectivity of copper-based catalysts for methanol, Lehigh University discovered that heavy alkali promoters, particularly cesium, substantially enhance methanol yields from CO/H_2 while retaining 99 percent selectivity to methanol, when used in optimum concentrations.

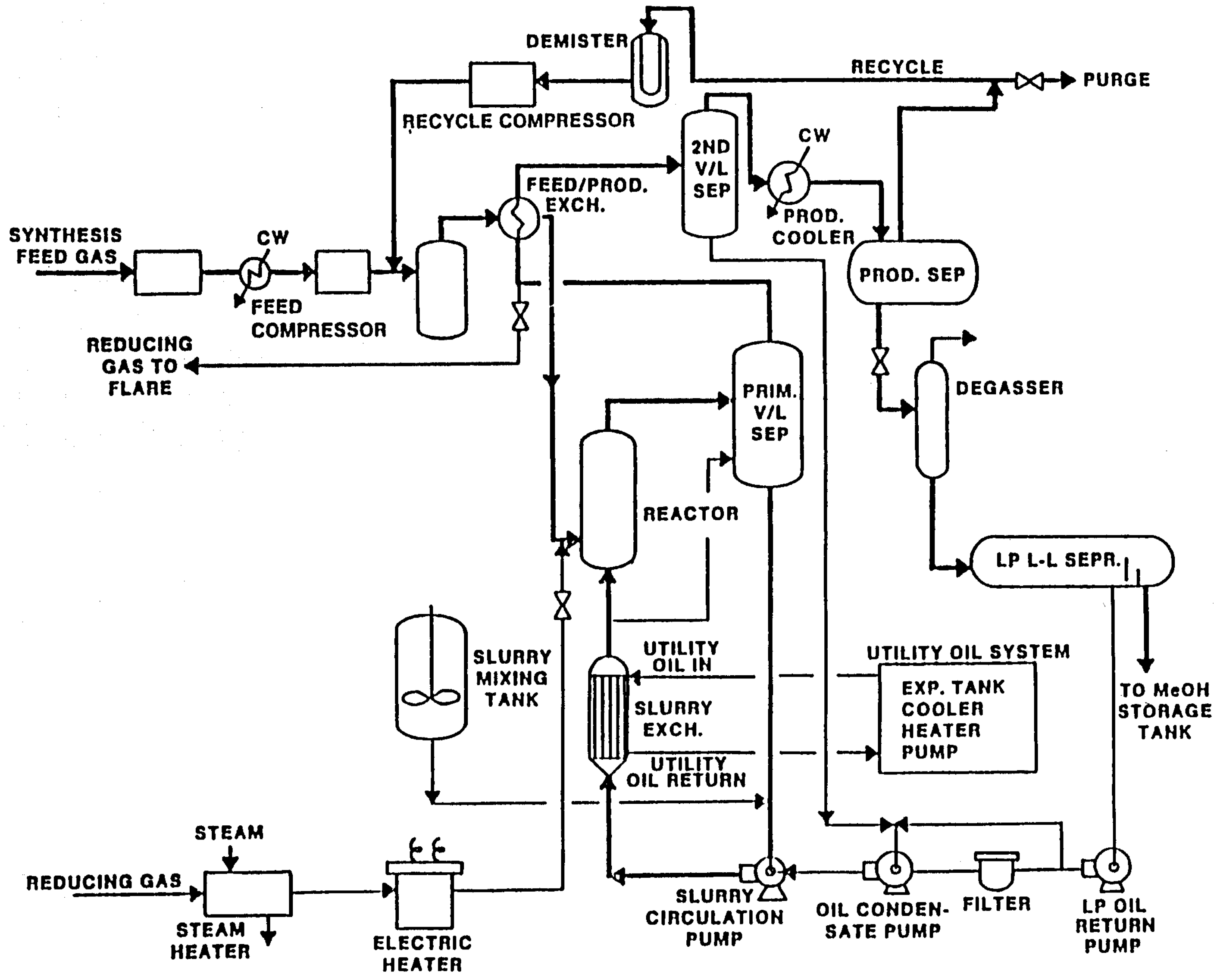
A. The APCI/Chem Systems Liquid-Phase Methanol Process

An engineering concept by which the reaction heat released in methanol synthesis is efficiently transferred to the surroundings utilizes a suspension of the heterogeneous catalyst in a liquid phase. In 1972 M.O. Tarhan of Bethlehem Steel was awarded a patent for methanol synthesis (actually by the reaction $3CO + 2H_2O \rightarrow 2CO_2 + CH_3OH$) utilizing Cu/ZnO catalysts suspended in water (46). In the mid-1970's Chem Systems developed a liquid-phase methanol synthesis in which a solid catalyst was fluidized or entrained in a hydrocarbon liquid, usually a mineral oil (47). The presence of the liquid renders the reactor virtually isothermal, and potentially higher conversions per pass could be achieved without catalyst deactivation in the hot spots of the reaction exotherm. Early research at Chem Systems utilized pelletized catalyst (3-6 mm particles) in an ebullated-bed reactor.

In 1981 DOE began supporting research on a liquid-phase methanol process in a Process Development Unit (PDU) at the LaPorte, Texas, plant operated by Air Products and Chemicals, Inc. (APCI). The Electric Power Research Institute (EPRI) cosponsored the program because of EPRI's interest in the economically attractive coproduction of methanol and electricity in integrated gasification-combined cycles (IGCC) (48). The LaPorte PDU was commissioned in March 1984. Five major synthesis runs and numerous hydrodynamic and analytical runs have been carried out. The flow diagram of the LaPorte PDU is shown in Figure 5-9.

The process operates at 3.5-6.3 MPa, 220-270°C, liquid-fluidized space velocity (l/kg cat/hour) 1000-4000, liquid-entrained catalyst loading 10-33 weight percent, and $H_2/CO/CO_2/(N_2 + \text{inerts})$ compositions 35/51/13/1 (CO-rich SG) and 55/19/5/19 (balanced SG). The CO-rich gas is representative of SG from modern coal gasifiers. These gases are suitable for once-through methanol synthesis in an IGCC process. The

Figure 5-9. Simplified Process Flow Sheet for LaPorte PDU



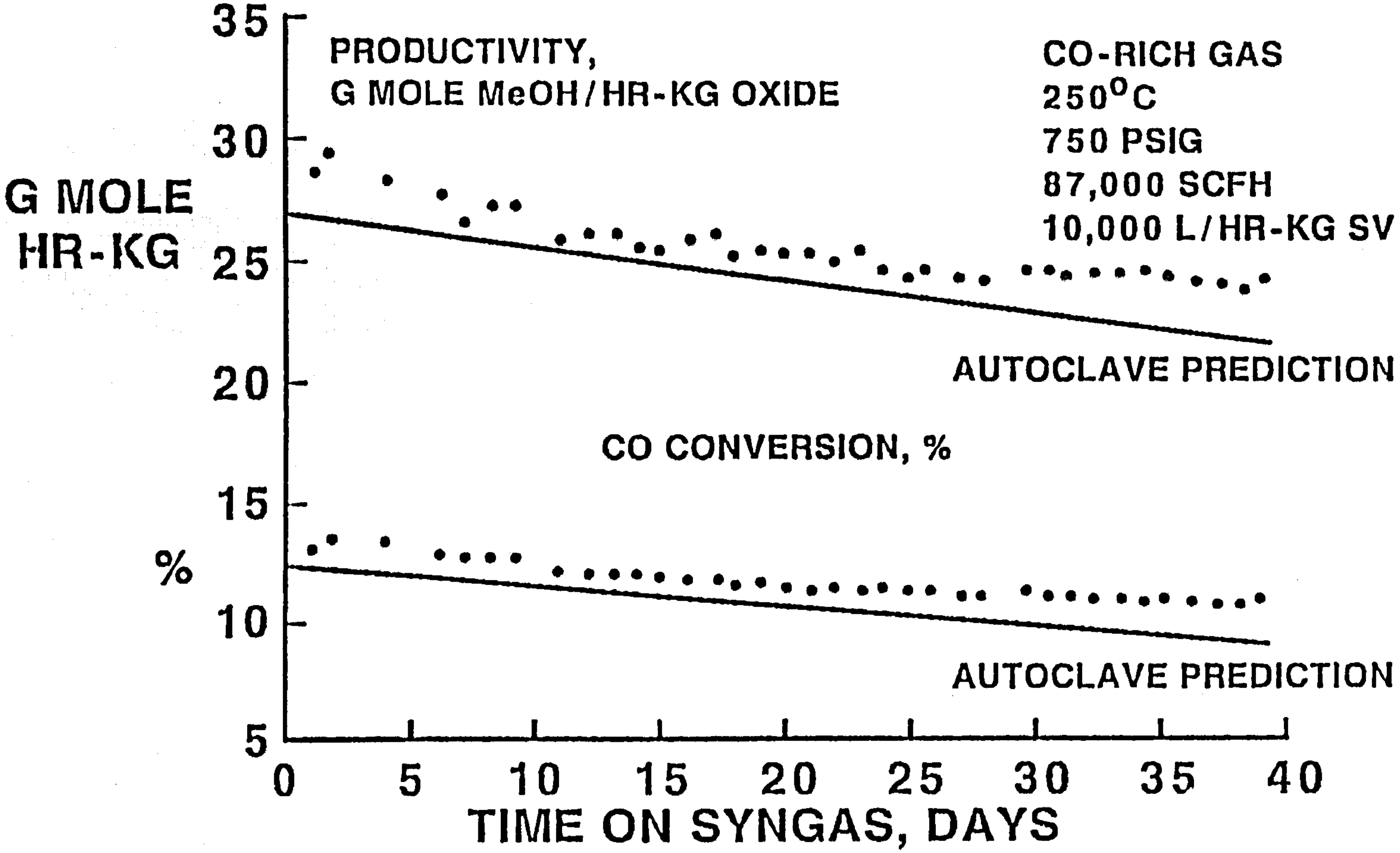
catalyst used was of Cu/ZnO/Al_2O_3 composition, and its powder slurry was circulated through the liquid-phase reactor.

The performance of the LaPorte process utilizing purified gases and metallurgical improvements aiming at minimizing catalyst deactivation by iron and nickel carbonyls is shown in Figure 5-10. Here it should be noted that the productivity expressed in Figure 5-10 in mol MeOH per kg catalyst per hour converts to STY in kg MeOH per hour per l of the liquid slurry in the reactor by a factor 0.032 (for the molecular weight of methanol in kg) x 0.25 (for 25 weight percent catalyst in slurry) = 0.008, giving an initial STY of 0.232 and an STY after 40 days (~1000 hours) of 0.19. The STY of the run reported in Figure 5-10 is less than 25 percent of the commercial ICI or Lurgi vapor phase processes, but a deactivation rate of 2.2 percent per 100 hours compares favorably with that for the vapor-phase process in Figure 5-6. It appears that the main factor reducing the STY in the liquid-phase process is the dilution of the catalyst by the liquid phase, and further development with a higher slurry density is underway (47).

B. The Gas-Solid-Solid Trickle Flow Reactor (GSSTFR)

In 1986 Hydrocarbon Processing reported an interesting engineering approach to shifting the equilibrium of reactions [1] and [2] in favor of the methanol product by adsorbing the synthesized methanol directly in the catalytic reactor (49) and removing it by a flow of the solid sorbent down the catalytic bed. The synthesis is conducted in a column reactor filled with a stationary bed of 5x5 mm cylindrical pellets of the catalyst (commercial BASF copper catalyst Type S3-85 was used in the Twente development work (49)) mixed with 7x7x1 mm Raschig rings. The SG is introduced at the bottom, and the selective adsorbent powder (amorphous LA-25 low-alumina AKZO cracking catalyst with mean particle diameter 90 μm) is introduced at the top and trickles downward over the catalyst pellets. The LA-25 sorbent adsorbs methanol at the reaction temperatures of 220-250°C, is collected in a bottom vessel, and is presumably ready for separation of methanol and recirculation of the sorbent.

Figure 5-10. LaPorte PDU 40-Day Run Performance, May/June 1985



Westerterp and Luczynski (49) estimated that the STY's of methanol are increased by 40 percent and 25 percent and more steam is produced in their type of GSSTFR compared to conventional reactors. The basic assumption was that the increased efficiency is due to shifting the equilibrium of reaction [1] or, in the presence of CO_2, of reaction [2]. Complete conversion of SG is achievable despite the unfavorable chemical equilibrium. The Twente University project has been sponsored by the Royal Dutch Shell Group since 1982, and Shell owns the patent (49).

C. New Catalytic Systems for Methanol Synthesis

This paragraph summarizes some new reports on heterogeneous and homogeneous catalysts for methanol synthesis, deferring the discussion of systems that make methanol with significant portions of higher oxygenates to Section 5.3.2. Moreover, one approach to the direct synthesis of dimethyl ether is discussed here.

Copper-Based Catalysts

Copper-based catalysts that are mixed, often on a nanometer scale, with the oxides of Zn, Al, Cr, Sc, V, Ti, Si, Mg, Th, and lanthanides, have been investigated in many recent studies. Some of these studies are summarized in Table 5-2. Most of these investigations are aimed at resolving mechanistic questions and effects of supports, dopants, and different preparation modes.

No higher activities or selectivities than those of the industrial $Cu/ZnO/Al_2O_3$ (58) or model binary Cu/ZnO (59) catalysts were reported, but the following established properties of copper-based catalysts were confirmed.

- The $Cu/ZnO/Al_2O_3$ and Cu/ZnO catalysts can produce methanol with near - 100 percent selectivity.
- The STY's of copper-based catalysts for methanol under the low pressure ($<$ 10 MPa) conditions are the highest of all selective catalysts known today.

Table 5-2. **Activities and Selectivities to Oxygenates (Methanol and C_2+ Alcohols) of Catalysts Based on Copper**

Sources: 9th ICC, July 1988 and References 58-62.

General Conditions: 1-5 MPa, $H_2/CO/CO_2$ = variable, given in footnote, GHSV 4,000-10,000.

Catalyst	Selectivity to oxygenates percent	T °C	STY[a] of oxygenates g/kg(l)cat/hour	Ref.
$Cu/ZnO/Al_2O_3/Cr_2O_3$	$^{\sim}100^{b}$	230	12.0^{c}	50
$Cu/ZnO/Al_2O_3/Sc_2O_3$	$^{\sim}100^{b}$	230	11.6^{c}	50
$Cu/ZnO/Al_2O_3/V_2O_3$	$^{\sim}100^{b}$	230	7.4^{c}	50
$Cu/ZnO/Al_2O_3$	$^{\sim}100^{b}$	230	5.0^{c}	50
Cu/ZnO	99	250	796.0^{d}	51
Cu/TiO_2	0.5	250	2.1^{e}	51
$Cu/ZnO/Al_2O_3$	$^{\sim}100^{b}$	250	800.0^{f}	52
$Cu/ZnO/Al_2O_3$	$^{\sim}100^{b}$	215	1216.0^{g}	53
$Cu/ZnO/ZrO_2$ aerogel	96	300	432.0^{h}	54
Cu/ZrO_2^{j}	n.a.	$160\text{-}300^{k}$	$453.0^{i,k}$	55
$Cu/Co/ZrO_2$	64	250	$28^{l}.0$	56
$Cu/Co/TiO_2$	25	250	27.0^{l}	56
$Cu/Co/SiO_2$	66	250	9.0	56
Cu/Co/MgO	85	250	$19^{l}.0$	56
$Cu/Co/Al_2O_3^{m}$	-	-	-	57
$Cu/ZnO/Al_2O_3$	>99	230	1430.0^{n}	58
Cu/ZnO	>99.8	250	1350.0p	59
$CuI/NaOCH_3$	n.a.	110	85.0^{q}	60
Cu/CeO_2	80-98	240	816.0^{r}	61
Cu/La_2O_3	n.a.	240	384.0r	61
Cu/ThO_2	n.a.	250	960.0^{s}	62

[a] STY = Space Time Yield, given in g of oxygenated product per kg of catalyst (including support) where available, otherwise per liter of catalyst.

[b] Only methanol reported, pressure not given.

[c] $H_2/CO/CO_2$ = 66/28/6, GHSV 6000.

[d] Pressure 1.7 MPa.

[e] This catalyst is very active in methanol decomposition, however.

[f] Pressure 5 MPa, $H_2/CO/CO_2$ = 70/25/5.

Table 5-2 (continued)

[g] Pressure 5 MPa, $H_2/CO/CO_2$ = 65.5/30.9/3.6.

[h] Pressure 3.2 MPa, $H_2/CO/CO_2$ = 9/0/91.

[i] Pressure 5 MPa, $H_2/CO/CO_2$ = 80/0/20.

[j] Urea-precipitated catalyst.

[k] Precise reaction temperature at which the tabulated STY was obtained is not given.

[l] Pressure 1 MPa, $H_2/CO/CO_2$ = 67/33/0.

[m] Study of preparation only; hydrotalcite precursors give rise to homogeneous Cu-Co-Al mixed oxide spinel-type structure which upon reduction yields small crystallites of Cu and Co metals and $CoAl_2O_4$ spinel.

[n] Pressure 5 MPa, $H_2/CO/CO_2$, GHSV 10,000.

[p] Pressure 7.5 MPa, $H_2/CO/CO_2$ = 70/24/6, GHSV 5000 per kg of catalyst.

[q] Pressure 13.5 MPa, $H_2/CO/CO_2$ = 50/50/0, STY estimated from a batch autoclave experiment, methanol and methyl formate (1:1:8).

[r] Pressure 5 MPa, $H_2/CO/CO_2$ = 50/50/0, GHSV 72,000 per liter of catalyst = 180,000 - 240,000 per kg of catalyst.

[s] Pressure 6 MPa, $H_2/CO/CO_2$ = 70/30/0, GHSV 22,000.

- CO_2 can be hydrogenated to methanol as efficiently as or faster than CO, but the highest rates are obtained with $H_2/CO/CO_2$ feed in which CO/CO_2 ratios = 10/1 - 4/1 are used.
- Addition of a Group VIII metal such as Co lowers the selectivity to methanol and increases the selectivity to C_2+ alcohols but also increases the hydrocarbon make.

A relatively novel support for methanol copper catalysts is ZrO_2, an amphoteric solid that imparts stability on the catalyst while preserving high selectivity and yields of methanol. On the other hand, TiO_2 drastically lowers both the selectivity to and the yields of oxygenates and promotes hydrocarbon formation.

The question of the nature of active forms of copper (Cu^+ vs. Cu°) was re-investigated in several papers, and a number of reports were published, some inconclusive (51, 55), some favoring Cu^+ (50, 53, 54) and another favoring Cu° (52). Obviously, while much evidence in favor of electron-deficient copper has been gathered (58), the nature of the catalytically active valence state of copper deserves further attention. The question is an important one because if Cu^+ is the active state, then catalysts can be designed so that Cu^+ is maximized. This was attempted by Tsai et al. (50) through doping the $Cu/ZnO/Al_2O_3$ catalyst with a trivalent element M^{3+} of ion size compatible with the ZnO lattice such as Cr^{3+}, Sc^{3+}, and V^{3+}. These trivalent ions dispersed in ZnO stabilize Cu^+ by valence induction, $2\ Zn^{2+}{}_{Zn} = Cu^+{}_{Zn}M^{3+}{}_{Zn}$. Tsai et al. obtained evidence by Auger spectroscopy that the valence induction doping procedure was particularly successful with Cr^{3+} and Sc^{3+}, and more active catalysts relative to his reference $Cu/ZnO/Al_2O_3$ were obtained. Unfortunately, the reaction pressure in Tsai's et al. work was not given, and the STY's over all their catalysts appeared low for the normal range of pressures used, which is around 5 MPa.

Researchers at the U.S. Bureau of Mines at Reno discovered that Cu/ThO_2 catalysts prepared from intermetallic $CuTh_x$ alloys by a redox process were active in methanol synthesis (62). Following this discovery, ICI researchers probed into a larger class of intermetallic

$CuMe_x$ (Me = Ce, La, Pr, Nd, Gd, Dy, Zr, Ti, and Th) alloys as precursors of Cu/Me_2O_3 and Cu/MeO_2 catalysts, and found that the $CuCe_{0.5}$, $CuLa_{0.45}$, and $CuPr_{0.5}$ precursors also resulted in very highly active catalysts for the synthesis of methanol from CO/H_2 (61). These catalysts were severely poisoned by small amounts (1-2 percent) of CO_2 and often contained copper metal of low dispersion (very large particles, Cu metal area < 1 m^2/g). An electropositive copper species analogous to that proposed by Klier et al. for the Cu/ZnO catalyst (59), Baglin et al. for the Cu/ThO_2 catalyst (62), and Shibata et al. for the Cu/ZrO_2 catalyst (63) was tentatively suggested to be the active component. Alternative candidates for the site for methanol synthesis were suggested to be extremely small copper particles (<1 nm diameter) or intermetallic hydrides.

Because of the lack of tolerance to CO_2, the Cu intermetallics-derived catalysts, although very highly active, were not considered practical as industrial SG invariably contains amounts of CO_2, and CO_2 removal (to below 0.1 percent) may adversely influence process economics. The oxygenate selectivities of these catalysts of 80-98 percent are acceptable in their upper limit but not in the lower limit. After initially higher activities, steady states were attained in 20-40 hours, and these are reported in Table 5-2, Rows 19 and 20. The concentration of CO_2 in the exit gas was typically less than 0.1 percent and that of H_2O approximately 1 percent of condensable products, or <0.05 percent by volume of the exit gas. The effect of water on the activity of the $CuMe_x$ intermetallics-derived catalysts has not been studied. Taking into account the very high activities, the lack of precise oxygen balances, the lack of precise determination of CO_2 effects at concentrations <1 percent, and the lack of data on water effects on the synthesis, it appears that these novel copper-based catalysts derived from intermetallics have not yet been studied in full detail and further research into their improvement is to be expected.

The Brookhaven Process for Methanol Synthesis

A 1984 report by Brookhaven scientists on a novel approach to methanol synthesis (64) received considerable attention. In this approach two catalyst components are used in the liquid phase, a metal (molybdenum) carbonyl that activates carbon monoxide and a hydride that hydrogenates the carbonyl to methanol and is regenerated by a reaction with hydrogen. In 1986 a further process development was reported by O'Hare et al. (65) wherein synthesis temperatures of 100°C were used, indicating extraordinary activities of the methanol synthesis. A. G. Mills points out (66) that there have been reservations about the practical operation of the Brookhaven process, for example, in terms of deactivation of the catalyst by CO_2 in the SG. Also, specific technical information has not been made public, and therefore the Brookhaven process yields and selectivities have not been verified. In the older version the selectivity ratio of methanol to methane that has been reported for temperatures around 200°C and pressures 2-5 MPa was between 45/55 and 55/45 (65). On the other hand, every new catalytic system that displays activity for methanol synthesis at temperatures below 200°C merits attention for possible future improvements of selectivity and stability, and further development of the Brookhaven system is to be expected.

Union Carbide's Soluble Cu(I) Catalysts for Methanol Synthesis

Union Carbide carried out research into soluble homogeneous catalysts for methanol under DOE contracts and published a final technical report in January 1987 (60). Ruthenium, cobalt, copper, and other catalysts were investigated. The ruthenium system, when promoted with iodine and lanthanide salts, yielded oxygenates with up to 80 percent of C_2+ alcohols, but the STY's of 60-100 g/l/hour were thought to require improvement to achieve commercially attractive yields. Although good stability of the halide-promoted ruthenium catalysts for direct conversion of syngas to alcohols was obtained, solvent degradation was found to be a problem with a number of solvents investigated. The homogeneous cobalt catalysts also produced alcohols but invariably at low rates, often with large amounts of methane side product; they also catalyzed solvent decomposition. Other catalysts based on soluble complexes of Fe, Re, Pd and Rh were found to produce very small or no amounts of alcohols.

Among the copper-containing catalysts studied, a very active copper-alkali system was investigated that produced significant amounts of methanol (30 g/l/hour) and methyl formate (55 g/l/hour) at temperatures as low as 110°C. The Union Carbide research aimed at the testing and improvement of a Japanese invention (66) that claimed a soluble copper catalyst for the production of methanol (MeOH) and methyl formate (MeOF) at moderate pressures (3-13 MPa) and very low temperatures (80-120°C) when sodium methoxide ($NaOCH_3$) was used as a promoter. Some of the results with the copper-sodium methoxide catalysts are summarized in Table 5-3. The data in run 86 in this table correspond to STY's of 85 g (MeOH + MeOF) per liter of the solution per hour at 110°C and show that the copper-sodium methoxide system is indeed active as well as selective, in the sense that it produces only MeOH + MeOF. However, mechanistically MeOF is a precursor of methanol in this system (cf. Section 5.3.1.4), and it is probably this mechanistic feature that gives rise to higher yields of MeOF than of methanol in this system. The copper-sodium methoxide catalyst has been found unstable and rapidly deactivated by precipitation of metallic copper from the solution of cuprous halide or hydride exposed to the synthesis gas $H_2/CO = 1/1$.

Although a selective homogeneous catalyst for methanol that could be considered as a replacement for the existing low-pressure heterogeneous catalysts such as the $Cu/ZnO/Cr_2O_3$ and $Cu/ZnO/Al_2O_3$ has not yet been found, several initially very active homogeneous catalysts have been reported as demonstrated above. There are incentives to continue a search for active and selective homogeneous methanol synthesis catalysts. Among the advantages of successful homogeneous catalysts are the following often-listed items (68):

- Liquid-phase systems in general have excellent heat-removal capability, and the added advantage that no cumbersome slurry handling or engineering is necessary with homogeneous soluble catalysts -- it can be expected that a good homogeneous

Table 5-3. **Reactivity of Copper Hydride Systems (Soluble Copper Catalyst)**

	SGHAM-G-#	RUN 86
1.	Catalyst	CuH
2.	mmoles	5
3.	NaOMe, mmol	110
4.	Solvent[a]	DEC
5.	mL	75
6.	Additive[b]	none
7.	mmol	0
8.	Press, psi	2000
9.	H_2/CO	1:1
10.	Temp., °C	110
11.	Time, hr	3
12.	Uptake, psi	4480
13.	Wt. % MeOH	7.0
14.	Wt. % MeOF	12.6
15.	Other Prods	none

[a] DEC = Diethyl carbitol

[b] NaOEt = sodium ethoxide

[c] Products included ethanol and ethyl formate derived from ethoxide.

catalyst in the APCI/Chem Systems liquid-phase process (Section 5.3.1.3) would be an attractive replacement for the slurried commercial catalyst that has been designed for vapor-phase processes.

- Homogeneous catalysts often allow improved selectivities under mild conditions -- this is not really the case in methanol synthesis, which is already 99.5 percent selective over heterogeneous catalysts, but can be the case in the related higher-alcohol synthesis.
- The absence of surface effects can lead to higher specific activity since the homogeneous catalyst is molecularly dispersed, and all catalyst molecules participate in the chemical reaction, as opposed to heterogeneous catalysts where supports and subsurface atoms do not.
- The claim of longer catalyst life has yet to be substantiated for heterogeneous methanol catalysts, the heterogeneous counterpart of which is usable for 3-4 years.
- The manufacture of homogeneous catalysts is simple and reproducible.
- A further advantage of homogeneous catalysts is that reaction kinetics in solutions are usually simpler than on the surfaces of heterogeneous catalysts, and the intermediates are somewhat more easily characterizable.

The Shell Process for Direct Synthesis of Dimethyl Ether (DME)

In 1983 L. H. Slaugh of Shell Oil Co. was awarded a patent for direct synthesis of DME from SG (69). Although DME -- CH_3OCH_3-- contains two carbon atoms, it is often classified as a C_1 chemical because the carbon atoms are connected by an oxygen bridge rather than being joined by a C-C bond. The Shell catalyst consists of the Cu/ZnO components for methanol synthesis supported on a 150-500 m^2/g gamma alumina. It can be assumed that two consecutive reactions occur on the catalyst, the methanol synthesis [1] and methanol dehydration to DME [8],

$$2CH_3OH \rightarrow \underset{\text{DME}}{CH_3OCH_3} + H_2O \qquad [8]$$

the reaction [1] occurring on the Cu/ZnO component and reaction [8] on the gamma-alumina component. Reaction [8] is usually acid-catalyzed, and it is expected that the gamma alumina imparts the acidic function onto the catalyst. Sodium impurities must be avoided as they could neutralize the surface acidity. Reaction [8] represents a sink for methanol, and the overall process [9] can be run with a minimum concentration of the methanol intermediate.

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O \qquad [9]$$

Selectivities up to 97 percent to DME, with 1.5 percent MeOH and 1.5 percent hydrocarbons coproduced, were achieved with the Shell catalyst at 6 MPa, 292-300°C, GHSV 3000, and the STY of DME exceeded 0.8 kg/l cat/hour, i.e., rates comparable to those of methanol synthesis at 250°C were achieved.

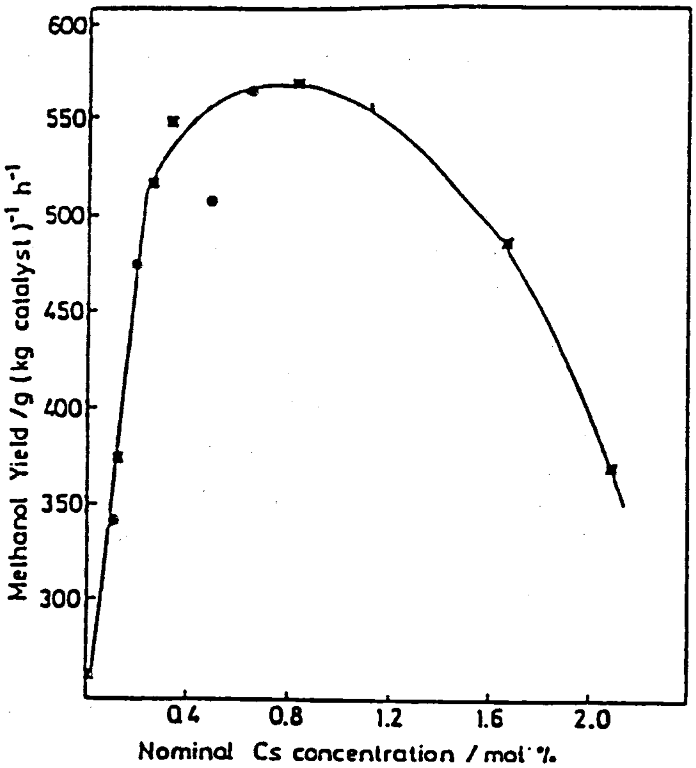
The Shell process for DME from SG utilizing modified low-pressure methanol synthesis catalysts is an example of a method of how SG can be converted to value-added chemicals via methanol as an intermediate. In conjunction with indirect liquefaction, the process for direct synthesis of DME may have an application in utilizing DME as a source for aromatic gasoline produced by the Mobil process utilizing the ZSM-5 zeolite. This concept would constitute a modification of the three-stage MTG process in which methanol is synthesized from SG and converted in a separate reactor over an acid catalyst to DME, with the DME being fed to the ZSM-5 to produce aromatic gasoline; the first two stages are integrated via Reaction [9] in the Shell DME process.

Enhancement of Methanol Yields over Cu/ZnO Catalysts by Alkali Dopants

After initial work that established the ion-specific promotion effects of Cu/ZnO catalysts by alkali hydroxides, Cs > Rb > K > Na,Li, for methanol and higher-alcohol synthesis (70), Lehigh University researchers have demonstrated that the alkali-promoted Cu/ZnO catalysts are quite selective for methanol under the usual methanol synthesis conditions, e.g., 7.6 MPa, 250°C, GHSV 6000, and $H_2/(2CO + 3CO_2) = 1.15$, and the methanol synthesis rates are at the same time enhanced. Further, it was found that several types of the dopant alkali compounds may be used, e.g., formates instead of hydroxides. The alkali dopants must used in their optimum concentration, as exemplified by the effect of cesium in Figure 5-11. It is seen from the data in this figure that the rate of methanol synthesis from H_2/CO was enhanced by a factor of 2.15 in the presence of the optimum Cs concentration of 0.3-0.8 percent and an STY of 0.56 kg MeOH/kg cat/hour at 7.6 MPa, 250°C, GHSV 6000 and $H_2/CO = 2.33$ was attained. With the use of higher-surface-area $Cu/ZnO/Cr_2O_3$ catalysts, 3 percent Cs doping increased the STY from 0.56 to 1.05 kg MeOH/kg cat/hour at the same conditions (except GHSV = 10,000) (72). For the Cs/Cu/ZnO catalyst the selectivity to MeOH was 99 percent and for the $Cs/Cu/ZnO/Cr_2O_3$ catalyst 98 percent, the main side products being methyl formate (0.6 percent for the Cs/Cu/Zn/Cr catalyst) and ethanol (1.3 percent for the Cs/Cu/Zn/Cr catalyst). Thus, STY's from a CO_2-free H_2/CO SG were achieved by Cs doping of the copper-based catalysts that are characteristic of the performance of copper-based methanol synthesis catalysts only in the presence of CO_2.

The activity of the Cs/Cu/ZnO catalysts was also investigated with a feed gas containing water ($H_2/CO/H_2O = 2.3/1/0\text{-}0.4$), and it was found that the alkali dopant promoted the methanol synthesis rates also in the presence of large amounts of injected water. The kinetic behavior is complex and is shown in Figure 5-12. Although most of the injected water is converted to CO_2 by the water gas shift reaction [3], the direct effect of CO_2 in the feed gas on the STY of methanol has not been reported by the Lehigh group.

Associated with the Cs promotion of methanol synthesis exemplified in Figure 5-12 is the promotion by Cs of the water gas shift activity of the Cu/ZnO catalysts. The effects are large, up to by a factor of 2.3 (73), and it is evident that a very highly active WGS catalyst has been discovered in the studies of alkali-doped copper-based methanol synthesis catalysts. The long-term stability of the $Cs/Cu/ZnO/(Cr_2O_3)$ catalysts has been studied under the higher-alcohol synthesis conditions (Section 5.3.2.2), and a deactivation rate of 1.6 percent of converted CO per 100



Yield of methanol as a function of Cs loading over the calcined-doped (■) and reduced-doped (●) binary Cu/ZnO catalysts

Figure 5-11. Yield of Methanol as Function of Cs Loading

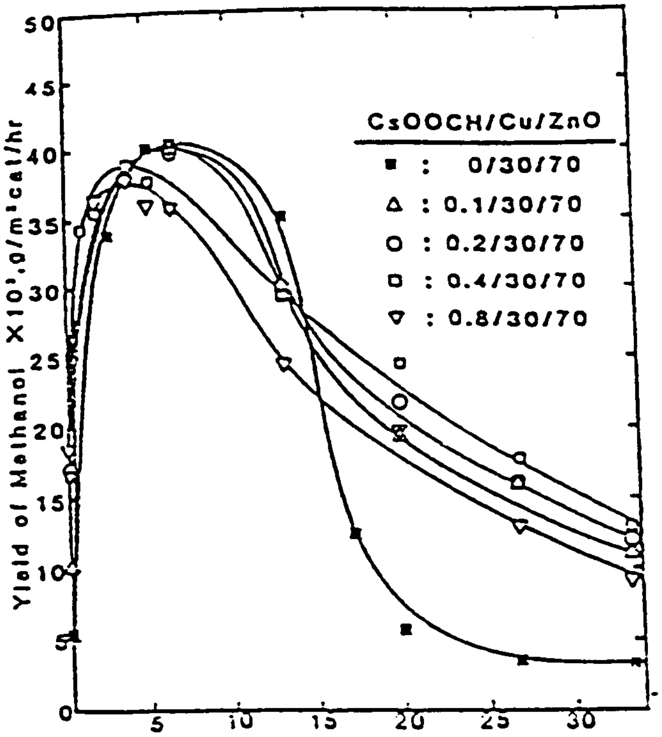


Figure 5-12. Yield of Methanol as Function of Water Injection Rate

hours has been established in a copper-lined reactor with carefully pre-purified gases. No deactivation rates were reported for the Cs/Cu/ZnO/(Cr_2O_3) catalysts under methanol synthesis conditions with variable concentrations of CO_2 in the SG.

5.3.1.4 Chemistry and Mechanism of Methanol Synthesis

The development of modern methanol synthesis technology has involved some seven decades of inventions, gradual improvements of catalysts, mechanistic work, and engineering design. The historic development was outlined in Section 5.3.1.1. Particular attention has been paid to the copper-based catalysts which are a key part of the most active and selective methanol synthesis technologies practiced today. New inventions are still occurring with copper catalysts and with copper-free catalysts in the area of both heterogeneous and homogeneous catalysis. It is desirable for methanol synthesis, as it is for any other process of importance, to resolve the chemical mechanism of key reactions, to analyze the intermediates, and to determine the functions of the individual catalyst components that steer the reactions to the most selective and efficient path. Finally, it is desirable to relate this mechanistic information to formal kinetics that could be used in process design.

Several reviews have been published on the mechanism of methanol synthesis over the copper-based catalysts only. The early, primarily kinetic studies of methanol synthesis were reviewed by Natta in 1955 (39), the mechanistic work by Kung in 1980 (74), the characteristics of the Cu/ZnO/M_xO_y catalysts along with the available mechanistic information by Klier in 1982 (38), new results on CO_2 versus CO hydrogenation and the role of metallic copper over the industrial Cu/ZnO/Al_2O_3 ICI catalysts by Chinchen et al. in 1987 (58), and most recently a comprehensive analysis of the current understanding of the copper-based catalysts by Bart and Sneeden (41), also in 1987. Subsequently and concurrently, a large number of papers have emerged that indicate that the mechanism and the kinetics of methanol synthesis are complex, may not be identical for different catalysts, and vary considerably with reaction conditions.

The reactions that result in the first C-H bond formation have been proposed to be

$$CO + H^{\ominus} \rightarrow \underset{\text{formyl}}{HCO^{\ominus}} \qquad [10]$$

$$CO + OH^{\ominus} \rightarrow \underset{\text{formate}}{HCOO^{\ominus}} \qquad [11]$$

$$CO_2 + H^{\ominus} \rightarrow \underset{\text{formate}}{HCOO^{\ominus}} \qquad [12]$$

Formyl may be formed directly from CO/H_2 or by hydrogenation of the formate. Both the formate and the formyl may be hydrogenated to methoxide

$$HCOO^{\ominus} + 2H_2 \rightarrow CH_3O^{\ominus} + H_2O \qquad [13]$$

which is then hydrogenated or hydrolyzed to form methanol. Formate and methoxide are readily detected under reaction conditions by IR spectroscopy (75-77), and formyl has been reported to form on co-adsorption of CO and H_2 over the Cu/ZnO catalysts (78). Initially, a hydroxycarbene route

$$CO + H_2 \rightarrow \underset{\text{hydroxycarbene}}{\underset{\updownarrow}{HCOH}} \qquad [14]$$

was postulated (81), but later it was pointed out that the catalyst would have to lower the 200-kJ/mol thermodynamic barrier of hydroxycarbene formation for this path to be effective (76).

With the help of labeled compounds, attempts have been made to resolve the proportion with which the different mechanisms operate. Takeuchi and Katzer (79) used a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ that produced $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$, but not $^{13}CH_3{}^{18}OH$ and $^{12}CH_3{}^{16}OH$, methanol over Rh/TiO_2 catalyst. This result favors the formyl path [8] and rules out the formate paths [11] and [12] for the Rh/TiO_2 catalyst under the conditions employed. However, the Cu/ZnO catalysts promote a rapid scrambling of $^{13}C^{16}O$ and $^{12}C^{18}O$ that is accelerated by preadsorbed water (80). This isotope flow is consistent with a reversible course of the formate mechanism [11]. To establish the kinetic role of water in methanol synthesis via route [11], Vedage et al. (80) injected D_2O into the CO/H_2 mixture to obtain methanol singly deuterated on the CH_3 group, $CH_2DO(H,D)$. Quantitative evaluation of the isotope flow led to the conclusion that reaction [11] accounted for at least 65 percent of the methanol synthesis from $CO/H_2 + H_2O$, again under the conditions employed in Reference 80.

Evidence for path [12] that utilizes CO_2 as the primary reactant has been obtained by hydrogenating $^{12}CO/^{14}CO_2$ and $^{14}CO/^{12}CO_2$ mixtures to methanol (81-83). For example, with $^{12}CO/^{14}CO_2$ mixtures, the ^{14}C label appeared in the product methanol for a large range of CO/CO_2 ratios, and a quantitative analysis of ^{14}C as a function of the flow rate of the reactants over the catalyst led to the conclusion that CO_2 hydrogenation is the exclusive primary path to methanol under the industrial conditions (temperature 250°C, pressure 40-50 atmospheres, and GHSV range of 10,000 - 120,000 $hour^{-1}$) that are utilized with the ICI $Cu/ZnO/Al_2O_3$ catalyst (86). In an earlier paper (84) the first step of CO_2 hydrogenation was proposed to be a formate-forming reaction between adsorbed CO_2 and hydrogen. Thus, based on the evidence utilizing the $^{13}C^{16}O$ + $^{12}C^{18}O$ mixtures, D_2O, and $^{14}CO_2/^{12}CO$ and $^{12}CO_2/^{14}CO$ mixtures as reactants, paths [10] - [12] are all feasible, but their dominance is dictated by the catalyst and the reaction conditions.

Reaction [11] is well known to occur under mild conditions even in aqueous solutions of alkali hydroxides (85). The details of this reaction have recently been investigated by reaction path calculations

(86,87) with the result that a facile nucleophilic attack of CO

$$HO^{\ominus} + CO \longrightarrow \underset{(I)}{\overset{\ominus}{\overline{H\text{-}O\text{-}C\text{-}O}}} \qquad [15]$$

is followed by an activated hydrogen transfer

$$\underset{(I)}{\overset{\ominus}{\overline{H\text{-}O\text{-}C\text{-}O}}} \longrightarrow \underset{(II)}{HCOO^{\ominus}} \qquad [16]$$

as represented in Figure 5-13, where T is the transition state. The stable structures of the metalloformate (I), formate (II), and the transition state (T) are shown in the figure.

The reaction [11] has been documented by Bogdan (87) using the Cu/ZnO and CsOH-doped Cu/ZnO catalysts. The IR spectrum of the formate formed from a surface hydroxyl and CO on the Cu/ZnO catalyst is shown in Figure 5-14a and that of formate on CsOH/Cu/ZnO catalyst in Figure 5-14b.

A formate specifically bonded to the Cs^+ ions is documented by the comparison of the spectrum in Figure 5-14b with reference spectra of HCOOCs. The facile formation of surface HCOOCs from CsOH and CO led Klier and coworkers to the probing of CsOH/Cu/ZnO and later HCOOCs/Cu/ZnO catalysts for methanol synthesis (71) and the WGS reaction (73). The promotion by Cs of the Cu/ZnO catalyst for methanol is shown in Figure 5-11.

As already mentioned, the promotion of the Cu/ZnO catalysts for methanol is ion specific as Cs>Rb>K>Na,Li (70), in the same order as the basic strength of the counterion of the surface alkali cation such as OH^-. The dependence of methanol activity on the concentration of the alkali surface dopant shown in Figure 5-11 has been explained as follows. The catalyst is bifunctional and contains a basic component (e.g., CsOH) that enhances activation of CO by reaction [11] and a hydrogenation component (Cu/ZnO) that activates hydrogen for the conversion $HCOO^- \rightarrow CH_3O^-$. The maximum methanol yield is obtained when the CO- and H_2-activating components are balanced. Although no calculations have been performed for the CO_2 hydrogenation path [12], it can be anticipated that this reaction will occur by a nucleophilic attack on the electropositive carbon of the (adsorbed) CO_2 molecule by a surface hydride with the

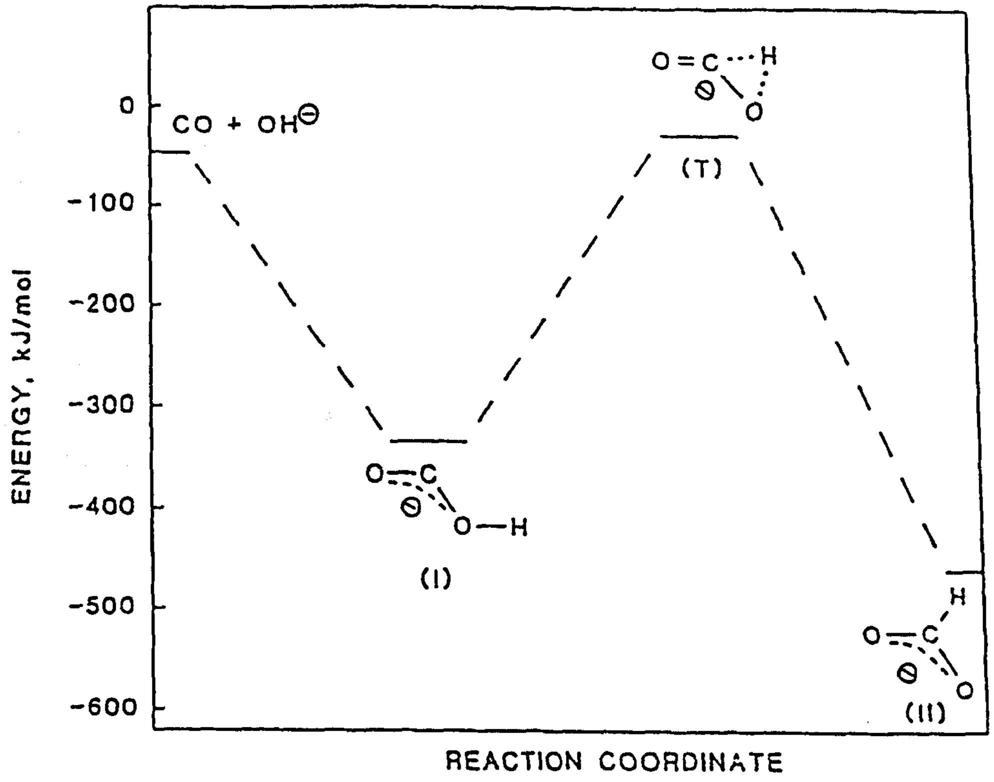
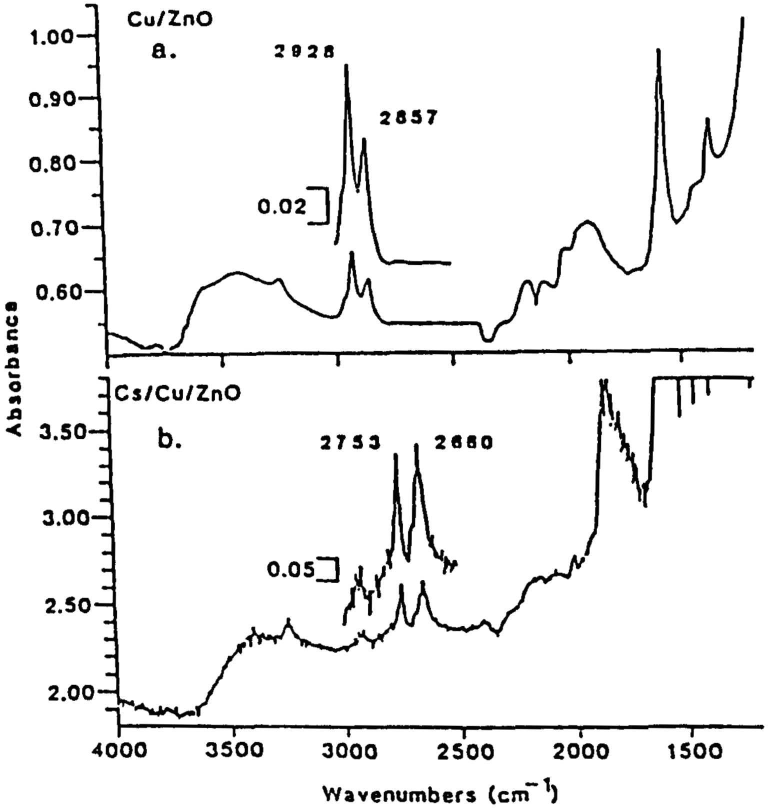


Figure 5-13. **MNDO Energy Diagram for Reaction of Carbon Monoxide with Hydroxide to Form Formate**



Infrared spectra of a) Cu/ZnO = 5/95 mol% and b) Cs/Cu/ZnO (50% surface coverage with cesium) obtained at 200°C and ambient pressure after carrying out methanol synthesis for 2 hr at 50 atm with H_2/CO = 0.50 synthesis gas.

Figure 5-14. Infrared Spectra

generation of surface formate $HCOO^-$. The hydride may also nucleophilically attack CO with the formation of surface formyl by surface reaction [10]. ICI researchers (88) have yet another picture in which the CO_2 molecule is adsorbed as $CO_2^{\ominus}$ and is attacked by "neutral" surface hydrogen atom to form the formate [17],

$$H_{(ads)} + CO_2^{\ominus} \rightarrow HCOO^{\ominus} \qquad [17]$$

The adsorbed hydrogen was presumed to be located on the metallic copper component of the $Cu/ZnO/Al_2O_3$ catalyst, although the same group recently reported, in the discussion at the 9th ICC, a large amount of hydrogen stored in the zinc oxide phase (89).

A pattern of base co-catalyzed CO hydrogenation, similar to that occurring over the copper-based catalysts, that gives a maximum methanol yield at an optimum alkali concentration was obtained with the alkali/MoS_2 catalysts as exemplified in Figure 5-21 in Section 5.3.2 on higher-alcohol synthesis. The catalyst requires a simultaneous presence of the alkali component and the MoS_2 component for developing alcohol synthesis activity. Consistent with the picture obtained for the Cs/Cu/ZnO catalysts, the Cs/MoS_2 catalyst appears to be a combination of a basic (CsOH) and a hydrogenation (MoS_2) component. The amount of the alkali component necessary to develop a maximum activity in MoS_2 is significantly larger than that in the Cs/Cu/ZnO catalyst because the alkali compounds agglomerate into approximately 20-nm particles which are in contact with the low-energy non-polar MoS_2 surface (90), while they are molecularly dispersed in a submonolayer on the polar Cu/ZnO surface (70).

A further example of a bifunctional base-hydrogenation catalyst for methanol that has recently been reported by Union Carbide (60) was presented in Section 5.3.1.3. This homogeneous catalyst consists of a Cu^+ compound and an alkali methoxide, and the hydrogenation component is believed to be the copper hydride CuH. The alkali methoxide may then serve as a base that activates CO by a nucleophilic attack [18] analogous to reaction [11] followed by hydrogenation of the metallocarboxylate III.

$$CH_3O^{\ominus}Na^{\oplus} + CO^- \rightarrow \underset{(III)}{CH_3OCO^{\ominus}Na^{\oplus}} \qquad [18]$$

The metallocarboxylate is then attacked by methanol to generate methyl formate and regenerate sodium methoxide [19].

$$CH_3OCO^{\ominus}Na^{\oplus} + CH_3OH \rightarrow CH_3O^{\ominus}Na^{\oplus} + HCOOCH_3 \qquad [19]$$

Methyl formate is then hydrogenated by the cuprous hydride [20].

$$HCOOCH_3 + 2H_2 \xrightarrow[CuH]{} 2CH_3OH \qquad [20]$$

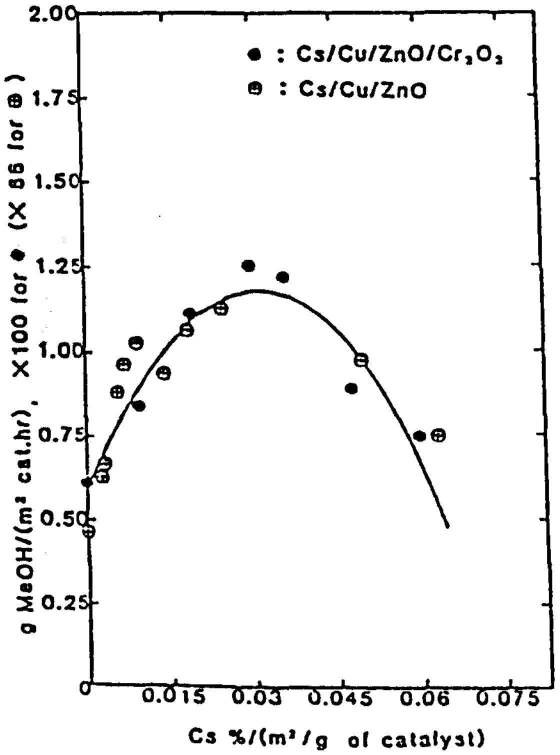
In summary, several new successful synthesis catalysts for methanol synthesis from CO and H_2 appear to be bifunctional, consisting of a basic component and a hydrogenation component. The $Cu/ZnO/Al_2O_3$ catalysts appear to hydrogenate CO_2 preferentially under industrial conditions. All three initial C-H forming reactions [10] - [12] have been found plausible for different catalysts and different sets of conditions. One major remaining task is to translate the mechanistic input into kinetic equations that describe the behavior of the synthesis reactions [1] - [3] in a wide range of conditions for each specific catalyst.

For a limited range of conditions and CO/H_2 synthesis gas only, methanol synthesis has been modeled as a function of surface Cs concentration for the Cs/Cu/ZnO and $Cs/Cu/ZnO/Cr_2O_3$ catalysts (<u>72</u>). The differential equation describing the cesium concentration dependence of the synthesis is

$$r_M = (k_1\theta_{Cs}\theta_{H2}(1-\theta_{Cs}) + k_0\theta_{CO}\theta_{H2}{}^n(1-\theta_{Cs}))(1-R/K_{eq})S \qquad [21]$$

The theoretical curves obtained by the best fit to the experimental methanol synthesis rates at 250°C and 75 atmospheres at $H_2/CO = 2.33/1$

Figure 5-15. **Correlation of Specific Methanol Activity as a Function of Normalized Cesium Surface Concentration**



Correlation of specific methanol activity as a function of normalized cesium surface concentration of Cs/Cu/ZnO (⊕) and Cs/Cu/ZnO/Cr_2O_3 (●) catalysts tested at 250°C and 75 atm with H_2/CO = 2.33 synthesis gas at GHSV = 6120 (unsupported) and 10,000 (Cr_2O_3-supported) ℓ(STP)/kg catal/hr.

are shown in Figure 5-15. The key term in Equation [21] proportional to $\theta_{Cs}(1-\theta_{Cs})$ reflects the bifunctionality of the synthesis, the rate of activation of CO being proportional to θ_{Cs} and that of hydrogen to the free Cu/ZnO surface through $(1-\theta_{Cs})$.

Both the methanol synthesis [1] and the side reactions occurring therein display chemical patterns that are indicative of the kinetic and mechanistic significance of an aldehydic C_1 intermediate. This intermediate may be formed directly as formyl by Reaction [10] but where the formate routes [11] and [12] are more efficient as on the $Cu/ZnO/M_2O_3$ catalysts, by a subsequent reduction

$$HCOO^{\ominus} + H_2 \rightarrow H_2O + HCO^{\ominus} \qquad [22]$$

or

$$HCOO^{\ominus} + {}^{1}/2\ H_2 \rightarrow \underset{\text{dioxymethylene}}{H_2COO^{\ominus}} \qquad [23]$$

Formyl $HCO^{\ominus}$ has been represented in Reactions [10] and [22]. Other forms of an aldehydic intermediate that have been proposed include-bonded formaldehyde, its isomer hydroxycarbene, and dioxymethylene which, if bonded to surface cation(s), is an anion of hydrated formaldehyde $H_2C(OH)_2$. IR spectra in the 2700-3000 cm^{-1} region have been interpreted (91) as vibrational transitions of the CH_2 group of dioxymethylene or adsorbed formaldehyde, but the evidence for hydroxycarbene is lacking.

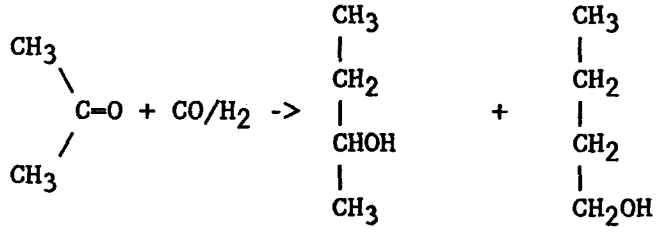
A number of chemical trapping reactions provide support for the aldehydic C_1 intermediate. Vedage et al. (92) utilized the reaction

$$R_1R_2NH + CO/H_2 \rightarrow R_1R_2NCH_3 + H_2O \qquad [24]$$

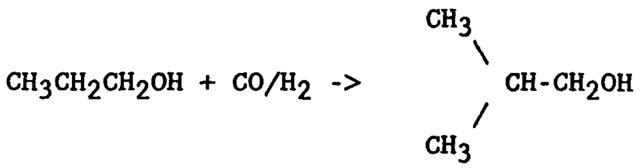
in which the CH_3 group of the product amine $R_1R_2NCH_3$ was synthesized via R_1R_2NH amine-C_1 aldehyde coupling. Deluzarche et al. (93) used methyl iodide to trap formyl with the result

$$CH_3I + CO/H_2 \rightarrow CH_3CHO\ (+\ I^{\ominus}_{ads}) \qquad [25]$$

and Young et al. (72) used various alcohols and ketones, e.g.,



$$(CH_3)_2C{=}O + CO/H_2 \rightarrow CH_3CH_2CHOHCH_3 + CH_3CH_2CH_2CH_2OH \qquad [26]$$



$$CH_3CH_2CH_2OH + CO/H_2 \rightarrow (CH_3)_2CH\text{-}CH_2OH \qquad [27]$$

to demonstrate that the addition of the C_1 intermediate formed from CO/H_2 occurred preferentially in the β position of the C_n alcohol of ketone. Such a reaction is typical of aldol condensation followed by hydrogenation, with some specific features regarding oxygen retention that are discussed in detail in Section 5.3.2.2. The high rates with which all of these reactions occur over the copper-based catalysts under synthesis conditions indicate that the C_1 aldehydic intermediate is a kinetically and mechanistically important reactive species.

As the side products are formed, particularly under the higher-alcohol synthesis conditions, higher aldehydes and ketones become important as chain building blocks, giving rise to a regular synthesis pattern of aldehyde coupling reactions that are reflected in the characteristic higher oxygenate product composition. The chemistry of these C_2+ syntheses is described in Section 5.3.2.

5.3.1.5 Research Trends

Research trends in methanol synthesis appear to be motivated by the desire to

- understand the function of the existing highly active and selective low-pressure methanol synthesis catalysts,

- understand the mechanisms of CO and CO_2 hydrogenation to methanol over a variety of catalysts based on copper, Group VIII metals, sulfides, and their combination with alkali compounds,
- develop a highly selective and stable homogeneous catalyst for methanol,
- develop reliable and reproducible methods for catalyst preparation based on detailed understanding of the solid state and surface chemistry of heterogeneous catalysts, and solution chemistry of homogeneous catalysts, and
- develop a high degree of control of the water gas shift reaction and its reverse as it occurs simultaneously with methanol synthesis from $H_2/CO/CO_2/(H_2O)$ SG.

Specific items that appear of interest are the following:

- Determine the active state of copper in heterogeneous and homogeneous copper-based catalysts and methods for optimizing its concentration (valence doping $Zn_2^{II} \rightarrow Cu^{I}Cr^{III}$, $Cu^{I}H$, Cu intermetallics).
- Further develop promising homogeneous catalysts for methanol, and invent novel ones.
- Develop active and selective heterogeneous catalysts for methanol based on alkali containing hydrogenation catalysts that are free of copper. An example of such catalysts that are not yet selective enough for methanol but show a good total oxygenate synthesis activity is the alkali/MoS_2 catalysts described in Section 5.3.2.2.
- Determine the long-term performance of the promising alkali/Cu/ZnO/Cr_2O_3 catalysts under methanol synthesis conditions and in the presence of CO_2.
- Determine the state of and resistance to various impurities, such as iron and nickel carbonyls and S-, Cl-, H_2O-, and CO_2-containing gases, in all heterogeneous and homogeneous catalysts that show promise for industrial applications.

5.3.2 Higher Alcohols

5.3.2.1 Introduction and Historic Notes

Mixtures of methanol with higher alcohols (mainly C_2-C_6) can be used pure or as an additive to gasoline as transportation fuels (94-100). In the United States, however, the Clean Air Act prohibits selling new unleaded fuels, or fuel additives in unleaded fuels, unless specifically waived by EPA. Four EPA waivers were granted between 1979 and 1985, and a new waiver for the Lurgi OCTAMIX alcohol product is reported to have been granted in February 1988 (101). The EPA waivers granted for methanol/higher alcohol blends are summarized in Table 5-4. An alcohol blend acceptable under the DuPont waiver is listed in Table 5-5.

In addition, the use of 10 percent ethanol in gasoline is covered by a 1978 waiver and MTBE (methyl tertiary-butyl ether) by a 1979 waiver based on a request by ARCO to allow MTBE and TBA (tertiary-butyl alcohol). The DuPont and Lurgi waivers allow a wider range of alcohols than ethanol, TBA, and the ethers MTBE and TAME (tertiary-amyl methyl ether), and cover alcohol mixtures that can be directly synthesized from synthesis gas (SG). However, certain EPA restrictions, particularly the volatility specifications (evaporative index, EI), have imposed economic penalties on alcohol blends and have impeded their acceptance by refiners and blenders. It is not known at this time whether the February 1988 Lurgi waiver relaxes the EI specifications.

The technical advantages of using the alcohol (C_1-C_6) blends with gasoline are the following:

- improvement of octane number to fill the gap left by banning the use of lead-containing antiknock agents,
- improved hydrocarbon solubility compared to pure methanol-gasoline blends,
- improved water tolerance compared to pure methanol-gasoline blends,

Table 5-4. EPA Waivers Granted For Methanol/Cosolvent Alcohol Blends

Applicant	Blend	Date Granted
SUN	MeOH/TBA (0-5.5%)	6/14/79
(Anafuel Unlimited) American Methyl	"Petrocoal" Up to 12% MeOH Up to 6% C_4OH's Max. 15% MeOH Proprietary Corrosion Inhibitor	9/28/81
ARCO	"Oxinol" 4.8% MeOH 4.8% TBA 3.5% Max. O_2	11/7/81
DuPont	Up to 5% MeOH 3.7% Max. O_2 Must Meet Evaporative Index	1/14/85
Lurgi	"Octamix" Blending Specifications and Evaporative Index Requirements not yet Published by EPA	2/1/88

Table 5-5. Acceptable Methanol/Cosolvent Alcohol Blend Under the DuPont Waiver

	2 parts Methanol	+	1 part Cosolvent Alcohol	=	2:1 Methanol/ Cosolvent Alcohol Blend	
Composition, Wt. %						
Methanol	100%		0-5.0		68.33 Max	
C_2-C_4 OH			90.0 Min		30.00 Min	
C_{5+} OH			0-5.0		1.67	
Ketones			0-2.0		0.67 }	1.67 Max
Esters			0-2.0		0.67 }	
Ethers			0-2.0		0.67 }	
Aldehydes			0-2.0		0.67 }	

- o improved driveability, and
- o good control of volatility.

Fuels containing higher-alcohol blends have been in use in West Germany (ca. 3-5 mol percent) for automobile transportation.

Other potential uses of higher alcohols include: fuel for combined cycle peak electric power generation, manufacture of olefins (ethylene from ethanol, propene from propanol, iso-butene from isobutanol), substitution for propane in LPG applications, alkylation and solubilization of coal, and transportation medium for coal in slurry pipelines.

As pointed out above, higher alcohols can be produced directly from SG by catalytic processes. The early processes for higher-alcohol synthesis (HAS) were practiced in Germany. BASF reported as early as 1913 cobalt- or osmium-catalyzed synthesis of a mixture of alcohols, aldehydes, ketones, acids, and other oxygenated compounds as well as hydrocarbons at 10-20 MPa and 300-400°C. In 1923-24 the Fischer-Tropsch "Synthol" process for alcohol mixtures was developed. Later, higher alcohols were found to be coproducts of methanol synthesis over ZnO/Cr_2O_3 catalysts (BASF, 1920's), alkalized ZnO/Cr_2O_3 catalysts (Natta, 1928), and alkalized copper-based catalysts (Natta, 1958). Toward the end of World War II, I.G. Farben and Ruhrchemie in Germany developed the "Synol" process that was based on low-temperature (<200°C) medium-pressure (20 atm) Fischer-Tropsch synthesis utilizing iron catalysts. The process incorporated several reactor stages with intermediate CO_2 removal and gas recycle (<u>100</u>). In 1984 the Dow Corporation announced a new process for higher alcohols based on alkalized MoS_2 catalysts (<u>103</u>) and Union Carbide filed patent applications the same year (<u>104</u>).

5.3.2.2 <u>Present Technology</u>

Currently, a large number of plants for alcohols other than methanol or for methanol/higher-alcohol mixtures are completed, under construction, engineered or planned, with a total annual capacity of over 2.6 billion kg (37). Some of these plants entail processes for fermentation ethanol, and others for specialty alcohols such as the plasticizer and solvent 2-ethylhexanol. But the overall build-up of large capacities for fuel alcohols by catalyzed processes is evident.

This section focuses on HAS from coal-derived SG, i.e., on indirect liquefaction of coal to C_1-C_4 alcohols. The technology for HAS has been demonstrated on both bench- and pilot-plant scale, and a large plant with the capacity of 15,000 tons/yr was operated for six years. The processes are based on (1) modified high-pressure methanol technology utilizing alkalized zinc oxide-chromia catalysts, (2) combined methanol-Fischer-Tropsch technology utilizing copper-cobalt-oxide catalysts, (3) modified low-pressure methanol catalytic technology utilizing alkalized copper oxide catalysts, and (4) the Dow-Union Carbide technology utilizing alkalized molybdenum sulfide catalysts.

Recently proven processes for HAS from SG that have been demonstrated either on industrial scale, on pilot-plant scale, or by extensive experimentation on bench scale are reviewed here in some detail, and they include (1) the SEHT (MAS) process, (2) the IFP (Substifuel) process, (3) the Dow HAS process, (4) the Lurgi OCTAMIX process, and (5) the Lehigh University (LU) HAS process. The basic operating characteristics for these five HAS processes are summarized in Table 5-6. For this table the entries for the MAS, IFP and OCTAMIX processes were taken from Reference 101 and cited literature, those for the Dow HAS process from patent literature and Lehigh University's DOE reports, and those for the LU HAS process from Reference 105.

A. The SEHT (MAS) Process

The technology for higher alcohols based on alkali-promoted ZnO/Cr_2O_3 methanol synthesis catalysts that had been used since the1920's for the high-pressure methanol synthesis was further developed by Snamprogetti, Enichem, and Haldor Topsoe A/S (SEHT) and used the acronym MAS from the Italian for "Metanolo piu Alcoli Superiori" (methanol plus

Table 5-6. Comparative Operating Characteristics for Various Alcohol Processes

Process Main Characteristics	1	2	3 MoS_2-based HAS				4	5	
	SEHT (MAS) Process	IFP (Substifuel) Process	Dow HAS Process	UCC HAS	LU HAS	Dow HAS	Lurgi OCTAMIX Process	LU[a] HAS Process	LU[a] HAS
Main Constituents of Catalyst	K/Zn/Cr	K/Cu/Co/Al	$K/Co/MoS_2$	Cs/MoS_2	Cs/MoS_2	K/MoS_2	Alkali/Cu/Zn/Cr Promoters	Cs/Cu/ZnO	$Cs/Cu/ZnO/Cr_2O_3$
Catalyst Stability (life), h	8,000	-2,000	>8,000	n.a.	>200	n.a.	8,000	>1,200[b]	>750[b]
Operating Temperature, °C	350-420	260-320	306	300	295	255	285-300	300	300
Operating Pressure, MPa	10-18	6-10	10.3	2.75	8.2	10.3	6-9	9.1	9.1
Syngas Space Velocity, 1000 h^{-1}	3.0-8.0	3.0-6.0	3.8	12.0	7.8	3.2	3.0-6.0	3.265	3.255
Syngas Feed H_2/CO Ratio	2-3	1-2	1[c]	1	0.96	1.02[c]	0.5-1.0	0.7	0.7
Syngas CO_2 Content, vol.%	1.0-6.0	2.5-3.5	0.0	0.0	0.0	0.0	1.0	0.0	0.0
Performance Characteristics									
Thermal Efficiency, %	56	-	-	-	-	-	60	-	-
CO Conversion Per Pass[d], %	14	12-15	16	4.8	9.1	12.3	13-30	22	25.5
Liquid Product Selectivity, %	90	70-75	88	80	77	85	95	>96	>96
C_2^+OH Selectivity, %	20-30	25-50	51.6	32.8	37.3	32.2	20-30	31.3	36.5
Alcohol Space Time Yield, kg/ℓ cat/hr[e] or kg/kg cat/hr[f]	0.21[e]	0.1-0.15[e]	0.23-0.30[f]	0.256[f]	0.32[f]	0.19-0.32[f]	0.46[e]	0.373[f]	0.46[f]

[a] Lehigh University
[b] Deactivation data in text and in reference 114.
[c] Contained 50 ppm H_2S
[d] CO conversion exclusive of CO_2
[e] STY in kg oxygenate product per hour per ℓ catalyst
[f] STY in kg oxygenate product per hour per kg catalyst

higher alcohols). The SEHT MAS process built on the expertise of Snamprogetti in catalysis of SG reactions; Haldor Topse's expertise in the development of new processes and catalysts, and manufacture of industrial catalysts; and Enichem's know-how in product evaluation gained through marketing of oxygenated compounds.

After catalyst and process development and preliminary economic evaluation, the SEHT group decided to forgo building a pilot plant and instead opted for an industrial prototype plant. This plan was accomplished by modifying a high-pressure methanol plant, closed in 1963, at Pisticci in Southern Italy. The Pisticci plant was operated at 15,000 tons per year of MAS between August 1982 and 1987 (101) but is now closed. The plant consists of three sections -- a unit for the preparation of SG starting from natural gas, a synthesis unit for the production of crude MAS, and a distillation unit. The flow diagram of the MAS process is shown in Figure 5-16. The MAS process operates at 9-18 MPa, 330-430°C, and gas hourly space velocity (GHSV) of 3000-15,000 with H_2/CO ratios of 0.5-3. The catalyst, principally $K/ZnO/Cr_2O_3$, is covered by Italian (106) and U.S. (107) patents. A life test up to 8000 hours has shown good performance and no deactivation for 6000 hours (108), although the initial activity of the catalyst in the plant was some 40 percent lower than the initial activity in the laboratory. Operating characteristics are listed in Table 5-6, Column 1.

The typical composition and properties of MAS are given in Table 5-7. The crude MAS product contains some 20 percent water because it is operated at high temperatures and a significant portion of CO_2 that iseither the product, a reactant, or a recycled gas is converted to water by the reverse water gas shift reaction. Although the MAS process could be operated to obtain ratios of methanol to higher alcohols from 60/40 to 80/20, the target choice 70/30 has been considered a good compromise between economic factors and performance. The main advantages of the MAS product for gasoline blending were considered to be as follows (108):

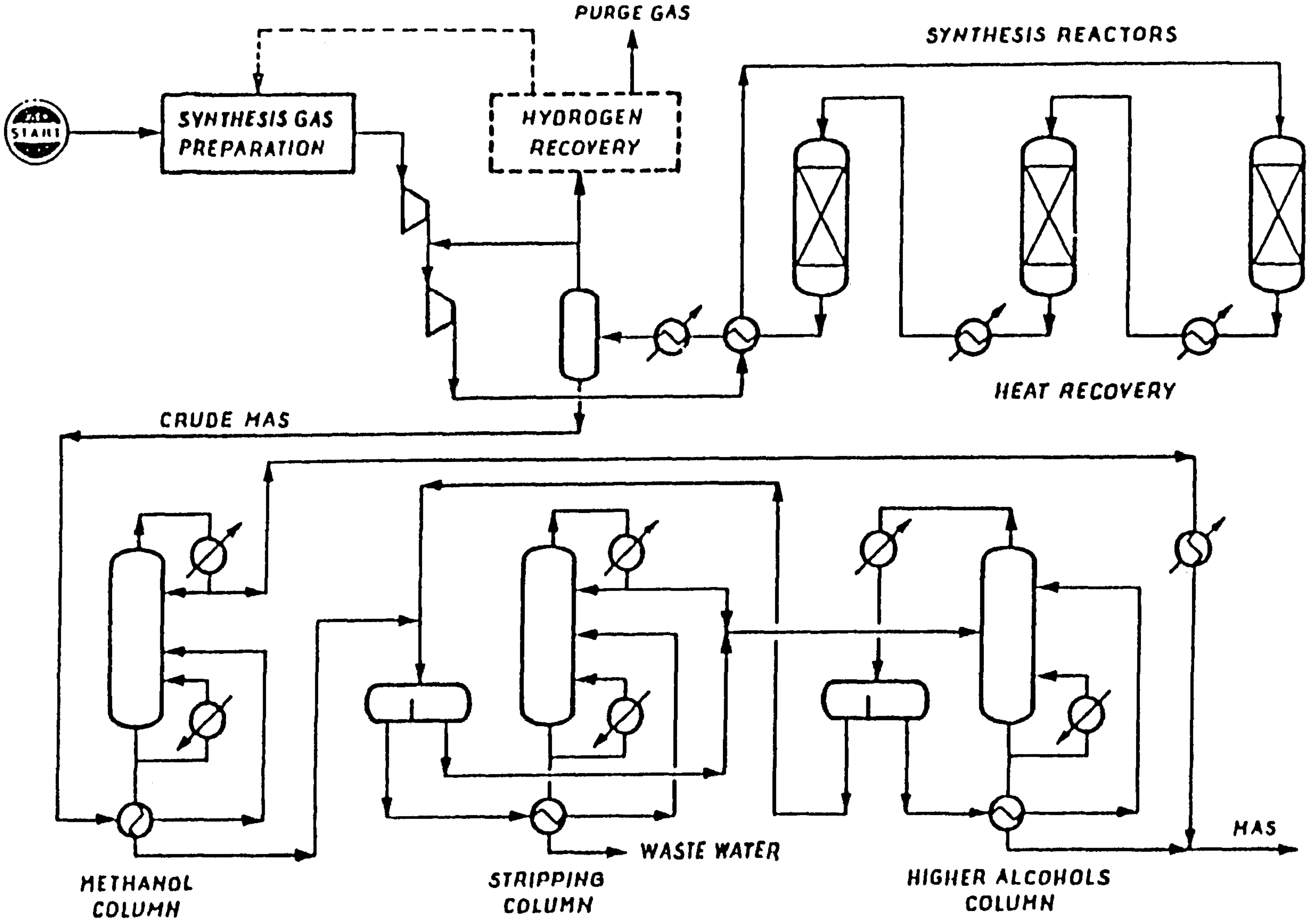


Figure 5-16. Flow Diagram of MAS Process

Table 5-7. Typical Composition and Properties of MAS

Typical Composition	Weight Percent Min	Weight Percent Max
Alcohol C_1	68.0	72.0
Alcohol C_2	2.0	3.0
Alcohols C_3	3.0	5.0
Alcohols C_4	10.0	15.0
Alcohols C_5+	7.0	12.0
Ketones and Aldehydes		2.0
Esters		0.1
Acidity (as acetic acid)		0.007
Water		0.1
Ash		0.001
Copper		0.1 ppm
Appearance Clear and free of suspended matter		

Typical Properties		
Density at 20 °C	kg/l	0.804
R.V.P	bar	0.230
Evap. at 70-100-150 °C	% vol.	61-85-95
Lower Heat Value	kcal/kg	5870
Oxygen content	wt. %	41
Octane "blending"		
- research method		120-135
- motor method		93-106
- $\frac{\text{research + motor}}{2}$		106-121

- Low tendency to phase separation in the presence of water,
- a strong reduction of volatilitiy due to methanol addition,
- high octane blending characteristics,
- good fuel properties,
- reduction of exhaust emissions,
- good compatibility with the materials normally employed in the automobile fuel system,
- excellent driveability,
- no influence on fuel consumption.

MAS-gasoline blends containing 5 percent MAS were distributed in one hundred AGIP PETROLI and IP filling stations under the name "SUPER E".

B. <u>The IFP (Substifuel) Process</u>

The IFP (Institut Francais du Petrol) higher-alcohol synthesis technology utilizes alkalized copper-cobalt-oxide catalysts covered by IFP patents (<u>109</u>-<u>112</u>). In the case of (alkalized) ternary Cu-Co-Cr-oxides, the diagram in Figure 5-17 shows which compositions of these catalysts promote methanol synthesis, hydrocarbon synthesis and higher alcohol synthesis. The copper-chromia component being a methanol synthesis catalyst and the cobalt component a Fischer-Tropsch hydrocarbon synthesis catalyst, the IFP Cu-Co-Cr oxide catalyst can be viewed as a combination of C_1 oxygenate and C_n ($n = 1$) hydrocarbon-forming functions. This is reflected in the proposed mechanism discussed in Section 5.3.2.5.

A demonstration plant with capacity of 7000 bbl/yr (670 tons/yr) utilizing the IFP Substifuel technology and process design has been built by Idemitsu Kosan at its research facilities in Chiba, Japan. The first demonstration was carried out from December 1984 to March 1985 under the Japanese government-sponsored RAPAD (Research Association for Petroleum Alternative Development), and a report on this operation was presented in 1986 (<u>114</u>). The source of syngas was natural gas. The block diagram of the IFP/Idemitsu Kosan process is shown in Figure 5-18.

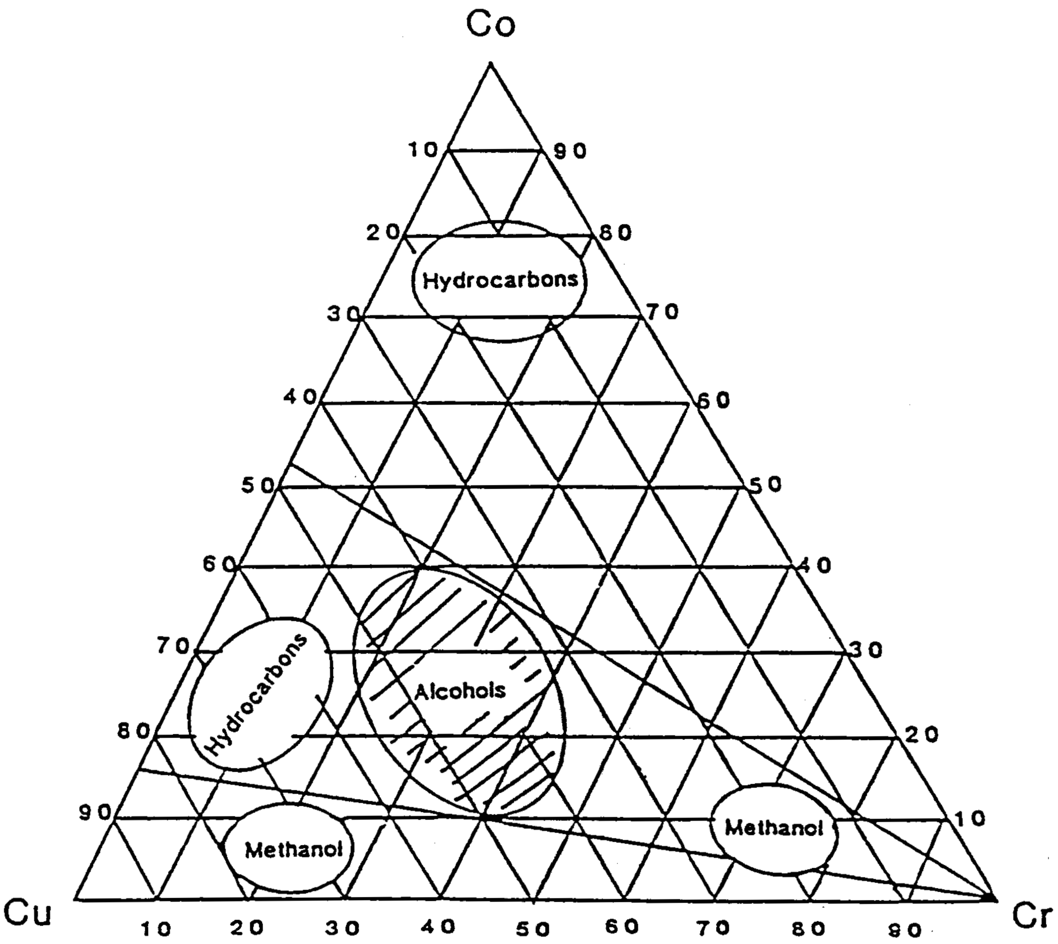
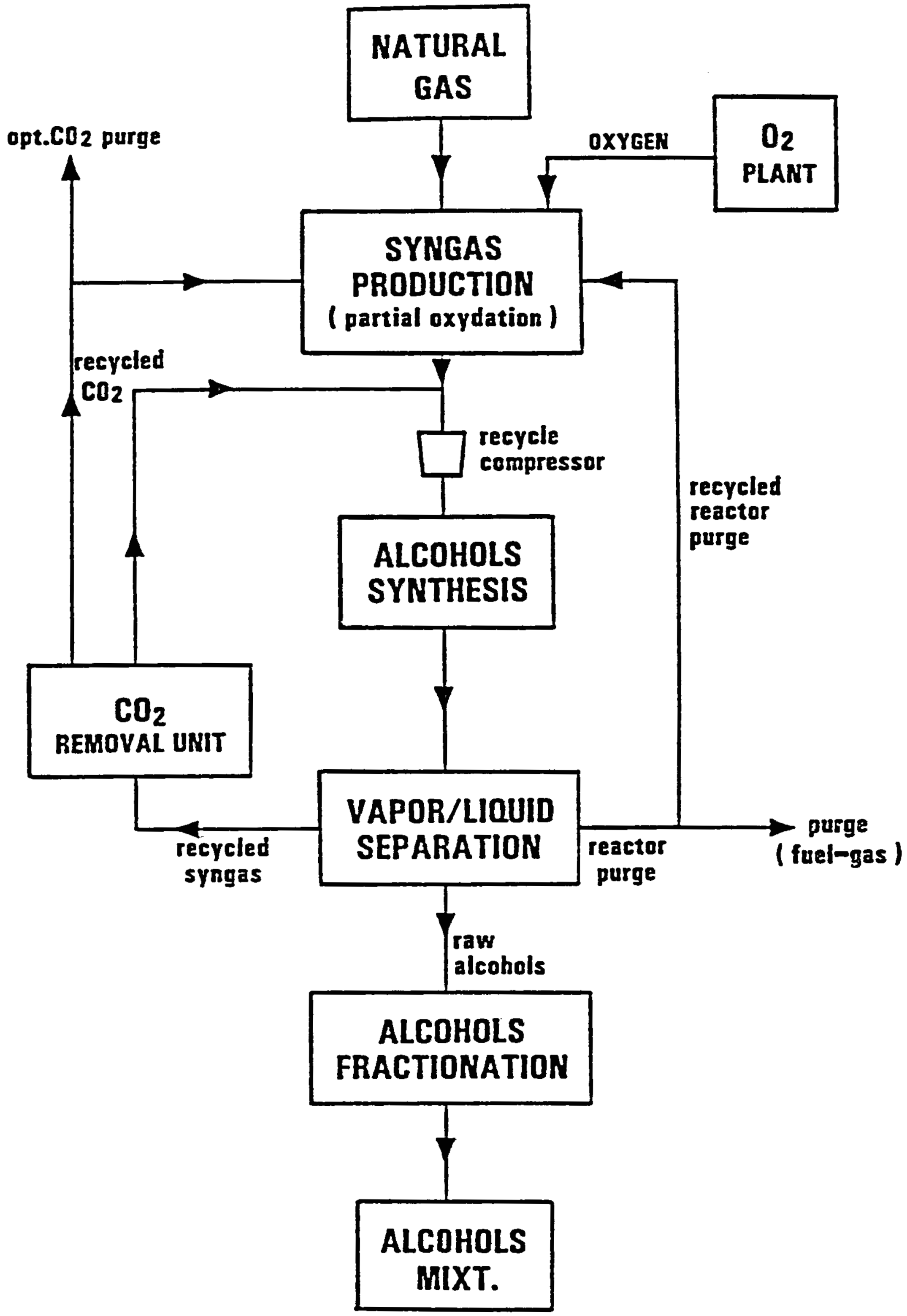


Figure 5-17. Influence of Composition on the Selectivity of IFP-1 Catalysts

Figure 5-18. Block Diagram of the Integrated Natural Gas to Alcohols Complex



In this process the separation section serves to remove water from the crude alcohol product (2.5-5 weight percent) to less than 0.2 percent, and includes azeotropic distillation with water entrainment. The reactor section is shown in Figure 5-19. Two reactors equipped with multiquenched bed systems to achieve good heat transfer are used in series with intermediate cooling, yielding high CO conversion after CO_2 removal and recycle.

The IFP process operates at 6-10 MPa, 260-320°C, and GHSV 3000-6000 with H_2/CO ratios of 1.0-2.0. Catalyst life has been reported suffering from deactivation caused by coke deposition, separation of Co from the originally homogeneously distributed Co and Cu phases, loss of cobalt as carbonyl, and formation of surface carbides (113). The performance and the composition of four IFP catalysts are presented in Table 5-8. It is presumed that the IFP/Idemitsu Kosan plant uses the second-generation IFP catalyst (catalyst 2 in Table 5-8). Some of the data in this table are at variation with those for the IFP process in Table 5-6, Column 2, which are documented in the MITRE report (101), partly based on an IFP report (114). The typical composition of the IFP fractionated higher-alcohol product is listed in Table 5-9, and their octane blending values in Table 5-10.

The gasoline compatibility of the IFP/Idemitsu Kosan alcohol product was found comparable to that of the methanol/TBA mixtures that are the ARCO gasoline additives. Provided that most of the butane is removed from the gasoline pool before blending, the alcohol-gasoline blends can be used as high-octane lead-free gasoline during summer time in many countries (114). An extensive evaluation program with a series of tests on a fleet of cars under the RAPAD program has been announced (114). Economic analysis of the IFP/Idemitsu Kosan process has also been performed, and the production cost of the alcohol product is represented in Figure 5-20.

Figure 5-19. Reactor Section of IFP/Idemitsu Kosan Process

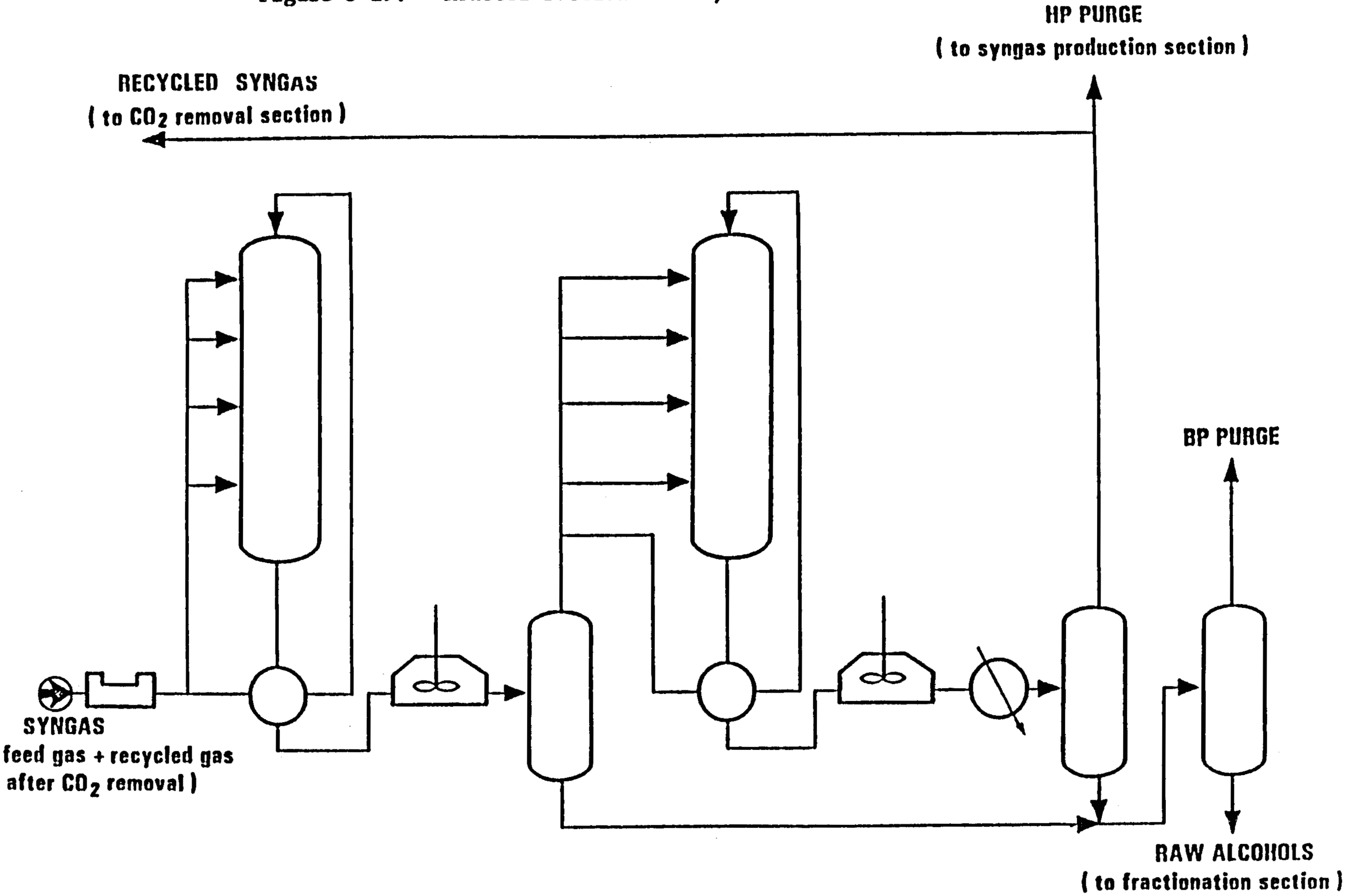


Table 5-8. Performance and Composition of IFP Catalysts

Cat.	Composition Atomic ratio	MeOH%	C_2+OH%	S_a[A]	Yield(C_1-C_4OH)[B]
1[C]	$CuCoM_{0.8}A_{0.09}$ M = Cr, Fe, V, or Mn A = alkali U.S. Pat. 4122110	20-26	74-80	90-95	0.27-(1.29)0.92
2[C]	$CuCo(M_1+M_2)_{0.8}A_{0.09-0.1}M_3$ M_1 = Cr, Mn, Fe, or V M_2 = rare earth M_3 = noble metals (0.005-0.5 wt%) A = alkali U.S. Pat. 4291126	20-24	76-80	ca. 95	0.27-0.40
3[D]	Cu/Co/Al/A/(M_1)(M_2)(M_3)(Zn)(Cr) M_1 = Mn, V, Fe, Re M_2 = Sc, Yb, Th, Zr, or rare earth M_3 = noble metals (0.02-0.8 wt%) A = alkali G.B. Pat. 2118061	28-61	39-72	62-70	0.11-0.15
4	Cu/Co/Zn(B)/Al(C)/A/(M) A = alkali or alkaline-earth B = Cd or Mn^{2+} C = Cr, Mn^{3+}, or Ti M = group VIII metals (Rh, Ru, Pd, Os, Ir, or Pt) G.B. Pat. 2158730	-----	20-77[E]	50-77[E]	0.06-0.09[E]

[A] S_a is the selectivity towards all alcohols.
[B] The yield is in g (ROH) hr^{-1} $gcat^{-1}$.
[C] The stability is unknown.
[D] The longest time was 8000 hr.
[E] Data after 1000 hr on stream.

Table 5-9. Composition of Fractionated Alcohols from Demonstration Unit

Composition of Fractionated Product
(fractionated C_1 - C_6 alcohols)

	Wt %		
Methanol	63.5	C_2	69.5
C_2+ Alcohols	35.8	C_3	17
Alcohols	99.3	C_4	6.5
C_5+ Hydrocarbons	0.2	C_5	3
Esters	0.3	C_6	4
Other Oxygenates	0.2		100
	100.0 (water content 0.16%)		

Table 5-10. Motor-Fuel Properties of Fractionated Alcohols from Demonstration Unit

Typical blending values*
of fractionated C_1 - C_6 alcohols

Alcohols	C_1	C_2	fract. C_1 - C_6 alcohols	nC_3	iC_3	nC_4	tC_4	nC_6
R.O.N								
add. 5% Vol.	134	135	120.8	117	122	94	108	56
add. 10% Vol.	132	132	120.8	118	120	96	110	56
M.O.N.								
add. 5% vol.	98	100	97.4	92	96	80	94	41
add. 10% vol.	100	104	98.4	90	96	78	93	46

* Fractionated C_1 - C_6 alcohols: T.O.B.V. with D gasoline sample.
Individual alcohols: Hinkamp, J., Oil and Gas Journal, 1983.

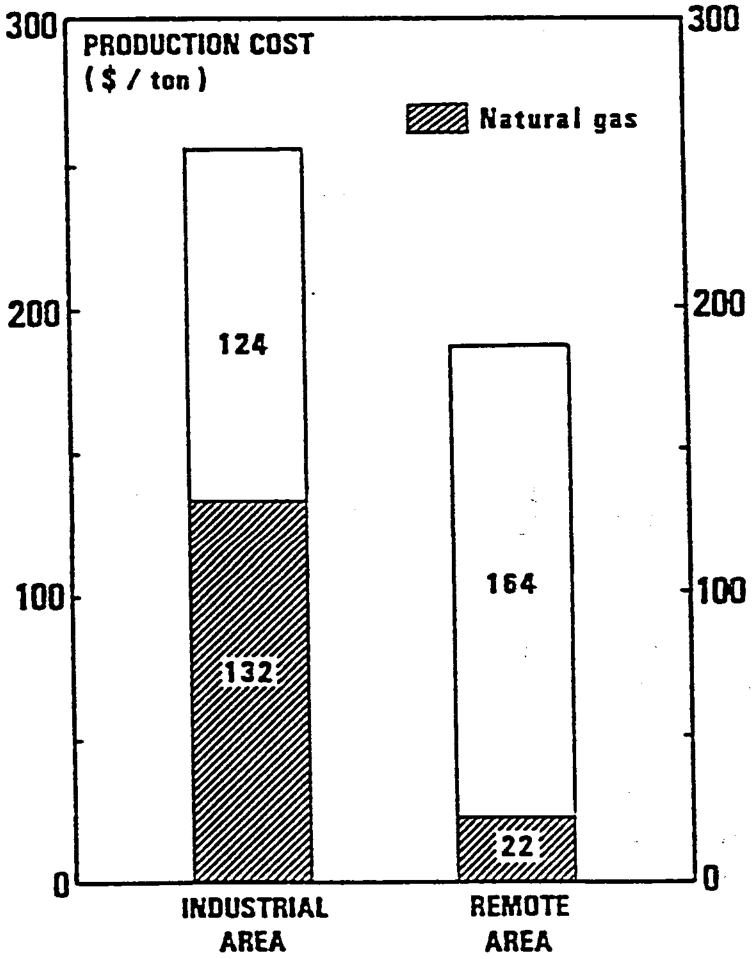


Figure 5-20. Breakdown of Production Cost of C_1-C_6 Alcohols

C. The Dow HAS Process

The Dow technology utilizes alkali/MoS_2 and alkali/Co/MoS_2 catalysts to steer the synthesis to C_1-C_4 alcohols with methanol/ethanol mixtures in various proportions being the dominant product. The process was announced in 1984 (103) after the Dow 0.2-0.225 tons/day (equivalent to 82 tons/yr if continuously operated) pilot plant in Midland, Michigan, operated since 1979 for Fischer-Tropsch synthesis of hydrocarbons was switched to alcohol production in 1982. The Dow alcohol synthesis pilot plant project was concluded in 1984. Patents covering alkali/MoS_2 catalysts were filed by the Dow (103) and Union Carbide (104) Corporations, and additional work was performed at Lehigh University that not only verified the Dow patents, but added specific information on the efficiency of different alkali promoters, catalyst preparation and improvements, and the mechanism of chain growth (90, 115). Research into the alkali/TX_2 catalysts (T, transition metal; X, chalcogenide) for alcohols continues under DOE sponsorship at Union Carbide Corporation (UCC) (116) and Lehigh University (117).

The Dow/UCC process has been demonstrated to operate at 7-20 MPa, 280-310°C, and GHSV 5000-7000 with H_2/CO ratios of 0.9-1.2 with space time yields of 170-400 g alcohol product per kg catalyst per hour. For typical operating characteristics and yields, see Table 5-6. A year-long life test at Dow revealed an extraordinary stability. The catalyst is highly tolerant to sulfur in the feed gas unlike any of the copper-based or Fischer-Tropsch catalysts. A very marked promotion effect of H_2S on increased ethanol yields via methanol homologation over the alkali/MoS_2 (but not alkali/Co/MoS_2) catalysts has been reported (118). The alkali components promote the highest rates of alcohol synthesis at an optimum concentration, as exemplified in Figure 5-21.

Because of the very short chain length n for the C_n ($n \geq 2$) alcohols, the alcohol product can be recycled to the extinction of methanol (103,118), and C_2+ alcohol fuel rich in ethanol can be obtained. It is probable that the Dow process utilizing coal-derived synthesis gas can economically compete with fermentation ethanol, although the

Figure 5-21a. Effect of Cs Content of the MoS_2 Catalysts on the Product Yield

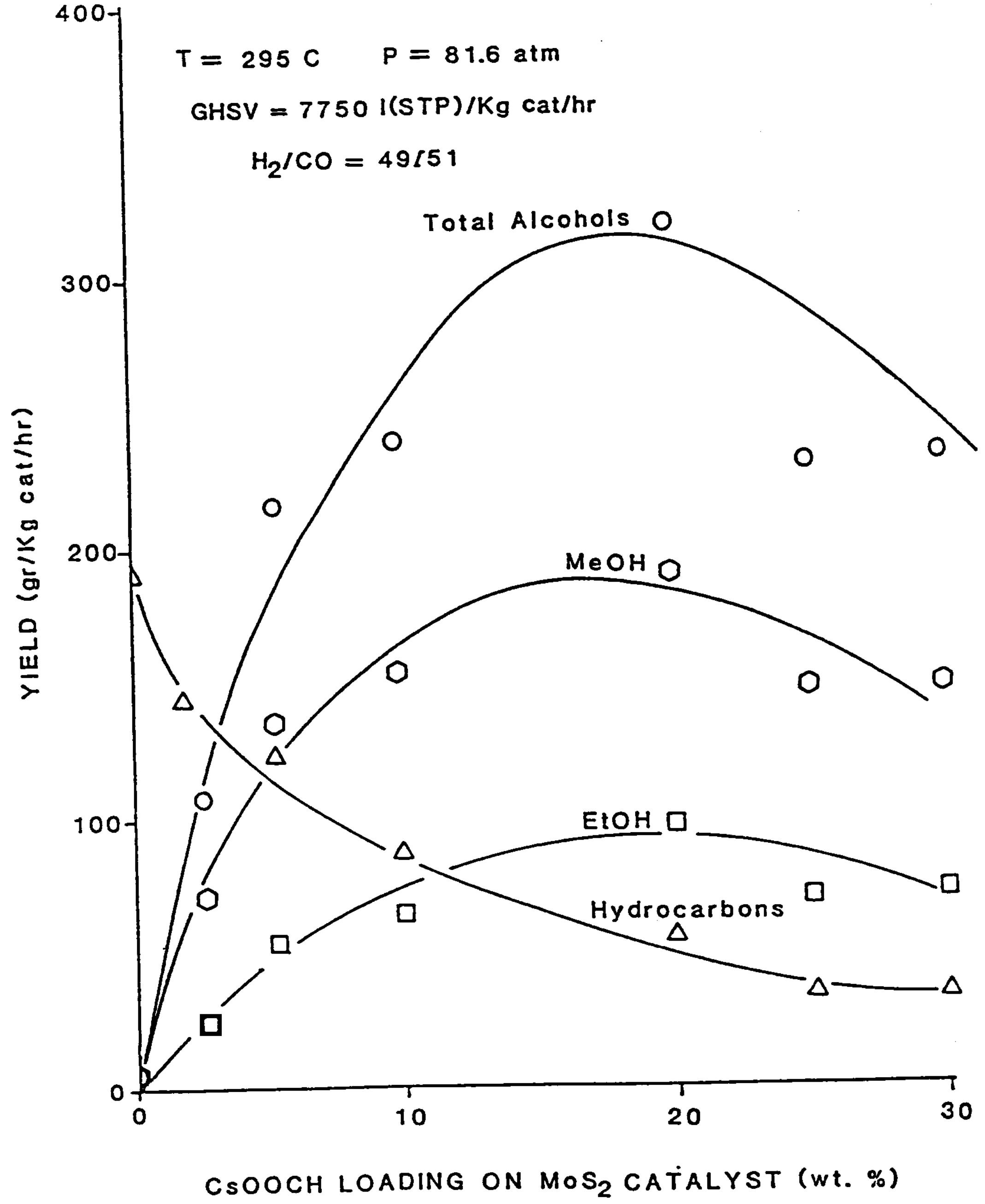
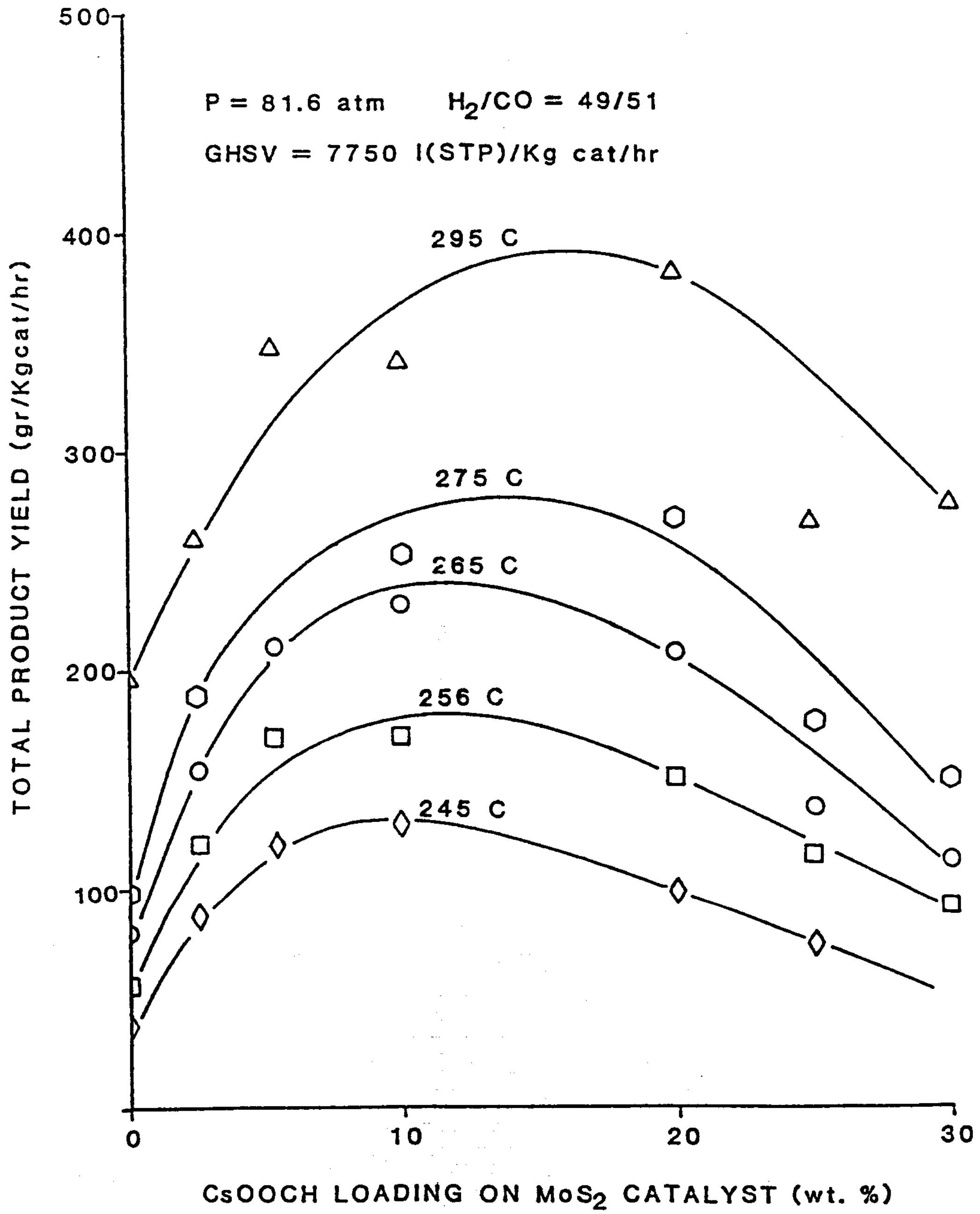


Figure 5-21b. Effect of Cs Content of the MoS_2 Catalysts on the Total Product Yield as a Function of Temperature



side-product hydrocarbon makes still appears too high (cf. Table 5-6, Column 4).

D. The Lurgi OCTAMIX Process

In contrast to the SEHT (MAS) Process that utilizes alkali-modified high-pressure methanol synthesis catalysts, the Lurgi OCTAMIX Process utilizes copper-based low-pressure methanol synthesis catalysts. The Lurgi catalysts are engineered (1) to reach a long service life of the copper catalyst under the higher-alcohol synthesis conditions that are more severe (higher temperatures, lower H_2/CO ratios) than methanol synthesis conditions, (2) to adjust the water gas equilibrium in such a way that the water which inevitably occurs in higher-alcohol synthesis is used up for the conversion of CO to CO_2 and hydrogen, and (3) to achieve satisfactory space time yield for the higher-alcohol mix (119).

The flow sheet for the Lurgi process is shown in Figure 5-22. The OCTAMIX process operates at 6-9 MPa, 285-300°C, and GHSV 3000-6000 with H_2/CO ratios of 0.5-1 and 1 percent CO_2. The catalyst stability over 8000 hours has been reported (101) based on the operation of a 3,650-tons/year pilot plant in Frankfurt, Germany. A 73,000-tons/year plant is planned adjacent to a refinery, possibly also combined with ammonia synthesis. Operating characteristics and space time yields are listed in Table 5-6 Column 4, and the typical composition of the OCTAMIX fuel in Table 5-11.

The properties of OCTAMIX as gasoline blends were established for three types of gasolines of different origins -- a cat cracker type, a reformate gasoline, and a mix containing a significant portion of petrochemical products. The density and the blending density of OCTAMIX are presented in Table 5-12, showing that the density of the gasoline plus oxygenate fuel mix is only about 0.5-0.7 percent higher than of the gasoline above. The boiling behavior and the Reid vapor pressure of OCTAMIX are superior to those of methanol/gasoline mixtures, and are comparable with those of the methanol/TBA blend (OXINOL), a property that is also applicable to the SEHT (MAS) product. The tolerance of various

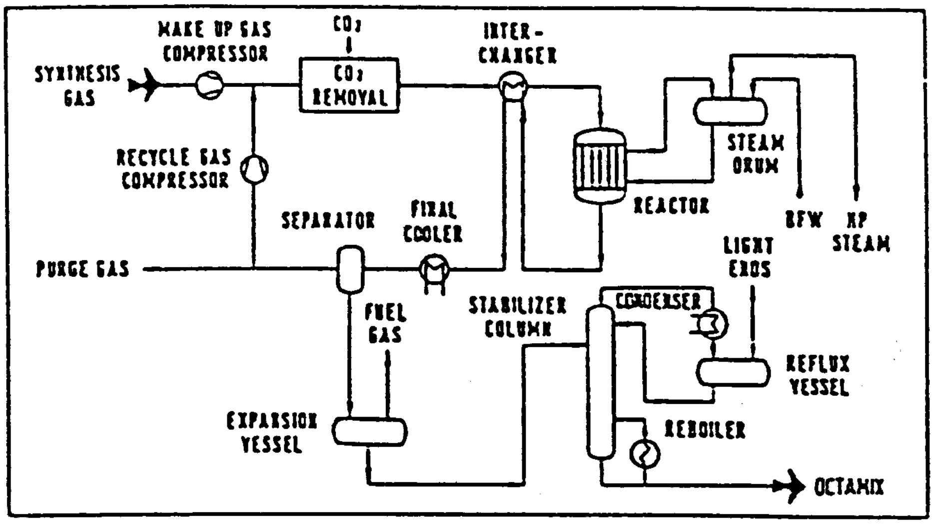


Figure 5-22. Flowsheet for the OCTAMIX Synthesis

Table 5-11. OCTAMIX Compositions

Compositions in Wt %

	OCTAMIX 40A			OCTAMIX 40B			OCTAMIX 50		
	Total	Alcohols	Esters Ketones	Total	Alcohols	Esters Ketones	Total	Alcohols	Esters Ketones
C_1 - Oxygenate	59.7	59.7	-	59.6	59.6	-	49.8	49.8	-
C_2 - Oxygenate	7.4	7.4	-	15.1	15.1	-	9.3	9.3	-
C_3 - Oxygenate	3.7	3.7	-	6.0	6.0	-	4.7	4.7	-
C_4 - Oxygenate	8.3	8.2	0.1	6.6	6.6	-	10.3	10.2	0.1
C_5 - Oxygenate	5.1	3.6	1.5	3.8	3.2	0.6	6.4	4.5	1.9
C_6 - Oxygenate	7.7	3.3	4.4	4.1	2.8	1.3	9.6	4.1	5.5
C_7 - Oxygenate	4.9	3.0	1.9	3.1	1.8	1.3	6.1	3.7	2.4
C_8 - Oxygenate	2.8	0.5	2.3	1.2	0.3	0.9	3.4	0.6	2.8
Hydrocarbons	0.1	-	-	0.1	-	-	0.1	-	-
Water	0.3	-	-	0.4	-	-	0.3	-	-
	100.0	89.4	10.2	100.0	95.4	4.1	100.0	86.9	12.7
H_2/CO Syngas		1.0			1.0			0.95	
P reaction, bar		70.0			70.0			100.0	
T reaction, °C		270.0			270.0			275.0	
Recycle C_1+ Light Ends		-			0.3			-	

Table 5-12. Blending Densities of OCTAMIX

Density at 15°C

	Pure Component	Blending Density
OCTAMIX 40 A	0.8078	0.8253
OCTAMIX 40 B	0.8055	0.8242
METHANOL 60% HA 40%	0.793	0.8087

gasoline/alcohol blends to water was investigated, with the result that the high-olefin gasolines such as the cat cracker gasoline are much less tolerant to water than the reformate type with its low olefin and high aromatics content. The materials compatibility of the OCTAMIX/gasoline blends poses no problem, as at least in Europe it has been common practice for some years to use methanol-resistant plastics in all new cars (119).

E. The Lehigh University HAS

Lehigh University (LU) engaged in higher-alcohol synthesis (HAS) on copper-based catalysts since 1982 (105-120). Although research has not been done on a pilot-plant scale, the data obtained are believed to be directly applicable for scale-up. The selection of the alkali component of the copper-based low-pressure methanol catalysts has been addressed systematically. The catalysts have been optimized, and activity and selectivity tests conducted in a wide range of conditions. An engineering model based on mechanistic input has been developed, and long-term tests performed in which the deactivation of the catalysts by carbonyls, the retention of the alkali component, and the physical changes have been established for continuous periods of operation up to 1250 hours.

The tubular stainless steel reactor of 1.9 cm diameter was provided with an outer brass sleeve to minimize longitudinal exotherms. Both the reactor and the inlet SG lines were alternatively equipped with a variety of purification devices and materials such as guard beds, charcoal traps, zeolite traps, copper lining, brass fittings, and aluminum containers. The engineering model was developed for both the differential and integral operation of the reactor, which can be viewed as an element of the Lurgi multi-tubular reactor. In the mechanistic studies that provided the basis for the engineering model, additional liquids--primarily methanol and other alcohols -- were injected into the SG at variable rates by a liquid metering pump. The schematic of this experimental system is shown in Figure 5-23.

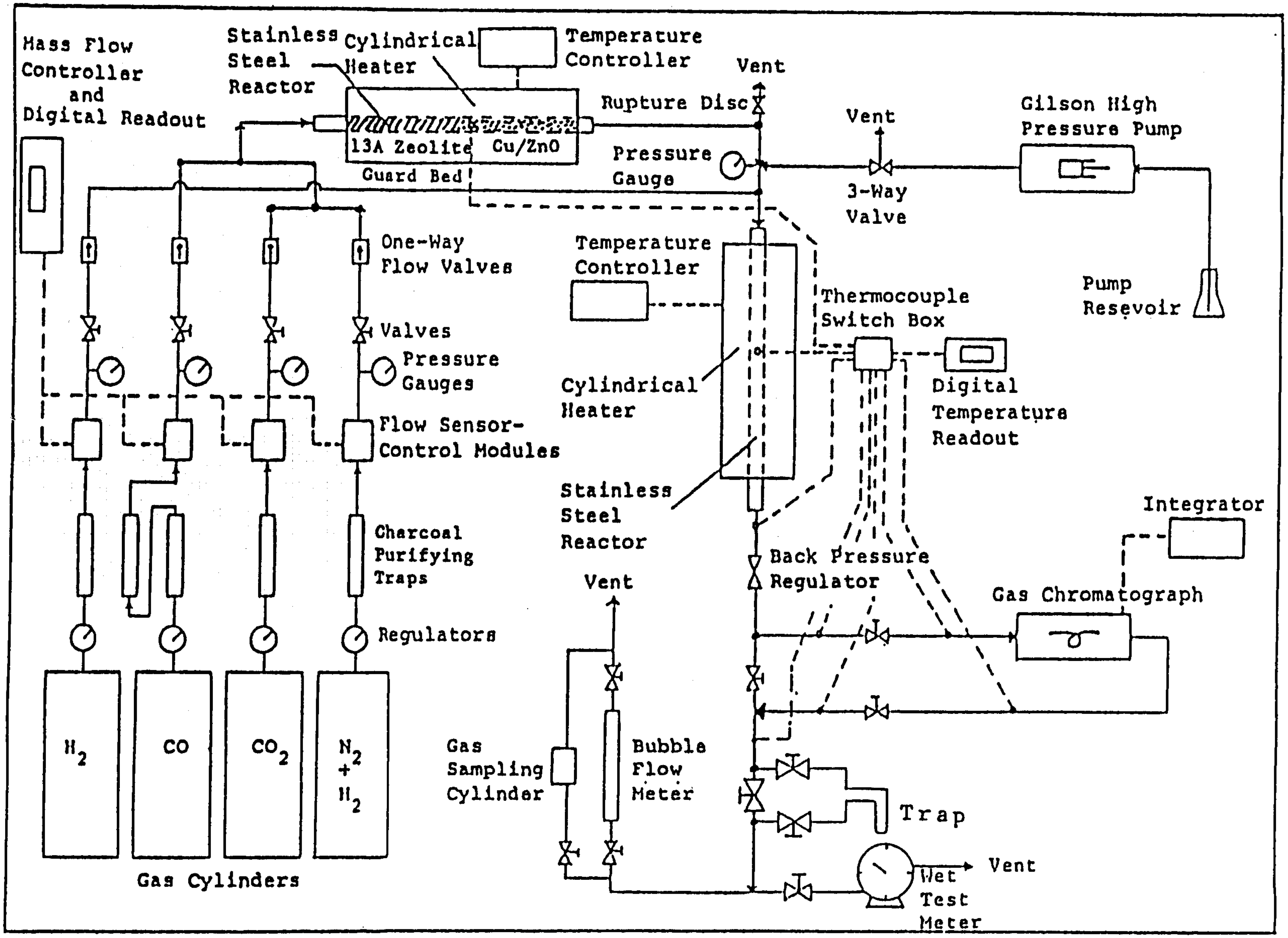


Figure 5-23. Schematic of the Catalytic Testing System

The heavy alkali-doped copper-based catalysts are also excellent water gas shift catalysts (73), and the LU HAS system produced a low water content similarly as the Lurgi OCTAMIX process. The LU HAS was run at 7.6-9.1 MPa, 260-325°C, and GHSV 3000-10,000 with H_2/CO ratios of 0.45-0.7. The synthesis gas contained no CO_2 in the feed, but CO_2 was a product of HAS. The operating characteristics and the space time yields are listed in Table 5-6, Column 5. A more detailed account of initial activities and selectivities for various Cs/Cu/ZnO, Cs/Cu/ZnO/Al_2O_3, and Cs/Cu/ZnO/Cr_2O_3 catalysts is given in Table 5-13. The effect of the different cesium promoter loading of the binary Cu/ZnO catalyst on the selectivity for higher (C_2+) oxygenate synthesis shown in Table 5-15 demonstrates that (1) the alkali dopant enhances both the total yield and particularly dramatically the selectivity to C_2+ oxygenates, and (2) there is an optimum concentration of the alkali promoter (0.34 percent Cs for the binary Cu/ZnO catalyst) for the maximum yield of alcohols and maximum selectivity for C_2+ oxygenates.

It is also apparent from Table 5-14 that among the supported Cs/Cu/ZnO/M_2O_3 (M = Al, Cr) the Al_2O_3-supported catalyst gives high yield of alcohols but poor selectivity to C_2+ oxygenates. The Cr_2O_3-supported catalyst gives both high yields and high selectivities for C_2+ oxygenates. Therefore, Cr_2O_3 is a support of choice, at least with the class of hydrotalcite-based precursors employed in the LU work. Under the methanol synthesis conditions (250°C, 7.6 MPa, H_2/CO = 2.33, GHSV = 10,000), the 3-percent Cs/Cu/ZnO/Cr_2O_3 catalyst gave a space time yield of 1.05 kg of methanol/kg catalyst/hour with 98 percent selectivity, the only side products being ethanol (1.3 percent) and methyl formate (0.6 percent) (105). These are the highest STY's and selectivities reported for methanol synthesis from CO_2-free synthesis gas.

A kinetic model was developed for the LU HAS based on the chain growth mechanism described in Section 5.3.2.6. The chain growth reactions are schematically shown in Figure 5-24 where 1, b_1, and a_o are kinetic constants for linear growth (1) and beta-addition (b_1), $C_n + C_1$

Table 5-13. Operating Characteristics for Cs-doped Copper-Based Catalytic Processes Obtained at Lehigh University

Syngas Content of CO_2 was zero. Initial Activities.

Main Characteristics			LU HAS	Catalyst No.		
Main Constituents of Catalyst	Cu/ZnO	0.34 percent Cs/Cu/ZnO	2.5% Cs/Cu/ZnO/ Al_2O_3	0.4% Cs/Cu/ZnO	0.25% Cs/Cu/ZnO	3% Cs/Cu/ZnO/ Cr_2O_3
Operating Temperature, °C	310	310	310	300	300	300
Operating Pressure, MPa	7.6	7.6	7.6	9.1	9.1	9.1
Syngas Space Velocity, 1000 h^{-1}						
Syngas Feed (H_2/CO) Ratio	0.45/1	0.45/1	0.45/1	0.7/1	0.7/1	0.7/1
Performance Characteristics						
Thermal Efficiency, %	~60	~60	~60	~60	~60	~60
CO Conversion Per Pass, %						
Liquid Product Selectivity, %	94.7	97.4	97.0	~96.0	n.a.	n.a.
(C_2+OH) Selectivity, %	30	58	5.6	26-27	25-30	~35
Alcohol Productivity, kg/kg cat/h	0.314	0.440	0.542	0.373-0.436	0.439	0.458

A detailed typical composition of the LU HAS product is given in Table 5-14.

Table 5-14. Comparison of Product Compositions

Comparison of the product compositions obtained from H_2/CO - 0.45 synthesis gas at 310°C, 7.6 MPa, and GHSV - 3260 1(STP)/kg cat/hr over binary Cu/ZnO and 0.34 mol% Cs/Cu/ZnO catalysts.

Product Type	Product	Yield, g/kg cat/hr Undoped Cu/Zno	 0.34 mol% Cs/Cu/ZnO
Hydrocarbons Water & CO_2	Methane	3.4	7.6
	Ethane	11.3	4.7
	Propane	2.1	1.1
	Water	1.3	1.7
	CO_2	367.0	403.0
Linear Primary and Secondary Alcohols	Methanol	204.0	157.0
	Ethanol	22.6	17.0
	1-Propanol	10.1	38.1
	1-Butanol	3.4	8.2
	2-Butanol	0.7	1.8
	1-Pentanol	0.9	4.7
	2-Pentanol & 3-Pentanol	0.8	3.0
	1-Hexanol	2.0	5.5
Branched Primary and Secondary Alcohols	2-Methyl-1-Propanol	20.7	48.6
	2-Methyl-1-Butanol	8.6	15.5
	3-Methyl-2-Butanol	1.7	1.7
	2-Methyl-1-Pentanol	5.1	12.4
	2-Methyl-3-Pentanol	2.0	4.1
Aldehydes	Propanol	-	1.6
	2-Methylpropanol	0.7	1.9
Ketones	2-Butanone	0.7	2.1
	3-Pentanone	-	2.3
	2-Methyl-3-Pentanone	3.0	5.4
Methyl Esters	Methyl Formate	3.6	2.4
	Methyl Acetate	10.5	9.9
	Methyl Propanoate	4.6	14.0
	Methyl Butanoate	1.0	2.7
	Methyl Isobutanoate	4.1	13.7
	Methyl Pentanoate	1.2	1.6
	Propyl Acetate	2.0	1.4

Table 5-15. Effect of Cesium Loading of Catalyst on Selectivity

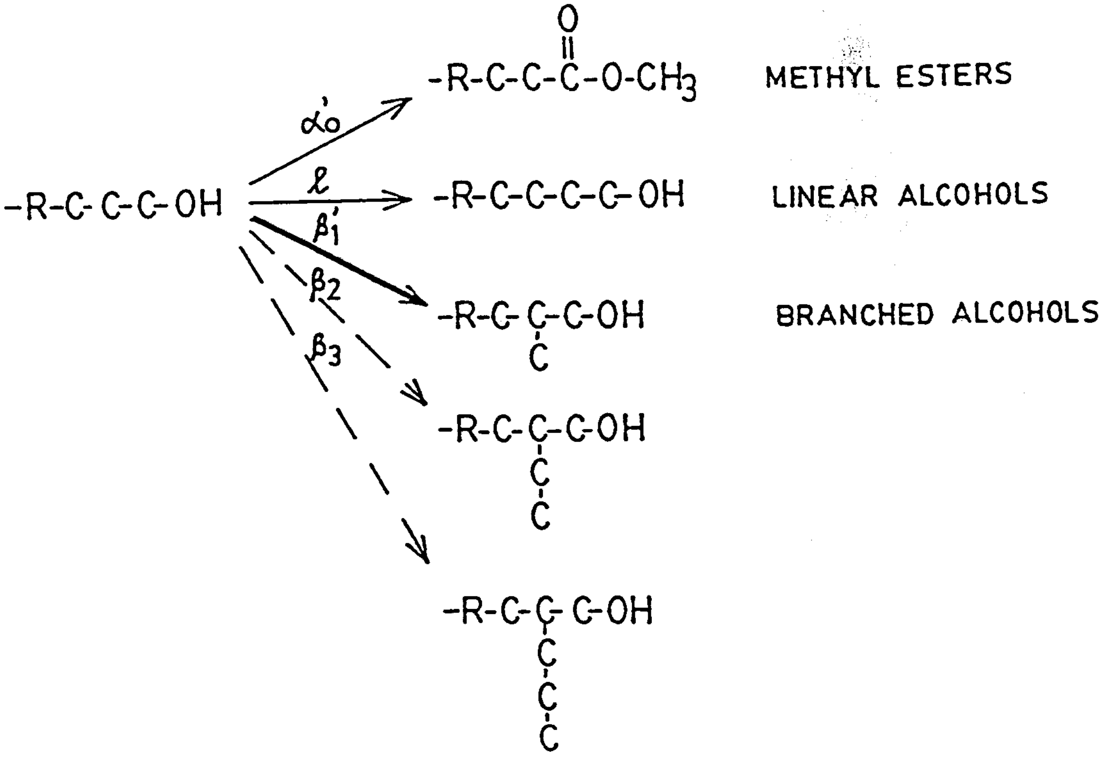
Effect of Cesium Loading of the Binary Cu/ZnO catalyst on the Selectivity (S) for Higher-Oxygenate Synthesis, where S is defined as

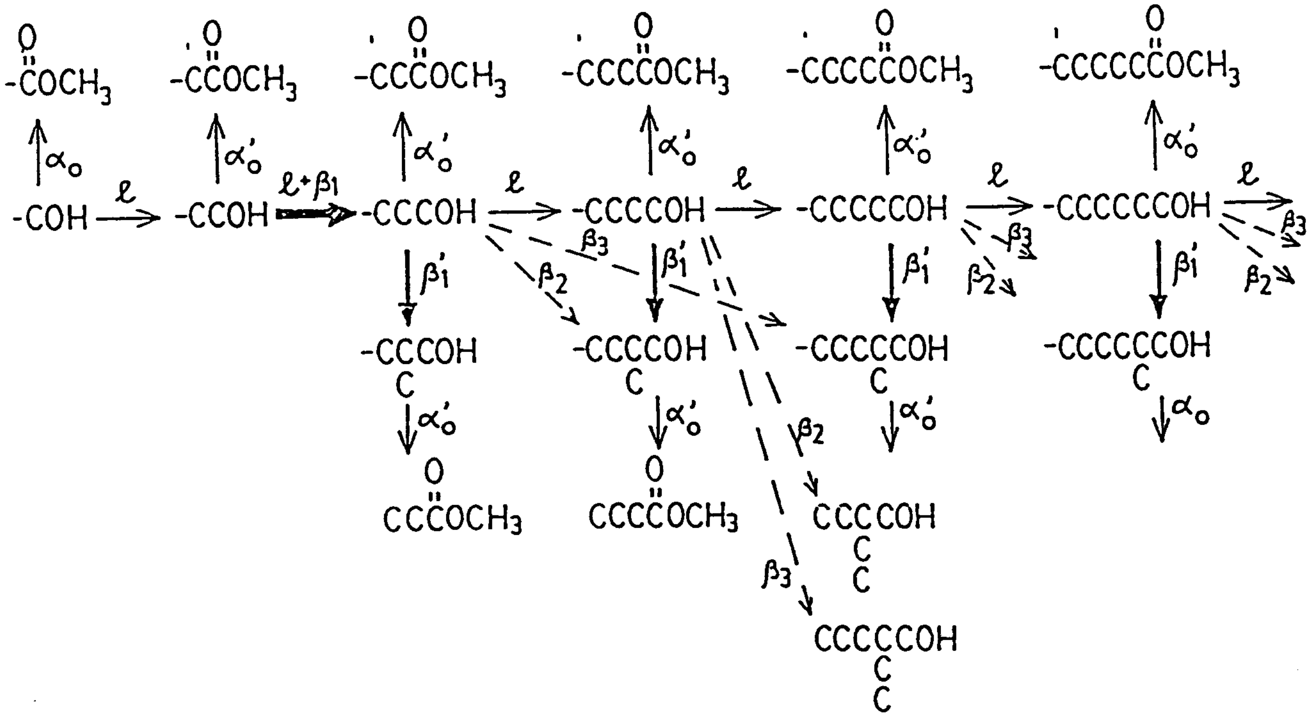
$$\frac{>C_1 \text{ Oxygenates}}{\text{Methanol} + (>C_1 \text{ Oxygenates})} \times 100$$

in wt%.

Catalyst	Product Yield, g/kg cat/hr		S, Wt.%
	Methanol	$>C_1$ Oxygenates	
Undoped Cu/ZnO	204	110	35.0
0.25 mol% Cs/Cu/ZnO	181	165	47.7
0.34 mol% Cs/Cu/ZnO	157	220	58.4
0.43 mol% Cs/Cu/ZnO	162	137	45.8
1.5 mol% Cs/Cu/ZnO	213	42.8	16.7

Figure 5-24. Chain Growth Reactions





-> C_n+1 and a_o that for methyl ester formation from C_n chains; b_n are kinetic constants for minor paths in which a C_m (m = 2,3) intermediate is added to a C_n ($n \geq 2$) growing chain. The model for the integral reactor is schematically represented in Figure 5-25 where k stands for the set of kinetic parameters 1, b_1, etc., and C_j/C_1 are the ratios of the concentration of products of chain length j to that of methanol. An example comparing the observed and predicted product yields with an optimized set of the parameters k for one set of HAS conditions is shown in Figure 5-26. An overall correlation of calculated and observed HAS product yields over the Cs/Cu/ZnO and Cs/Cu/ZnO/Cr_2O_3 catalysts with variable Cs concentrations is shown in Figure 5-27, demonstrating that the model is successful for large numbers of catalysts.

The catalyst life data were also reported for the LU HAS (105). All the Cu-based catalysts rapidly deactivated in stainless steel units, primarily due to iron carbonyl poisoning. However, deactivation rates as low as 1.8 percent/100 hours in terms of loss of CO conversion activity were achieved in copper-lined reactors, pipes and fittings utilizing a well-purified SG under the severe HAS conditions of 300°C, 9.1 MPa, and $H_2/CO/CO_2$ = 0.7/1.0/0.0. There was a larger loss of selectivity to C_2+ alcohols (but not to total alcohols) during the life tests, most of which could still be traced to residual iron deposits that give rise to the growth of hydrocarbon residues on the catalyst surface. A minor deactivation was due to physical deactivation of the catalyst by sintering. The alkali promoter, Cs, was not lost or redistributed in the reactor bed in tests up to 1250 hours.

Comparison of the LU HAS product (Table 5-14) with the Lurgi OCTAMIX product (Table 5-11) shows a similar composition in that methanol and 2-methyl-1-propanol (iso-butanol) are the dominant alcohols. It is therefore expected that the February 1988 EPA waiver will apply equally to the (refined) LU HAS and the OCTAMIX blends, and the characteristics of these two products will be similar. The differences between LU HAS and the Lurgi OCTAMIX processes are in the catalyst formulation and

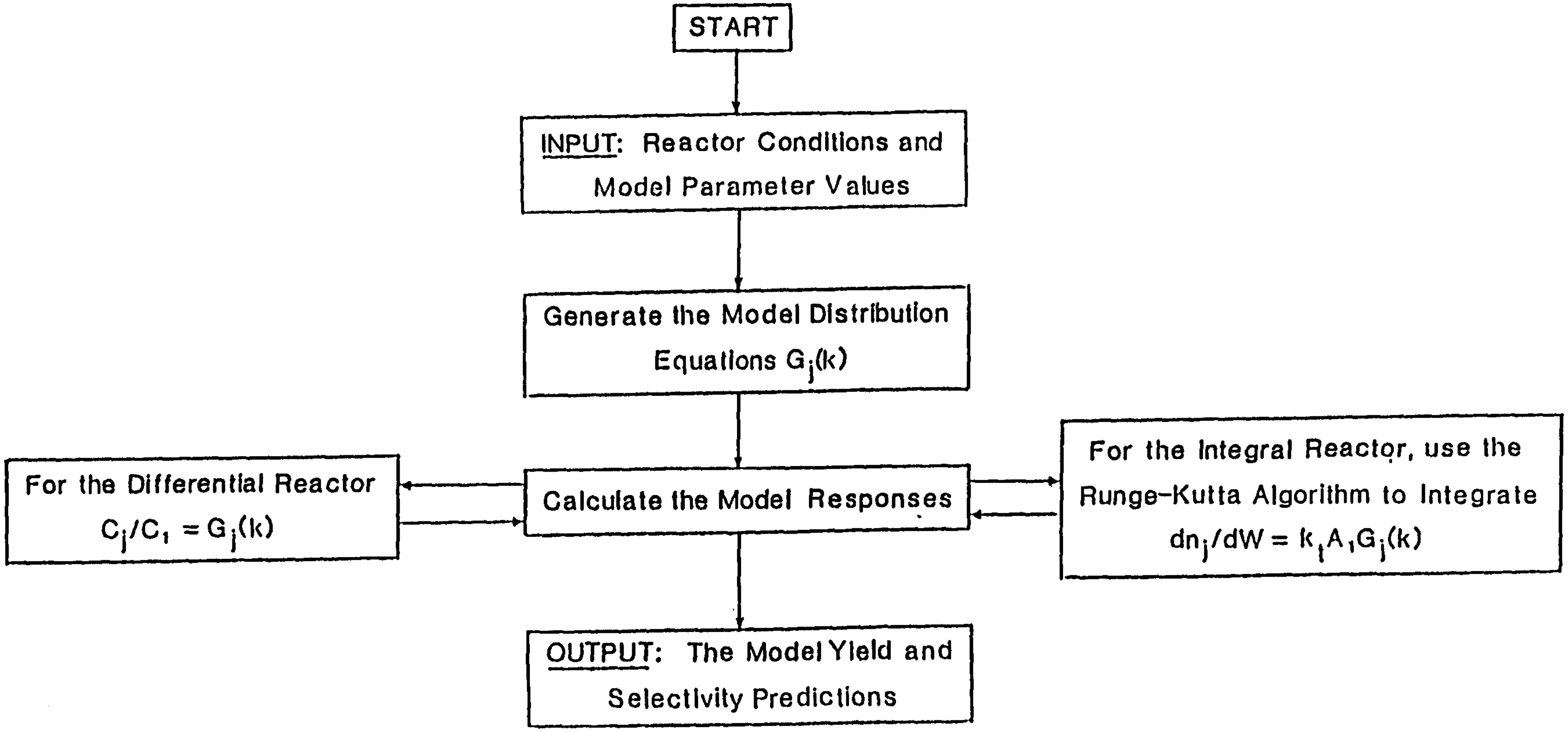


Figure 5-25. Integral, Isothermal, Plug-Flow, Fixed-Bed Kinetic Model

Figure 5-26. Measured and Predicted Product Yields

Measured product yields* for a 0.4 mol% CsOOCH promoted Cu/ZnO catalyst at 583K, 9.1 MPa, $H_2/CO = 0.45$, and GHSV = 3265 ℓ(STP)/kg cat/hr compared with the predicted oxygenate yields based upon a reaction network to be presented in the next section of this report. The estimated kinetic parameters are $\ell = 0.254$, $\beta_1 = 3.299$, $\beta_2 = 0.121$, $\beta_3 = 0.152$, and $\alpha_o' = 0.221$.

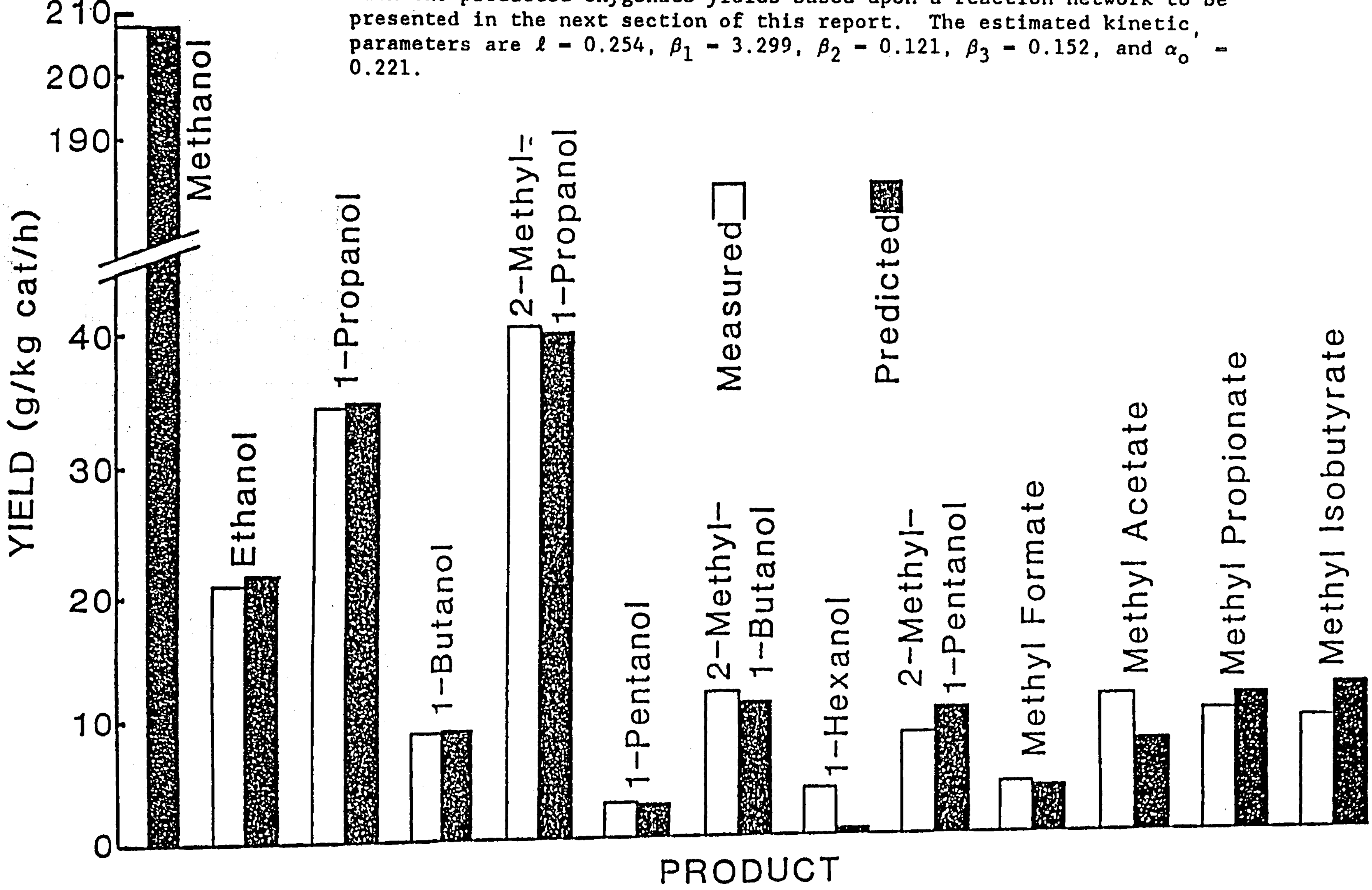
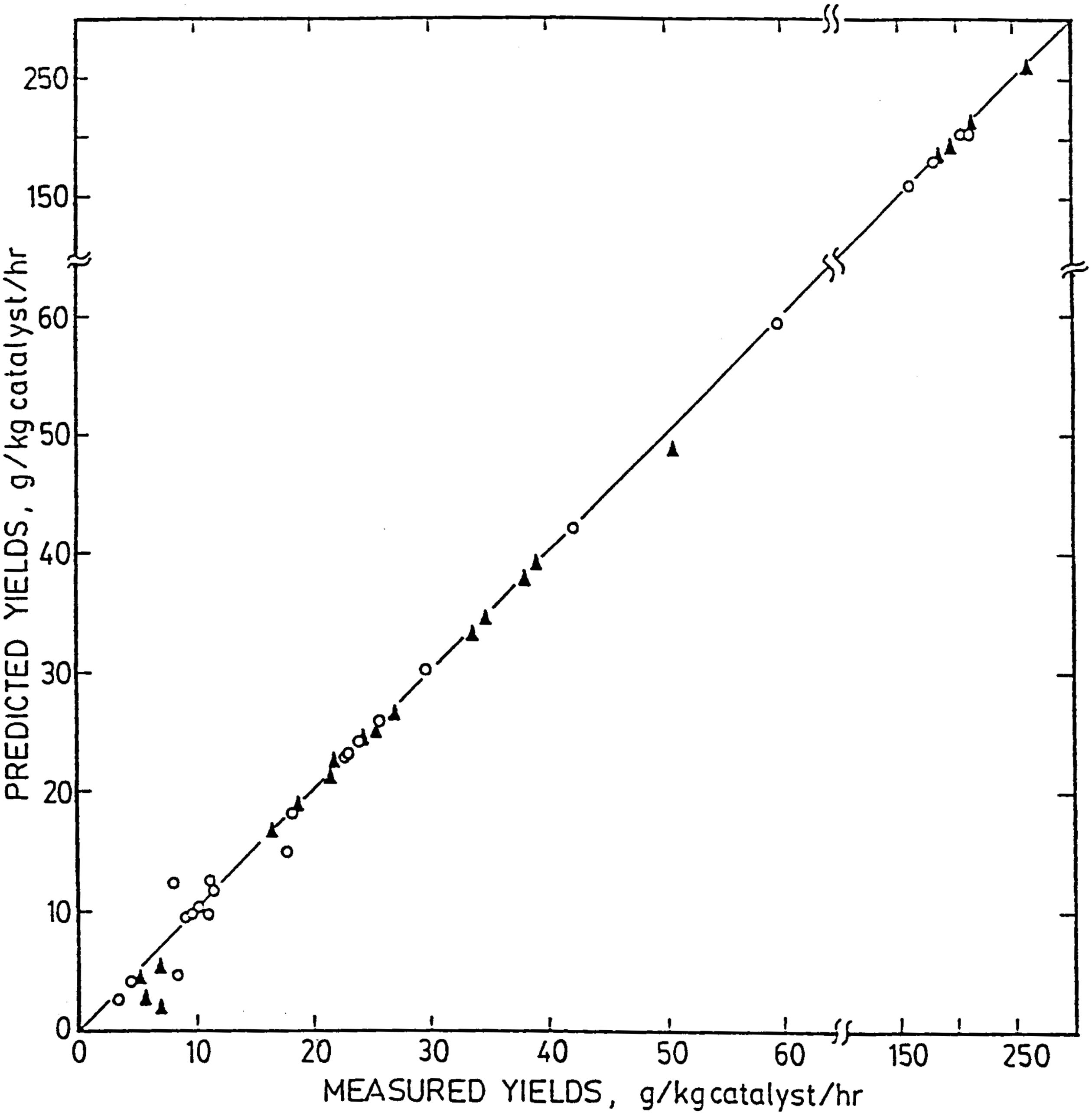


Figure 5-27. Comparison of Measured and Predicted Yields



Comparison of the measured* and predicted yields of the individual oxygenate components for the Cs/Cu/ZnO (o) and Cs/Cu/ZnO/Cr_2O_3 (▲) catalysts, with Cs concentrations in the range 0-1.5 mol% and 0-5 mol%, respectively. The predicted oxygenate yields are based on the kinetic model.
The yields were measured at 583K, 7.6 MPa, $H_2/CO = 0.45$ and GHSV = 3265 L(STP)/kg catalyst/hr and 5330 L(STP)/kg catalyst/hr for the Cs/Cu/ZnO and Cs/Cu/ZnO/Cr_2O_3, respectively.

possibly composition, as well as in selectivities under given conditions to C_2+ oxygenates.

5.3.2.3 General Remarks on Higher-Alcohol Technology and Its Economics

The most recent evaluation of the HAS technology and its economics by MITRE Corporation (101) arrived at the following conclusions:

- The 1988 price of methanol is \$0.72/gal, of OCTAMIX estimated at \$0.89-0.90/gal (approximately 25 percent higher than methanol) and of MTBE \$1.01/gal (approximately 40 percent higher than methanol).
- There is a market for 46 million barrels per year of oxygenated octane-enhancing fuel-blending compounds; currently this market is split about 50:50 between ethanol and MTBE, with MTBE rising.
- The use of MTBE is projected to reach a limit because of a limited capacity for the source isobutene, which is mostly obtained from petroleum, and a higher production cost due to a two-stage process less efficient than the direct synthesis of higher alcohols.
- Isobutanol (2-methyl-1-propanol) is a better cosolvent than ethanol, and acceptable blending characteristics are obtained with isobutanol/methanol mixtures but not with pure methanol.

The final version of the MITRE report (101) will be published sometime in Fall 1988, and therefore the above statements are tentative as of the writing of the present report.

5.3.2.4 Chemistry and Mechanisms of Higher-Alcohol Synthesis

The mechanisms of methanol synthesis were discussed in Section 5.3.1. Although chemical mechanisms, particularly those of catalyzed reactions, are often difficult to resolve, much progress has been made in the understanding of C_2+ oxygenate syntheses. The various early hypotheses as well as current views are summarized herein, and the contrasting catalytic functions that result in the synthesis of ethanol-rich or isobutanol-rich C_2+ oxygenates are emphasized.

The first step in higher-alcohol synthesis over metal oxide catalysts involves the formation of a carbon-carbon bond. The first hypothesis of a mechanism for this process was advanced by Fischer (121) who suggested that higher alcohols are formed from methanol and carbon monoxide, as depicted by Equations [1] and [18-20].

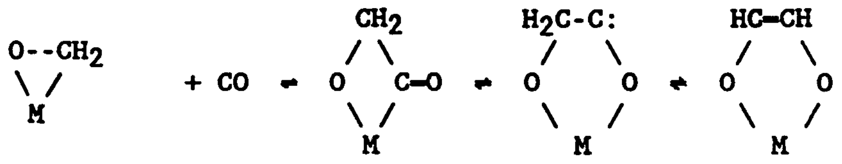
$$CO + 2H_2 \rightarrow CH_3OH \qquad [1]$$

$$CH_3OH + CO \rightarrow CH_3COOH \qquad [18]$$

$$CH_3COOH + H_2 \rightarrow CH_3CHO + H_2O \qquad [19]$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \qquad [20]$$

This reaction sequence would involve CO insertion into the OH bond of methanol to form the C-C bond, followed by sequential hydrogenation. A similar homologation of methanol by CO/H_2 has been proposed by Natta et al. (99) and Vedage et al. (70). More recently, it has been proposed (122) that the homologation of methanol by CO proceeds via a symmetric intermediate, as shown by Equation [21].



[21]

In contrast, Frolich and Cryder (123) and Morgan (124) concluded that the synthesis of higher alcohols occurs predominantly by condensation of lower alcohols. Using the Frolich and Cryder proposal that the controlling reaction in the synthesis of higher alcohols was the condensation of two methanol molecules to produce ethanol via dehydration and elimination of water (Equation [22]), Graves (125) was

$$2CH_3OH \rightarrow CH_3CH_2OH + H_2O \qquad [22]$$

able to qualitatively predict the presence or absence of certain higher alcohols when simple rules for addition were involved. Because of the observations of Brown and Galloway (126) that appreciable yields of dimethylether were formed during methanol synthesis over ZnO/Cr_2O_3 catalysts, a two-step dehydration mechanism involving dimethyl ether as an intermediate (Equations [23] and [24]) was considered, but this was discounted because the "information was insufficient to warrant any definite conclusion" (97).

$$2CH_3OH \rightleftarrows (CH_3)_2O + H_2O \qquad [23]$$

$$(CH_3)_2O \rightleftarrows CH_3CH_2OH \qquad [24]$$

An aldehyde condensation mechanism [25]

$$2HCHO \rightarrow CH_2OH\cdot CHO \xrightarrow{H_2} CH_3CHO + H_2O \qquad [25]$$

has been invoked by Fox et al. (127) for non-catalytic alcohol synthesis over alkali acetylides, where the formaldehyde molecules are derived from methanol. The latter mechanism is reminiscent of the first steps of homogeneous base-catalyzed formose chemistry (128).

The proposed mechanisms for C-C bond formation that yield C_2-C_5 alcohols can be classified as

- CO insertion into a methyl-metal bond or into the C-O bond of methoxide,
- CO homologation of methanol via a symmetric intermediate, and
- Coupling of aldehydic or alcoholic species.

These three mechanistic pathways were recently distinquished by ^{13}C-NMR analysis of the products formed when small amounts of $^{13}CH_3OH$ or $CH_3{}^{13}CH_2OH$ were injected into the H_2/CO synthesis gas feed over Cu/ZnO and Cs/Cu/ZnO catalysts (129) and over Cs/MoS_2 and $K/CoS/MoS_2$ catalysts (90). The results of these ^{13}C-labeling studies will be summarized, and it will be shown that higher alcohols are formed over the alkali/MoS_2 catalysts by a different mechanism than the way they are formed over the Cs/Cu/ZnO catalysts.

Over the alkali-promoted copper-based catalysts, the C_2+ oxygenates are favored by low H_2/CO (1.0-0.5) ratios and high temperatures (>550°K (277°C)) (70, 105). The main products aside from methanol are ethanol, 1- propanol, and 2-methyl-1-propanol, and the alkali dopants enhance the rates of the chain growth. Over the alkali/MoS_2 catalysts C_2+ oxygenate synthesis has been demonstrated (90, 103, 104) at $H_2/CO = 1$ and temperatures of 523-603°K (250-330°C) to yield mainly C_2+ linear alcohols, and the presence of cobalt in the catalyst has been found to greatly enhance the methanol homologation C_1->C_2 (103, 118). Thus, there is a tendency for the alkali/Cu/ZnO catalysts to produce branched alcohols and for the alkali/MoS_2 catalysts to produce linear alcohols, and it will become clear that this is a reflection of the different dominant mechanisms for C-C bond formation that are occurring over these catalysts.

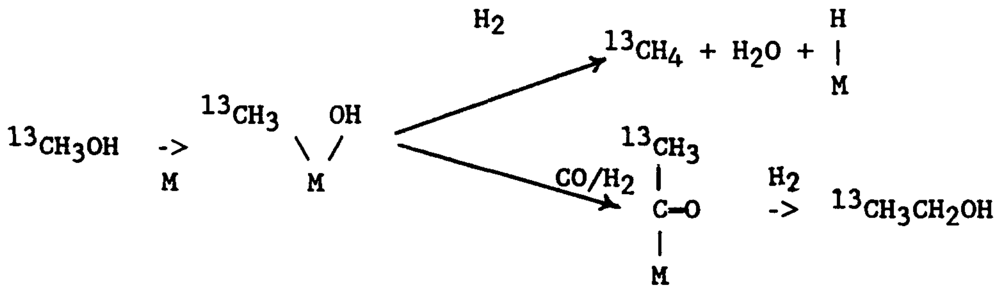
A. C_1->C_2

Injection of $^{13}CH_3OH$ yields C-2 labeling of ethanol over the Cs/MoS_2 and alkali/Co/MoS_2 catalysts (90), as represented by Equation [26].

$$^{13}CH_3OH + {}^{12}CO/H_2 \xrightarrow[\text{alkali/(Co)/MoS}_2]{} {}^{13}CH_3{}^{12}CH_2OH \qquad [26]$$

This outcome [26] indicates a CO insertion into the CH_3-O bond for linear alcohol growth over the MoS_2 catalysts. This path is enhanced by the presence of cobalt and accounts for the dominance of linear alcohols over alkali/MoS_2 catalysts.

Further support for the CO insertion mechanism over these catalysts is provided by the observation that methane produced as a side-product was also labeled by the ^{13}C. This side-reaction can be represented by Equation [27].



[27]

Injection of $^{13}CH_3OH$ into the $^{12}CO/H_2$ synthesis gas stream yields doubly labeled ethanol over the Cu/ZnO and Cs/Cu/ZnO catalysts (129)

$$^{13}CH_3OH + CO/H_2 \xrightarrow[(Cs)/Cu/ZnO]{} {}^{13}CH_3{}^{13}CH_2OH\ (+\ CO/H_2) \qquad [28]$$

This was interpreted as the C_1->C_2 step occurring by coupling of two C_1 aldehydic species by a mechanism similar to that proposed by Fox et al. (127). This outcome [28] rules out any ^{12}CO insertion mechanism such as several previously proposed (70,99,121,122) and is opposite to that [26] observed over the alkali/MoS_2 catalysts.

B. C_2->C_3

Injection of $CH_3{}^{13}CH_2OH$ over the Cu-based catalysts or growth of $^{13}CH_3{}^{12}CH_2OH$ over the alkali/MoS_2 catalysts yields different isotopic 1-propanols over the two types of catalysts.

Over alkali/MoS_2 and alkali/Co/MoS_2 catalysts, the C_2->C_3 step occurs by the same type of linear growth via CO insertion as in the C_1->C_2 step, as evidenced by the isotope reaction

$$^{13}CH_3CH_2OH + {}^{12}CO/H_2 \xrightarrow[alkali/(Co)/MoS_2]{} {}^{13}CH_3CH_2{}^{12}CH_2OH \qquad [29]$$

Over Cs/Cu/ZnO catalysts at high temperatures, path [30] occurs selectively (129)

$$CH_3{}^{13}CH_2OH + CO/H_2 \xrightarrow[Cs/Cu/ZnO]{} {}^{13}CH_3CH_2CH_2OH \qquad [30]$$

Result [30] is consistent with aldol-type β-addition with oxygen retention reversal, as shown in reaction sequence [31].

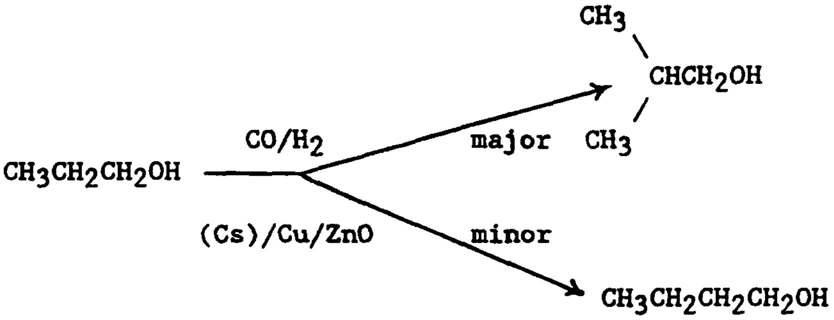
$$\begin{array}{l} CH_3{}^{13}CH_2OH \underset{H_2}{\overset{-H_2}{\rightleftharpoons}} CH_3{}^{13}CHO \underset{H^{\ominus}}{\overset{-H^{\ominus}}{\rightleftharpoons}} {}^{\ominus}CH_2{}^{13}CHO \quad \text{(enolate or carbanion)} \\ {}^{\ominus}CH_2{}^{13}CHO + H_2CO \underset{\beta\text{-addition}}{->} [{}^{\ominus}OCH_2CH_2{}^{13}CHO] -> {}^{\ominus}OCH_2CH_2{}^{13}CH_3 \\ \hspace{9cm} H^{\ominus} \downarrow \\ \hspace{8.5cm} HOCH_2CH_2{}^{13}CH_3 \end{array} \qquad [31]$$

The retention of the anionic oxygen in the $[{}^{\ominus}OCH_2CH_2{}^{13}CHO]$ intermediate is specific to the Cs promoter that prevents the dehydration of the alcoholate oxygen and favors hydrogenation of the free ${}^{13}CHO$ group. Such a path constitutes a reversal of the normal aldol synthesis pattern in which $CH_3CH_2{}^{13}CH_2OH$ propanol would be formed in the presence of hydrogen.

C. C_3->C_4

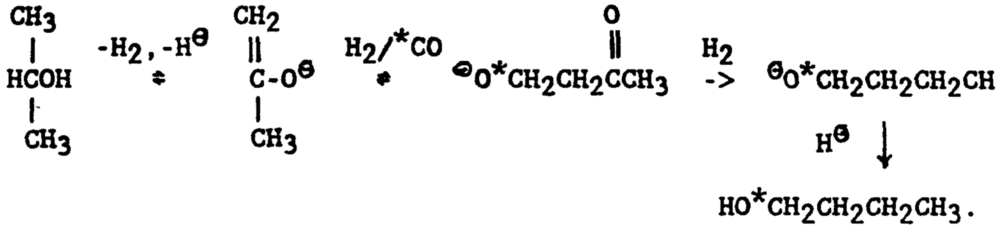
Over the alkali/MoS_2 and alkali/Co/MoS_2 catalysts, the C_3->C_4 growth step occurs mainly by linear CO insertion, giving rise to the dominance of 1-butanol in the C_4 product (90), and the ${}^{13}C$ label in ${}^{13}CH_3CH_2CH_2OH$ is found in the C-4 carbon of 1-butanol.

Over the Cu/ZnO and Cs/Cu/ZnO catalysts, injection of 1-propanol yields dominantly 2-methyl-1-propanol (with 1-butanol as a minor product), and the Cs promoter enhances the rate of the β-branching (72),



$$CH_3CH_2CH_2OH \xrightarrow[(Cs)/Cu/ZnO]{CO/H_2} \begin{cases} \xrightarrow{major} \overset{CH_3}{\underset{CH_3}{CHCH_2OH}} \\ \xrightarrow{minor} CH_3CH_2CH_2CH_2OH \end{cases} \qquad [32]$$

The dominant β-addition to form 2-methyl-1-propanol occurs via a mechanistic path analogous to [31] as indicated by the ^{13}C isotope experiments of Nunan et al. (129). This aldol path with oxygen retention reversal is further corroborated by the outcome of 2-propanol injection into the synthesis gas (92) that resulted in the dominance of 1-butanol in the C_4 product,



$$\underset{CH_3}{\overset{CH_3}{HCOH}} \underset{}{\overset{-H_2,-H^\ominus}{\rightleftharpoons}} \underset{CH_3}{\overset{CH_2}{\overset{\|}{C-O^\ominus}}} \overset{H_2/^*CO}{\rightleftharpoons} {}^\ominus O^*CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{H_2} {}^\ominus O^*CH_2CH_2CH_2CH_3 \xrightarrow{H^\ominus} HO^*CH_2CH_2CH_2CH_3. \qquad [33]$$

D. $C_4 \rightarrow C_5 \pm$

The patterns of steps $C_1 \rightarrow C_4$ continue over the different catalysts as shown above with the exception that 2-methyl-1-propanol does not give rise to any C_5 products over the copper-based catalysts. This is a known feature of β-addition not occurring at branched carbons in aldol synthesis. The α-addition of the type [25] between a branched C_4 and a C_1 aldehydic intermediate also appears to be forbidden, perhaps for steric as well as for electronic reasons. The high rate of β-addition at C_3 and the termination of the synthesis at the branched C_4 alcohol are the major factors determining the high selectivity for 2-methyl-1-propanol.

5.3.2.5 Other Catalytic Systems for Higher Alcohols

The activities and selectivities of copper-based catalysts were summarized in the review of methanol technology in Section 5.3.1.1 and in Section 5.3.2.2 in the summary of the IFP, Lurgi OCTAMIX, and LU HAS processes. In addition, a large number of Group VIII metal-based catalysts for C_1-C_5 alcohols has been investigated. In the 9th International Congress on Catalysis, a total of 21 reports dealt with Rh-based (8 papers) and Fe-, Co-, Ni- and Ru-based mixed catalysts (13 reports), primarily for methanol and ethanol mixtures. Several papers also reported on reactions of synthesis gas (SG) with olefins, methanol and amines, or initiated by acetylenes. The space time yields (STY's), selectivities, and reaction conditions are summarized in Table 5-16.

The impetus for research utilizing the Rh-based catalysts can be traced to the discovery at Union Carbide of a good selectivity of Rh-Fe catalysts to ethanol (130) and to the early work of Ichikawa (131) in which effects of various supports on the selectivity of Rh catalysts, particularly for ethanol, have been disclosed. Among the newer reports, particle size effects have been discovered (132) and confirmed (133) such that very small Rh particles (dispersion ≥ 0.6) promote the SG conversion to ethanol while large particles drive the synthesis to hydrocarbons and acetic acid. Arakawa et al. (134) classify the promoters of rhodium-based catalysts to those that increase dispersion, decrease dispersion, and those that accelerate CO dissociation. The suggested effects on selectivity in oxygenate synthesis are schematically represented in Figure 5-28. The investigations of the group of Rh-based catalysts represented in Table 5-16 and references therein demonstrate that 80-90 percent selectivity to oxygenates can be achieved. The STY's attain in some cases respectable values, e.g., 0.55 kg oxygenates/kg catalyst/hour over the $Rh/Mo/Al_2O_3$ catalyst (133). Further increases in selectivity appear to result in lower STY's, however.

Following another Union Carbide discovery (150) that Pt, Pd and Ir supported on silica are very selective catalysts for methanol, attempts

Table 5-16. Activities and Selectivities to Oxygenates (C_1-C_5 Alcohols, Acetic Acid, Esters) of Catalysts Based on Group VIII Metals

Source: 9th ICC, July 1988.

General Conditions: 1 - 10 MPa, H_2/CO - 1-2, low CO conversions, GHSV 5000-13,600.

Catalyst	Selectivity to oxygenates %	T °C	STY[a] of oxygenates g/kg(l)cat/hour	Reference
Rh/Fe^{I}II/SiO$_2$	45	150	20[b]	135
Rh/Mo/Al$_2$O$_3$	66	250	555	136
Rh/Mn/Li/SiO$_2$	80[c]	260	136[d]	134
Rh/Ti/Fe/Ir/SiO$_2$	69[c]	260	341	134
Rh/Fe^{I}II/SiO$_2$	88[e]	272	115	137
Rh/ZrO$_2$/K,P,Y,Mo,Mn	<50	250	113	138
Rh/Mn/Fe/SiO$_2$	77	220	n.a.[f]	139
Rh/SiO$_2$	93->30[g]	280	3->41	133
Fe/Pt,Pt,Pd/SiO$_2$	100	150	24	135
Fe/Ir/SiO$_2$	84	272	144	137
Fe/Rh,Pd,Ir,Pt/SiO$_2$	52-87	272	<80	137
Fe/N[h]	16	150-300	n.a.	140
Co/Ir,Pt	68-93	272	<80	137
Co/Cu/MgO	95->15	225->300	99->15	141
Ni/Ir	70	272	<15	137
Ni/ZnO	85	300	159	142
Ni/Pt	93	272	<30	137
Ni/Mo/K/SiO$_2$	55	300	296	143
NiPd/Cu membrane	<50	n.a.	n.a.	144
Ni/Pt				137
Ru/HT[i]	22	275	n.a.	144
Fe/acetylene[j,k]	>50	110-130	n.a.	146
Co carbonyl[k]	oxo reaction	110-270	n.a.	147
Co[k]	MeOH incorporation	180-200	n.a.	148
Ru,RuRh[k,l]	amine synthesis	120-260	-	149
NaOCH$_3$[k]	carbonylation	70-110	-	142

Table 5-16 (continued)

[a] STY = Space Time Yield, given in g of oxygenated product per hour per kg of catalyst (including support) where available, otherwise per liter of catalyst.

[b] Estimated.

[c] Ethanol plus acetic acid >50 percent of oxygenated product.

[d] Estimated, assuming runs were over 1 g of catalyst.

[e] Mainly methanol.

[f] Purpose of experiment was surface ketene trapping.

[g] Purpose of experiment was to establish Rh particle size effect; the smallest particles give the highest selectivity to oxygenates.

[h] Nitrided iron catalyst.

[i] HT – Hydrotalcite $Mg_3Al(OH)_8(CO_3)_{0.5} \cdot 2H_2O$ basic support.

[j] Reaction of synthesis gas initiated by acetylenes over Fischer-Tropsch iron catalysts.

[k] Reactions of synthesis gas with acetylene, olefins, methanol and amines

[l] Aminomethylations with synthesis gas and ammonia or amines.

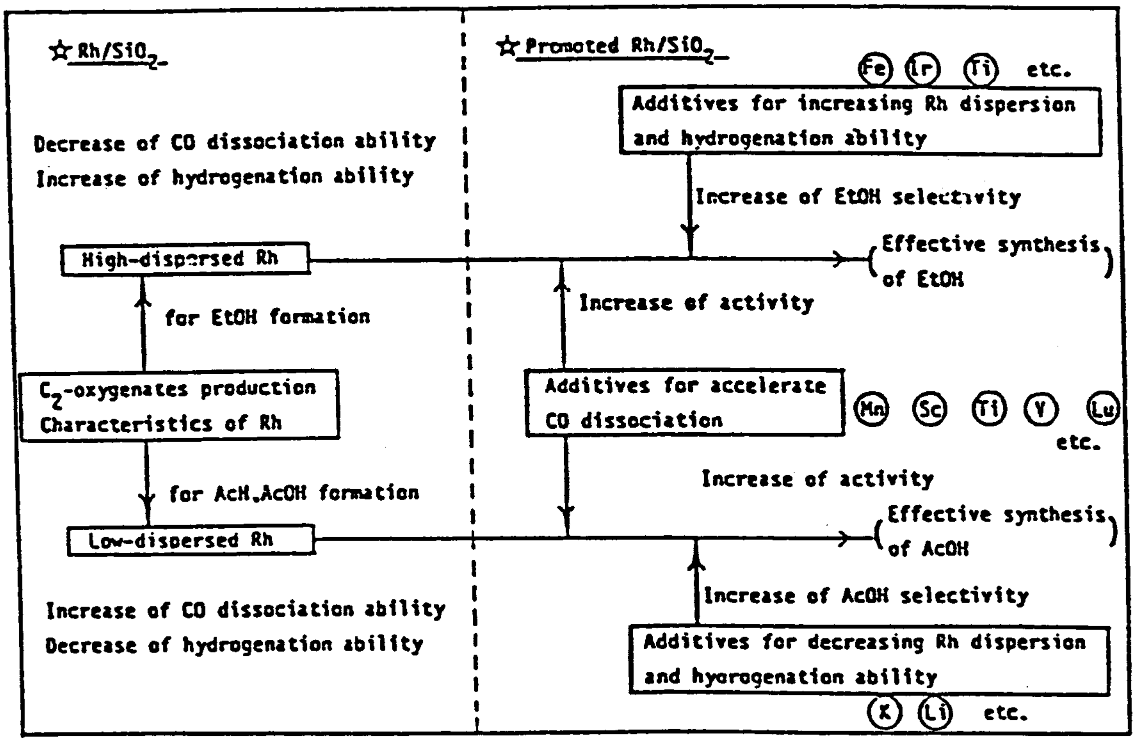


Figure 5-28. The Roles of Additives for Effective Synthesis of EtOH and AcOH

were made to improve their activity by adding a non-noble Group VIII metal such as Fe, Co, and Ni. The results are summarized in the second section of Table 5-16. In some cases high selectivities to oxygenates were attained at temperatures of 150-300°C, but both the maximum and the average STY's were lower than for the Rh-based catalysts.

More encouraging results were obtained when a non-noble Group VIII metal such as Fe, Co, and Ni was mixed with a component that is a known methanol synthesis catalyst such as ZnO, Cu, or Cu/ZnO (cf. Table 5-16, second section) but the selectivities to, and STY's of, oxygenates were significantly lower than in the systems described in Section 5.3.2.2.

In the third section of Table 5-16 are described some novel and improved processes for adding building blocks formed from SG to olefins (the oxo reaction), methanol (homologation and carbonylation), and amines (aminoalkylation). Included as well are SG polymerizations initiated by acetylenes at mild conditions wherein the group originating from the acetylene ends up as a terminal block of an oligomer formed by successive CO insertions. Although generalizations are premature, the results summarized in Table 5-16 indicate that the Rh-based catalysts give higher yields of alcohols and, except for supported Pt and Pd, also higher selectivities than the remaining Group VIII metals studied (Fe, Co, Ni, Ru, Fe/Pt, Fe/Ir, Fe/Rh, Co/Ir, Co/Pt, Ni/Ir, Ni/Pt, nitrided iron, and similar catalysts). Of the Rh-based catalysts a combination with molybdenum reported by Mills et al. (136) gives oxygenate yields comparable to or higher than those over the alkali/copper-based or alkali/MoS_2 catalysts, but the selectivities to alcohols appear lower. Among the C_2+ alcohols ethanol appears to be the main product over the Rh-based catalysts, and if ethanol is the desired product, the singly or doubly promoted Rh catalysts hold greater promise than the remaining Group VIII metals.

Some new reports also dealt with the alkali/MoS_2 catalysts with or without additional Group VIII metal sulfides such as CoS, NiS, or FeS, and effects of various supports were studied. These developments are summarized in Table 5-17, in which some of the information overlaps with

Table 5-17. Activities and Selectivities to Oxygenates (Methanol and C_2+ Alcohols) of Catalysts Based on Alkalized MoS_2

Source: 9th ICC, July 1988.

General Conditions: 5 - 20 MPa, $H_2/CO=1/1$, GHSV 2000-13,600.

Catalyst	Selectivity to oxygenates %	T °C	STY[a] of oxygenates g/kg(l)cat/hour	Reference
$K/CoS/MoS_2$	90	290	238[b,c]	118
$K/CoS/MoS_2$	84	305	275[b,d]	118
$K/CoS/MoS_2$	85	310-320	374[b]	118
$K/NiS/MoS_2$	80	310-320	314[b]	118
$K/FeS/MoS_2$	72	310-320	205[b]	118
Cs/MoS_2	84	295	310[e]	90
Cs/MoS_2	80	300	256[g]	104
Rb/MoS_2	66	300	101[g]	104
K/MoS_2	81	300	144[g]	104
Na/MoS_2	53	300	19[g]	104
Li/MoS_2	24	300	13[g]	104
K/Ketjen-165 ($K/CoS/MoS_2/c\text{-}Al_2O_3$)	13	~300	16[b]	118
K/MoS_2	86	320	500[f]	151
K/MoS_2	94	300	330[f]	151

[a] STY - Space Time Yield, given in g of oxygenated product per kg of catalyst (including support) where available, otherwise per liter of catalyst.

[b] STY in g/l cat/hour; pressure 10.3 MPa; H_2/CO - 1; ca. 50 percent Ethanol in product.

[c] GHSV - 2000.

[d] GHSV - 3300.

[e] STY in g/kg cat/hour; pressure 8.2 MPa; H_2/CO - 1; GHSV - 7750; ca. 30 percent Ethanol in product.

[f] Pressure 10 MPa, H_2/CO - 2/1, GHSV - 5000.

[g] Pressure 2.7 MPa, H_2/CO - 1/1, GHSV - 12,000, STY in g/l cat/hour.

that discussed in greater detail in Section 5.3.2.2 under the heading The Dow HAS Process.

Following the announcement by Dow Chemicals of a new process for mixed alcohols in 1984 (103) that utilizes alkalized MoS_2 catalysts, a series of patent applications, patents, and papers dealt with the selectivity, STY's, long-term performance, resistance to poisons, and effects of sulfur-containing compounds in the feed (70-77). The essential features of this interesting system are summarized below:

- It has now been established by several independent laboratories that C_1-C_4 alcohol STY's above 300 g/kg (l) cat/hour can be obtained at pressures below 10 MPa and temperatures $\leq$ 300°C over the alkali/MoS_2 catalysts; a claim that STY's greater than 1000 g/l cat/hour can be reached -- a result comparing favorably with commercial methanol production (118) -- is likely to be substantiated.
- Selectivities to C_1-C_4 alcohols of both the alkali/MoS_2 and the alkali/MeS/MoS_2 (Me = Co, Ni) are in the range of 80-90 percent; the remaining products are hydrocarbons, primarily methane, and small amounts of esters; the selectivity is not a strong function of temperature.
- Group VIII metal sulfide promoters to alkali/MoS_2 catalysts enhance the formation of ethanol both directly from SG and by homologation of methanol. These promoters are preferred in the order CoS > NiS > FeS. 50 percent selectivity to ethanol in the oxygenated product is readily attained.
- Over alkali/MoS_2 catalysts, 30/70 ethanol/methanol mixture can be obtained at high STY's and selectivity to oxygenates; heavy alkali are better promoters than light alkali, Cs > K.
- H_2S in small concentrations (10-40 ppm) doubles the selectivity of the K/MoS_2 (but not K/Co/MoS_2) catalysts to C_2+ alcohols; this remarkable effect is reversible upon removal of H_2S.
- The alkali/MoS_2 and alkali/MeS/MoS_2 catalysts are remarkably stable, resistant to S-containing and $Fe(CO)_5$ poisons, and have been demonstrated to perform over a year-long period of time.

5.3.2.6 Research Trends

The research trends in higher-alcohol synthesis appear to be motivated by the desire to develop catalysts that

- minimize the hydrocarbon, particularly methane, make
- have a high productivity (STY's) for C_2+ alcohols (ethanol in one case and isobutanol in another)
- have a high water gas shift activity
- have a good heat conductivity
- minimize the production of C_6+ oxygenates, and
- improve the stability and long-term performance of the most active catalysts.

Several of these requirements have already been satisfied by reactions and processes reviewed in Sections 5.3.2.2 and 5.3.2.3. Further improvements can be expected with existing catalytic systems by manipulating the reaction conditions (including optimizing the pressure, temperature and the CO_2 content in SG for the best performance of a given catalyst) and by characterizing the catalysts in all stages of preparation and use.

Specific items that appear desirable are the following:

- Achieve a uniform dispersion of the catalyst components. This has been cited as a key to the successful preparation of the IFP catalysts. In terms of the dispersion of alkali promoters, it is known that they are distributed in molecular submonolayer dispersion on certain preparation of the copper-based catalysts (105) but are agglomerated in large particles, perhaps accompanied by a fine dispersion, on the MoS_2-type catalysts (90).
- Suppress the formation of hydrocarbons, particularly methane, over the Group VIII metal and MoS_2-based catalysts. This will be a difficult task as, at least for the latter catalyst, it was shown that methane and ethanol have a common precursor (90).

- Stabilize the catalysts by properly chosen, preferably heat conducting, supports. Under the HAS conditions, this does not appear to be a problem for the MoS_2-based catalysts which excel by extraordinary ruggedness and stability. On the contrary, the alkali-doped copper-based catalysts exhibit a strong dependence of selectivity on the choice of support such as Al_2O_3, Cr_2O_3 or Ga_2O_3 (<u>105</u>).

- Investigate further the influence on selectivity and activity of oxide (Mo, Zn and others) components in the Group VIII (particularly Rh) metal-mixed oxide catalysts.

- Investigate the effects of alkali promoters on the performance in HAS of the very highly active copper-based catalysts derived from intermetallics described in Section 5.3.1.

- Explore and investigate novel low-temperature, low-pressure catalysts for HAS, for both heterogeneous and homogeneous catalysts.

5.3.3 Water Gas Shift (WGS) Technologies

The WGS technologies are well-developed and commercially proven. Kuo (<u>152</u>) has given a concise review of WGS catalysts and chemistry. The high-temperature shift (440-700°C) Cr-Fe oxide or Zn-Cr oxide catalysts, low-temperature shift (230-350°C) Cu-Zn-Al or Cu-Cr oxide catalysts, and raw-gas shift (180-550°C) Co-Mo sulfide catalysts and their performance were also summarized in the 1987 DOE Coal Gasification report (<u>1</u>). The water gas shift reaction [3] has been proposed to occur by two

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad [3]$$

principal mechanisms, the redox mechanism [25], where M stands for an

$$\begin{aligned} CO + O_{(ads)}\text{-}M &\rightarrow CO_2 + M \\ H_2O + M &\rightarrow O_{(ads)}\text{-}M + H_2 \end{aligned} \qquad [50]$$

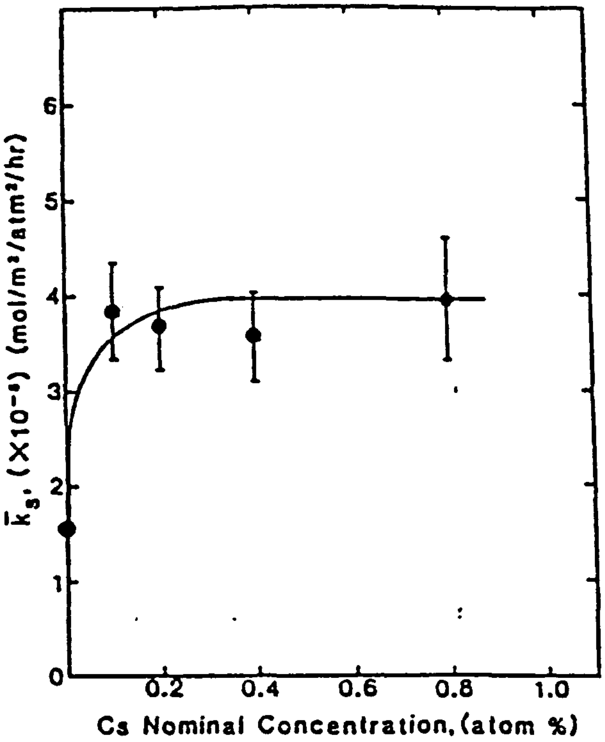
oxidizable free site on the catalyst surface and $O_{(ads)}$ for the adsorbed oxygen atom generated by oxidation of the free site by water, and the associative formate mechanism [51], in which the first step is identical

$$
\begin{aligned}
&CO + HO^{\ominus}_{(ads)} \rightarrow HCOO^{\ominus} \\
&2HCOO^{\ominus} \rightarrow 2CO_2 + H_2 + 2e^- \qquad [51] \\
&2H_2O + 2e^- \rightarrow 2HO^{\ominus}_{(ads)} + 2H_2
\end{aligned}
$$

with the first step [4] in methanol synthesis discussed in Section 5.3.1.4 and is followed by the decomposition of the formate $HCOO^{\ominus}$ and reoxidation of the catalyst by water. The formate mechanism [51] therefore also involves partial redox reactions, but the difference between [51] and [50] is in the mechanism of the formation of CO_2, via reaction of CO with surface hydroxyls [51] or directly with chemisorbed oxygen [50].

ICI researchers presented arguments that the low-temperature $Cu/ZnO/Al_2O_3$ WGS catalysts operate via the redox mechanism [50] where M is the copper metal surface atom (83). On the other hand, Klier et al. (73) improved the WGS activity of the Cu/ZnO catalysts by cesium hydroxide or cesium formate doping, taking the approach that the formate mechanism [51] is operating, at least on the alkali-doped catalyst. The WGS rates were increased by a factor up to 2.3 by additions of small amounts (0.1-0.8 wt percent) of cesium compound to the Cu/ZnO catalyst, as shown in Figure 5-29. The WGS rates were determined concurrently with methanol synthesis and not at low pressures, at which the WGS takes place without methanol synthesis. Also, the long-term stability of the Cs/Cu/ZnO catalysts and the effects of supports such as Cr_2O_3 or Al_2O_3 were not determined. However, the heavy alkali doping has been demonstrated as a promising route to improved low-temperature WGS catalysts.

Alkali doping also imparts a significant WGS activity on the MoS_2 catalysts, and the chemistry of WGS in this system has yet to be resolved. If the formate route [51] operates, all reactions may occur on the alkali component with the electrons released in the second step and consumed in the third step being accepted and re-supplied by MoS_2.



Average forward WGS rate constants $\bar{k}_S$ (ordinates) as a function of cesium concentration (abscissas) in the HCOOCs/Cu/ZnO catalysts for the pressure 75 atm, temperature 235 °C, and H_2/CO = 2.33 synthesis gas.

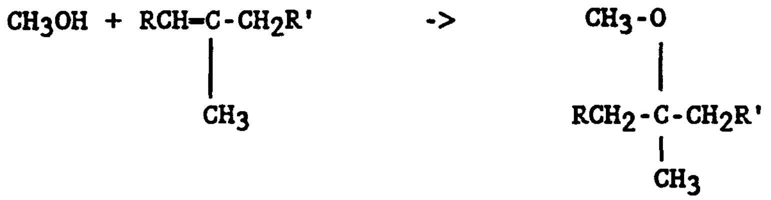
Figure 5-29. Average Forward WGS Rate Constants

In conclusion, although the WGS technology is mature and is in a wide commercial use, improvements are still possible and being reported, and certainly a great deal of effort is needed to unambiguously resolve the WGS mechanism for each individual catalyst.

5.3.4 The Methyl Tertiary-Butyl Ether (MTBE) and Tertiary-Amyl Methyl Ether (TAME) Technology

5.3.4.1 Introduction and Historic Notes

MTBE and TAME are produced by reactions of methanol with tertiary olefins,



$$CH_3OH + RCH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CH_2R' \rightarrow RCH_2{-}\overset{\overset{\displaystyle CH_3{-}O}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_2R' \qquad [52]$$

where R=R'=H for isobutene that gives rise to MTBE, and R=CH_3, R'=H for 2- methyl-2-butene (isoamylene) and R=H, R'=CH_3 for 2-methyl-1-butene, both of which give rise to TAME. The ethers MTBE and TAME constitute the fastest growing use of methanol, along with petroleum-derived hydrocarbons C_4H_8 or C_5H_{10}, in the U.S. and Europe (153 - 157). MTBE and TAME are rated with octane RON/MON 118/101 and 105-122/96-105, respectively. When blended into gasoline at a level of 10 percent, these ethers increase the RON and MON by 2-3 units (153). MTBE and TAME can be used as octane enhancers by themselves but also as cosolvents for blends of methanol in gasoline, since methanol is less expensive and has higher octane than both gasoline and MTBE or TAME.

The world's MTBE and TAME capacity has grown significantly recently, the newly plants built, under construction, or engineered in 1986-1988 totaling more than 4.7 billion kg in annual capacity (37).
Between 1986 and 1987 the world's production of MTBE alone rose from the 24th to the 18th place among organic chemicals to 1.5 billion kg in 1987, averaging 50.7 percent annual growth (158). Currently, MTBE occupies approximately 50 percent of the oxygenate blending agents market, and its

use is rising. However, El Sawy (101) anticipates constraints for future increases of MTBE production in the limited supply of isobutene and in a cost factor (1.4 compared to methanol and 1.12 compared to higher alcohols) that will make alcohol fuel blends economically competitive with MTBE and possibly reverse the trend. A similar consideration applies to TAME.

Currently, in the production of MTBE (TAME), one carbon atom originates from methanol that could be made from coal-derived SG (but most of which is made today from natural gas or naphtha), and four (five) carbon atoms originate from petroleum in the form of specific olefins as indicated by Equation [52]. Thus, MTBE and TAME production still relies on petroleum (at least to 80-83 percent) as a raw material, and currently there are no indications of switching to coal resources. There are known chemical paths to MTBE, however, that permit the total use of coal-derived SG as a raw material, e.g., via isobutanol (2-methyl-1-propanol) directly synthesized from SG as shown in Section 5.3.2.1. Isobutanol can then be catalytically dehydrated to isobutene and MTBE synthesized by the process represented by reaction [52] with R=R'=H. Some other approaches are mentioned in Section 5.3.4.3.

MTBE was introduced commercially in Europe in 1973 using Snamprogetti technology (153, 157, 159). In the U.S. after the first MTBE plant was built in 1979, 14 plants were running in 1983, and the capacity is growing worldwide.

5.3.4.1 The MTBE and TAME Technology

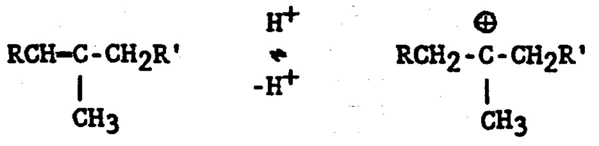
J.D. Chase reviewed the basic features of the MTBE and TAME technology in 1983 (153). These ethers are produced with high (97-99 percent) selectivity by solid acid-catalyzed coupling reactions [52] under mild conditions at 0.7- 1.4 MPa, 70-110°C, and a liquid hourly space velocity of 13.5 (based on the olefin), with conversions of 86-96 percent. The STY's are also high, being in the range of 0.022-0.05 kg of isobutene consumed per kg catalyst per hour in MTBE manufacture. MTBE is produced at an 85-percent higher initial rate than TAME under comparable conditions.

In the Gulf Canada process (161) methanol is used in two-fold excess to the stoichiometric amount required by reaction [52]. The unreacted methanol is removed by adsorption in glycol rather than by distillation, which is rendered impractical due to the existence of methanol-C_4 azeotropes. A schematic flow sheet for the Gulf Canada MTBE process is shown in Figure 5-30. A patent covering the Gulf Canada combined process for MTBE and TAME was awarded in 1980 (162). The Institute Francais du Petrol (IFP) has a process utilizing an alternative approach of separate reactors for MTBE and TAME (163). The largest TAME plant, under construction at Feyzin, France, utilizes the IFP technology and the largest MTBE plant, at Al Jubail, Saudi Arabia, the Snamprogetti technology.

The catalysts for both the MTBE and the TAME manufacture are cation exchange resins that are exchanged with protons to impart surface acidity (160, 164), and they are used in the liquid phase. Despite the fact that high synthesis rates, liquid-phase conditions, large catalyst particle sizes, and low temperatures are used, the process is believed to occur in the kinetic reaction regime and not to be mass-transfer limited. The reaction rate is first order in the tertiary olefin concentration and zero order in methanol when a stoichiometric excess of methanol is used. Thus, simple, efficient, and selective production processes exist for MTBE and TAME, and the underlying chemistry is well understood in terms of carbenium intermediates as discussed in the next section.

5.3.4.3 Chemistry and Mechanism

The tertiary olefins involved in reaction [52] readily make tertiary carbenium ions through the equilibrium [53], and these react with methanol



$$RCH{=}\underset{\substack{|\\ CH_3}}{C}{-}CH_2R' \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} RCH_2{-}\underset{\substack{|\\ CH_3}}{\overset{\oplus}{C}}{-}CH_2R'$$

[53]

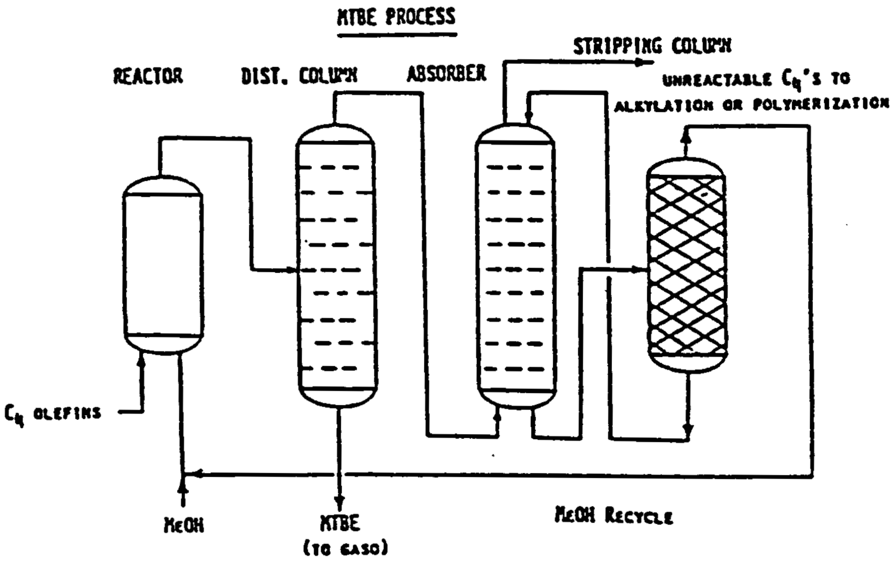
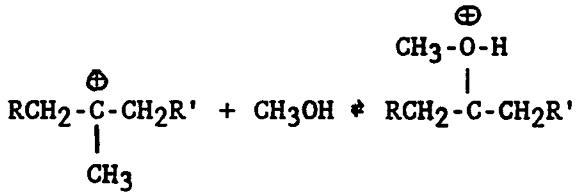
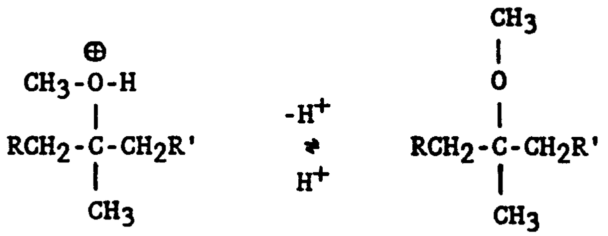


Figure 5-30. A Schematic Diagram of the Methyl Tertiary-butyl Ether (MTBE) Process

to form an oxonium intermediate [54] which upon the loss of proton converts to the product ether, [55].

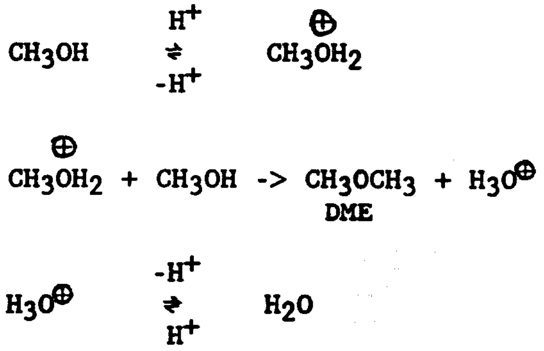


$$RCH_2-\underset{CH_3}{\overset{\oplus}{C}}-CH_2R' + CH_3OH \rightleftharpoons RCH_2-\overset{\overset{\oplus}{CH_3-O-H}}{C}-CH_2R' \qquad [54]$$



$$RCH_2-\underset{CH_3}{\overset{\overset{\oplus}{CH_3-O-H}}{C}}-CH_2R' \ \underset{H^+}{\overset{-H^+}{\rightleftharpoons}}\ RCH_2-\underset{CH_3}{\overset{\overset{CH_3}{O}}{C}}-CH_2R' \qquad [55]$$

Reactions [54] and [55] may occur in a concerted fashion. Competing undesirable side reactions may involve acid-catalyzed olefin oligomerizations that also occur via carbenium intermediates, and acid-catalyzed dehydration of methanol to dimethyl ether (DME) that occurs via an oxonium mechanism [56].



$$CH_3OH \ \underset{-H^+}{\overset{H^+}{\rightleftharpoons}}\ CH_3\overset{\oplus}{O}H_2$$

$$CH_3\overset{\oplus}{O}H_2 + CH_3OH \rightarrow \underset{DME}{CH_3OCH_3} + H_3O^{\oplus} \qquad [56]$$

$$H_3O^{\oplus} \ \underset{H^+}{\overset{-H^+}{\rightleftharpoons}}\ H_2O$$

The extent to which the side-product olefin oligomers and DME appear in the product has not been reported in detail, although the selectivities for the main reaction [52] are known to have attained 97-99 percent at conversion levels up to 96 percent.

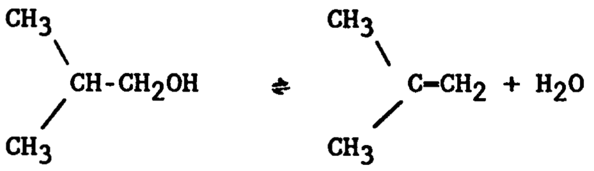
5.3.4.4 Novel Synthesis of Octane-Enhancing Ethers from Alcohols

A direct coupling of alcohols to ethers by the general reaction [57] has recently been reported to occur on superacid resins (165). Here the

$$CH_3OH + ROH \rightarrow CH_3OR + H_2O \qquad [57]$$

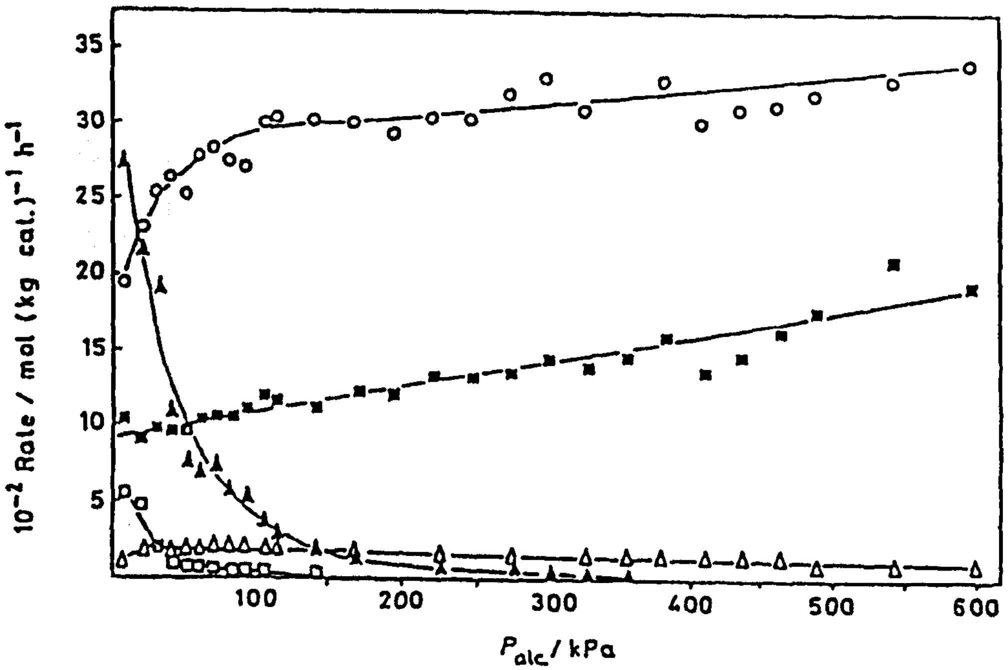
source of the methyl-alkyl ether is methanol and an alcohol ROH (R = higher alkyl) instead of methanol and an olefin in reaction [52]. Research into the synthesis [57] was motivated by the fact that methanol-isobutanol (R = 2-methyl-1-propyl) mixtures can be synthesized directly from coal-derived SG, and therefore all carbons in the ether CH_3OR produced by reaction [57] would originate from coal.

When isobutanol was coupled as ROH with methanol over a Nafion-H resin, the ether produced was methyl-isobutyl ether (MIBE), or 1-methoxy-2-methyl propane, rather than MTBE, showing convincingly that reaction [57] did not proceed via dehydration of isobutanol to isobutene [58] followed by reaction [52] because in that case MTBE would be the



[58]

expected product. The formation of MIBE indicates a different mechanism involving oxonium or surface sulfate ester intermediates (165). The side products of the MIBE generating reaction [57] (with R = 2-methyl-1-propyl) are butenes, DME, di-isobutyl ether (DIBE) and octenes; the olefin formation can be suppressed by pressure. At pressures exceeding 0.4 MPa, the olefin formation is negligible at temperatures below 130°C. Interestingly, the mixed ether MIBE is preferred to DME and DIBE in the product as shown in Figure 5-31. The Nafion-H resin is stable up to 200°C. Steady yields of MIBE of 0.23 kg/kg cat/hour were obtained at a temperature of 160°C and a pressure of 7.6 MPa with 42 mol percent selectivity. The conditions for alcohol coupling [57], although mild in general terms applied to catalytic



Variation of product yield with alcohol mixture partial pressure at a steady-state reaction rate. Reactants, MeOH-Bu^{i}OH (2:1); alcohol feed, 15.59 mol (kg cat.)$^{-1}$ h^{-1}; N_2 feed, 186 mol (kg cat.)$^{-1}$ h^{-1}; catalyst (Nafion-H Micro-Saddles) wt., 1.0 g; *T*, 389 K. ○, MIBE; ■, Me_2O; ▲, butenes; □, octenes; △, $Bu^i{}_2O$.

Figure 5-31. Variation of Product Yield with Alcohol Mixture Partial Pressure

processes, are slightly more severe than for the methanol-olefin coupling [52], and the selectivities of the MIBE process [57] are lower than of the MTBE process [52].

The octane-enhancing value of MIBE has not been determined, and there are some reservations concerning the stability of MIBE upon long-term exposure to air. Therefore, it is likely the MTBE will remain the most attractive octane-enhancing ether. Should the coal technology of the future aim at MTBE from the coal-derived methanol-isobutanol mixture, the chemical path involving a catalytic dehydration of isobutanol [58] followed by the established MTBE technology (Section 5.3.4.2) appears more feasible.

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CHAPTER 6

REVIEW OF PYROLYSIS[1]

6.1 INTRODUCTION AND SUMMARY

6.1.1 Introduction

Pyrolysis is the thermal cleavage of coal to produce char, tar, and gas. It is a low-temperature variation of coking, which has long been used in the metallurgical industry. Pyrolysis was considered to be an inexpensive liquefaction process, because it is carried out at low pressure and without catalyst or hydrogen consumption. Several pyrolysis processes to produce liquid fuels were under development in the 1970's, by FMC, Consolidation Coal, Toscoal, Lurgi Ruhrgas, Occidental Petroleum, and others. Occidental's process utilized flash hydropyrolysis to increase liquid yield. Pyrolysis economics were disappointing, due principally to small tar yields and low product value, especially of the char.

In 1980, Utah Power and Light (UP&L) considered expanding its electrical generating capacity by using pyrolysis char as a supplemental boiler fuel that was to be made by either the Tosco or the Lurgi Ruhrgas process. The liquid was to be upgraded on site and then sold to a refinery, and the gases were to be reformed to make hydrogen for the upgrading. UP&L's interest dwindled when demand for electricity fell. Before that happened, the individual steps of the process -- pyrolysis, utilization of the char as a boiler fuel,.and upgrading of the tar oil to a syncrude -- had been tested successfully.

After that program closed down, there were no large-scale pyrolysis developments until interest was revived recently by the Morgantown Energy

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[1] This chapter was prepared by Harvey Schindler, SAIC, and SAIC staff, from sections of References 1 - 6.

Technology Center (METC). In METC's program the pyrolysis processes being investigated appear to be similar to those used in the past; the major emphasis is on better utilization of the char and upgrading of the liquid to higher-value-added products. These are two major areas of concern in pyrolysis. The char, which constitutes at least half of the weight of the coal feed, has a per-pound value lower than that of the coal feed, and the pyrolysis liquid has a high heteroatom content, which requires extensive hydrotreating to be reduced to an acceptable level. But certainly, the low liquid yield is the major characteristic of pyrolysis and the reason for the lack of interest by DOE in recent years.

This chapter on pyrolysis was developed from sections of six reviews (1-6), the last of which was published in 1987. These reviews should be consulted for more detail. The Bechtel study (6) is an economic analysis of the UP&L project, including the costs of mining and product upgrading. The MITRE study (5) is a review of four processes under development in the 1970's. The review by Brandes (2) contains recent research results, including work on catalytic hydropyrolysis, which has achieved liquid yields of over 50 percent in laboratory tests. This approach brings liquid yields close to those from direct liquefaction but at the expense of foregoing the main processing advantage of pyrolysis, i.e., thermal liquefaction at low pressure.

6.1.2 Summary

This chapter describes some of the important research in coal pyrolysis, much of which is intended to increase liquid yields. Major efforts have been expended to achieve a better understanding of coal structure and changes in structure during heating, in the belief that pyrolysis conditions can be tailored to change the yield structure. Interesting work has been done on pyrolysis pathways, pretreatments, reactive atmospheres, and the study of process parameters. Nevertheless, it was the opinion of the assessment panel that this work will lead to only relatively small increases in liquid yields and small improvements in pyrolysis economics.

Thus, the panel made the near-unanimous recommendation to study catalytic hydropyrolysis (Recommendation No. P1), which has demonstrated significantly greater liquid yields. Admittedly, these yields are achieved with a more expensive pyrolysis system -- one whose conditions of high hydrogen partial pressure and an added catalyst approach direct liquefaction technology. The economic studies described in the chapter illustrate, however, that the pyrolysis section constitutes perhaps only one-sixth of the total plant investment. This indicates that a more costly pyrolysis section, but one that increases liquid yield by two- to three-fold, may be warranted. Another related recommendation is to study staged catalytic hydropyrolysis (No. P5), in which the tar made in the first catalytic stage is hydrotreated/hydrocracked in a second stage to produce an acceptable refinery feed.

Currently, no large-scale pyrolysis developments are being funded. The developments reviewed in this chapter were all terminated by the early 1980's. The assessment panel agreed that such large-scale developments are not justified until the economics of pyrolysis are improved substantially. For processes such as those described in this chapter, this improvement depends on converting the char to a product that has a market value greater than that of boiler fuel. The assessment panel did recommend studies to find more uses for the char (see Table E-1 in Appendix E, Pyrolysis Research Need 2.4), but this was not considered to be of high priority. This area has been well researched in the past, with little success. A related recommendation which was prioritized is to conduct a systems analysis of pyrolysis coupled with gasification/combustion for char utilization (No. P4).

After the highest-priority recommendation to study catalytic hydropyrolysis, the panel recommended the characterization of coal fundamental groups and their relationship to pyrolysis/hydropyrolysis reactivity (No. P2). Also of some interest was to compare pyrolysis yields and products with and without reactive atmospheres (No. P3). The study of the chemistry and reaction networks in pyrolysis reactions to establish optimum operating conditions was also recommended (No. P6).

However, in summary, the panel was lukewarm about the prospects for dramatic improvements in conventional pyrolysis technology. The panel therefore primarily endorsed research on catalytic hydropyrolysis, which has the potential of achieving major increases in liquid yield, and may thus be competitive with direct liquefaction.

6.2 FUNDAMENTAL AND APPLIED RESEARCH

6.2.1 Coal Structure and Physicochemical Properties as Related to Pyrolysis

The strategy supporting the development of pyrolysis processes in general has been shaped by several inherent assumptions regarding the structure of coal. One of these key assumptions is that the molecular building units in coal are of relatively low molecular weight, i.e., one- and two-ring structures. If this assumption is valid, then pyrolysis conditions which produce and recover primary fragments would result in maximum liquid yields of these desired liquids. This concept has been tested by providing high heating rates at reduced pressure to permit rapid production and recovery of small molecules as liquids. Heat- and mass-transfer considerations necessitate feeding small particles so that primary pyrolysis fragments form quickly and diffuse rapidly to the surface where they are vaporized and recovered.

In reality, a major part of the primary liquids recovered is relatively high boiling. Generally, the higher the liquid yields from pyrolysis, the greater is the proportion of high-boiling species. This observation strongly suggests that the basic building blocks in coal are higher in molecular weight than desired for commercial liquid fuels. Shifting the liquids toward lower-molecular-weight, lower-boiling products necessitates increasing residence time and temperature, resulting in secondary cracking with a reduction in liquid yield.

Various models of coal structure as a multi-ring, higher-molecular-weight compound have been proposed, based on numerous analytical measurements and experimental results (see Chapter 4). Howard (7) discussed various models and their relationship to pyrolysis reactions in his review of coal pyrolysis. There have been many investigations to elucidate the mechanisms by which the functional groups in coal are transformed into volatile matter. These investigations have generally involved a careful study of appropriate model compounds based on the premise of free radical reactions to form stable gaseous, liquid, or solid products. The plastic or caking behavior of coal upon heating has also been the subject of investigations as it impacts on the practical aspects of handling coal in various reactor configurations. The occurrence of the plastic state is associated with and kinetically similar in many ways to pyrolysis, with temperature limits and the time duration of plasticity depending on the heating rate (7).

In many investigations the pyrolysis of model compounds representing important structural features and functional groups in a coal molecule has been studied in the presence of a hydrogen donor such as tetralin. Researchers believe that preasphaltenes are formed by the scission of C-C bonds in the ethylene bridges that connect the aryl groups and have found that model compounds break down faster when heated with ground coal (vitrinite). They suggest that the slower asphaltene and oil formation results from ether bond cleavage and more C-C bond cleavage, and that the carbon-to-sulfur and carbon-to-nitrogen bond breakage occurs throughout both stages of hydrogenolysis. Based on a study of 9-benzyl 1,2,3,4,-tetrahydrocarbazole (9-BTHC) as a model compound to represent the types of structural configurations and connecting bridges believed to be present in bituminous coal (8), it can be inferred that the pyrolysis of bituminous coal is a second-order reaction.

The thermal decomposition of diaryl ether in tetralin has been studied (9) to understand the behavior of oxygen-containing structures in coal during pyrolysis. These data indicate that at coal liquefaction temperatures (450°C) the bond scission of oxygen-containing polynuclear aromatic structures occurs mainly at methylene or ether bridges.

Miller and Stein (10) and Stein (11) have shown the usefulness of thermochemical and kinetic analysis as tools for the critical evaluation of the reaction pathways of model-compound reactions used to elucidate details of coal liquefaction chemistry. Use of thermokinetic principles shows that the several decomposition pathways proposed in the literature are too slow to explain observed rates. McMillen and co-workers (12) explained the mechanisms by which methylene and ether linkages undergo C-C and C-O scissions in tetralin at 400°C to form hydroxylated rings. The observed reaction rates for certain classes of compounds--(hydroxyphenyl) phenyl methanes and p-hydroxy phenyl ether -- were too rapid to be accounted for by simple bond-scission/radical capping mechanisms used to explain many coal-model studies with rates estimated through thermochemical techniques.

Vernon (13) reported that the pyrolysis products of bibenzyl at 450°C depend upon the hydrogen environment. In the absence of a hydrogen donor source, the major products are toluene and stilbene. In the presence of a donor solvent (tetralin), toluene is the only major product. However, in the presence of molecular hydrogen, the major products are toluene, benzene, and ethyl benzene with the product distribution depending on the hydrogen pressure. He proposed a simple reaction mechanism consistent with all these results.

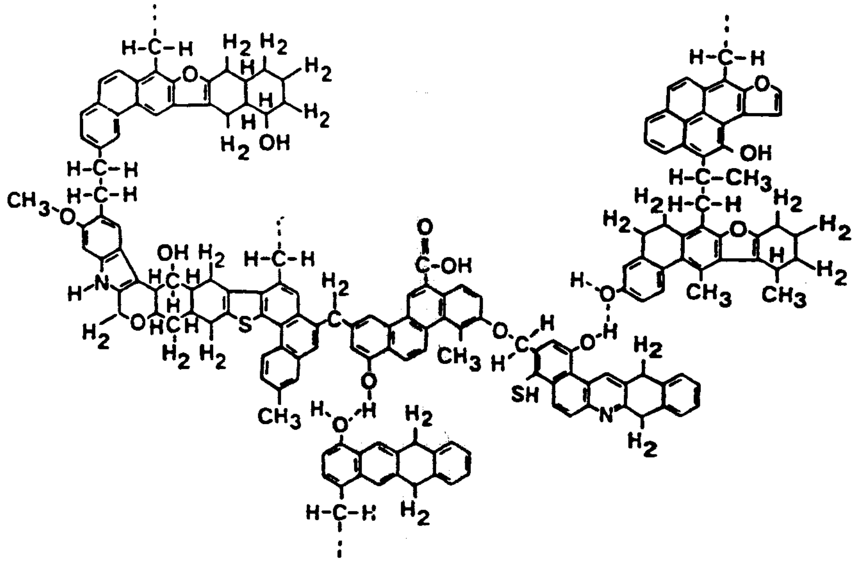
Siskin and Aczel (14) studied the phenolic and etheric oxygens in coal to elucidate the thermal mechanisms leading to the formation of hydroxyaromatics, and to ascertain the nature and the environment of those bonds cleaved and rearranged in this process. They concluded that phenols in the pyrolysis liquids derive from the cleavage of etheric bonds not directly attached to the functionalized site of furanic and thiophenic structures. Their data also indicated that most of the one-ring phenols found in pyrolyzates are formed during pyrolysis.

Recently, Solomon et al. (15, 16) used Fourier-transform infrared spectroscopy (FTIR) to verify the relationship between the functional group distribution in coal and its thermal decomposition behavior. They obtained rate constants for the evolution of each species. The rate constants are claimed to be independent of coal rank with differences between coals attributed to differences in the mix of sources (functional groups) in those coals. Based on a variety of analytical and thermal decomposition data, Solomon (17) proposed a coal structure model for a Pittsburgh seam coal and its thermal decomposition products (Figures 6-1 and 6-2). His coal model differs from other proposed models in having more oxygen in rings, nitrogen only in rings, explicit hydrogen bondings, and larger cluster size. It also has more easily broken aliphatic linkages and a higher value for aromatic hydrogen.

Given (18) and Solomon (19) both represent coal as having small aromatic clusters connected by bridging groups. These bridges can be methylene, acetylene, ether, or thiol ether. It is at the bridges where the coal is most readily broken under pyrolysis conditions. It is these bonds that are, therefore, most often modeled. Additionally, functional sites (alcohols, phenols, amines, and sulfur groups) and the way they react and are transformed are of considerable interest for modeling studies. Talwalkar (1) reviews the post-1978 literature of model-compound studies.

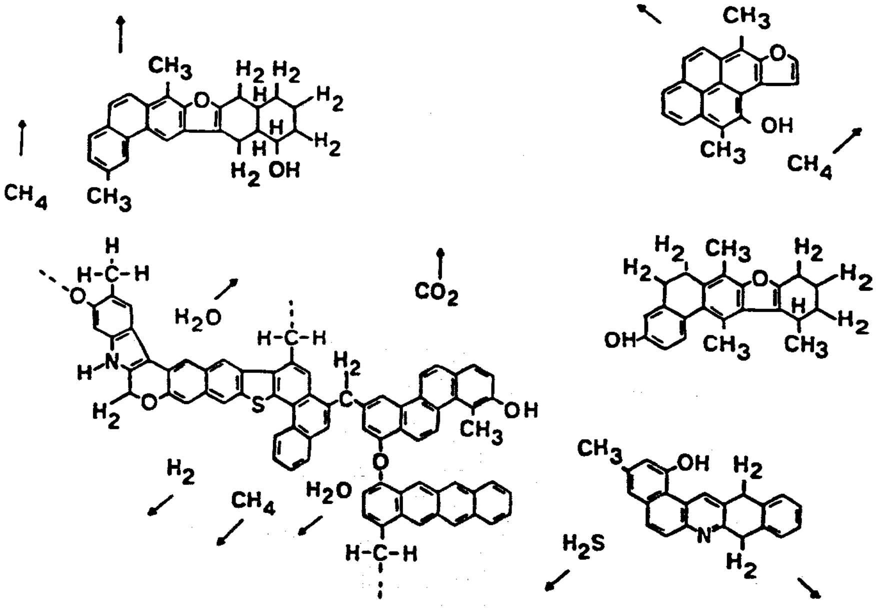
Pyrolysis studies of coal and model oxygenated compounds were carried out by Siskin and Aczel (20). Their goal was to ascertain the nature and the environment of the etheric bonds which cleave to form phenols under pyrolysis conditions. Both the coals and the model compounds were derivatized with KOH to replace all the hydroxyaromatic protons with potassium ions. Both the derivatized and the starting materials were pyrolyzed at 600°C, and the pyrolysates were analyzed. The conclusions reached from this model compound work were that phenols derive mainly from cleavage of alkyl C-O bonds, diaryl ethers are stable, and dialkyl ethers form mostly hydrocarbons and CO.

McMillen et al (21) demonstrated that coal structures are not well represented by monocyclic aromatic structures which are unsubstituted (such as bibenzyl). They showed that by substitution in the aromatic rings, the central bonds are sufficiently weakened to account for the bond rupture evident in coal at temperatures around 400°C. If the substituted group on a diaryl methane is hydroxyl, there need not be a weak C-C or C-O bond to cause reaction of the structure at 400°C at a rate commensurate with coal dissolution.



Source: Ref. 17.

Figure 6-1. **Summary of Coal Structure Information in a Hypothetical Coal Molecule**



Source: Ref. 17.

Figure 6-2. **Cracking of Hypothetical Coal Molecule During Thermal Decomposition**

It is possible to study the structure and the chemical makeup of coal by studying its components. Pyrolysis, because there need not be any interfering substances to confuse the product spectrum, is an ideal way to produce fragments of the coal for study. Solomon and Hamblen (22) assume, for the formulation of a model for coal pyrolysis, that tars are representative fragments of whole coal. They back this up with evidence that FTIR and NMR spectra of bituminous coal and tars produced from that coal are virtually identical.

Unger and Suuberg (23) studied the products of the pyrolysis of four coals to trace the pathway from the coal to the final tar and/or soot formed in the pyrolysis process. A number of steps were taken to minimize secondary reactions. These included prevention of exposure of the products to light and minimization of the time interval between collection and analysis. They found that the molecular-weight distribution of the tar product fell in the 100 to 4000 range, the peak being at 250 to 750 with the majority of the tars having weights below 1500.

A broad study designed to examine all the volatile matter produced during pyrolysis and hydropyrolysis of Louisiana lignite was carried out by Wu and Harrison (24). Individual volatile components of the complex tar mixture were assigned to one of eleven groups. The groups were designated in the following way: benzenes, alkane-alkenes, phenols, naphthalenes, polyaromatics, indenes, benzofurans, thiophenes, other ring compounds, other compounds, and unidentified. Volatile matter was collected in CH_2Cl_2-filled traps and then injected into a gas chromatograph. Regardless of the temperature (500-800°C) or the atmosphere of pyrolysis (N_2 or H_2), the majority of the yield was in the alkane-alkene group, followed by benzenes and phenols. The production of benzenes was, however, double in an H_2 atmosphere at the expense of the alkane-alkene yield.

The origin of benzene as a pyrolysis product was investigated by Finn et al. (25). Both single- and two-stage reactors were utilized.

Varying the temperature in the two stages of the reactor independently allowed for optimization of the benzene yield. The parameters of solids and vapor residence times, heating rate, pressure, and coal rank were investigated. Six aromatic model compounds were also used to study further the production of benzene in hydropyrolysis. They found that there is a temperature dependence of the benzene yield, higher temperatures increasing the proportion of benzene.

Vassallo et al. (26) were able to measure changes in aromaticity which occur as coal is pyrolyzed. Solid-state ^{13}C-NMR was performed as well as H-NMR of the product tars. For the coals studied, four of the five showed an increase in percent aromatic carbon in the products over the starting coal. The aromatic carbon found in the char was always less than the amount of aromatic carbon in the starting coal. As the aromatic carbon content of the coal increased, a greater proportion of the aromatic carbon remained in the char. It was also found that a significant portion of the aliphatic carbon in the starting coal undergoes conversion to aromatic carbon.

Changes in the structure of coal as it undergoes pyrolysis has been the topic of much recent discussion. The plastic properties of the coal strongly influence the heat and mass transfer during pyrolysis. Talwalkar (1) reviews the work which relates coal structure to pyrolysis. He states that the onset of plasticity is similar to pyrolysis. Many authors consider it to be the first stage of pyrolysis. Various theories have been proposed to explain the softening of coal. It has been suggested that hydrogen bonds and Van der Waals forces begin to weaken and the mobility of the micellar structure of the coal increases.

A study of the cross-linking in coal as it undergoes pyrolysis was conducted by Suuberg and Unger (27). Different rank coals were pyrolyzed, and the chars were subjected to a swelling experiment. Lignites were found to cross-link at lower temperatures than bituminous coals. The molecular mass of the resulting pyrolysis tars decreases as the temperature increases. The authors claim that this phenomenon is consistent with polycondensation occurring as the coal is pyrolyzed.

Redistribution of the sulfur in the native coal to gas, tar and char formed during pyrolysis has a direct influence on the potential for each of these products as a fuel. Solomon (28) showed that the sulfur content of the char is almost always lower than that of the high-volatile bituminous starting coal. There is a pyrolysis temperature dependence of the sulfur content of the char which is related to the coal type. This dependence in turn is related to the proportions of organic and inorganic sulfur in the coal. The pyrolysis tars are slightly enriched in sulfur. There is, however, an erratic temperature dependence between sulfur content in the chars and pyrolysis temperature.

Cleyle et al. (29) have shown that the inorganic sulfur (contained in pyrite) is liberated as the coal pyrolyzes and is trapped in the coal matrix. Working with high-sulfur coals in which at least half the sulfur occurs as pyrite, they showed that for non-isothermal pyrolysis to 1000°C, some of the sulfur is evolved as H_2S, but not enough to account for all of the pyrite-to-pyrrhotite reaction which occurred by thermal decomposition of the coal. It was found that the released inorganic sulfur is converted to H_2S, which migrates through the pore structure of the coal. The H_2S reacts with active carbon sites trapping the sulfur in the carbon matrix as organic sulfur.

Calkins (30) characterized sulfur structures in the coal by pyrolyzing the coal and analyzing the pyrolysis products. Gaseous sulfur compounds accounted for 25-50 percent of the sulfur found in the coal. Gases that were emitted included: H_2S, COS, CS_2, CH_3SH, and SO_2. Condensibles incorporating sulfur in their structure were thiophenic compounds (thiophene, thianaphthene, dibenzothiaphene, and methyl derivatives of these compounds). For a bituminous coal (Pittsburgh No. 8) only 1.7 percent of the original sulfur appeared in the char after pyrolysis at 850°C. For a lignite 30 percent remained in the char.

Torrest and Van Meurs (31) showed that pyrolysis in steam can effectively reduce the level of sulfur in the residual char of Texas lignite. This sulfur reduction would make the char a potential feed for combustion as the Btu content was not that much lower than the starting coal. Nitrogen pyrolysis at 578°C resulted in a char with 20 percent less sulfur than the starting coal. Steam pyrolysis at 760°C resulted in the production of a char containing 38 percent less sulphur than the starting coal.

6.2.2 Chemistry and Mechanisms of Pyrolysis Reactions

The following section addresses priorities in understanding coal devolatilization mechanisms, including the status of research in such areas as secondary reaction minimization, role of particle size and free radicals in pyrolysis chemistry, reaction kinetics based on coal particle studies, steam-enhanced pyrolysis, and impact of reactive atmospheres on coal devolatilization. Each of these areas was given a high priority by the expert review panel.

Several process parameters are important in pyrolysis processes. Following is a brief review of the effects of such parameters. More detailed reviews can be found in the literature (1, 2, 3, 7, and 32).

Time -- Different periods of time are of concern, including residence time of the coal in the heated zone, which depends on both the kind of reactor (e.g., fixed-bed, entrained flow, screen) and the coal properties. For example, agglomerating coal will stick to the walls of a reactor, creating conditions for long solids residence times. Residence time of the pyrolysis products in the reaction zone correlates with the residence time of the atmosphere in which the pyrolysis is occurring. This period of time includes time for transport of the products out of the coal particle, a process related to the coal particle size and porosity. Finally, there is the actual time for the reaction to occur, which depends on the kinetics.

Studies of the dependence of tar and light hydrocarbons yields on these different periods of time have been made, many with the intention of formulating a model for the kinetics of the pyrolysis reaction. The current approach to modeling the complicated events of coal pyrolysis is to use a set of parallel first order reactions whose activation energies are described by a statistical distribution (DAE, Distributed Activation Energy, models).

Lowenthal et al. (33) correlate the swelling of the coal particle to tar formation under rapid pyrolysis conditions. The swelling properties of the coal directly relate to the solids residence time and the time of transport of the products out of the coal particle. In addition, the swelling influences the heat transfer properties to the particle. These authors also report that there is a correlation of vitrain swelling with tar formation. Predictability of the behavior of the coal based on maceral content can thus be used for reactor design.

Temperature -- The onset of significant decomposition for most coals begins at approximately 300°C. The effect of increasing the peak temperature of pyrolysis has the predictable effect of producing a larger volatiles yield from the coal; however, a plateau that is strongly dependent on heating rate and residence time is reached in volatiles production. At this point, secondary reactions and the retrogressive formation of solid coke take over.

Solomon (28) showed that the percent of tar product increases to a temperature of about 650°C before leveling, independently of the coal rank or the hold time at a given temperature. He showed that the temperature dependence of the devolatilization product distribution was the same for all the coals studied, with the exception of the evolution of CO_2 from a lignite. Water, tar, and light hydrocarbon evolution increased with temperature, then attained a plateau. Hydrogen and CO were evolved at higher temperatures and did not show a maximum even up to 1000°C.

Suuberg and Scelza (34) investigated low temperature pyrolysis of a North Dakota lignite. They used high heating rates and very short residence times at peak temperatures. They found that the evolution of CO_2 started at temperatures much lower than the evolution of hydrocarbon gases and at the same temperature as the onset of tar evolution (300°C).

Volumetric swelling studies made of heated coal samples at different maximum temperatures of heating show that there is a decrease of swelling for a bituminous coal which corresponds to the end of the tar evolution. As for the lignite studied, the swelling ratios decreased very early in the temperature history and continued to decline with increasing temperature, indicating that the onset of cross-linking occurs much earlier in lignites than in bituminous coals (35).

Xu and Tomita (36) analyzed the pyrolysis products of seven different coals in the temperature range of 445-920°C. They compared the temperature dependence of the product yield to the coal rank. They found, as Solomon (28) did, that there is no dependence on rank. Product materials were divided into four groups: I. inorganic gases (IOG), II. hydrocarbon gases (HCG), III. light hydrocarbon liquids (HLC), IV. tar (defined as Total Volatile Material = IOG+HCG+HCL). Each group showed a characteristic temperature dependence independent of coal type or rank. The tar yield increased with temperature up to 627°C where it then leveled off.

Collin et al. (37) showed by NMR that as the flash pyrolysis temperature increases, the chemical nature of the product tar changes. Above 600°C the tars contain more fused aromatic rings and a decreased phenol content. It has also been found that the carbon content of the tars increases slightly with temperature, as the carbon content of the char also increases. The hydrogen content of both the tar and the char correspondingly decrease, and consequently, the H/C ratio of both the tar and the char decreases with increasing temperature. This change of the

H/C ratio would indicate that a better-quality tar would be produced at lower temperature.

Pressure -- the effect of changing system pressure on weight loss is reviewed by Howard (7) and Gavalas (32). Briefly, as the pressure of an inert atmospheric pyrolysis is increased, the yields of light hydrocarbons and tar decrease; the opposite is also true. The effect is reported to be noticeable only above 600°C. Total volatiles yield and tar yield decrease; methane and hydrocarbon gases actually increase slightly. For hydropyrolysis the effect of increasing the hydrogen pressure is to increase the tar yields. Arendt and van Heek (38) addressed the question of pressure on tar yield and found that the production of tar at elevated H_2 pressure has a strong dependence on heating rate as well.

Graff et al. (39) have reported that for steam pyrolysis of a bituminous coal at 20 psi, tar yields are higher by about 10 percent than those of the same bituminous coal obtained at 750 psi (40). There may, however, be a residence-time effect as the yields at the two different pressures were obtained in two different reactor configurations. Tamhankar (41) also showed that in a N_2/65-percent-water atmosphere the effect of raising the total pressure at temperatures below 1000°C is to increase the percentage of the coal which pyrolyzes. Sharma et al. (42) pyrolyzed an Indian coal (Godavari) in a mixture of steam and hydrogen. They found that as the total pressure of the system is increased, total volatile yields are increased.

Noor et al. (43), looking at the pressure dependence of tar yield in hydropyrolysis utilizing slow heating rates, found that maximum yields of tar require optimum hydrogen-to-coal ratios. To achieve the maximum yield, they found that it is not necessary to work at very elevated pressures, only to have the appropriate ratio.

Atmosphere -- Very little reference is found in the literature to pyrolysis work involving atmospheres other than inert gas or hydrogen.

The use of hydrogen clearly promotes the formation of more tar and light volatile matter, and results in a better char (7 , 32). There are a few references in the literature which show that hydrogen is not the only atmosphere that promotes tar formation. Graff et al. (44) show that yields of tar and volatile-matter are improved significantly over inert gas pyrolysis if the pyrolysis atmosphere is steam. Sharma et al. (42) pyrolyzed coal in hydrogen, argon, steam, and mixtures of steam and hydrogen. They found that pyrolysis in steam enhances total volatile yields, and in a mixture of steam and hydrogen, tar yields are enhanced over those obtained at the same pressure as the partial pressure of the hydrogen in the mixture. These workers also pyrolyzed coal in a mixture of synthesis gas and steam with the aim of reducing the necessary hydrogen pressure in the system to produce the same or better yield. As with the steam-hydrogen mixtures, the volatile matter production was slightly enhanced (7 percent) over that with just hydrogen alone in the system.

Stompel et al. (45) compared the product tars from two experiments. In the first a bituminous coal was pyrolyzed in a fluid bed with hot flue gases (70 percent N_2) as fluidizing and heat-transfer agent. In the second experiment the same coal was pyrolyzed with the hot gases obtained during steam-air gasification of a pyrolysis char (46 percent N_2 and 22 percent CO). Although total yields did not differ outside the range of experimental variation, the quality of the tars did differ from one experiment to the other, especially in their oxygen contents. The coal tar from pyrolysis in the N_2-rich environment contained 11.4 percent oxygen whereas the tar from the CO-enriched environment contained only 8.3 percent.

Sundaram et al. (46) performed flash pyrolysis experiments in 'reactive atmospheres' (H_2, CH_4, CO). They reported that the total carbon conversion of the coal in pyrolysis in these three gases was 37.6, 30.4, and 17.5 percent, respectively. The yield for pyrolysis in CO was equivalent to what the authors found for pyrolysis in inert gas. The yield in methane, however, is almost double that value. In contradiction to these findings, Caulkins and Bonifaz (47) reported on work where a Texas lignite was flash pyrolyzed in a methane atmosphere. They found that there was no improvement in the yield of volatiles from the coal, only conversion of the methane itself.

To track the movement of hydrogen from the pyrolyzing atmosphere to the products and to determine what portion of the hydrogen originally in the coal ended up in the products, Noor et al. (48) pyrolyzed Manvers coking coal in a deuterium atmosphere. Pressure and other conditions were adjusted to those which gave maximum tar yields with pure H_2. They concluded from this study that the deuterium which incorporates in the product tars is the result of exchange with H atoms in the aromatic rings. They found that the distribution of deuterated species was what would be expected from random scrambling. There was, however, an excess of weakly deuterated species. These were postulated to have arisen from deuteration of molecules "...imbedded in the solid coal-coke".

Rank and Coal Type -- Coal is classified by type and by rank. The rank of the coal indicates its age or degree of maturation. Chakrabarty and duPlessis (49) state that pyrolytic behavior can not be predicted by coal rank. However, the maceral composition, or type of coal, plays a major role in yield structure. They developed the following generalizations based on studies of European, African, and Australian coals (See Chapter 4 for a discussion and a definition of maceral types):

- "* good oil yields result from a high percentage concentration of the exinite group of macerals in coal
- "* vitrinite in high concentrations also contributes to the oil yield but produces strongly phenolic oils
- "* dull coals with a low concentration of exinite (and vitrinite), known as 'gray durain', are unsuitable for oil production by low-temperature pyrolysis
- dull coals with a high concentration of exinite, known as 'black durain', give very rich oil yields. The hydrogen content of this type of coal generally exceeds 5.2 percent."

Solomon et al. (22) concluded from their experiments that rank has little importance as the cause of the scatter of kinetic data found in the literature for coal pyrolysis. They found that variations in coal rank cause only a factor of 5 variation in the rate constant for material losses in pyrolysis. Davies et al. (50) found that in relatively slow heating in a thermogravimetric analyzer, there was a rank dependence. From the derivative curves it was apparent that there was a correspondence between the point of maximum rate of weight loss and temperature and rank. The higher-rank coals required a higher temperature to release volatiles at a rapid rate.

Ko, Peters, and Howard (51) give a correlation for tar yields from pyrolysis with coal type and pressure. Their model incorporates the idea that the number of labile bridges and the amount of abstractable hydrogen are directly proportional to the tar yields and the number of cross-linked bridges is inversely proportional. They also correlate labile bridges with aliphatic carbon content and cross-link bridges to ether and thio-ether structure. Abstractable hydrogen is that which is attached to aliphatic carbon (with a small correction made for -OH groups). The predicted tar yield based on this model works fairly well with the exception of a number of different coals.

Heating Rate -- Traditionally, pyrolysis of coal was performed at very slow heating rates. This resulted in the optimization of the char yields by the promotion of secondary reaction of the tar. This slow pyrolysis (referred to as low-temperature carbonization) resulted in a solid fuel for domestic use and coke for metallurgical purposes.

Arendt and van Heek (38) pyrolyzed a number of coals, changing only the manner in which they were heated and thus effectively changing only the heating rate. The heating rates varied from 0.05°C/s to 3°C/s for pyrolyzing coal in a thermobalance experiment and 200°C/s to 1200°C/s for pyrolyzing coal spread on a wire mesh. Their results were plotted as a function of reaction pressure, and they showed that for the higher heating rates, at all pressures, the amount of tar formation is increased.

Howard (7) claims that there is no effect of heating rate on total volatile matter released. He claims that the different techniques to produce the different heating rates influence the outcome. Such factors as particle size and reactor type (which influences residence times) and the final temperature reached in the experiment influence the production of volatiles. He explains that the time-temperature profile for maximum yield does change with heating rate. As the rate increases, so does the temperature where the maximum yield is found. As the rate increases, the time at the maximum temperature to achieve the maximum yield goes down. As the rate increases, the range of temperature for devolatilization increases; consequently, at higher heating rates there is more time for the occurrence of secondary reactions.

Coal Handling -- Coal handling is differentiated from coal pretreatments on the basis of coal environmental and physical aspects. Coal handling includes oxidation (or weathering), crushing, and grinding (particle size).

Oxidation -- One of the most widely observed phenomenon occurs when a fresh coal face is exposed to air at ambient conditions. This effect, known as weathering, reduces yields of coal-derived liquids (52). Ignasiak et al. (53) and Liotta et al. (54) showed that the process involves the formation of ether links in the coal. The more highly cross-linked structure which results destroys plastic and dilation properties. Furminsky et al. (52) claimed that oxidation decelerates pyrolysis reactions that yield volatile products. Solomon et al. (55) correlated the yield of volatile material producible with the organic oxygen content as measured by ultimate analysis and the aliphatic hydrogen concentration as determined by FTIR. The amount of CO, CO_2, and H_2O is increased as the oxygen content of the coal increases. The yields of oils, BTX (benzene, toluene, and xylene), and tar are expected to increase as the aliphatic hydrogen present increases, it being a likely abstractable source for stabilizing free radicals as they are thermally formed.

Particle Size -- Thermal alteration of coal particles strongly depends on the mass- and heat-transfer properties of the particle and the system in which it is pyrolyzed. Tsai and Scaroni (56) found that pyrolysis in their entrained-flow reactor occurred under nonisothermal conditions and was thus governed by the heat-transfer rate to the particles. They found, however, an independence of final volatile yields on particle size. The same conclusions were reached by Scaroni et al. (52). Work was done by Stubington and Sunaryono (58) with very large particles (1-15 mm) of coals ranging in volatile-matter content between 19 and 44 percent. They showed that as the particle size increases, the likelihood for secondary reactions increases as the pyrolysis products pass through the pores of the particle to the surface of the particle. There is, consequently, an increase of the char yield as particle size goes up.

For very small particles the rate of pyrolysis is controlled by chemical kinetics (7). As the particle size increases, a critical size is reached at which heat and/or mass transfer becomes limiting, and this size appears to be <2 mm for heating rates <1000°C/s.

Pretreatments -- Pretreatments are considered to be conditions imposed on the coal prior to further processing which are not indigenous to the natural environment in which the coal is found or handled. Such conditions could include, for example, chemical reactions, temperatures and pressures above or below ambient, and mixture with foreign substances (material not found in the native coal structure, or not found in such excess).

Native Mineral Matter -- The influence of mineral matter on the pyrolysis of coal has been extensively studied. Gavalas (32) distinguished two forms that mineral matter can have which influence the yield from coal pyrolysis. One form is the inherent mineral matter of the coal or material added by ion exchange with the coal. The other is by mechanical mixing of inorganic material with the coal.

On the whole, the addition of minerals to the coal either by ion exchange or mechanical mixing has the effect of reducing tar yields and increasing the yield of solid char (59). Franklin et al. (60) investigated the importance of native mineral matter in the rapid pyrolysis of coal and correlated the mineral content of the coal to yields of char, tar, and light gaseous volatiles. They concluded that the total yield of volatiles and tar is unaffected by most of the minerals. However, they claimed that montmorillonite, pyrite, and kaolinite cause significant reductions of tar yields. Both CaO and $CaCO_3$ increase char yields, at the expense of the tar. Franklin and coworkers also reported on the effects of mineral matter on the yields of C_3-C_8 hydrocarbons (61).

Morgan and Jenkins (62) found that pyrolysis of a lignite which had been exchanged with Group I and II metals showed a reduction of the total volatiles yield from 50 to 30 percent by weight. They also clearly showed that by removing the mineral matter from the coal by acid washing, the total pyrolysis weight loss increased 20-30 percent (depending on residence time).

Chemical and Physical Pretreatments -- There are a large number of references in the literature dealing with pretreatment of fossil fuels followed by extraction, liquefaction, and study of the transformed material. Very little reference is found, however, to pretreatment of coal followed by pyrolysis or hydropyrolysis.

Preliminary treatment of coal before pyrolysis has been used to study the reactivity of different bonds in the coal and to improve the tar yields from pyrolysis. Predrying coals to improve the economics of handling the raw coal has been a standard practice (63). A secondary advantage of the predrying is to reduce the steam/carbon reaction which will occur between the released water and the carbon in the char on pyrolysis. Preheating coals in an inert atmosphere at temperatures substantially below pyrolysis temperatures has, however, been shown to produce no improvement in pyrolysis tar yields (64). Preheating in steam at 50 atmospheres and temperatures below 360°C dramatically improves tar yields and also improves gas make in subsequent pyrolysis (Graff and Brandes (1984)).

Rose et al. (65) modified coals by attaching labeled organic groups to the coal structure. These groups were placed in the structure at key points so that upon pyrolysis the course of various reactions could be monitored by tracing the labeled groups. Using first O- and C-benzyl, later O-phenylmethyl and O-methyl (66), and most recently O-(2-phenylethyl) derivatives (67), researchers have been able to elucidate mechanisms of fragment formation.

6.2.3 Catalysis

Recent hydropyrolysis research has used catalyst admixed with coal to double the tar yield, bringing it close to liquid yields from direct liquefaction. The char yield is reduced to the order of 20 percent, implying that the char may be consumed internally as a source of hydrogen. A process based on this catalytic mode of pyrolysis would require an as-yet undetermined catalyst consumption, in addition to the costs associated with hydrogen production and high-pressure hydrogenation. Although no process has yet evolved from catalytic hydropyrolysis, it has the potential to compete with direct liquefaction as a source of coal liquids. (As the result of its assessment, the panel recommended that the study of catalytic hydropyrolysis be given the highest priority in pyrolysis research.)

Typical reaction conditions are 500°C and 2200 psi hydrogen pressure. The catalyst is applied to the coal surface by techniques including: (1) physical mixing of catalyst and coal, (2) catalyst dispersal on the coal surface, followed by ion exchanges, and (3) melting the coal with a catalyst solution. Pyrolysis yields (68) obtained by the Coal Research Establishment (Stoke Orchard, England) are:

	Wt% MAF Coal*
Tar	59
Methane	5
C_2-C_x gases	6
Char	21

*0.4% Mo as MoS_2 added to coal

The tar composition had the following elemental composition:

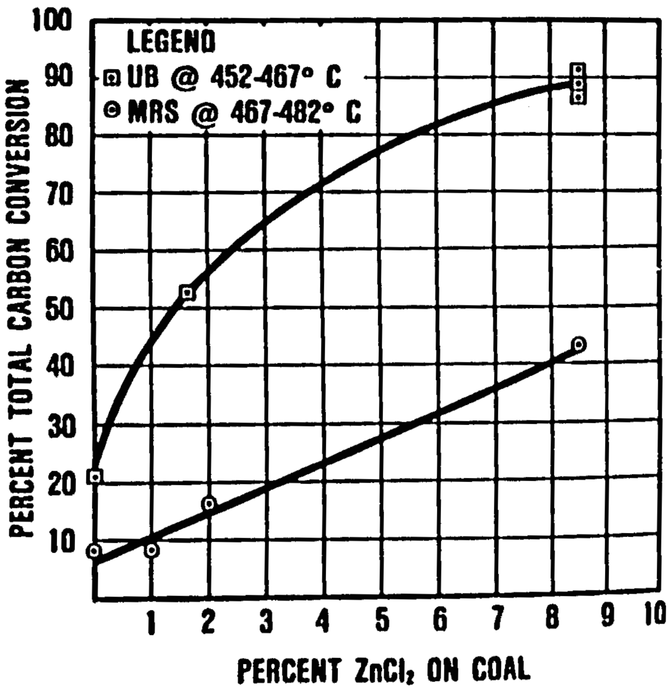
	Wt% Tar
C	86.1
H	7.0
O	3.6
N	1.7
S	0.4
OH	3.0

Furfari and Cypres (69) studied the hydropyrolysis of a high-sulfur, high-calcite Italian Sulcis Coal in a fixed-bed semi-batch reactor under a pressure of 1 to 3 MPa from 580° to 850°C. They used a heating rate of ~10°C/min for this subbituminous coal and determined the catalytic effect of calcite on the hydropyrolysis yield. They found a correlation between the amount of heat released during hydrogenation and the amount of water formed. A significant portion of the CO_2 evolved from the decomposition of the mineral carbonates. A portion of the CO evolved from the degradation of phenols catalyzed by calcite and/or lime, and as a result the oil yield was reduced.

Butler and Snelson (70) investigated bituminous coal hydrogenation in the presence of $AlCl_3$ and $AlCl_3$ plus chlorides of Cu, Zn, Fe, Cr, Mo, and Ni. The mixed halides $MoCl_3$ + $AlCl_3$ and $NiCl_2$ + $AlCl_3$ were found to be superior catalyst combinations. Up to 75 percent carbon conversion to low-molecular-weight hydrocarbons were obtained at 300° to 400°C and initial H_2 pressures of 4.1 to 6.9 MPa with the former.

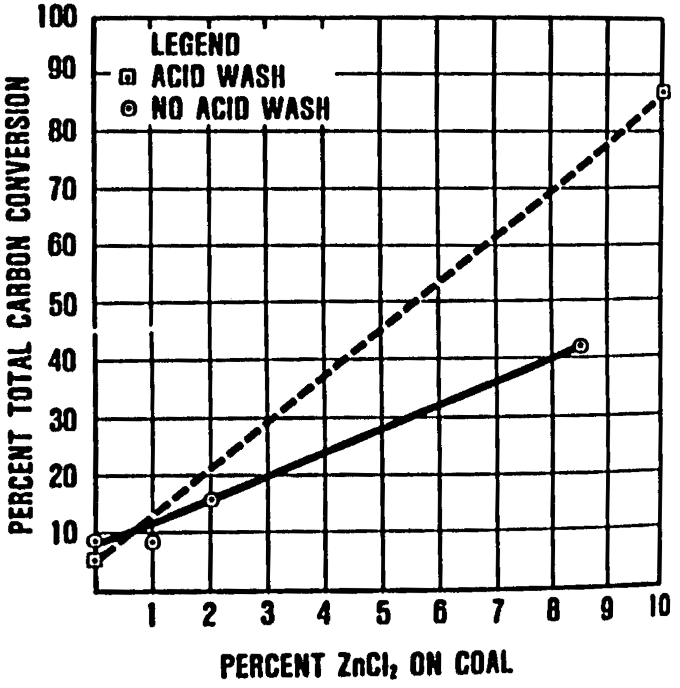
Oko (71) evaluated the effect of catalysts on the hydropyrolysis of Utah bituminous and Montana Rosebud subbituminous coals. Zinc chloride showed the highest catalyst activity ratio with a 10-fold increase in total conversion and a 13-fold increase in liquid product for both coals (Figure 6-3). The effect of acid-washing the coal prior to $ZnCl_2$ impregnation is shown in Figure 6-4. There is apparently a synergistic effect of acid-washing and $ZnCl_2$ addition which suggests that Bronsted acid character is needed on the catalyst. The results of the evaluation of various potential catalysts on MRS coal are shown in Table 6-1. Both nickel compounds caused modest improvements in the liquid yields, but were not nearly as effective as $ZnCl_2$. $FeCl_2$ also caused a mild increase in conversion, but did not increase the selectivity to liquid products. Acid pretreatment did not enhance the catalytic effect of $FeCl_2$, as was observed with $ZnCl_2$. The other catalyst candidates had either no effect or a negative effect. Ammonium molybdate, which is a proven catalyst for hydrogenation, was not effective at the operating conditions used in this study. Moderate improvements in gas yields were observed for $ZnCl_2$, $FeCl_2$, HCOONa and silica-alumina (Si/Al) catalysts. The other catalyst candidates had a negative effect on the gas yield. The gasification yield with $ZnCl_2$ was also significantly enhanced by acid pretreatment.

Qader (72) described the catalytic hydropyrolysis of coal in a hanging-basket reactor (HBR) and a fluidized-bed reactor (FBR) at high pressure and relatively low temperature (550°C). Hydrogen pressure did not affect the non-catalytic conversion but did significantly increase the catalytic conversion. The catalytic product was lighter and contained substantial amounts of light and middle oils. The absence of an improved non-catalytic conversion with hydrogen pressure, in contrast to other studies, was attributed to the high-pressure operation (2000 psi). The effect of temperature, pressure, and reaction time on catalytic and non-catalytic hydropyrolysis in a hanging basket reactor is shown in Figure 6-5. The crucible was lowered into the hot zone after the system stabilized and was kept there for different periods of time. A pre-reduced tungsten disulfide catalyst was used, and significant



Source: Ref. 17.

Figure 6-3. Effect of $ZnCl_2$ on Total Carbon Conversion of MRS and UB Coals at 13.8 MPa H_2 Pressure



Source: Ref. 17.

Figure 6-4. Effect of Acid Washing on MRS Coal with $ZnCL_2$ at 467° to 482° Reactor Temperature, 13.8 MPa H_2 Pressure.

Table 6-1. Effect of Additives on Conversion of MRS Coal at 467° to 482°C, 13.8 MPa

Catalyst	Wt % Added	Actual % C Converted			Catalyst Activity Ratio		
		Total	To Gas	To Liquids	Overall	Gasification[4]	Liquefaction
None	0	8.6	3.1	5.5	1	1	1
HCOONa	10	9.6	4.8	4.8	1.1	1.5	0.9
$(NH_4)_6Mo_7O_{24}4H_2O$	10	6.1	1.5	4.6	0.7	0.5	0.8
$Ni(NO_3)_2$	10	18.5	3.1	15.4	2	1.0	2.8
$NiCl_2$	10	17.1	2.3	14.8	2	0.7	2.7
$FeCl_2$	10	14.0	5.7	8.3	1.6	1.8	1.5
ZnS[1]	10	4.2	2.1	2.1	0.5	0.7	0.4
FeS[2]	10	3.8	1.9	1.9	0.4	0.6	0.3
Si/Al[3]	10	6.2	3.9	2.3	0.7	1.3	0.4
$AlCl_3$	10	6.9	1.9	5.0	0.8	0.6	0.9
$FeCl_2$/HCl Wash	10	6.9	2.3	4.6	0.8	0.7	0.8
HCl Wash	--	5.6	1.8	3.8	0.6	0.6	0.7
ZnCl/ZnS[1]	1/9	8.8	2.2	6.6	1.0	0.7	1.2
$ZnCl_2/FeCl_2$	2/8	16.1	3.8	12.3	1.9	1.2	2.2
$ZnCl_2$	8.5	43.7	4.2	39.5	5.1	1.4	7.2
$ZnCl_2$/HCl Wash	10	87.8	13.9	73.9	10.2	4.5	13.4

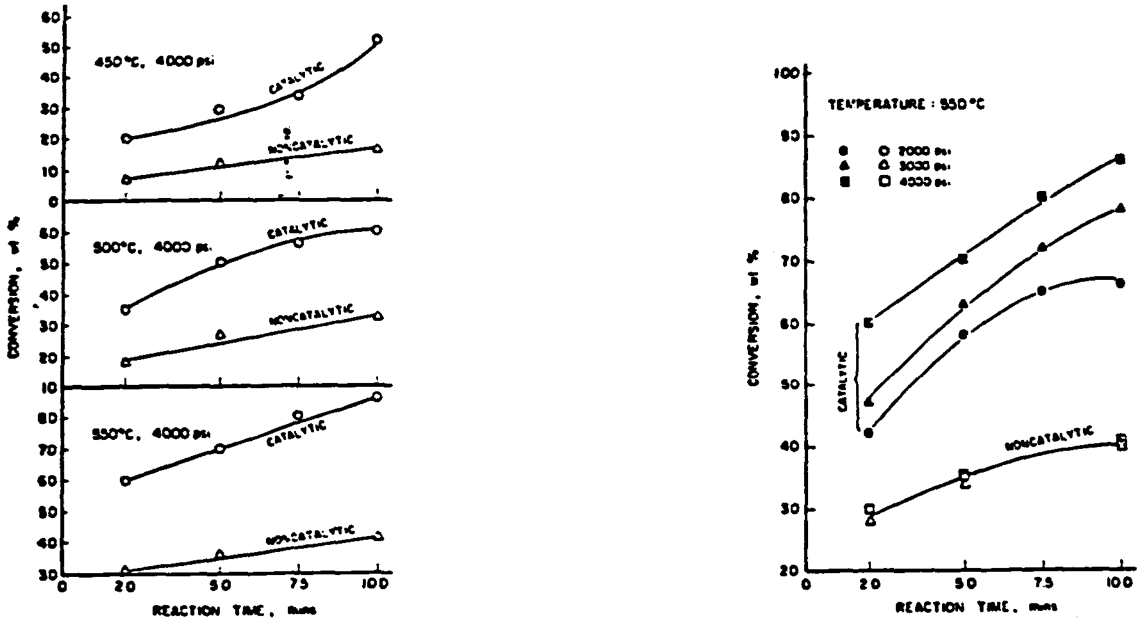
[1] Zinc Sulfide Concentrate (59% S, 20% FeS and 2% CuS)

[2] Iron Sulfide Concentrate (58.7% Fe, 38.6% S, .2% Zn and .3% Cu)

[3] Silica-alumina Catalyst (Aero-Cat cracking catalyst by American Cyanamid)

[4] Calculated by IGT

Source: Ref. 71.



a. **Effect of Temperature and Reaction Time on Conversion**

b. **Effect of Pressure and Reaction Time on Conversion**

Source: Ref. 72.

Figure 6-5. Effect of Temperature and Pressure on Catalytic and Noncatalytic Hydropyrolysis .

improvements in yield with the catalyst were seen in all cases. The improvements increased at higher temperatures and pressures.

Exploratory experiments in an entrained-flow reactor with New Mexico subbituminous coal impregnated with 10 weight percent Na_2CO_3 were performed to study its catalytic effect. There was no significant effect on the product yields or the temperature of the maximum BTX yield from rapid hydropyrolysis as compared with the results obtained for untreated coals (73).

6.2.4 Characteristics and Properties of Pyrolysis Products

Preceding sections in this review of pyrolysis as a coal liquefaction technology have dealt with coal structure, the chemistry and the mechanisms of pyrolysis reactions, and their catalysis. This section, drawn from Reference 5, contains a discussion of the characteristics and the properties of pyrolysis products. In addition to liquids, which are the main concern of this assessment, pyrolysis processes also produce char as a major product. Thus, the characteristics and the properties of both product liquids and solid char are important to the development of pyrolysis processes and are considered in this assessment of long-range research needs.

6.2.4.1. Properties of Pyrolysis Liquids or Tar

The point was made earlier that process conditions associated with maximum liquid yield produce increasing quantities of a high-boiling fraction as a major part of the recovered liquid. This point is illustrated in Table 6-2 where the elemental and distillation analyses of the liquids from three processes are shown: COED (74), Lurgi Ruhrgas (75), and Occidental Flash Pyrolysis (76). The heaviest fraction (+425°C or +400°C) represents 50 percent or more of the recovered liquids. Similar results were observed in the Consol program where the +400°C fraction represented 69 percent of the total liquid at the highest yield conditions (77). This characteristic indicates the need for hydrotreating to produce lighter products. Hydrotreating is also

Table 6-2. Characteristics of Liquids From Coal Pyrolysis Processes

	COED Process (A)	COED Process (B)	Lurgi Ruhrgas (C)	OR Flash Pyrolysis (D)
Elemental Analysis:				
H	9.6	7.7	6.4	7.2
C	84.2	82.9	82.3	77.6
N	0.7	1.2	1.3	1.2
O	5.1	6.8	8.3	13.6
S	0.4	1.4	1.8	0.4
Distillation Analysis (Wt. %) °C - 1 atm:				
-230	0	0	11.8	14.8(1)
230-270	10.0	10.0	3.2	
270-425	40.0(4)	30.0	18.6	28.0(2)
+425	50.0(5)	60.0	66.4	57.2(3)

(A) Utah Coal
(B) Western Kentucky Bituminous Coal
(C) West Virginia Bituminous Coal
(D) Wyoming Sub-bituminous Coal

(1) -260°C
(2) 260-400°C
(3) +400°C
(4) 288-460°C
(5) +460°C

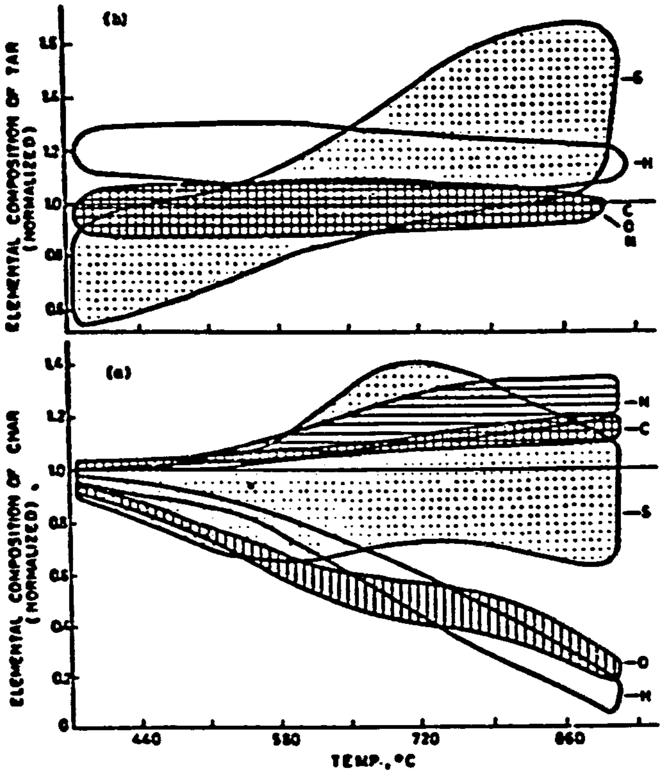
Source: Ref. 5.

required to eliminate the relatively high concentration of heteroatoms. These heteroatoms adversely affect storage stability and compatibility with petroleum-derived fuels. In addition, the nitrogen and sulfur contents would preclude meeting NO_x and SO_x environmental standards following combustion.

An attempt to determine how coal rank and temperature influence heteroatom distributions as well as distributions of major elements (H, C, and O) was made by Solomon (78) for a specific high-heating-rate reactor. The results of this study for 12 bituminous coals, showing elemental compositions of char and tar normalized to the compositions in the parent coal as a function of temperature during rapid pyrolysis, are shown in Figure 6-6. Tars are found to be virtually identical with their parent coals in carbon, oxygen, and nitrogen contents, but rich in hydrogen. The sulfur contents of both char and tar vary most widely with the nature of the parent coal. The large variations in the sulfur contents of tar and char produced from coal pyrolysis (as shown in Figure 6-6) are due to wide variations in the compositions of various forms of sulfur in coals. Tar containing a high oxygen content tends to be unstable (i.e., it polymerizes rapidly during storage). In general, oxygen and other heteroatoms (e.g., N, S) are found in greater concentrations in the higher-boiling fractions of tar. It needs to be stressed that the data presented in Figure 6-6 are typical examples of the distributions based on 12 bituminous coals. The distribution of species in coal tars and chars is a strong function of pyrolysis conditions and coal type (e.g., lignite versus bituminous).

6.2.4.2 Char Characteristics of Pyrolysis

The quality of the char produced in pyrolysis processes is a factor in char utilization. Char properties depend strongly on the coals from which the chars originated and the conditions of the particular pyrolysis process. The proximate and ultimate analyses of the feed coals and product chars from two pyrolysis processes are compared in Table 6-3. In both cases the hydrogen content and the H/C ratio of the chars are



Elemental Compositions of Char (a) and Tar (b) Normalized to the Compositions in the Parent Coal, as a Function of Temperature in the Rapid (e.g., ~10^4 °C/s) Pyrolysis. Based on the data of Solomon (1981) on 12 bituminous coals. Residence Time: 20 s.

Source: Ref. 78.

Figure 6-6. Elemental Compositions of Char and Tar Normalized to the Compositions in the Parent Coal

Table 6-3. Properties of Feed Coals and Product Chars

	COED		Occidental	
	Coal	**Char**	**Coal**	**Char**
V.M.	41.4	5.2	38.0	
Ash	8.5	17.3	6.6	13.8
Ultimate Analysis (% MF)				
C	75.3	79.5	68.22	76.7
H	5.7	1.4	4.7	2.3
N	1.2	1.3	1.1	1.3
S	0.6	0.5	0.6	0.6
O	8.7	---	18.8	5.3
Ash	8.5	17.3	6.6	13.8
Btu/Lb (Dry Basis)	13,860	12,180	9,400	11,940

Source: Ref. 5.

reduced as compared to the starting coals. Similar reductions in volatile matter are observed, with a corresponding increase in ash content. Oxygen content is reduced.

The elemental compositions of char from bituminous coals normalized to the compositions in the parent coal as a function of temperature during rapid pyrolysis were shown previously in Figure 6-6. It can be seen that the oxygen and hydrogen contents of char drop sharply with an increase in temperature. There is little change in the carbon and nitrogen contents.

In the case of low-rank coals exemplified by the Western subbituminous coal used in the Occidental process, a substantial loss of oxygen as CO and CO_2 is observed. Loss of oxygen results in a net increase in the Btu content of the char. If the Btu content of the char in the Occidental process is compared to that of the starting coal, a net increase of Btu content from 9400 Btu/lb to 11,940 Btu/lb is observed.

Because the volatile-matter content in the char is severely reduced, the char may be a substantially more refractory solid fuel for combustion. The sulfur and nitrogen contents in the char are essentially unchanged with respect to the levels in the feed coal. From the standpoint of meeting environmental standards, coals which require flue gas scrubbing would produce chars which must be handled similarly because the sulfur content of the recovered char is not reduced significantly compared to that of the starting coal.

6.2.5 Upgrading of Pyrolysis Products and Their Utilization

Efficient utilization of all generated solid, liquid, and gaseous products is vital for the overall process economics of a pyrolysis system. A number of viable alternatives can be considered for utilization of these products. The generated products may require varying degrees of treatment before they become usable. For example, the stream exiting the pyrolyzer unit will require separation of gas, liquid, and particulates. The unit operations (e.g., hot dust removal cyclones, quench/particulate scrubber towers, and Venturi scrubbers to remove tar mist) required for separation may be similar to those used for a fixed-bed gasifier (e.g., cold gas cleanup). The gas stream may require, depending on its end usage, a sulfur removal process. In addition, a pyrolysis plant will also require processes for wastewater treatment. Finally, environmental factors such as toxicology of the pyrolysis liquids need to be considered. An excellent investigation regarding the toxicological aspects of devolatilization products is available (79).

6.2.5.1 Upgrading of Pyrolysis Liquids

A. Solids Carryover with Liquid

The first issue involved in the upgrading of raw pyrolysis liquids is that of solids carryover. Processes which utilize a fluidized bed, an entrained bed, or mechanical mixing of char and coal all result in a significant carryover of char into the recovered liquid product. The particle size of the solids carried out is extremely small because of the size segregation produced by the gas used to sweep out the liquid products.

Filtration or other mechanical means of separating solids have not proven satisfactory because of the small size of the solids, the viscosity of the liquids, and the difficulty of scaling the separation device. The resulting clean liquid still contains sufficient solids to be unacceptable as feed for a fixed-bed hydrotreater without a severe economic penalty.

Attempts have been made to use hot cyclones and mechanical filters between the pyrolysis reactor and the liquid recovery section. With respect to filters, operations on a pilot scale have not been successful, resulting in rapid filter plugging. While cyclones are useful, in the case of the Lurgi Ruhrgas process, a char carryover exceeding 12 percent of the recovered liquid is observed. In the case of COED liquid, solids carryover from 2.5 to 10 weight percent of the recovered oil was reported. Lower solids carryover was observed in some of the other processes depending on the fraction of fine char produced and the ratio of sweep gas to coal.

External filtration was proposed in the COED and Occidental Flash Pyrolysis processes. While this approach is operable on a bench- or pilot-plant scale, it has not been demonstrated commercially in the sense that filtrate may still contain several thousand parts per million of solids, which in turn cannot be handled by conventional fixed-bed hydrotreaters. The whole question of scaling a pressure filter for commercial operation has not been addressed. Judging from the experience with pressure filters in direct liquefaction, pressure filtration is not a practical unit operation.

There are a number of alternatives which can be considered, some of which have been evaluated. These include:

- Solvent deashing with an antisolvent
- Hydrotreating with an expanded-bed catalyst reactor, e.g., H-Oil or L.C. Fining.

B. Upgrading of Raw Liquid Fuel

Because of their high-boiling character and high heteroatom content, raw pyrolysis liquids must be hydrotreated. First of all, their hydrogen content must be increased; in general, the H/C atomic ratio for pyrolysis liquids is lower than that for various petroleum feedstocks. This ratio varies from 1.8 to 1.9 for No. 2 fuel oil, and from 1.7 to 1.8 for No. 6 fuel oil. By comparison, the H/C atomic ratio for pyrolysis liquids ranges from 0.9 to 1.5. In addition, they appear to be significantly more aromatic (e.g., 50 to 70 percent) than petroleum-based fuels (e.g., No. 2 fuel oil has about 20 percent aromatic carbon, and No. 6 fuel oil about 40 percent aromatic carbon). Finally, the heteroatoms must be reduced so that the refined liquids will be stable during storage, compatible with petroleum derived fuels, and meet environmental standards when burned.

In the case of the raw tar from the COED process, a filtered sample was hydrotreated (<u>80</u>) under the following conditions:

Reactor Temperature	410°C
System Pressure	2450 psi
WHSV	0.44
Catalyst	Ni/Mo + Co/Mo

A comparison of the properties of the oil feed with those of the syncrude product is as follows:

	Feed	Syncrude
C,wt%	83.80	85.68
H,wt%	8.90	13.00
O,wt%	5.72	1.09
N,wt%	1.10	0.22
S,wt%	0.042	0.01
API°	-1.0	20.10

The yield of syncrude was 93.5 weight percent and 108.3 volume percent of the feed. The hydrogen consumption was 3300 SCF/bbl.

The syncrude contained 92 percent material identified as heavy oil and boiling above 200°C with an endpoint of 532°C. Naphtha content, a gasoline precursor, was very small. While the properties of the raw feed were improved, this product would only be useful as a distillate fuel oil. Additional hydrotreating-hydrocracking would be needed to produce a slate containing high-octane gasoline, diesel fuel, jet fuel, and distillate fuel oil.

The fixed-bed hydrotreater consisted of two identical vessels containing hydrotreating catalyst. The first reactor served as a guard chamber. The filtered feed contained in excess of 3500 ppm of solids (600 ppm ash), which is an order of magnitude higher solids loading than is considered acceptable for a fixed bed. Solids loading is normally about 100 ppm maximum for a petroleum feed to hydroprocessing. Such solids loadings will normally reduce the operating cycle from a practical

6 months to 1 year to a short period, with the obvious economic implications. This situation suggests that a practical commercial filter design and a practical fixed-bed hydrotreater configuration have not been demonstrated.

An independent study was reported by Occidental Research on hydrotreating the filtered flash pyrolysis "tar" (81) from a sub-bituminous coal. Fixed-bed hydrotreating was used. Conditions were similar to those reported by FMC for COED tar hydrotreating:

Temperature	400°C
Pressure	2500 psi
WHSV	0.95

An unidentified CoMo catalyst was used for the experiment. The feed analysis is compared with that of the hydrotreated syncrude:

	Feed	Syncrude
C,wt%	85.8	88.10
H,wt%	6.9	10.40
O,wt%	1.2	0.25
N,wt%	0.5	0.02
S,wt%	5.6	1.00
API*	-7.6	17.00

Hydrogen consumption was 3100 SCF/barrel.

The hydrotreating runs were of extremely short duration (40 hours) and do not demonstrate the suitability of a fixed-bed hydrotreater for a relatively heavy feed which still contained in excess of 2500 ppm of solids (300 ppm ash) after filtration, just as in the case of COED liquid. While a substantial improvement in liquid quality is observed, the large consumption of hydrogen does not produce the increased H/C ratio, nitrogen elimination, and oxygen reduction observed when direct liquefaction syncrudes are hydrotreated.

The properties of the hydrotreated pyrolysis liquids from COED and Flash Pyrolysis are compared in Table 6-4. Distillation of the hydrotreated syncrude upgrades the raw pyrolysis liquids but still leaves

Table 6-4. Key Properties of Hydrotreated Pyrolysis Liquids

	COED LIQUID		ORC FLASH PYROLYSIS LIQUID
C, wt%	85,7[1]	87.9[2]	88.10
H, wt%	13.00	10.20	10.40
O, wt%	1.10	1.30	1.00
N, wt%	0.22	0.60	0.25
S, wt%	0.01	0.03	0.02
API°	20.10	19.0	17.00
H/C	1.75	1.39	1.41
Sulfur in Feed Coal	0.60		0.80

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1. Fixed-bed hydrotreatement.
2. H-Oil hydrotreating of pyrolysis liquid derived from W. Kentucky coal.

Source: Ref. 5.

an undistilled residue. This residue may vary from 10 percent for liquid derived from Utah coal to 40 percent for a pyrolysis liquid from a high-volatile Eastern coal like Pittsburgh Seam or Western Kentucky.

The comparative hydrogen consumptions to prepare the respective products are 5000 to 6500 SCF/bbl for direct liquefaction and in excess of 3000 SCF/bbl to pre-refine the pyrolysis liquids. An additional 450 to 1300 SCF/bbl of hydrogen net is required to produce commercial products from liquefaction syncrudes. A similar amount will be required in addition to the 3000 SCF+ for pyrolysis liquids as a minimum. It must be recognized that in the case of pyrolysis liquids, the yield of high-quality transportation fuels is about 1.0 to 1.5 barrels/ton compared to 4+ barrels/ton from direct liquefaction.

The tar made by catalytic hydropyrolysis was upgraded in a fixed-bed hydrotreater (68). The catalyst was NiMo on alumina. The temperature was 400°C. Virtually all of the tar was converted to distillable material boiling below 400°C, with up to 40 percent boiling in the naphtha range.

Some important research needs in the upgrading of pyrolysis liquids can be identified as follows (3):

- Combustion characteristics of coal pyrolysis liquids need to be investigated. Fundamental aspects such as feeding, atomization, stability, combustion behavior, viscosity, pollution, and slagging potential of various coal tars need to be better understood.
- There is a pressing need to develop low-cost novel poison- and coke-resistant catalyst systems for reducing N and S compounds present in coal liquids. Deactivation of existing catalysts is a problem when the heavier fractions of pyrolysis liquids are processed by fluid catalytic cracking or catalytic hydrogenation.
- Further investigation regarding separation of fine suspended solids (e.g., inorganics) from liquid products is needed.

- Toxicological problems (e.g., mutagenicity, carcinogenicity, skin irritability, aquatic toxicity) are of enormous significance in proper utilization of pyrolysis products. Further studies are needed to define the potential toxicological and arcinogenicity problems. Needed information includes (a) the nature of products generated and their health and environmental impacts as a function of pyrolysis conditions such as varied residence time and temperatures, and (b) effects of catalytic materials on these products.

6.2.5.2 Char Utilization

As noted above, the char produced in coal pyrolysis processes can amount to 50 percent or more of the weight of the dry coal feed. The efficient, economic utilization of this solid product is vital to the overall process economics of a pyrolysis process. Pyrolysis char has a number of potential applications:

- On-site char combustion for production of energy which can be supplied to the pyrolysis process.
- Off-site char combustion in an electric power plant.
- Gasification to produce H_2 (for hydropyrolysis or tar hydrotreatment, if included in the process).
- Other applications (e.g., production of activated carbon, molecular sieves).

As discussed above, the properties of chars depend strongly on the coals from which they originated, and on the conditions at which the coals are processed. For example, the chars produced from lignites (which contain relatively higher surface areas and more well-dispersed metal cations than those noted for cokes produced from bituminous coals) are relatively more reactive in combustion and gasification conditions.

Pyrolysis char can perhaps be most efficiently utilized as boiler fuel (4). When an existing boiler is employed, problems may be encountered which result from the char having a lower volatile content, higher ash-content, different reactivity, and different particle-size distribution than the coal for which the boiler was designed. These different char properties introduce major uncertainties in the use of char for combustion in conventional combustors. However, the literature contains a recent review (82) of the data and the theory regarding combustion of char in the pulverized-coal boilers. This analysis showed that retained volatile matter was not an important parameter in judging the suitability of char for combustion in conventional boilers. During the pyrolysis process rapid heating of the coal appears to favor production of a reactive-pore structure in the char particles.

Unfortunately, the sulfur content of the coal splits between the gas, liquid, and char pyrolysis products. For this reason, pyrolysis alone is not a simple solution to the control of sulfur emissions from combustion of high-sulfur coal. The lower water and hydrogen contents of char in comparison to coal will increase the efficiency of boilers slightly. In come cases, cyclone-type furnaces will be more attractive for burning char than pulverized-coal burners. Since char is dusty, bulky, and perhaps pyrophoric, there is considerable incentive to burn the char directly without intermediate storage or shipment. The heat content of the hot char can also be conserved when the char is burned without cooling.

Fluidized-bed boilers are being employed for industrial use, and larger utility-size boilers are under development. There are excellent opportunities to combine coal pyrolysis with atmospheric fluidized-bed boilers, and high-pressure hydropyrolysis processes with pressurized fluidized-bed boilers. However, additional experiments need to be performed to examine the viability of coal-char combustion using a wider selection of feedstocks. There are considerable data gaps on the combustibility of char-water mixtures, such as ignition, flammability, and slagging characteristics.

Finally, char can be gasified to produce hydrogen, which can be used in the pyrolysis plant if the process requires hydrotreatment (e.g., tar upgrading or hydropyrolysis). Using char as the feedstock for hydrogen production instead of raw coal preserves the pyrolysis liquid and gases for higher-value uses.

Because a large portion of the product from pyrolysis is char, the usage of char is one of the most important determining criteria for the viability of a pyrolysis process. Some research needs in char utilization are summarized below (3).

- Combustion of Char: The volatile-matter content of the char, depending on the pyrolysis process, is significantly lower than in the parent coal. Therefore, ignition and combustion characteristics of char may impose serious limitations on its use in existing pulverized combustors. Fundamental aspects of combustion of char and char-coal mixtures need to be addressed (e.g., ignition flammability, flame stability, and slagging characteristics). Finally, the links between devolatilization conditions of coal and the reactivity of the resulting char need to be better defined.

- Processing of Char: Relatively little is known regarding the linkage of heteroatoms (N, S) and minerals in char. Very little information is available regarding the possibility of removal of these materials (N, S, and mineral matter) by subsequent treatment. For example, treatment of char with steam or a steam/carbon dioxide mixture may facilitate removal of these materials. Further work needs to be done in these areas.

- Char Slurry: The feasibility of producing a char-water slurry for pipeline transport needs to be considered (e.g., solid loadings in the slurry as a function of char characteristics need to be determined).

- Slagging Characteristics of Char: Fundamental studies regarding the slagging nature of chars and the corresponding coals need to be performed.

- Alternative Usages of Char: The feasibility of combustion of char in fluidized-bed combustors needs to be further examined. The concept of gasification of char as a means of producing H_2 to upgrade tar appears to be attractive; the economic feasibility of this concept needs further studies.

6.3 PROCESS DEVELOPMENT

6.3.1 Descriptions of Advanced Low-Temperature Pyrolysis Processes

In a recent analysis by the MITRE Corporation (5), the advanced low-temperature pyrolysis process being developed by FMC, Consolidation Coal Company, Lurgi Ruhrgas, and Occidental Petroleum were examined. Some of the results of that study are summarized here. The overall characteristics of these processes and their scale of operation are summarized in Table 6-5 (5). Fluid-bed, mechanically stirred, and entrained-bed configurations were studied in this development work. The developments of Consolidation Coal and Lurgi Ruhrgas were supported privately, and as a result, details are lacking. A range of coals of different rank was explored in these developments. Temperature conditions and vapor/solid residence times were selected to maximize liquid yields.

6.3.1.1 FMC-COED Process

The COED process (74) uses multi-stage fluidized-bed carbonization of coal at ambient pressure. A simplified process configuration is illustrated in Figure 6-7. The hot fluidizing gases flow counter-currently to the net forward flow of solids, thereby heating the solids to successively higher temperatures. Heat and fluidizing gases are simultaneously generated for combusting part of the char with oxygen in the last fluidized stage (IV), which is operated at the highest temperature. The process was developed by FMC under contract to the Office of Coal Research. Process development was carried out in a 3-inch bench-scale unit, an integrated process development unit handling 1 ton of coal per day, and an integrated pilot plant converting 36 tons per day with product oil hydrotreating facilities.

Dried coal (-1/8" particle size) is fed to Stage I where it is heated to 315°C by hot oxygen-free fluidizing gas entering at about 482°C. Moisture and about 10 percent of the total tar yield are driven off from the coal. The tar is recovered as part of the total tar yield.

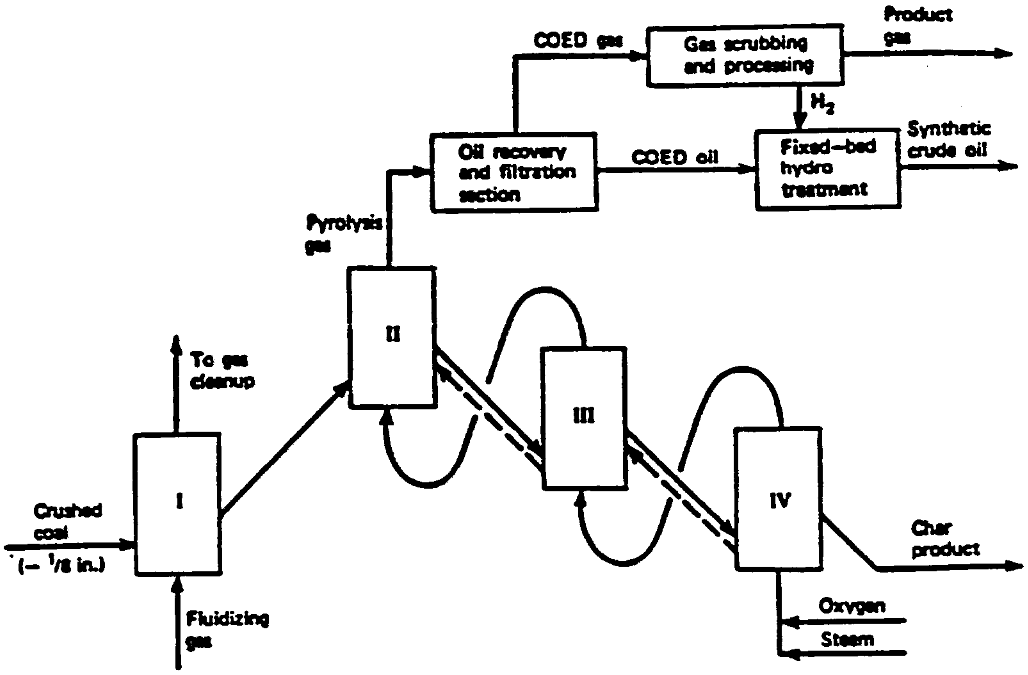
Table 6-5. Status of Advanced Pyrolysis Developments

Process	Coals Tested	Capacity (TPD)	Reactor Type	Residence Time (Seconds)	Temperature (°C)	Reactors
COED	Lignite-Bituminous	36	Multiple Fluid Bed	200-1000	450-540	4
Consol	Bituminous	24	Single Fluid Bed	3-10	500	1
Lurgi-Ruhrgas	Lignite-Bituminous	1.3-880	Stirred	1-5	650	1
Occidental	Bituminous Subbituminous	3	Entrained	3	650	1

Solids Residence Time

COED	1.4 hours
Consol	0.6-2 hours
Lurgi-Ruhrgas	>20 seconds
Occidental	3 seconds

Source: Ref. 5.



Source: Ref. 5.

Figure 6-7. COED Coal Pyrolysis

The coal softening temperature is increased so that the coal can be transferred from Stage I to Stage II, which is operated at 454°C. Heat is supplied to the second stage by hot gases from the third stage plus hot char from Stage III.

Most of the tar and pyrolysis gases are recovered from Stage II. Char from Stage II moves forward to Stage III, which operates at 538°C. When the process is operated with younger coals, Stage III temperature is adjusted to minimize vapor-phase coking of tar vapor. Heat is supplied to Stage III from Stage IV via hot gases and char. The balance of the tar is recovered from Step III via Stage II.

Stage IV generates heat and fluidizing gas to pyrolyze the coal using oxygen/air and steam. Ideally, the last stage is maintained at the highest temperature consistent with avoidance of clinkering. Only 5 percent of the coal as char is required to supply process heat. The rest of the char is recovered as product representing up to 63 percent of the dry coal.

A series of coals were investigated as feedstocks for this process. These ranged in rank from North Dakota lignite to a high-volatile (Ab) caking Pittsburgh seam coal. Product yields for four coals are summarized in Table 6-6 (80). Tar yields varied from 5.3 percent of the dry coal for lignite to 21.5 percent in the case of Utah coal. Char, the principal product, comprised 55 to 63 weight percent of the coal feed. The liquid product yields varied from 0.22 bbl/ton to 1.2 bbl/ton of coal. These yields are to be compared with direct liquefaction yields of 3.5 to 4.5 bbl/ton or more of a completely distillable syncrude, most of which is lower boiling than the tar from pyrolysis. The distillation analysis of this pyrolysis tar and its quality are examined in Section 6.2.4.1.

6.3.1.2 Consolidation Coal Studies

Consolidation Coal carried out an extensive program on fluidized coal pyrolysis, emphasizing conversion of highly caking Eastern coals.

Table 6-6. COED Process Product Distribution

	Coal			
	N.D. Lignite	Utah	Illinois	W. Kentucky
Yields, Dry Coal Basis (Wt. %)				
Char	55.8	54.5	59.5	63.0
Tar	5.3	21.5	19.3	17.3
Gas	37.6	18.3	15.1	13.0
Aqueous Liquor*	1.3	5.7	6.1	6.7

*Water containing water soluble organics produced during pyrolysis

Source: Ref. 5.

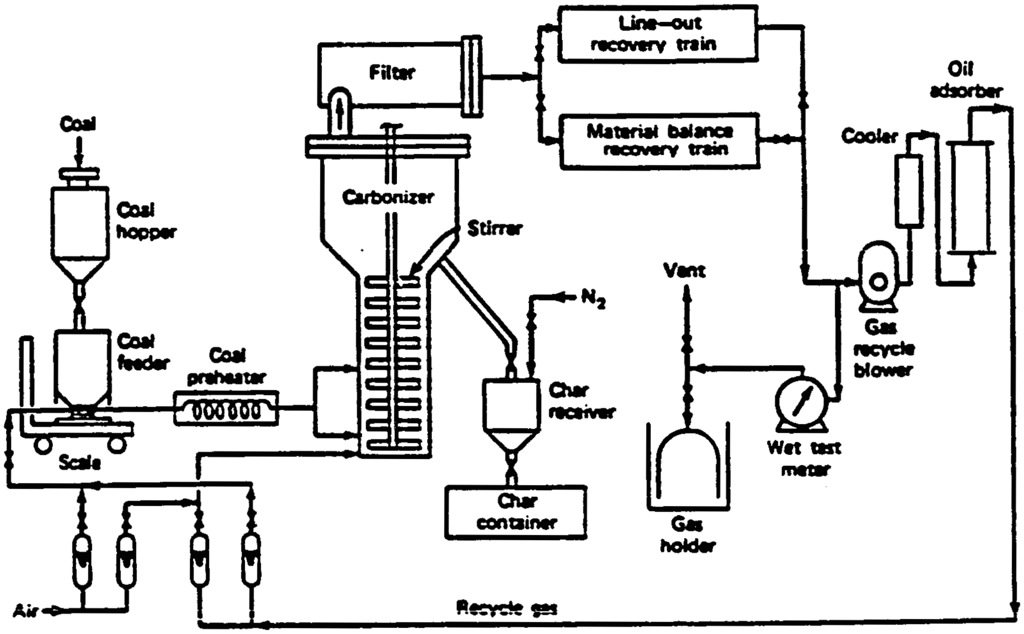
The study progressed from laboratory bench scale through PDU, culminating in the operation of a 36-tons/day pilot plant (76). Utilization of the liquid products for chemicals and the char as a utility fuel was planned.

The handling of highly caking coals necessitated preoxidation plus dilution by hot char in the fluid bed. A broad variable study was carried out in which the effects of sweep gas ratios, preoxidation level, and tar/char residence time were studied. This broad study was made possible by incorporating a stirrer in the fluid bed. A schematic diagram of the stirred carbonizer is shown in Figure 6-8. This scheme permitted the use of sweep gas rates in a PDU to match rates used in a commercial-size bed with adequate heat transfer and mixing to minimize agglomeration and defluidization. It was possible to operate this unit without any preoxidation even with strongly agglomerating Eastern coals.

The yield of tar (77) as a function of sweep gas rate (5 to 60 CF/lb MAF coal) increases with increasing sweep gas rate from 20 weight percent to 26 weight percent as compared with 15 percent in a Fischer assay (Figure 6-9). The increased yield is contributed entirely by material boiling above 400°C, indicating that the sweep gas volatilizes the heavier coal pyrolysis products before they can polymerize.

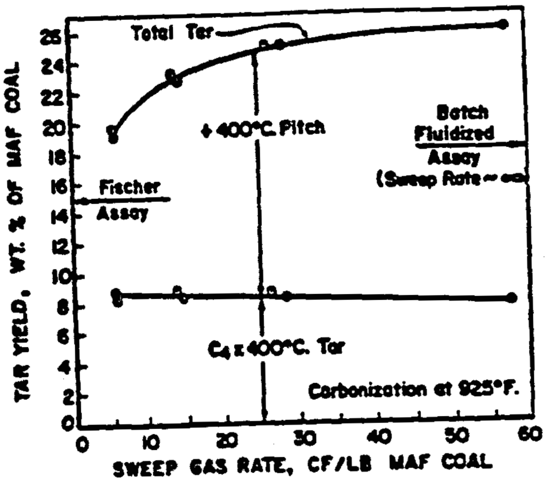
It was observed that in the large pilot plant which did not have the benefit of a mechanical stirrer, about 5 weight percent oxygen was required to avoid agglomeration when processing a highly caking coal. To evaluate the effect of preoxidation over a range of pretreatment levels, coal was preoxidized at 382°C followed by pyrolysis at 495°C in the stirred unit. The tar yields were combined from both stages. The yield decreased from 19.3 without preoxidation down to 13.5 percent with 6 percent preoxidation. Good agreement with the pilot-plant results was observed at 5 percent preoxidation.

The effect of solid and vapor residence times on tar yields was examined, and the results are shown in Table 6-7. It was observed that tar yields are independent of solids residence time over the range shown



Source: Ref. 5.

Figure 6-8. Stirred Carbonizer Unit



Source: Ref. 5.

Figure 6-9. Effect of Sweep Gas on Yields with Preoxidized Coal in Table 6-7. Vapor residence time was varied from 22 to 84 seconds. Yield decreased slightly with increasing residence time as a result of tar vapor cracking, but the effect is small. The maximum tar yield was observed at 480° to 510°C. These conditions should be compared with those in the Lurgi Ruhrgas unit, in which the residence time is much shorter and maximum tar yield requires temperatures of 620° to 650°C.

6.3.1.3 Lurgi Ruhrgas (LR) Process

Lurgi Ruhrgas developed a flash pyrolysis process which produced yields as high as 30 weight percent of the feed coal, when processing high-volatile coals. Caking coals can be used, but non-caking or slightly caking coals are preferred. Between 1940 and the early 1960's, this process was tested on a pilot scale at the Dorsten, West Germany, facility. Units capable of processing up to 10 metric tons per hour were available. A small commercial plant with a capacity of 800 tons/day has been operated in Yugoslavia since 1963.

A schematic flow diagram is shown in Figure 6-10. Coal is pyrolyzed rapidly by being mixed with a circulating hot char in vessel 2 with a mechanical mixer. Pyrolysis is completed at 750°C in vessel 4. The char mix is split into two streams. Product char leaves the system for use as a fuel. The other char is mixed with air, which preheats the char and lifts it into the hot char bin (2). Product gas liquor and tar are recovered from vessel 6, leaving the top of cyclone 5.

The product distribution from pyrolysis of a high-volatile West Virginia bituminous coal is as follows:

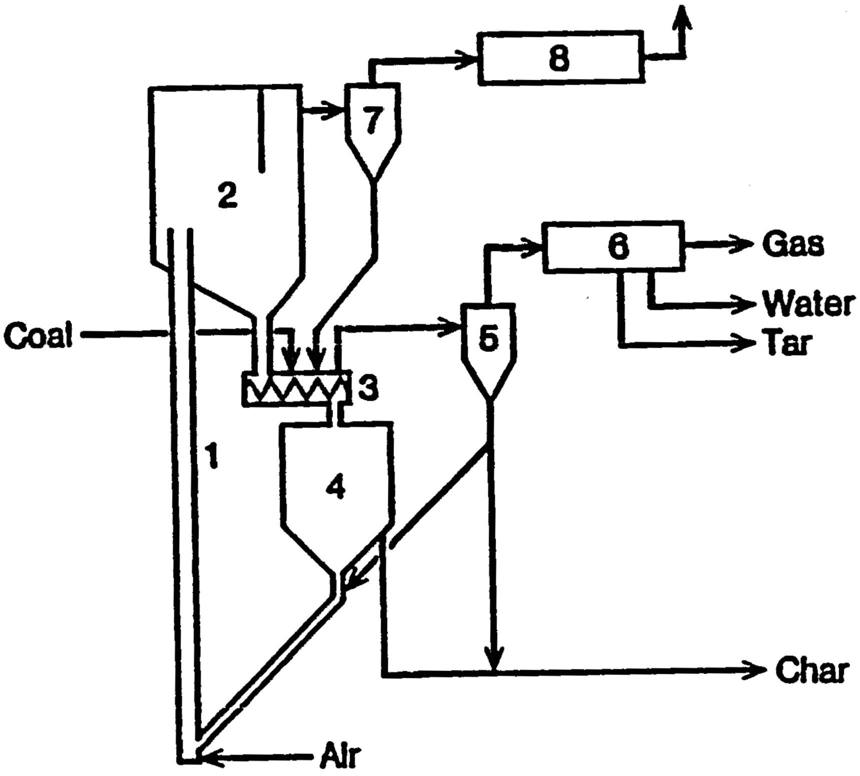
	Wt. % (MF Coal)
Gas + Liquor	14.0
Tar	28.0
Char	58.0

Yields of solids-free tar as high as 73 gal/ton (MAF coal) have been demonstrated. In common with other low-temperature pyrolysis processes, a major part of the tar is very high boiling (above 425°C).

Table 6-7. Effect of Vapor Residence Time on Tar Yield at 925°F

Vapor Residence Time (Sec.)						
Run No.	In Bed	Above Bed	Total	Solids Residence Time (Minutes)	Sweep Gas (Cf./Lb. MAF Coal)	Tar Yield (Wt. % of MAF Coal)
29	3	19	22	121	28	25.1
14	7	45	52	44.5	26	24.9
17	5	34	39	58	15	22.7
16	11	73	84	127	14	23.2

Source: Ref. 5 .



Source: Ref. 5.

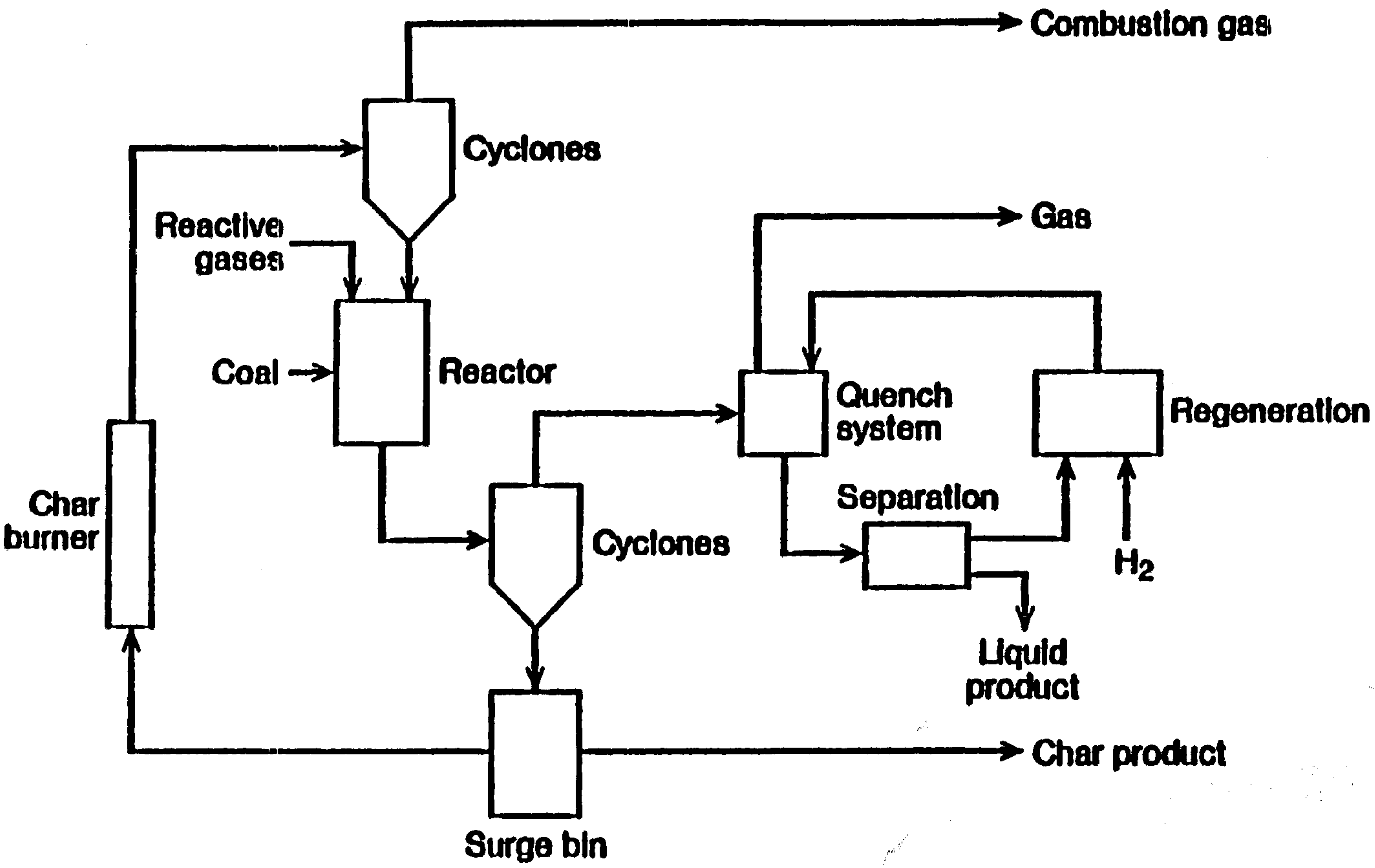
Figure 6-10. Lurgi Ruhrgas Flash Carbonization Process

6.3.1.4 Occidental Flash Pyrolysis Process (14)

The Occidental process (76) was designed to maximize liquid yield and handle a range of coals including agglomerating coals without preoxidation. The process is based on rapid pyrolysis by providing extremely high heating rates (6000°C/second), hot char, high coal dilution with char, and low partial pressure of tar vapor with inert sweep gas. Since 1970 Occidental Research Company (ORC) has built and operated four small-scale bench reactors and a 3-tons/day PDU.

A schematic flow sheet of this entrained pyrolysis process is shown in Figure 6-11. A portion of the char collected in cyclones downstream from the reactor is heated by direct heat exchange with char combustion gases. The reheated char is returned to the reactor to be mixed with coal. Vapor residence time in the reactor is short (2 seconds). The reactor configuration is designed to minimize contact between individual coal particles during the period when the coal particle is sticky. By use of high heating rates and appropriate upper temperature, the duration of this "sticky" period is obviously very short. Provisions for upgrading of crude tar and desulfurization of char were considered because of the problem of marketing both tar and char.

Yields of liquid as high as 36 weight percent were reported at temperatures of 580°C for a particular coal (81). The conditions required for these high yields were not demonstrated at steady-state conditions. The contractor concluded that a modified PDU was required for testing highly caking coals. The system worked well for a non-caking subbituminous coal, which produced 20-22 percent yield of tar on a MAF basis.



Source: Ref. 5.

Figure 6-11. Occidental Research Pyrolysis Process Flow Scheme

6.3.2 Technology Assessment and Economics.

6.3.2.1 Bechtel Group, Inc. Analysis

A technical feasibility study for demonstration- and commercial-scale pyrolysis plants was performed by Bechtel Group, Inc., for Utah Power & Light (6). This study included cost estimates for complete projects, including costs for the upgrading of the pyrolysis tar to a refinery feedstock, based on the Lurgi and Tosco pyrolysis processes and using Utah bituminous as feedstock. This coal produces a high yield of pyrolysis tar. The yields and the economics of this study, therefore, are not generally representative of pyrolysis processes, but apply only to a particular application of this technology. Nevertheless, the study was a thorough engineering evaluation of the technical readiness and the economics of pyrolysis at the time it was performed. It can serve to guide pyrolysis research in directions that will make the most significant improvements to the technology.

A. Background

Utah Power & Light (UP&L) evaluated the potential for reducing power generation costs through the use of coal pyrolysis in conjunction with electric power production. This potential cost reduction was to be realized through the sale of hydrocarbon liquids produced in the pyrolysis plant and the use of char fuel in place of coal in power station boilers. UP&L selected two sizes of pyrolysis plants for evaluation by Bechtel Group, Inc. (Bechtel): a demonstration-scale plant with a nominal coal capacity of 1000 short tons per day (TPD) and a commercial-scale plant with a nominal coal capacity of 20,000 TPD. For each size of plant, UP&L selected two coal pyrolysis technologies for evaluation: the Lurgi Ruhrgas (Lurgi) process and the Toscoal process.

The major objectives for this economic and technical feasibility study were:

- To develop conceptual process designs and capital and operating cost estimates for the demonstration- and commercial-scale pyrolysis plants

- To prepare a project implementation plan and schedule for the demonstration- and commercial-scale plants
- To evaluate the Lurgi and Toscoal technologies

The costs estimated by Bechtel in 1982 and the major conclusions of the study are summarized in the next sections.

B. Process Descriptions

In the Lurgi retort dried coal is pyrolized by contact with a large flow of hot recycle char that has been heated by partial oxidation with air and by combustion of fuel gas in an entrained-flow lift pipe. The Lurgi retort is a horizontal twin-screw mixer in which the coal and the recycle char are blended. At the exit of the retort, the hot pyrolysis gases separate, and the char falls into a surge bin from which both recycle and product char are withdrawn. The pyrolysis gases from the retort are next sent through condensers to collect the hydrocarbon liquid product (tar).

The Lurgi retort operates at a temperature of approximately 1150°F and produces a char product with a volatile-matter content of approximately 3 weight percent. The tar yield from the retort is approximately 1.2 bbl/ton of coal feed.

In the Toscoal retort dried coal crushed to minus 3/8 inch is preheated and then pyrolized by contact with 1/2-inch-diameter hot ceramic balls that have been heated through combustion of desulfurized fuel gas. The retort is a horizontal rotating cylinder in which the coal and the heated balls are quickly and uniformly blended. At the exit of the retort, the hot pyrolysis gases separate, and the ceramic balls are screened from the smaller product char particles. As in the case of the Lurgi process, the pyrolysis gases from the retort are next sent through condensers to collect the hydrocarbon liquid product.

The Toscoal retort operates at a temperature of approximately 930°F and produces a char product with a volatile-matter content between 15 and 17 weight percent. The tar yield from the retort is approximately 1.0 bbl/ton of coal feed.

The tar and naphtha products from the commercial-scale Lurgi and Toscoal pyrolysis plants are upgraded to refinery-feedstock quality in ebullated- and fixed-bed hydroprocessing units and are then sold. The tar and distillate products from the demonstration-scale plants are combined to form a synthetic oil to fuel a boiler and, therefore, need not be upgraded. The overall processing schemes for the demonstration-scale and commercial-scale plants are shown in Figures 6-12 and 6-13.

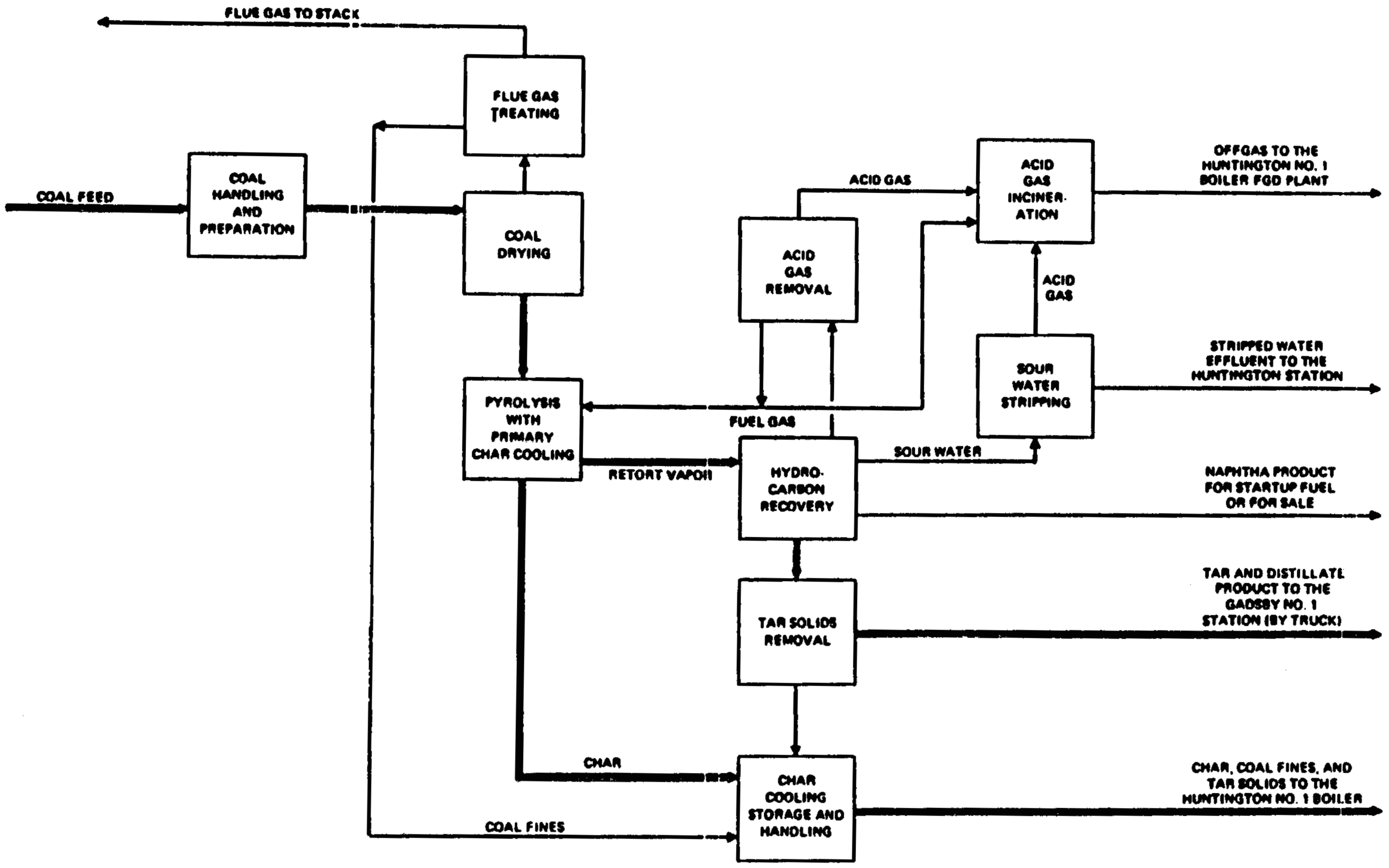
C. Conceptual Process Designs

Design and cost information was supplied to Bechtel by Lurgi Kohle and Mineraloltechnik GmbH (Lurgi) and Tosco Corporation (Tosco) for the coal drying, coal retorting, hydrocarbon recovery, and char-cooling sections of the pyrolysis plants. The supplied information was based on bench-scale testing of Utah coal by Lurgi and Tosco, and included pyrolysis product yields; rates and components of major process streams; characteristics of char, tar, and gas products; and utilities consumption (or generation).

Additional design and cost information was supplied to Bechtel by Combustion Engineering (C-E) Lummus and Tosco for the LC-Fining section of the commercial-scale Toscoal plant. The supplied information was based on bench-scale testing of Utah coal tar by Lummus, and included LC-Fining product yields, rates and components of major process steams, characteristics of the liquid and gas products, and utilities consumption (or generation).

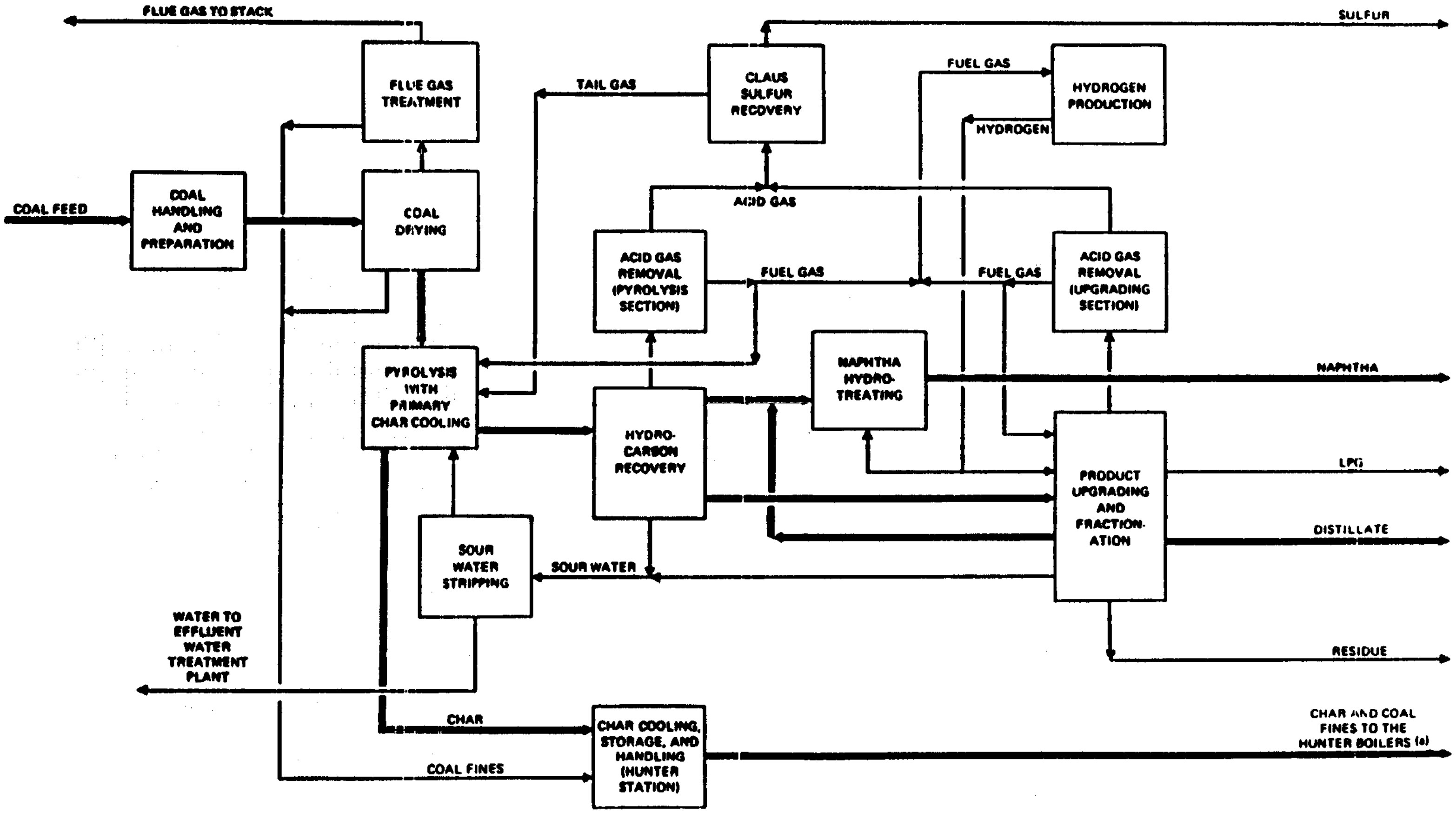
D. Coal Feed Rates and Retort Capacities

The coal feed rates to the Lurgi and Toscoal demonstration-scale



Source: Ref. 6.

Figure 6-12. Demonstration-Scale Pyrolysis Plant



(a) OPTIONALLY, SOME OF THE CHAR AND COAL FINES MAY BE DIVERTED TO THE HUNTINGTON STATION FOR FIRING IN THE BOILERS. FOR THIS, AN AERIAL TRAMWAY SYSTEM, TOGETHER WITH FACILITIES TO RECEIVE AND STORE THE CHAR AND COAL FINES AT THE HUNTINGTON STATION, HAS BEEN INCLUDED.

Source: Ref. 6.

Figure 6-13. Commercial-Scale Pyrolysis Plant

plants are 1000 and 1030 TPD, respectively. Each of the plants employs a single operating retort with no spare capacity.

The coal feed rates to the Lurgi and Toscoal commercial-scale plants are 18,000 and 21,630 TPD, respectively. The Lurgi plant employs four retorts, each with a coal capacity of 4,500 TPD (as received). The Toscoal plant employs two retorts, each with a coal capacity of approximately 10,500 TPD (as received). No spare retorting capacity is provided for either of the commercial-scale plants.

E. Product Yields

The major product yields from the demonstration-scale plants are given in Table 6-8.

The retort char, total boiler fuel (including char), and salable hydrocarbon liquid yields per ton of coal feed for the commercial-scale plants are as follows:

o Lurgi commercial-scale plant	
- Char yield, tons/ton of coal	0.47
- Total boiler fuel, yield, tons/ton of coal	0.56
- Hydrocarbon liquid yield, bbl/ton of coal	1.20
o Toscoal commercial-scale plant	
- Char yield, tons/ton of coal	0.60
- Total boiler fuel yield, tons/ton of coal	0.64
- Hydrocarbon liquid yield, bbl/ton of coal	1.00

The pyrolysis units and the related upgrading facilities were not optimized with respect to product yields or economic performance. For this reason, the relative yields of char and hydrocarbons may be subject to some degree of adjustment. The major product yields from the commercial-scale plants are given in Table 6-9.

F. Capital Costs

The capital cost estimates for the pyrolysis plants are order-of-magnitude, venture guidance types. The cost estimates are based on

Table 6-8. Major Product Yields from the Demonstration-Scale Plants

Item	Lurgi	Toscoal
Salable hydrocarbon liquids		
- Naphtha, BPD	-	51
- Tar, BPD(a)	1,111	966
Boiler fuels		
- Char, TPD	472	622
- Char and coal fines, TPD	20	28
- Fuel gas, MMSCFD	3.60	(b)

(a) Excludes tar loss with solids removal from tar products.

(b) Small quantity of excess gas is incinerated.

Table 6-9. Major Product Yields from the Commercial-Scale Plants

Item	Lurgi	Toscoal
Salable hydrocarbon liquids		
- LPG, BPD	812	818
- Naphtha, BPD	6,963	7,769
- Distillate, BPD	13,752	13,104
Boiler fuels		
- Char, TPD	8,493	13,060
- Char and coal fines, TPD	474(a)	610
- Residuum, BPD	1,683	772
- Fuel gas MMSCFD	29.1	(b)

(a) Excludes 91 TPD of flue gas desulfurization waste that is mixed with the recovered char and coal fines.

(b) Gas produced is all consumed for plant fuel and hydrogen plant feed.

third-quarter-1981 equipment, material, and labor prices. The capital costs for the demonstration- and commercial-scale pyrolysis plants are summarized in Table 6-10 and broken down by major categories in Figures 6-14 and 6-15. The proprietary technology related to the pyrolysis and the coal drying accounts for about 30 percent of the capital cost for the demonstration-scale plant and about 20 percent for the commercial-scale plant.

The Lurgi plant costs are higher than the Toscoal plant costs. There are four principal reasons for this:

- The larger number of Lurgi retorts (four versus two) and the associated flue gas combustion and heat recovery systems
- The larger number of Lurgi primary tar quench systems (four versus two) and the larger quantity of noncondensible distillation gas processed through the Lurgi system
- The larger Lurgi tar feed to the LC-Fining (tar upgrading) plant
- The requirements for sulfur removal from the Lurgi flue gases (SO_2 is released by combustion of char and sulfur-containing fuel gas in the Lurgi lift pipe)

G. Product Revenues and Operating Costs

Revenues from the liquid hydrocarbon product, the gas product, and other byproducts were estimated by UP&L using the unit prices listed in Table 6-11. The char price was estimated by UP&L, based on the capital and operating costs developed by Bechtel and on the product revenues.

The annual operating costs for the demonstration- and commercial-scale pyrolysis plants are summarized in Table 6-12. The operating costs are presented in third-quarter-1981 dollars and are based on an annual production factor of 90 percent for all plants. The Lurgi operating costs are lower than the Toscoal operating costs, primarily because of the differences in coal throughput.

Table 6-10. Capital Cost Summary

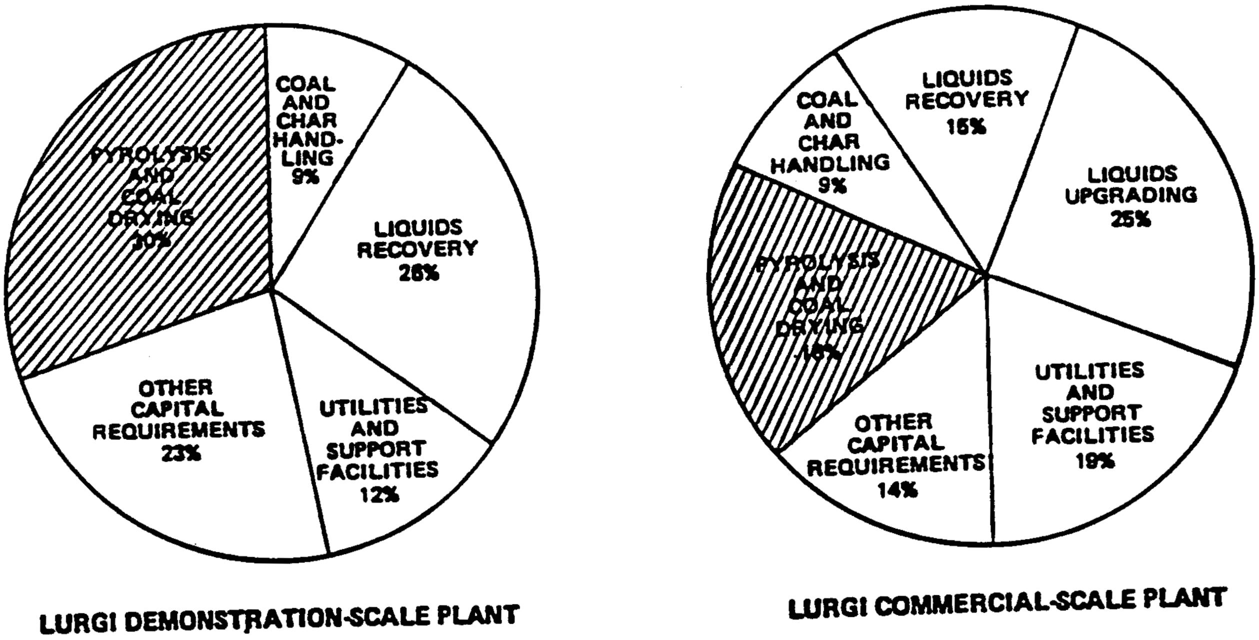
Item	Capital Costs, $ Million				
	Demonstration-Scale Plants		Commercial-Scale Plants		
	Lurgi	Toscoal	Lurgi	Toscoal	Toscoal(a)
Total plant investment(b)	61.0	44.0	694	630	663
Other capital requirements(c)	17.8	16.9	112	100	102
Total capital requirements	78.8	60.9	806	730	765

(a) Includes costs of associated facilities for handling and transporting 4,500 stpd of char from the Hunter Station to the Huntington Station.

(b) Includes contingency of 25% for demonstration-scale plants and 20% for commercial-scale plants.

(c) Other capital requirements include: initial catalyst and chemical charges, prepaid royalties, water purchase charge, preproduction (startup) costs, other owners' costs (e.g., costs for pilot plant testing and tradeoff studies), working capital, and land. An allowance for funds during construction (i.e., interest accrued on debt and commitment fees) has not been included in the other capital requirements.

Source: Ref. 6.

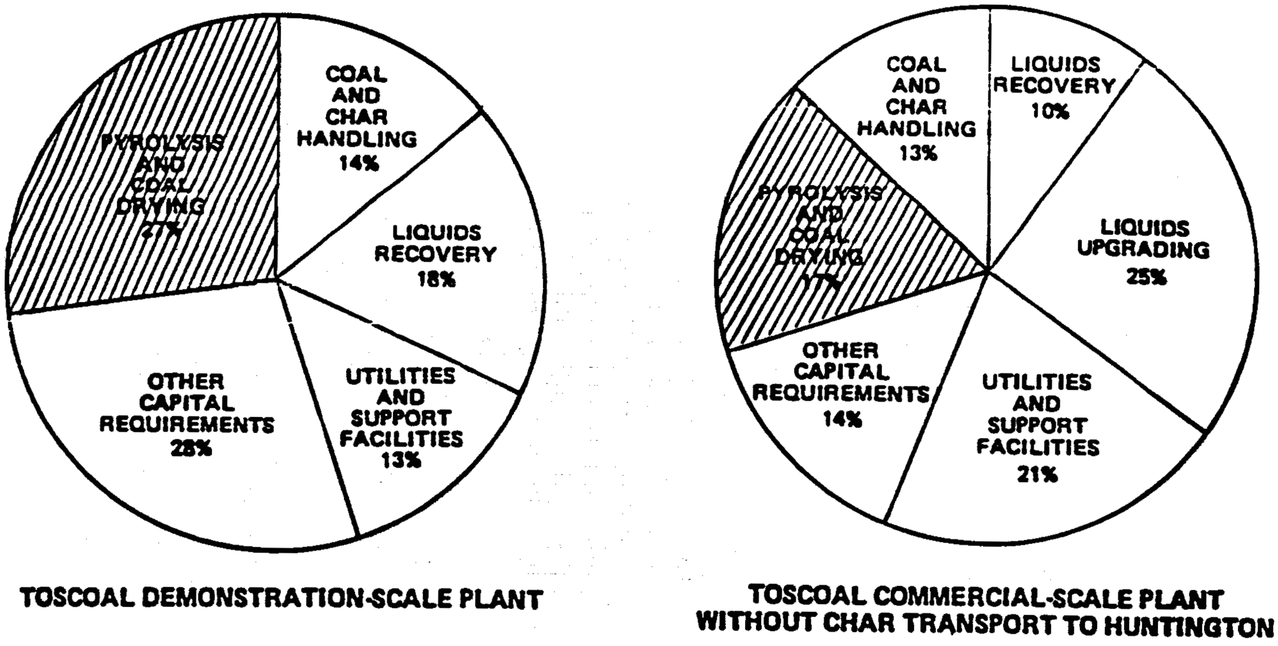


LURGI DEMONSTRATION-SCALE PLANT

LURGI COMMERCIAL-SCALE PLANT

Source: Ref. 6.

Figure 6-14. Breakdown of Capital Costs for Lurgi Plants



TOSCOAL DEMONSTRATION-SCALE PLANT

TOSCOAL COMMERCIAL-SCALE PLANT WITHOUT CHAR TRANSPORT TO HUNTINGTON

Source: Ref. 6.

Figure 6-15. Breakdown of Capital Costs for Toscoal Plants

Table 6-11. Product Unit Prices

Product	Unit Price	Notes
Demonstration-scale plants		
Condensate (C_4-400°F)	$36/bbl	(1)
Tar (400°F+)	$27.50/bbl	(2)
Centrifuge-cake	$1.36/MMBtu	(3)
Coal fines	$1.36/MMBtu	(3)
Commercial-scale plants		
Sulfur	$140/short ton	(2)
LPG	$22/bbl	(4)
Naphtha (C_4-400°F)	$36/bbl	(1)
Distillate (400°F-900°F)	$39/bbl	(5)
Residue	$1.36/MMBtu	(3)
Fuel gas	$1.36/MMBtu	(3)
Coal fines	$1.36 MMBtu	(3)

Notes:

(1) Based on a price of $1.00/gallon for 94 octane gasoline in Chicago, less the catalytic reforming process charge and transport charge from Chicago to Utah by pipeline.
(2) Price furnished by UP&L.
(3) Coal value per Btu.
(4) Estimate obtained from a major petroleum company for the price of LPG in Utah.
(5) Based on 50% of the product sold as No. 2 fuel in Chicago at $1.00/gallon and 50 percent sold as No. 5 fuel oil in Chicago at $0.90/gallon, less transport charges from Chicago to Utah by pipeline.

Source: Ref. 6.

Table 6-12. Annual Operating Cost Summary

Item	Annual Operating Costs, $ Millions				
	Demonstration-Scale Plants		Commercial-Scale Plants		
	Lurgi	Toscoal	Lurgi	Toscoal	Toscoal[(a)]
Coal	10.51	10.83	189.2	227.4	227.4
Purchased utilities[(b)]	1.04	1.19	33.8	33.8	33.8
Catalysts, chemicals, and lime	.03	—	3.8	3.1	3.1
Maintenance materials, miscellaneous supplies, and ceramic balls	.85	.64	9.7	9.3	9.7
Labor	5.91	5.59	23.0	21.0	21.6
Property taxes, insurance, and general corporate expenses	1.41	1.16	11.4	10.5	11.0
Total operating costs (third-quarter-1981 dollars)	19.75	19.41	270.9	305.1	306.6

(a) This Toscoal plant has additional facilities for handling and transporting 4,560 stpd of char from the Hunter Station to the Huntington Station. The differences in operating costs between the two plants are due to the increased capital required for the char handling and transportation.

(b) Purchased utilities includes costs for electric power, boiler feedwater, cooling water, and waste disposal. The electricity costs are based on nonregulated industry electricity pricing. For regulated utility financing, the electricity costs would decrease.

Source: Ref. 6.

Table 6-11 shows the product prices that Bechtel used in its economic study. The current low cost of crude oil would be reflected in significantly lower product prices today. Capital costs, however, would have escalated since 1981 when this study was made. Consequently, the economic attractiveness of this venture would be greatly diminished is considered today.

It is worth noting that the upgraded distillate products were assigned a value of about \$6/MMBtu, compared to \$1.36/MMBtu for heavy liquid and solid products. This value comparison clearly illustrates that pyrolysis technology must increase the yield of high-valued liquid products if if is to receive serious consideration for commercialization.

H. Project Risks and Uncertainties

The ultimate success of the UP&L coal pyrolysis project would have hinged primarily on its ability to produce a char suitable for burning in power station boilers at a cost per Btu lower than that of the parent coal. Unfavorable changes in the estimates of the following economic and process parameters reduced the chances of project success, and these changes constituted the major elements of project risk:

- Market value of liquid products
- Liquid yield and properties
- Char combustion and handling properties
- Plant operability
- Plant capital requirement
- Demand for char
- Scaleup

6.3.3 Environmental Considerations

Refer to Section 4.3.4. The environmental literature for direct liquefaction technologies suggests that direct liquefaction experience may be directly applicable to other liquefaction processes, including pyrolysis.

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CHAPTER 7

REVIEW OF COAL/OIL COPROCESSING[1]

7.1 INTRODUCTION AND SUMMARY

7.1.1 Introduction

Coprocessing is the simultaneous reaction of coal and petroleum resid, or crude oil, with hydrogen to produce distillable liquids. The technology may rightly be considered a variation of direct liquefaction, but its rapid development to commercial readiness entitles it to consideration as a separate technology. Petroleum liquids have been used as a liquefaction solvent since the early days of direct liquefaction, but principally for start-up or other situations in which coal-derived liquids were unavailable. It has only been within the last few years that serious consideration has been given to the process possibilities of hydrocracking petroleum resid while liquefying coal in the same reactors.

After a brief but successful development program, Ohio-Ontario Clean Fuels, Inc. (OOCF) has received a $45 million Clean Coal Technology award to build a plant in Warren, Ohio, to coprocess daily 800 tons of Ohio bituminous coal and approximately 8,000 barrels of Cold Lake (Alberta) reduced crude to produce 11,700 barrels of distillate liquids. This plant will be the first commercial application in this country of direct liquefaction technology. It is, therefore, incumbent on the research community to recognize coprocessing as an independent technology with its own unique features that require understanding and development.

This chapter reviews the fundamental research, the process developments in the 1980's, and the economics that are projected for the

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[1] This chapter was written by Christine W. Curtis, Auburn University, and Richard A. Winschel, Consolidation Coal Company.

Ohio-Ontario plant. Because coprocessing is a relatively new liquefaction technology, many researchers may not be familiar with its beginnings. The next section of this review describes the background of this technology. The reviews by Curtis (Section 7.3, Fundamental and Applied Research) and Winschel (Section 7.4, Process Development) show that the early research consisted principally of combining coal with various aromatic petroleum streams, such as heavy crudes, resids, and decant oils. More recent research has emphasized the ability of catalysts to increase coal conversion. The last sections of this chapter are based on process developments and economic evaluation by HRI, which is applying its Catalytic Two-Stage Liquefaction Process (see Chapter 4, Section 3) to coprocessing.

The following summary highlights the results of the panel's discussions concerning the status of coprocessing and the high-priority research recommendations developed by the panel.

7.1.2 Summary

Coprocessing is a relatively new approach to liquefaction, in which considerable fundamental research must be performed to support the ongoing process development and commercial demonstration. The current status of coprocessing is similar to that of direct liquefaction in the 1970's; process development has progressed rapidly, with fundamental research lagging. Much of the direct liquefaction research, particularly in the areas of hydrogen transfer and catalysis, may not be applicable because of the very different nature of the petroleum solvent/reactant.

Coprocessing research has emphasized the role of catalysts in effecting the simultaneous conversion of coal/petroleum resid. However, the major difference between direct liquefaction and coprocessing is the paraffinic nature of the oil (where oil is used generically to refer to petroleum streams), and this difference has thus far received little attention. Research in coprocessing must elucidate the solvating/hydrogen-transfer properties of the oil. Since the oil is also a source of lighter liquid products, the question arises as to how much of the products (naphtha, middle distillate, etc.) comes from coal and how much comes from oil? How is this product split affected by reaction conditions such as catalyst activity for hydrogenation and cracking, coal rank, and "heaviness" of the oil.

Analytical procedures for characterizing liquid streams and products will have to be reviewed and modified because of the paraffinic nature of the starting material. New analytical procedures will be of special importance in monitoring the reactivities (conversions) of coal or coal resid, and oil, and the product distribution attributable to each feed.

With this information on the background of coprocessing, the panel developed a number of research recommendations for this technology, including general research needs as well as detailed ideas for projects. The complete list of recommendations is included in Table E-1 in Appendix E. As indicated by the discussion in Section 7.3.1, much of the chemistry involved in coprocessing remains to be defined, and answers must be found to many fundamental questions, as indicated above. The panel gave the recommendation to study the fundamental chemistry of coal/oil reactions in coprocessing (Recommendation No. C1) the highest priority for this technology. Included in this recommendation is the study of the fundamentals of hydrogen donor chemistry with petroleum streams. As discussed in Section 7.3.1.3, some current work illustrates the importance of this area to the further development of coprocessing. Finally, in recognition of the considerable amount of development work currently being conducted in coprocessing, the panel considered process studies to be second in importance (No. C2), to study the effects of different feeds on reactivity, reaction conditions, and product quality.

7.2 BACKGROUND OF COPROCESSING

7.2.1 Early Work

Coal/petroleum coprocessing has its earliest roots in the work of Friedrich Bergius, the Nobel laureate and inventor (1) of direct coal liquefaction. The vehicle used in many of Bergius' early batch tests in the 1910's and the early continuous tests in the 1920's was a petroleum "heavy oil" (2). Of course, the intent of this work was not to develop coprocessing; later long-term tests and commercial operations used a coal-derived vehicle. Bergius apparently used the petroleum vehicle because it was an available liquid hydrocarbon.

For the most part, petroleum-derived oils were used as coal liquefaction vehicles only in batch tests and as start-up oils in continuous-flow units for the next five decades. For example, petroleum-derived oil was sometimes used, after hydrogenation, as the start-up oils for the 3-tons/day H-Coal Process Development Unit (PDU) in Lawrenceville, New Jersey, and the 200-tons/day H-Coal pilot plant in Cattletsburg, Kentucky (3). Based on the literature, except for this somewhat loosely associated coal liquefaction work, very little research was performed on coprocessing, as it is now envisioned, until the 1970's.

Perhaps the first U.S. coprocessing patent was granted to UOP, Inc., in 1972 for a process whereby coal is solvent extracted with petroleum (4). Hydrocarbon Research, Inc. (HRI) was granted an early U.S. patent (5) on coprocessing in 1977 for the single-stage ebullated-bed COIL process, based on work performed in the early to mid-1970's (6) using HRI's H-Oil/H-Coal technology. Though the above UOP process was not developed, HRI's was. UOP and HRI continue to be two of the major coprocessing developers, as will be discussed below.

In 1978 Consol R&D tested the use of a South Texas heavy oil as the vehicle for coal hydroextraction but found that even after hydrogenation, the petroleum made a very poor liquefaction solvent (7).

Also in the 1970's, the Canada Centre for Mineral and Energy Technology (CANMET) developed the CANMET hydrocracking process for petroleum resids. Their research showed that small additions of coal (less than about 5 weight percent) to the petroleum feedstock significantly improved distillate product yields although yields were reduced with greater coal additions (8). A 5000-bbl/day plant using this process (including coal addition) was started up in 1985 by Petro-Canada near Montreal, Quebec (9).

Other than HRI's early work, there was little coprocessing activity in the U.S. until the 1980's. As petroleum prices stabilized and coal liquefaction became less of a near-term prospect, the U.S. interest in coprocessing appeared.

7.2.2 Advantages of Coprocessing

Coprocessing appears to have certain potential economic and processing advantages relative to either coal liquefaction or hydroprocessing of heavy petroleum residua (10). For example, coprocessing can provide a route to introduce coal liquids into commercial refineries and the market place slowly and thus to gain their acceptance while replacing imported oil with domestic resources and labor. Coprocessing may permit liquids to be extracted from coal at a lower processing cost than would be possible through a self-contained grass-roots coal liquefaction facility. From the capital-cost standpoint, the addition of coal feed to an already existing hydroprocessing facility used for upgrading heavy resids would require considerably less investment cost. Much of the downstream process and separations equipment already in place could be utilized with the combined feedstock. In coal liquefaction the largest capital expense item is the reactor system. Since liquefaction uses recycle ratios of 1.5/1 to 3/1, replacement of recycle oil with an unrefined crude oil would increase reactor throughput of fresh feed by 2.5 to 4 times, thus reducing costs.

Because petroleum residua are still hydrogen-rich materials (H/C = 1.5) compared to coal (H/C = 0.8), the amount of hydrogen required in a combined process should be less than that required to produce the same quality products from a stand-alone coal liquefaction facility. The liquids produced by combined processing may also be more amenable to downstream processing and further refining via existing technology and equipment, than would liquids from a purely coal-fed plant.

In turn, the upgrading of heavy petroleum resids would be improved via coprocessing. Coal liquids tend to be more aromatic than petroleum products. Thus, the octane number of the product gasoline from coprocessing should be improved by the presence of coal. Alternately, the aromatics can be hydrogenated to produce a jet fuel with higher density than that produced from petroleum only. High-density jet fuels have attractive military applications.

In coprocessing the petroleum metals that cause catalyst deactivation (e.g., Ni, V) deposit on the coal solids, thus enhancing demetallation while possibly extending catalyst life. Coprocessing provides feedstock flexibility and is reported to be more economic at smaller scale than liquefaction (11). A final important feature of coprocessing is the reported synergistic behavior of the two feedstocks such that the coprocessing product slate is better than that expected from the simple sum of the two feedstocks alone. Overall conversion to distillate liquid products is greater via coal/oil coprocessing than by separate processing. The presence of coal-derived liquids, with excellent hydrogen donor characteristics, enhances the conversion of the petroleum-derived residuum. CANMET's experience (8) with distillate yield was noted above. Other similar reports will be discussed below.

As might be expected based on its origin, coprocessing is operated at conditions similar to coal liquefaction. For example, temperatures of 750 to 825°F, 2000-psig hydrogen pressure, and alumina-supported (Co, Mo, Ni, or W) or disposable Fe catalysts are frequently employed. Space velocities depend on reactor type (thermal or catalytic) and on desired products, but may be as high as 400 $lb/hr/ft^3$ for a thermal reactor or as low as 0.25 $lb/hr/ft^3$ for a catalytic reactor.

7.3 FUNDAMENTAL AND APPLIED RESEARCH[2]

7.3.1 Chemistry and Mechanisms of Coprocessing Reactions

7.3.1.1 Importance of Hydrogen Donation in Coal Dissolution

Recent studies have shown the importance of hydrogen donors and hydrogen transfer reactions in the dissolution of coal (12-15). Curran et al. (15) postulated that hydrogen transfer from solvent to coal during liquefaction proceeds via a free radical mechanism. By comparing the dissolution of a hvC bituminous coal in tetralin, naphthalene, and dodecane, Neavel (12) demonstrated that the presence of hydrogen donors substantially enhances coal conversion at reaction times greater than 4 min. Derbyshire and Whitehurst (16) examined the stabilization of dissolving coal fragments by hydrogen transfer from the hydroaromatic fraction of the coal to an aromatic which, in turn, donates hydrogen to a coal free radical.

The basic premise that hydrogen transfer reactions play an important role in the dissolution of coal is generally well accepted. Many researchers (17-25) have attempted to qualitatively and quantitatively determine the hydrogen donors present in liquefaction solvents as well as to predict the efficacy of specific donors. In addition, catalytic dehydrogenation has been used to determine the hydroaromatic content of coals (20,21) and of process solvents (22). Model hydrogen acceptors have been employed to rank the efficacy of process solvents as well as to rank the reactivity of individual hydrogen donor compounds. Comparisons of the stability of radical anions formed during hydrogen abstraction has also been used to evaluate the relative propensity of hydrogen donation from different model donors (23,24). Thermodynamic considerations involving resonance energies of hydroaromatics and their aromatic analogs have been used to predict the hydrogen donor abilities of different hydroaromatics (25).

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[2] This section was written by Christine W. Curtis, Auburn University.

7.3.1.2 Coal Bonds to be Cleaved for Effective Dissolution During Coprocessing

The selectivity of hydrogen donors for breaking specific bonds in coal in coprocessing is largely unknown and must be determined for both selective and effective dissolution. Coal may be viewed as a large organic structure consisting of condensed or partially condensed polynuclear aromatic systems (the degree of condensation being dependent on rank) coupled by connecting linkages. Although the exact structure of the coal molecule is not known, from average properties obtained by a variety of methods (elemental analysis, IR, NMR, X-ray diffraction, etc.), it is possible to postulate the structure of an "average" molecule.

Such structures are very helpful in visualizing the chemical transformations required to convert coal to liquids. The coal structure is viewed to be predominantly aromatic with the percent of aromatic carbon varying from about 65-70 percent in lignite to over 90 percent in anthracite. The structure also contains hydroaromatic carbon and significant amounts of the heteroatoms -- O, N, and S. The various heteroatoms may occur as parts of rings such as dibenzothiophenic structures; as linkages between clusters, like sulfides and ethers; as side chains; or on ring structures, like phenols. A much more comprehensive review of the molecular structure of coal has been given by Davidson (26). If coal is heated to temperatures around 350°C, the weaker linkages in the coal structure begin to break thermally giving a large number of free radical species. For liquefying coal, the important linkages to break in the coal feed are methylene and ethylene linkages, ether groups, sulfur-sulfur bonds, sulfur-carbon bonds, oxygen-carbon bonds and nitrogen-carbon bonds.

7.3.1.3 Role and Importance of Hydrogen Donor Reactions in Coprocessing

The chemical composition of petroleum residua with an aromatic fraction of about 0.35 and a large proportion of alicyclic compounds make petroleum residua and crudes inherently poorer solvents for coal dissolution than coal liquids. Since coal liquids are derived from the coal itself, their chemical compositions are quite similar to that of coal, usually making them good solvating media for coal. The high aromatic content of coal liquids and their propensity for forming hydrogen donors during hydroliquefaction, thereby serving as hydrogen transfer sources to the dissolving coal matrix, are major factors causing coal liquids to be excellent solvents. These good solvating properties are particularly true for higher boiling coal liquids derived from hydroliquefaction.

In a recent study by Curtis et al. (27), coal dissolution and subsequent product formation in liquefaction reactions were compared in a heavy coal-derived solvent, a petroleum Maya Crude, and a Lloydminster Reduced Crude, under coprocessing conditions. In a N_2 atmosphere 79 percent of the coal was converted in the coal-derived solvent while Maya Crude and Lloydminster Reduced Crude yielded 28 percent and 13 percent coal conversion, respectively. In a H_2 atmosphere all of the coal conversions increased. When a catalyst was added to each of these systems, substantial increases in both coal conversion and the amount of pentane solubles produced were observed.

A direct comparison between the efficacy of tetralin and petroleum crudes and residua for coal conversion and production of a desirable product slate was made by Curtis et al. (28). These solvents were compared under three conditions: (1) a N_2 atmosphere at 400°C, (2) a H_2 atmosphere at 400°C, and (3) a H_2 atmosphere with a $NiMo/Al_2O_3$ catalyst at 425°C. In the N_2 atmosphere coal conversion in tetralin was ~57 percent while in the petroleum solvents coal conversions were ~30 percent. In H_2 all coal conversions increased, with tetralin yielding ~70 percent and the petroleum crudes and residua between 45 and 55 percent. Catalytic hydrotreatment increased coal conversions in all solvents by 10 to 15 percent, but the differential between tetralin and the petroleum solvents remained. The results from these experiments definitely indicate that petroleum solvents do not have the same inherent ability as a hydrogen donor, such as tetralin, to transfer hydrogen and dissolve coal. Therefore, either the reaction conditions need to be changed to induce hydrogen transfer from the residuum to coal, or hydrogen donors need to be generated in the petroleum solvents to make them more effectual solvents for coprocessing.

An interesting article concerning hydrogen transfer from cycloalkanes to coal during solvent extraction was published by Clarke et al. (29). In this work the authors examined the reactivity of cycloalkanes, i.e., naphthenes, alone and in conjunction with aromatics for the conversion of coal. They also measured the amount of hydrogen transferred during the reactions by the cycloalkanes. The solvent extraction experiments were performed thermally at 430°C for one hour; however, the other experimental details were very sketchy. The authors claimed that cycloalkane/aromatic mixtures containing decalin/phenanthrene and decalin/pyrene yielded much higher coal extraction yields than either the cycloalkane or aromatic alone. The products obtained from the reactions showed that the cycloalkanes had been converted to their hydroaromatic and aromatic analogues and, hence, some hydrogen had been released from the cycloalkane. The authors then postulated that in the presence of coal-derived radicals and polynuclear aromatic compound, cycloalkanes serve as hydrogen-donating species. This work has strong implications for coprocessing, suggesting that under a favorable set of reaction conditions and environment, possible hydrogen transfer may occur between the naphthenes present in the petroleum solvents and the hydrogen accepting components of the coal and the residuum.

Curtis et al. (30) have further examined the role and the importance of hydrogen donation reactions in coprocessing. They found that the availability of hydrogen to the coprocessing system was critical and that the hydrogen could be present either as molecular (gaseous) hydrogen or as hydrogen donors. Hydrogen donors tetrahydroquinoline (THQ), tetralin, and dihydrophenanthrene (DHP) were added to the thermal coprocessing system under both N_2 and H_2 atmospheres. The coal conversion in both N_2 and H_2 increased with increased donor concentration with THQ yielding higher conversion than tetralin and DHP yielding slightly more than THQ.

In terms of pentane solubles production, THQ was a detriment, particularly in N_2, while tetralin increased the amount of pentane solubles produced in reactions under both N_2 and H_2 atmospheres. Depending upon their chemistry, the addition of hydrogen donors can be beneficial to either coal conversion or pentane-solubles production.

Further examination of the role and the importance of hydrogen donation in coprocessing was performed by Curtis and Cassell (31). In the thermal coprocessing of Maya resid with Western Kentucky 9/14 coal, the addition of tetralin increased coal conversion from 48 percent to 70 percent. The influence of tetralin on the catalytic coprocessing with two different catalysts, $NiMo/Al_2O_3$ and Mo naphthenate, was also determined. When tetralin was added to the $NiMo/Al_2O_3$ coprocessing system, the combined effect of tetralin and hydrotreatment from $NiMo/Al_2O_3$ synergistically promoted coal conversion, increasing yields from 69 percent without tetralin to 82 percent with tetralin. In contrast, with Mo naphthenate as the catalyst, the addition of tetralin had no effect on coal conversion or the product slate attained. With $NiMo/Al_2O_3$ substantial solvent rehydrogenation occurred while with Mo naphthenate only a small amount occurred. Based upon these results, the effectiveness of hydrogen donation in coprocessing appears to be dependent upon the reaction conditions and the activity and the selectivity of the catalyst used.

7.3.2 Catalytic Coprocessing

The initial work in catalytic coprocessing was performed by Boomer and Saddington in which petroleum solvents were used to coprocess lignite, subbituminous, and bituminous coals from Alberta in the presence of molybdic oxide (32). Moschopedis and co-workers have performed extensive work in catalytic coprocessing reactions using $CoMo/Al_2O_3$ and Fe_2O_3 catalysts (32, 33). Their results indicate that the coal conversion to toluene solubles is improved with the addition of a $CoMo/Al_2O_3$ catalyst and that the product slate is dependent upon coal and solvent type as well as processing conditions.

A process for catalytic hydrocracking of coal-oil mixtures has been developed by HRI in which coal and heavy vacuum residuum are catalytically coprocessed in the presence of a $CoMo/Al_2O_3$ catalyst. Coprocessing reduced the amount of benzene-insoluble materials in the products as well as the sulfur content of the liquid boiling above 204°C. The synergistic effects of the coprocessing allowed operation at a lower severity than that of coal liquefaction (32).

Oil-soluble coprocessing catalysts -- phosphomolybdic acid and naphthenates of molybdenum, vanadium and chromium -- have been described as catalysts for coprocessing by Exxon. Aldridge and Bearden (34) used molybdenum naphthenate as a catalyst for coprocessing Athabasca bitumen and Wyodak coal. By using molybdenum naphthenate, they increased the liquid yield by 20 percent and decreased the coke formation. Aldridge and Bearden (35) also described a two-stage process in which bitumen is first hydrocracked and then hydrogenated with Wyodak coal using a phosphomolybdic acid catalyst in both stages. Compared to a single-stage process using a molybdenum catalyst, the two-stage process produced more residual oils boiling above 540°C, more char, and lower hydrogen consumption. Two-stage processing is described in a patent by Rosenthal and Dahlberg (36) in which oxides of cobalt-molybdenum, nickel-molybdenum, and nickel-tungsten were used for hydrocracking coal in heavy oil in the second stage. Chevron (37) has developed a coal-oil two-stage reaction process which is similar to that used for coal liquefaction. They stated that the advantages of corefining include increased yields, process stability, coal feed flexibility, ability to process residua with high-metals content, and efficient hydrogen utilization.

A process patented by Gatsis (38) converts coal to liquid products and reduces the residuum asphaltene content by solvent extraction in a heavy hydrocarbonaceous liquid using a finely divided unsupported metal catalyst. A review of coprocessing by Monnier (32) discusses the work of several other groups. Russian workers have used coal impregnated with (0.2 weight percent) Mo^{6+} and (0.75 percent) Fe^{3+} to achieve a coal conversion of 82 percent. Japanese workers have performed pilot studies investigating the solvolysis of coal in asphalt and residual oils. Two-stage processing was performed in which coal was dissolved at 390°C in the first stage and then hydrocracked over a catalyst in the second stage at 400°C. A number of different catalysts were used including oxides of nickel-molybdenum, cobalt-molybdenum, and nickel-tungsten on gamma-alumina. The $NiMo/Al_2O_3$ gave the best results, although zeolites and other commercial catalysts also performed well.

Recent work by Curtis et al. (39) has shown that highly effective and accessible catalysts are required to achieve high levels of oil production from the coprocessing of coal and heavy residua. In their work, powdered hydrotreating catalyst at high loadings and oil-soluble metal salts of organic acids as catalyst precursors achieved the highest levels of activity for coal conversion and oil production. On a weight-of-active-metal basis, the catalysts from the oil-soluble salts were the most effective in achieving both high levels of coal conversion and oil production. Pyrite was effective in achieving upgrading of asphaltenes from residuum and in achieving coal conversion in both single- and two-stage processing. Two-stage catalytic coprocessing using the first- and second-stage catalyst sequences of pyrite-$NiMo/Al_2O_3$ and $NiMo/Al_2O_3$-$NiMo/Al_2O_3$ sequence was much more effective in oil production. The products from the two-stage reactions were slightly more upgraded than those from the single-stage reaction.

7.4 PROCESS DEVELOPMENT[3]

7.4.1 Recent Development Work

Chevron studied coprocessing in the early 1980's and adapted its six-tons/day liquefaction (40) pilot plant in Richmond, California, to coprocessing in 1983 (41). The Chevron process was a close-coupled two-stage (thermal/catalytic) system. Shinn et al. (41) reported facile operation with a wide range of coals and heavy oils. A definite positive synergism was noted for resid conversion. Of particular interest was the great degree of demetallation from high-metals-content resids. Chevron demonstrated that catalyst life was prolonged by the coal because metals laydown was reduced. The lack of ensuing publications makes it appear that Chevron is no longer active in this area.

CANMET's discovery of improved distillate yields in coprocessing in their early work, in addition to the occurrence of coal and bitumen in close proximity in the provinces of Alberta and Saskatchewan, gave CANMET an incentive to consider true coprocessing. By 1981 CANMET (42) had tested coprocessing in a 1-kg/hr continuous unit using bitumen vacuum bottoms (535°C$^+$) and a low-rank (Sub C) coal. Coal concentrations of 6 to 25 weight percent were tested. The bitumen contained 5.5 percent S and 38 percent asphaltenes. CANMET uses a once-through process with a disposable Fe catalyst (43). Alberta Research Council (44) is currently testing the process in a 2-kg/hr unit.

Following the development of H-Coal (3) technology into a two-stage process (45), HRI also further developed the COIL (5) process into a two-stage process (6, 11, 45-49). HRI is now actively developing advanced two-stage catalytic coal/oil coprocessing technology. HRI's coprocessing technology is based on the commercial H-Oil Process (for upgrading heavy crudes and/or petroleum residua), the fully developed H-

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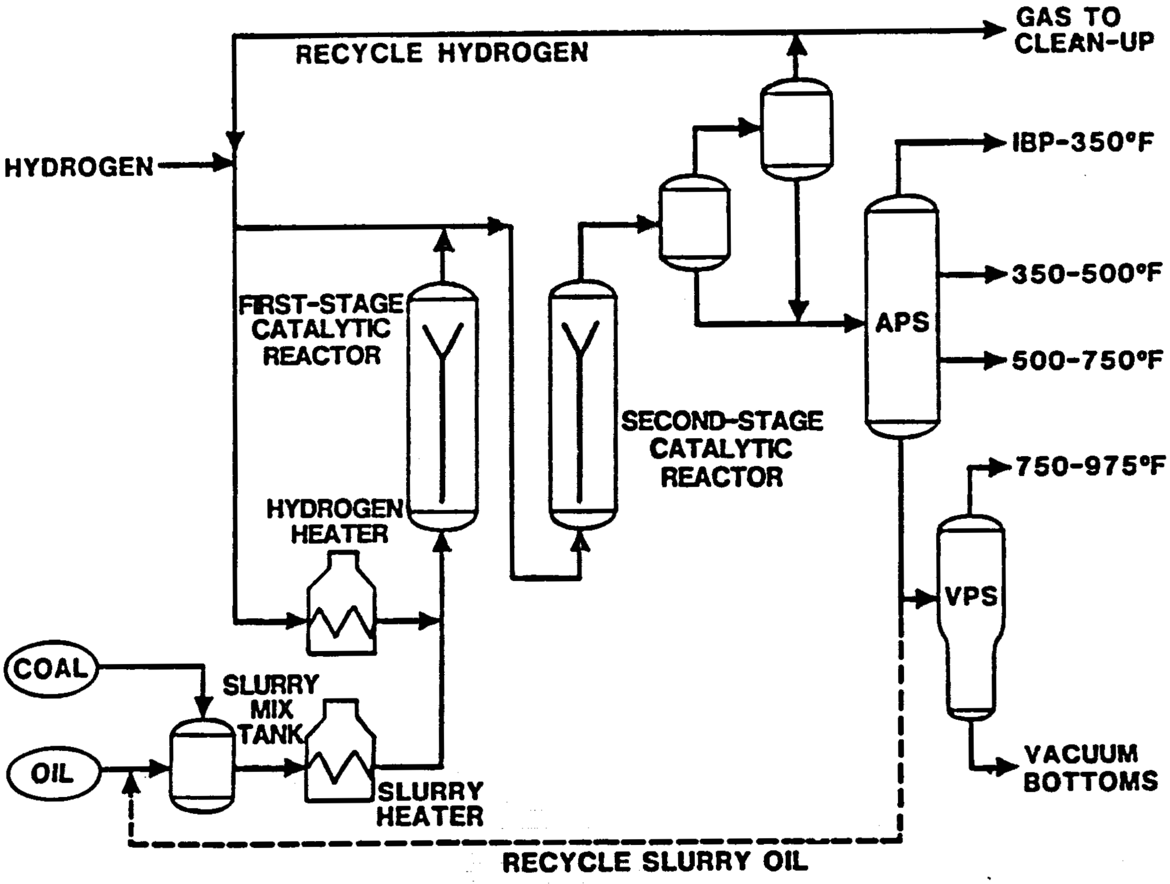
[3] This section was written by Richard A. Winschel, Consolidation Coal Company.

Coal process (for direct liquefaction of coal), and advances made at HRI in the Catalytic Two-Stage Liquefaction (CTSL) Process. HRI now considers all these processes to be one single flexible technology for the hydroprocessing of hydrocarbons using ebullated-bed reactors (50). HRI's continuous bench-unit program has received support from a variety of sources, notably the Electric Research Power Institute (EPRI), Alberta Research Council, Ontario-Ohio Synthetic Fuels Corp., Ltd., and Ohio-Ontario Clean Fuels, Inc. (OOCF).

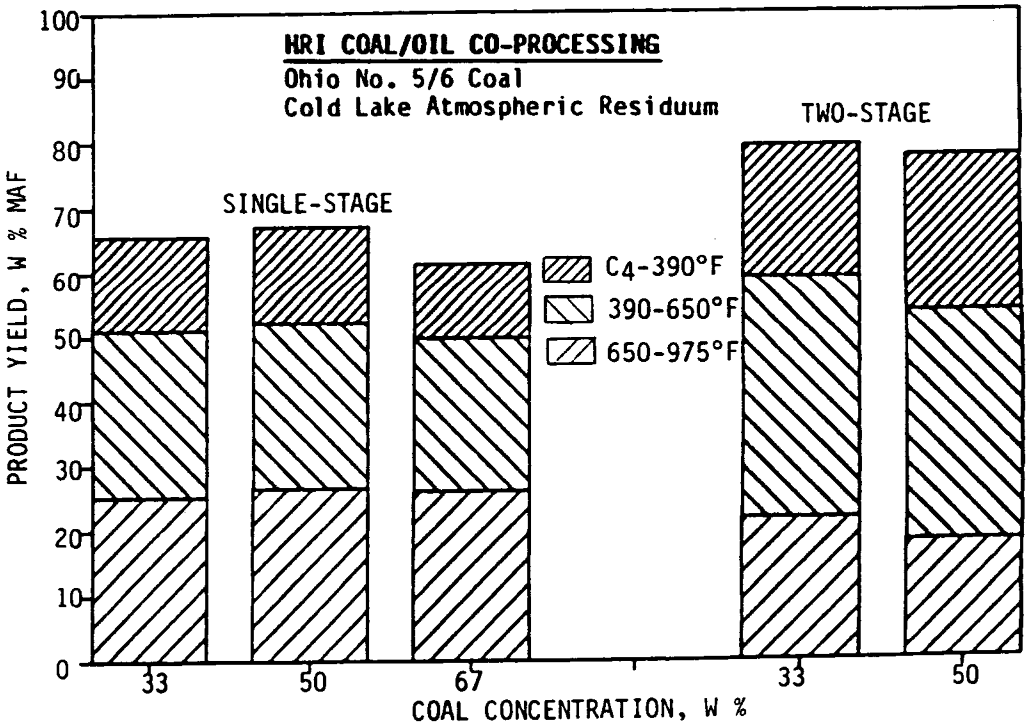
HRI's two-stage process is shown in Figure 7-1. Coal is slurried with petroleum-derived residual oil. Residual oils which can be used include atmospheric and vacuum residua, FCC clarified slurry oils, heavy crudes, tar sands bitumen, and shale oil. The feed slurry is pumped to reaction pressure, mixed with hydrogen, preheated, and fed to the ebullated-bed reactor. Both single-stage and two-stage process configurations have been demonstrated. The reactor effluent is separated into vapor and slurry streams. The vapor is treated to recover hydrogen and recycled back to the reactor. The slurry is depressurized and fractionated to produce high-quality distillate products and a non-distillate vacuum bottoms product, which contains all unconverted residual oil, unconverted coal, and ash. High concentrations of coal in the fresh feed are made possible by recycling a small amount of the coal slurry oil.

HRI has tested a wide variety of coals from lignite through high-volatile A bituminous and a wide variety of petroleum resids. Each combination showed a positive synergism toward resid conversion (46, 47), although a negative synergism was noted in some cases using a very high coal concentration (46). Typical liquid product yield data are shown in Figure 7-2. Metals were readily removed by the coal solids (47). Up to 67 weight percent coal in the fresh feed has been tested successfully. At coal concentrations lower than about 40 percent, no recycle is employed. At higher coal concentration a recycle must be used to supply part of the vehicle. A 50/50 ratio appears to be preferred (47).



Source: Ref. 47.

Figure 7-1. **Simplified Flow Plan of HRI's Two-Stage Process**



Source: Ref. 46.

Figure 7-2. Typical Coprocessing Liquid Product Yield Data

Overall, HRI's program has been successful in demonstrating the technical, economic, and commercial feasibility of coal/oil coprocessing and has produced some very important results (47):

The technical feasibility of coal/oil coprocessing was demonstrated in continuous bench-scale operations. Fifty-two days of continuous bench-scale operation were completed in both single- and two-stage process configurations. The feedstocks used were Ohio No. 5/6 coal and Cold Lake residuum. A wide range of process variables were evaluated including coal concentration from 33-67 weight percent of fresh feed, and temperatures from 750-825°F. 975°F$^+$ conversion levels were from 60 weight percent MAF to in excess of 90 weight percent MAF. Over this range of process severities no operability difficulties were encountered and product slates varied from all distillate (at high severity) to a high-residuum-containing product (at low severity).

Process synergy was demonstrated in both batch reactivity screening experiments and in continuous bench unit operations. This process synergy (as described earlier) occurs in at least two different ways. First, 975°F$^+$ conversion obtained in coprocessing is greater than expected based on separate processing of the individual feedstocks. The other aspect of the process synergy relates to the observed affinity of the coal-derived solids (unconverted coal plus ash) for organometallics (nickel and vanadium) contained in the oil feed. This was shown in continuous bench unit operations by analyzing the recovered coal solids for nickel and vanadium. Coprocessing reduces the metals contaminants on the spent catalyst by an order of magnitude compared to oil-only processing (H-Oil Process). This reduces the catalyst deactivation caused by metals deposition on the catalyst and allows the option of more efficient catalyst utilization through regeneration and/or cascading of catalyst in a two-stage system.

Excellent process performance was obtained in the continuous bench unit operations. In Bench Run No. 2 (two-stage), Condition 4 (at 50 percent coal in the fresh feed), the following process performance was obtained:

Process Performance	Wt % MAF
Coal Conversion	96
975°F$^+$ Conversion	90
Hydrodesulfurization	86
Hydrodenitrogenation	80
Demetallation	99

Also at this condition excellent product quality was obtained. As a measure of product quality, the vacuum gas oil (650-975°F) quality was closely monitored. The vacuum gas oil qualities for Bench Run No. 2, Condition 4, are shown as follows:

Vacuum Gas Oil Quality

Gravity, °API	13.30
Hydrogen, wt %	10.54
Sulfur, wt %	0.17
Nitrogen, wt %	0.35

These qualities meet or exceed the target qualities for a potential utility turbine fuel, without any further upgrading.

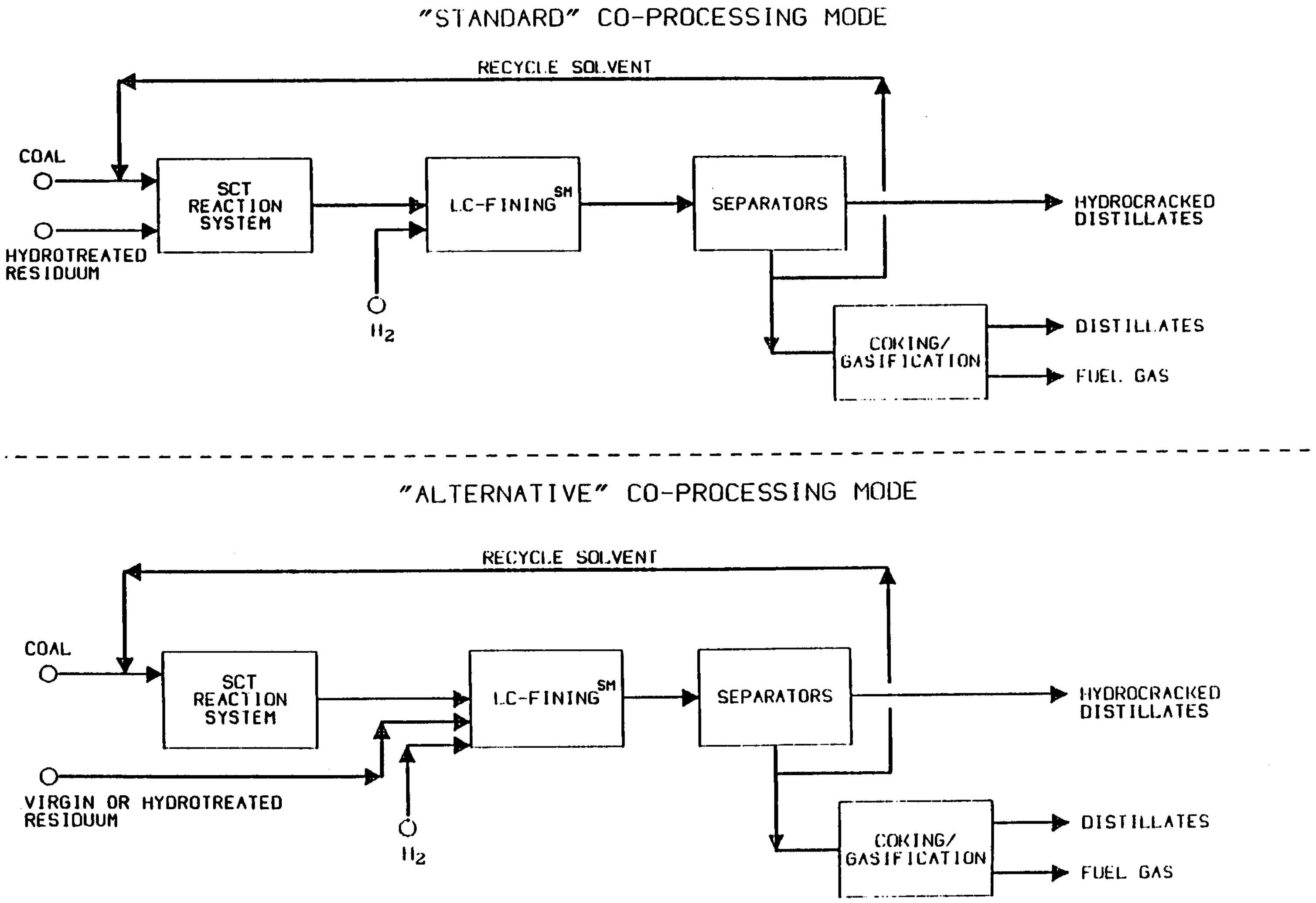
A 30-day continuous test (without catalyst addition/withdrawal performed by HRI using Ohio 5/6 coal and Cold Lake resid showed excellent operability and performance (47). After 25 days of operations, coal conversion was 95 percent; 975°F$^+$ conversion was ca. 88 percent; demetallation was ca. 99 percent; and sulfur and nitrogen removals were ca. 75 percent. About 77 weight percent of clean distillate was produced, half of which was naphtha. An OOCF project to use HRI two-stage coprocessing technology for a 12,000-BPSD prototype commercial plant in Warren, Ohio, was selected as one of the final candidates for funding by DOE's Clean Coal Technology program (47, 51, 52). Ohio 4/5 coal and Cold Lake resid are planned as feedstocks.

Kerr-McGee Corp. tested coprocessing in a 0.2-tons/day continuous bench unit during 1984 (53). The Kerr-McGee process can be envisioned as Wilsonville-style thermal/catalytic Integrated Two-Stage Liquefaction (ITSL) with a resid hydrotreater added at the front end. The bottoms product from the resid hydrotreater is used to replace about half of the liquefaction recycle oil. Distillate product streams are formed from the resid upgrader and the first liquefaction reactor. The latter reactor also produces a deashed resid net product. Although operations were successfully demonstrated with Ohio 5 coal and Cold Lake bitumen (53), development appears to be dormant for lack of funding.

Lummus coprocessing technology also grew out of thermal/catalytic two-stage direct liquefaction (54). Figure 7-3 is a schematic of two alternative processing schemes for the LCI coprocessing concept. In the standard mode coal is slurried with an externally hydrogenated petroleum feedstock, such as for example, the vacuum bottoms from an expanded-bed hydrocracker (LC-Fining^{sm}), and processed in a short contact time (SCT) thermal stage reaction system. The SCT reactor effluent is fed to an expanded-bed LC-Fining^{sm} reaction system in a close-coupled manner, i.e., without depressurization or deashing between stages. An ash-containing residual stream from the LC-Finate product separation system is recycled to the SCT reactor as necessary to supplement the solvency power of the petroleum component of the coprocessing feedstock. In the alternative mode the petroleum feedstock is injected between the stages at the inlet to the close-coupled LC-Finer^{sm}. All of the SCT slurry vehicle for the coal feed is derived by recycling an ash-containing heavy oil stream from the close-coupled LC-Finer^{sm}. In both modes bottoms processing is based on fluid coking of the coprocessed vacuum bottoms with subsequent gasification of the resultant fluid coke.

Net products are 650°F$^-$ distillates and a resid for hydrogen generation. Lummus has tested a wide variety of coal and resid feedstocks (55), but most of their continuous-unit tests have employed Pittsburgh seam coal and a hydrocracked vacuum resid from a commercial LC-Fining unit (56). Lummus also reports a synergism for resid conversion (54-59). Long-term tests (700 hours on-stream) using a 1/1 ratio of the above feedstocks and 30 percent recycle gave coal conversions of 94 percent, 975°F$^+$ conversions of 64 percent, and N and S removals of about 60 percent.

Signal Research/UOP coprocessing technology (60) had its origins in resid upgrading and differs from most of the other processes in that it is a single-stage entrained-catalyst system. A conceptual schematic flow diagram of the proposed process is shown in Figure 7-4. In this process hydrogen, finely ground coal, petroleum resid, and catalyst are mixed,



Source: Ref. 57.

Figure 7-3. Block Flow Diagrams of LCI Coprocessing Concepts

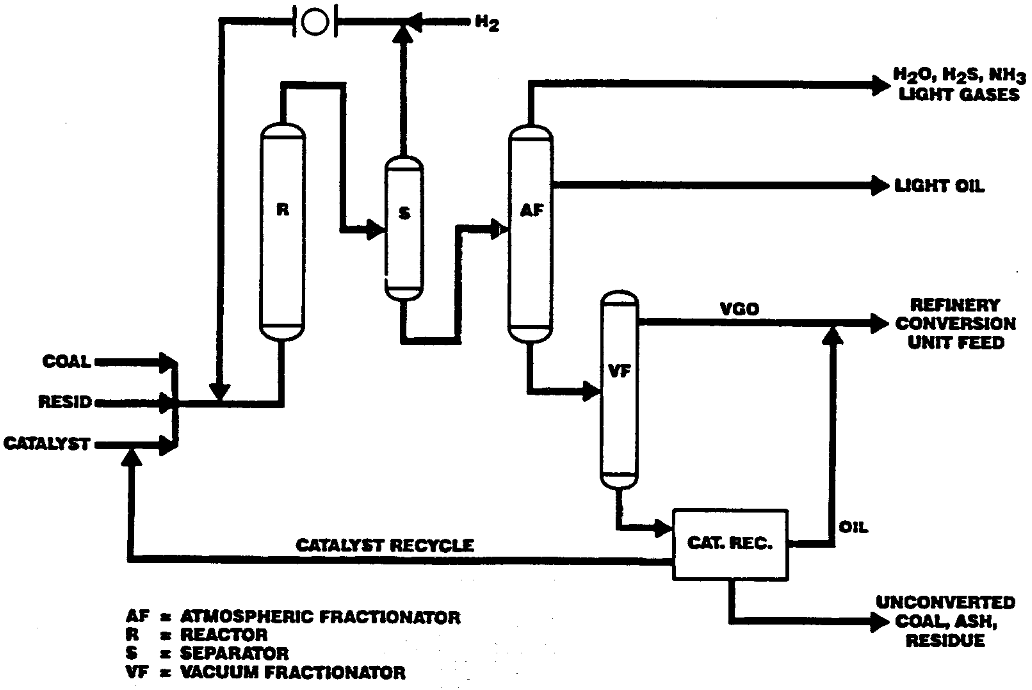


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Figure 7-4. Signal/UOP's Proposed Resid/Coal Processing Scheme heated, and then directed to a single-stage reactor where the simultaneous conversion of the petroleum resid and coal occurs. A hydrogen-rich gas is recovered from the reactor effluent and recycled back to the reactor inlet. The balance of the material is separated, and the light gases, light oil, and vacuum gas oil are recovered. The remaining material is sent to a catalyst recovery unit to recover additional oil product, unconverted coal, ash, residues, and the catalyst, if desired. The catalyst is recycled back to the reactor. The addition of a well-dispersed catalyst allows the unit to operate at relatively moderate temperatures while maintaining good coal and heptane-insoluble conversions. An added benefit to the low-temperature operation is that thermal degradation reactions and the cracking of the coal and resid feedstocks to light gases are minimized. Both a proprietary catalyst and a disposable Fe catalyst have been tested. The proprietary catalyst must be recovered and recycled for commercial use. Excluding the undefined catalyst recovery step, this process is quite simple.

A wide range of coals and resids have been tested in the UOP co-processing scheme in batch experiments (60); however, continuous bench-unit tests (ca. 200 g/hr) have used either Illinois 6 or Wyodak coal with Lloydminster resid. Typical resid/coal (MAF) ratios are 1.5/1 to 2/1 (60-65). Recently, a 12-week continuous test (1795 hours on-stream) used Illinois 6 coal and Lloydminster resid at 2/1 resid/coal (MAF) with the proprietary catalyst (64). The process operated well and gave stable yields: 89 percent coal conversion and 55 percent resid conversion.

The continuous unit operations of the last ten years have made it apparent that coprocessing is technically feasible. The cited literature shows, however, that most of the process developers believe their process is not yet optimized. Optimization requires small-scale exploratory work as well as process testing.

Miller (66, 67) demonstrated synergism for distillate production using Wyoming coal and several resids in exploratory batch tests. Curtis and coworkers (68-71) examined the roles of catalyst and hydrogen source in coprocessing. Alberta Research Council is investigating alkali-catalyzed coprocessing in syngas (72). Exploratory work also has recently started at Pittsburgh Energy Technology Center (73, 74) and North Dakota Energy Research Center (75). Battelle Pacific Northwest Laboratory (76, 77) has investigated the detailed chemical and toxicological properties of coprocessing products.

7.4.2 Characterization of Coprocessing Products and Their Upgrading

In its analysis HRI found that the products from coal/oil coprocessing should fit into the existing markets for liquid fuels (46). An overview of HRI's coal/oil coprocessing products, their probable dispositions, and possible further upgrading required, is shown in Table 7-1. The naphtha from coprocessing will go to gasoline blending pools. To prepare a high-octane gasoline blendstock, this naphtha will be hydrotreated and catalytically reformed. As shown in Figure 7-5, the coprocessing naphtha contains higher concentrations of naphthenes and aromatics compared to an H-Oil Process naphtha derived from processing Cold Lake atmospheric residuum. The resulting product from catalytic reforming will have a higher octane number, with higher volumetric yield, at lower operating severity. The mid-distillate and VGO products from coprocessing are extremely low in sulfur and considerably lower in nitrogen compared to products from direct coal liquefaction (see Table 7-2). These products could be combined and used as a low-sulfur fuel oil or turbine fuel for utility application, without further upgrading.

7.4.3 Economics of Coprocessing

A variety of analyses have been performed to estimate the economics of coprocessing (49, 52, 59, 65, 78). Apparently costs lie between those of coal liquefaction and resid upgrading. However, since coprocessing is a relatively immature technology that is not yet fully developed, there is reason to believe that the economics can be improved.

Table 7-1. Product Characterization Overview of Coprocessing Products

Coprocessing Product	Nominal Boiling Range	Probable Disposition	Possible Further Upgrading
Naphtha	IBP-390°F	Gasoline	Hydrotreating and Catalytic Reforming
Mid-Distillates	390-500°F 500-650°F	Jet Fuel Diesel Fuel No. 2 Fuel Oil Turbine Fuel* No. 6 Fuel Oil	Hydrotreating
Vacuum Gas Oils	650-850°F 850-975°F	Conversion No. 6 Fuel Oil Turbine Fuel* Recycle to Reactor	Hydrotreating, Fluid Catalytic Cracking, Hydrocracking
Resid (Excluding Solids)	975°F+	No.6 Fuel Oil Recycle to Reactor	
Resid (Including Solids)	975°F+	Partial Oxidation Direct Combustion Solids Separation Recycle to Reactor	Flaking, Fluid Coking

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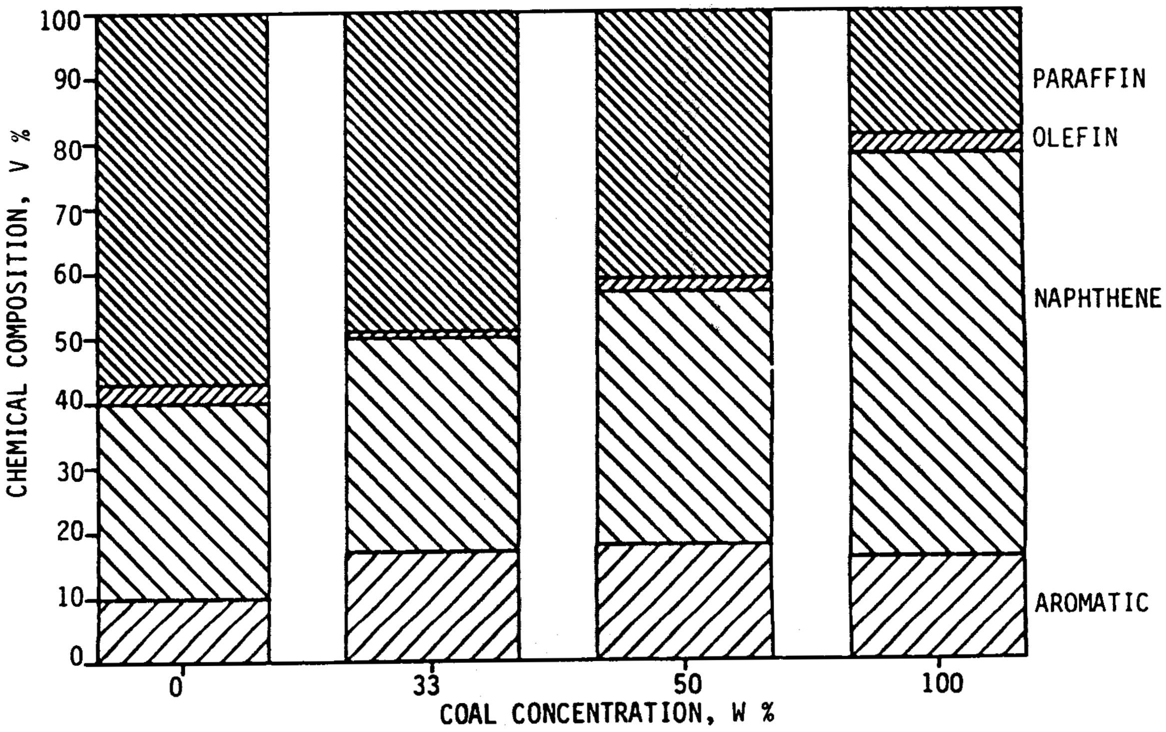
*Including oil-fired combined-cycle electric power generation.

Source: Reference 46.



Source: Ref. 46

Figure 7-5. **Chemical Composition of Coprocessing Napthas**

Table 7-2. Product Characterization

%Coal Feed	0	33-50	100
		Mid-Distillate	
°API	32	29	23
Hydrogen, wt%	12.5	12.0	11.0
Sulfur, wt%	0.7	<0.1	<0.1
Nitrogen, wt%	0.2	0.2	0.3
Cetane Index	41	36	28
		Vacuum Gas Oil	
°API	19	15	9
Sulfur, wt%	1.3	0.2	<0.1
Nitrogen, wt%	0.3	0.35	0.6

Source: Reference 46.

The results from economic screening studies performed by HRI (46) are typical. These studies showed that coal/oil coprocessing significantly reduces the cost of liquids from coal compared to direct liquefaction. Economics were calculated for a single-stage coprocessing add-on to an existing petroleum refinery. The objective of this economic screening study was to identify the preferred oil-to-coal feed ratio and operating conditions. Some coal/oil coprocessing vacuum bottoms processing options were also evaluated.

A summary of the cases evaluated is provided in Table 7-3. In the base Cases 1-5 the bottoms from coal/oil coprocessing are coked, and hydrogen is produced via steam reforming of natural gas. Each case is based on 3,000 TPSD of total coal plus oil feed. In Cases 1-3 the coal concentration increases from 33 to 67 weight percent, at otherwise constant operating conditions. Case 4 is based on high conversion at 33 weight percent coal, and Case 5 is based on low conversion at 50 weight percent coal. In Case 4A the coal/oil coprocessing bottoms are used to manufacture hydrogen via partial oxidation. Results are summarized in Table 7-4.

Product costs are shown versus percent coal in the fresh feed in Figure 7-6. Product cost components (capital, other operating cost, residuum and coal) are shown separately. As the coal concentration increases, the relative contribution of feedstock costs decreases as the cost of coal ($1.25/MMBtu) is considerably less than the cost of residuum ($15/bbl or about $2.50/MMBtu). The cost of capital and other operating expenses (labor, maintenance, natural gas, utilities), however, increases with coal concentration. As shown in this figure, 50 percent coal is slightly preferred to 33 percent coal with product costs of about $22-23/bbl. The product cost at 67 percent coal is considerably higher.

HRI also found from its commercial planning studies that there are a number of locations in the Great Lakes region where coal/oil coprocessing is commercially feasible. Commercial feasibility for coprocessing is generally defined as locations which have coal mines, crude oil pipelines, natural gas pipelines, existing refineries, and product pipelines in close proximity.

Table 7-3. HRI Economic Screening Studies Summary of Cases

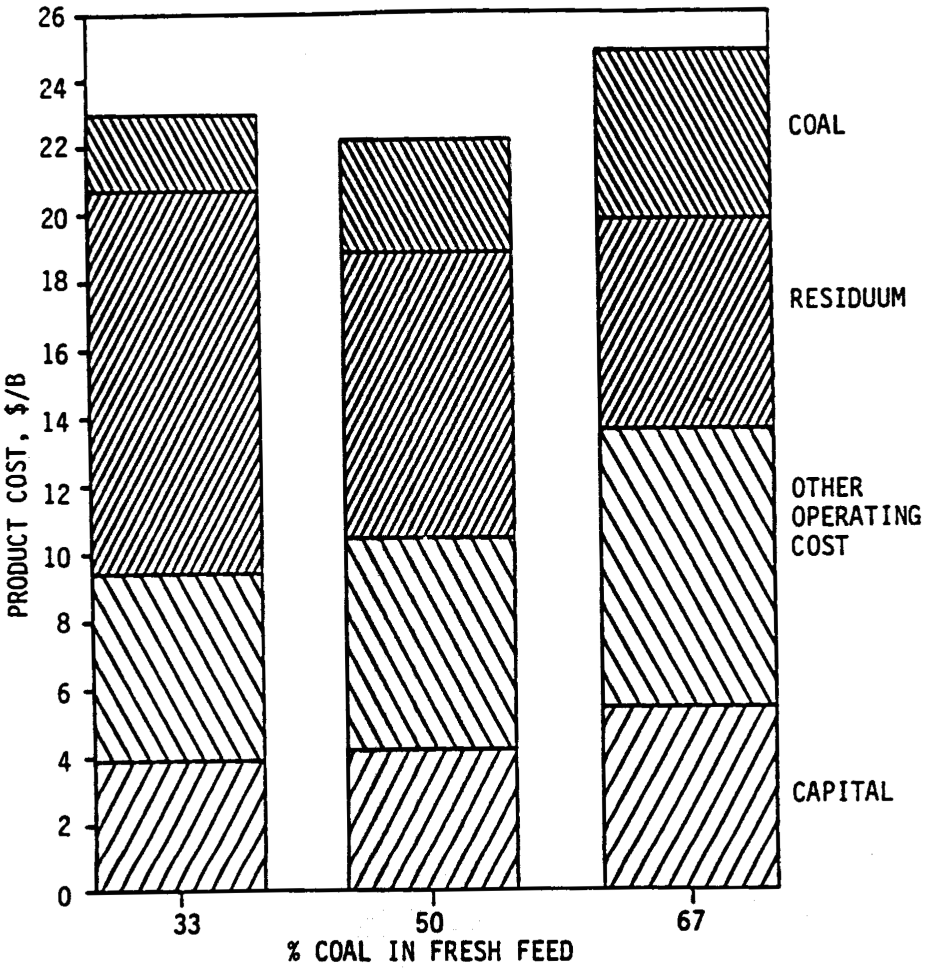
CASE	1	2	3	4	4A	5
Overall Feed Rate, TPSD	< ---------- 3000 ---------- >					
Percent Coal Feed	33	50	67	33	33	50
975°F+ Conversion, wt%	74	75	70	84	84	59
Coprocessing Bottoms Processes	< ------ Coking ------ >				POX	Coking
Hydrogen Source	< ------ Steam Reforming ------ >				POX	Steam Reforming
Recycle, wt% of FF	-	50	115	-	-	50

Source: Reference 46.

Table 7-4. HRI Economic Screening Studies
Summary of Results

CASE	1	2	3	4	4A	5
Percent Coal Feed	33	50	67	33	33	50
Feedrate, TPSD	< ---------------------- 3000 ---------------------- >					
C_4-975°F Product, BPSD	14100	14200	12750	14850	14000	12500
Estimated Investment, MM$	240	260	300	260	300	249
Operating Cost, MM$/Yr	93	89	87	97	93	87
By Product Revenues, MM$/Yr	(5)	(5)	(6)	(5)	(13)	(6)
Net Cost, MM$/Yr	88	84	81	92	80	81
First -Year Product Cost, $/Bbl	23.03	22.24	24.87	22.89	22.39	24.01

Source: Reference 46.



Source: Ref. 46

Figure 7-6. Coprocessing Product Cost Components

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CHAPTER 8

REVIEW OF BIOCONVERSION OF COAL[1]

8.1 INTRODUCTION AND SUMMARY

8.1.1 Introduction

Bioprocessing of coal, as related to conversion of coal and coal-derived products, is not well developed. Its advantages and disadvantages are currently unclear due to the limited state of development of the technology. However, if one assumes those advantages of known bioprocesses, the potential advantages appear to warrant more extensive investigation of coal bioprocessing and demonstration of viable concepts. In this review of bioconversion of coal, an attempt is made to briefly review the data relative to biological coal solubilization, and conversion of coal and coal-derived materials. A third area of coal bioprocessing -- desulfurization and coal cleaning -- is being actively developed but is excluded from this review because this technology is not concerned with the production of liquid fuels from coal.

Because bioconversion of coal is an embryonic technology, not very many researchers may be familiar with the general concepts involved. The next section of this review describes the background of this technology. The general concept of bioprocessing is described, and the potential advantages and disadvantages of this method are outlined.

After this background material, the balance of the chapter is concerned with biosolubilization, which is analogous to direct liquefaction, and biological indirect liquefaction, in which synthesis gas derived from coal is the feedstock to be converted to liquids via treatment with microorganisms. For each technology area, historical

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[1] This chapter was written by Michael E. McIlwain, Idaho National Engineering Laboratory.

background is presented, followed by a discussion of current Federal and private research agendas and objectives. It is too early for each technology to pursue significant development activities. A few process economics are presented, although most such studies indicate that much more data are needed before an accurate assessment of economics can be made. Research and development needs specific to each technology area are discussed.

These topical discussions are used to support a summary of the panel discussions concerning bioconversion of coal. What the expert panel regarded as the most important research needs and research directions for bioconversion of coal is highlighted in the summary which follows.

8.1.2 Summary

Bioconversion of coal is an embryonic field which has received considerable attention in the last four to five years. Bioconversion has the potential advantages of requiring relatively low-severity conditions for processing, low capital cost for the plant, environmentally safe effluents, and high chemical specificity. Bioprocessing could potentially have the disadvantages of high variable cost associated with nutrients and power requirements, and contamination of the process by foreign biological agents which result in production losses.

Research results on coal solubilization indicate that microorganisms do promote the water solubilization of pretreated coals. There appears to be additional degradation of the solubilized coal polymer occurring due to microbial action. Microorganisms have been identified that can convert carbon monoxide to acetate and ethanol. High conversion yields and short contact times have been found for synthetic gas mixtures representative of syngas. Analysis of process economics indicates that microbial-based processes may be comparable in cost to similar conventional chemical processes. However, neither type of process is viable in today's energy market.

All of these findings suggest that research and development in this area should be expanded. More effort is required on: bioreactor designs for solid substrates, product separation methods, larger organism scoping studies, better understanding of the structure of low-rank coals, more biochemistry related studies that support enzyme and genetic engineering studies, more emphasis on microbial systems able to metabolize and convert syngas and biosolubilized coal, and finally, scale-up of a microbial process to evaluate the costs associated with bioconversion of coals.

In its discussions regarding the potential of bioconversion of coal to produce liquid fuels, the panel concluded that this technology is in such an early stage of development that little background information and data are available upon which to develop and prioritize detailed research recommendations. The recommendations which were brought out in the panel meetings are listed in Table E-1 in Appendix E. As discussed in Sections 8.3.3 and 8.4.3 following, the most important research need is to identify useful microorganisms and enzyme systems, and this recommendation (No. B1) was endorsed by the panel as having the highest priority by far of all the recommendations discussed and evaluated. The panel further concluded that the type of research needed in this technology area should be termed "scoping studies" as it is too early to determine what the specific needs are in either fundamental or applied research.

8.2 BACKGROUND

8.2.1 Description of the Bioconversion Concept

Bioconversion of raw feedstocks is an embryonic technology. Although microorganisms have been used for many years to produce alcohol, food stuffs, and decomposition of wastes, the idea of using microorganisms to process materials from naturally occurring resources is relatively new. Microorganism-promoted extraction of minerals is approximately forty years old. Today, approximately 25 percent of the world's copper production is derived using microbial leaching of low-grade deposits and tailings. The use of microorganisms to process coal can be traced back to studies in the early 1950's (1) in which researchers were investigating the actions of microbes on coal. Today, research is being done on bioprocessing of coals in three areas: desulfurization, solubilization, and conversion of coal-derived materials. As yet, no technology related to the use of microorganisms to process coals has been demonstrated. However, a number of processes have been proposed to remove sulfur from high-sulfur coals (2) and to produce methane from low-rank coals (3).

A generic bioprocess is shown in Figure 8-1. The process is composed of four main elements: feedstock/culture preparation, organism/enzyme preparation, reactor, and product separation. The following gives a brief description of each element.

The feedstock/culture preparation element involves the creation of the medium in which the organism or enzyme will perform the desired chemical reactions. The raw material to be processed must be provided in a form that will be amenable to biological action. In the case of coal, the mean particle size must be reduced to a size less than 1 millimeter and in many cases to less than 100 microns. If the coal has chemical constituents which are known to inhibit organism growth, they are removed by washing or chemical treatment. If living organisms are to be used in

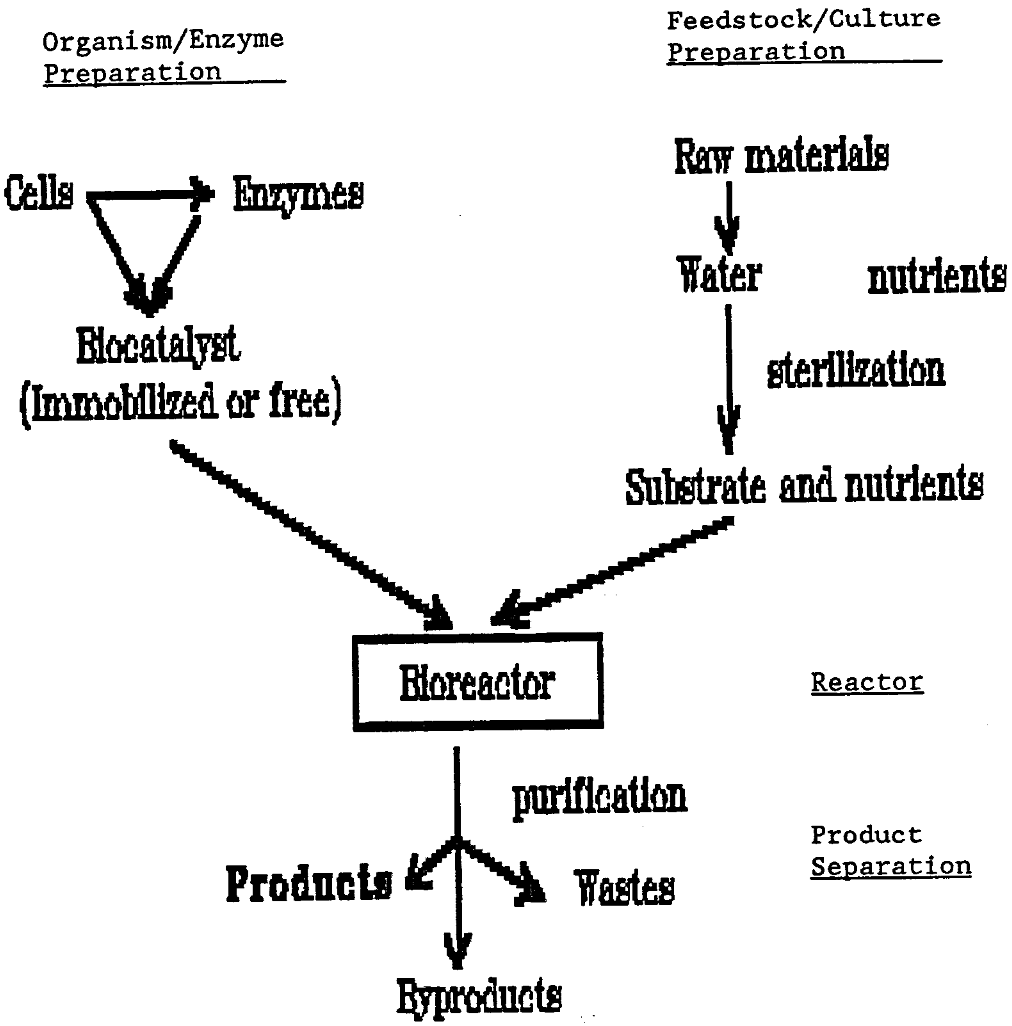


Figure 8-1. Schematic of a Generic Bioprocess

the process, inorganic salts and other additives are combined with the coal. The resulting solid is added to water. The amount of water used in the process varies with the reactor type. For example, a continuously stirred reactor will have a mass loading of 10 to 20 weight percent, requiring a copious amount of water for the process. In many commercial processes the resulting mixture is heated to kill all native organisms prior to its introduction to the bioreactor. If an enzyme is to be used, the coal and the enzyme co-factors are combined in water and added directly to the reactor.

In the organism/enzyme preparation element, a concentrated solution of biocatalyst is prepared. (Bioprocess reactions are catalyzed chemical reactions, except that the catalyst is biologically derived instead of being an inorganic material. For this reason the term biocatalyst has been chosen to describe an enzyme or whole cell used to catalyze the desired reaction.) When whole organisms are used as the biocatalyst, this element is called a primary fermentor. A small amount of culture containing pure-strain organisms is added to a sterilized volume of a premium medium. This medium is specially designed to provide a growth environment in which the organism can grow and reproduce rapidly. Most bioprocesses based on whole cells rely on the primary fermentation process to produce the majority of the cell mass. The conditions in the bioreactor are usually not suited for rapid cell production, or the time needed to attain high cell densities would be prohibitive. When the desired cell density is obtained, the contents of the primary fermentor are emptied into the main reactor and mixed with the waiting substrate. In processes based on an enzyme system, a solid enzyme preparation is mixed with water in the organism/enzyme preparation element. Any enzyme activation required is performed in this element.

In the reactor the biocatalyst performs the desired chemical conversion. The reactor conditions, such as temperature, pH, and species concentrations, are closely monitored and controlled. In systems based on whole cells, various types of gases may be added to the mixture by bubbling the gas through the mixture. Some bioconversions are inhibited by oxygen, and appropriate measures must be taken to insure that oxygen is excluded from the reactor. Since most whole-cell systems produce carbon dioxide as a result of cell metabolism, some mechanism must be provided to prevent the buildup of carbon dioxide.

Three types of bioreactor schemes are commonly employed in commercial activities: batch and continuous flow reactors, and heap leaching. Batch reactors process one volume at a time. At some point in time, the reactants have been depleted, products have increased to a maximal level, or inhibitors have increased significantly to cause reaction rates to decline. The reaction is then terminated, and the reactor is emptied into the separation element. The reactor is cleaned, sterilized, and prepared for the next batch. Continuous reactor schemes attempt to maintain a steady state of reactants, products, and inhibitors by continuously adding fresh substrate while withdrawing spent medium from the reactor. Film-type continuous reactors typical of liquid waste treatment operations maintain the biocatalyst on some type of solid support bed and trickle fresh substrate mixture on the top of the bed. Product and spent media are removed at the bottom of the reactor. Air-lift and fluidized-bed reactors continuously percolate the substrate mixture through an immobilized biocatalyst or a fluidized bed of biocatalyst. Fresh reactants are added at the bottom of the reactor, and products, carried by the percolation of liquid medium, are removed from the top.

A heap leach is used to process large volumes of solid materials. A biofilm is allowed to form on the surface of the particles on the top layer of the heap. In the case of coals or low-grade mineral ores, water is continuously added to the top of the heap. The organisms growing on the top of the heap metabolize components in the water or from heap constituents and liberate agents into the water. These agents, such as acid, act to leach the remaining portion of the heap as the water percolates downward. For low-grade mineral ores, products in the form of solubilized metal ions are removed with water from the bottom of the heap. In coal desulfurization pyrite is converted to water-soluble sulfate and metal ions, and the product, clean coal, remains in the heap.

In the product separation element the products are separated from the water, spent substrate, and unreacted material. No one separation scheme has been employed universally. Some of the separation schemes typically used include: filtration, distillation, evaporation, dialysis, and precipitation. This element of the process is relatively simple for coal desulfurization in which coal solid is the product. Coal solubilization may require acid precipitation or extraction of the depolymerized coal material. Conversion of coal-derived materials to alcohols may require distillation or membrane dialysis. The product separation area has received little attention in relation to coal processing, and better definition of the process must await further process development.

8.2.2 Advantages and Disadvantages of Bioprocessing

Bioconversion of coal is still in a very embryonic state of development, so that a discussion of the advantages and disadvantages of this approach to processing coal must be drawn from the general nature of biotechnology. As research and development progress, a better analysis will be possible. In general, bioprocesses have the following advantages:

- low process temperatures
- low process pressures
- environmentally safe effluents
- reduced capital costs
- high specificity of chemical reactions.

It is possible to compare a hypothetical bioprocess to depolymerize coal with a generic chemical approach. Chemical processes heat the coal to temperatures perhaps in excess of 400°C and maintain this temperature for the duration of the process. Bioprocesses operate at or near room temperature (25 to 35°C). If a sterilization step is required, coal and a small amount of water will need to be heated to 100°C for about 20 minutes, and process water can be sterilized by ultrafiltration. At some stage in the chemical direct liquefaction process, hydrogen at high pressure (>1000 psig) must be maintained in contact with the coal and the solvent. In the case of indirect liquefaction, gasifiers may be pressurized to levels as high as 1450 psig. Equilibrium formation of methanol is favored by moderately high temperatures (400°C for zinc oxide-chrome oxide to 260°C for copper-containing catalysts) and high pressure (300 atm, and greater than 50 atm for these two catalysts, respectively). The bioprocess proposed for direct liquefaction would operate at atmospheric pressure while that proposed for indirect liquefaction would be pressurized up to about 10 atm.

All chemical processes produce process water which must be treated to remove dissolved tar, oils, naphtha, phenols, heterocyclics, ammonia, hydrogen sulfide, organomercaptans, hydrogen cyanide, and trace metals. Bioprocess effluents could contain trace elements, cells, and some organics not removed by the separation process. In general, effluents from a bioprocess would resemble those coming from a water treatment plant, especially if a whole-cell process is used.

Capital costs of a conventional chemical liquefaction process are high. These costs are driven by the severity of the process conditions. In most cases bioprocesses do not have severe conditions and therefore will not require the additional cost associated with provisions for severe conditions. Finally, biochemical enzymes have a high degree of chemical specificity. An enzyme-promoted reaction will have only one product which is stereospecific. Inorganic catalysts may produce several products; the product distribution is controlled by the reaction branching mechanisms and reaction conditions.

The disadvantages of bioprocesses are associated with two factors: variable costs and process time. In systems using whole cells, various additives such as nutrients and salts are needed. Even if those materials are added in small amounts, associated costs may be sizeable. Power costs of a bioprocess may be high due to the cost of moving large amounts of water and gases through the process. These costs are independent of the biocatalysts used for the process.

Processing time becomes a major factor when considering wole-cell systems. Time is required for materials to diffuse in and out of cells. In addition, inside the cell the substrate must diffuse to the catalyst site. Processing times can be stretched to days as compared to hours for conventional catalysts to the size of the plant and, therefore, capital costs. An additional problem associated with whole-cell systems can arise from contamination of the process by an unwanted organism. For example, the cheese industry usually has three batches in one hundred destroyed by contamination of the batch by virus infections which kill the curd-forming bacteria.

8.3 DIRECT LIQUEFACTION (BIOSOLUBILIZATION)

8.3.1 Historical Background

8.3.1.1 Lignin Degradation

A variety of studies have shown that microorganisms have the ability to promote solubilization, depolymerization, and oxidation of coal and coal-derived materials (4,5). Most studies have used lower-rank coals, and some of these coals have undergone chemical pretreatments. These pretreatments are oxidative in nature and produce humic acid-like components in the resulting coals. Some "young" lignites can be characterized as containing as much as 35 to 70 percent lignin-like constituents. It is therefore appropriate to examine some of the chemistry associated with microbial interaction with lignin to possibly understand how microorganisms are interacting with coal.

White rot fungi, such as *Phanerochaete chrysosporium* and *Polyporus versicolor*, are known to be responsible for decomposition of woody tissues. The mechanism by which these fungi decompose lignin involve enzymes known as ligninase and laccase (6,7,8). The chemistry of these enzymes is associated with a nonspecific hydrolysis and ring cleavage of the phenylpropyl units in lignin. Figure 8-2a shows one of the proposed mechanisms for cleavage of lignin. Figure 8-2b illustrates the mechanism of ligninlytic activity shown by *Poria subacida* (9) which is known as an etherase. There does not appear to be a uniform route associated with fungal degradation of lignin. Each type of organism seems to have developed a unique set of enzymes to degrade lignin. For example, *P. chrysosporium* has been shown to have both an arylglycerol-β-aryl etherase (Figure 8-3a) and a 1-β and 4-β ligninase (Figure 8-3b). In general, the chemistry of microorganism attack on lignin appears to be associated with either the C_α and C_β carbons of the phenylpropyl subunits.

Although no accurate model of lignite or oxidized lignite currently exists, it is known that phenylpropyl units are not very prevalent in higher-rank coals (10). At present, it is uncertain as to the extent and

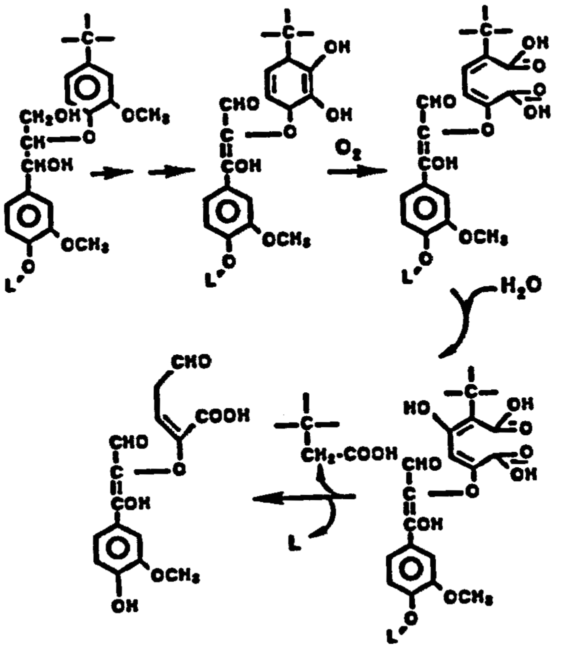


Figure 8-2a. Mechanism of Lignin Degradation

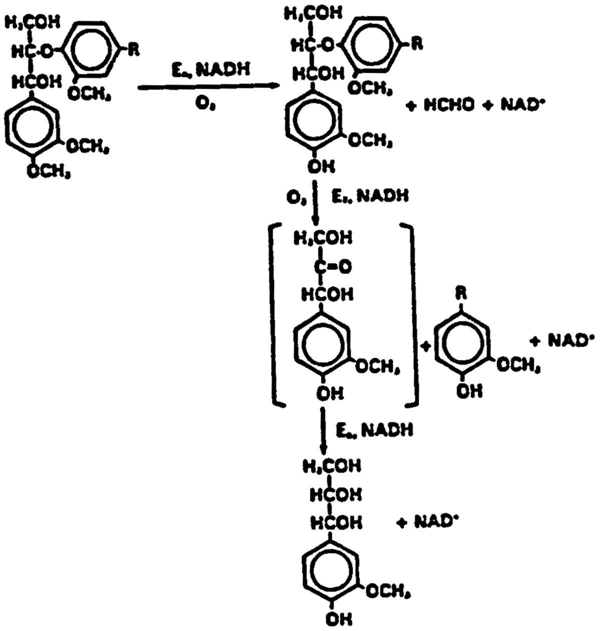


Figure 8-2b. Hypothetical Scheme of Cleavage of Ether Bonds by the Enzyme System of <u>Poria subacida</u>

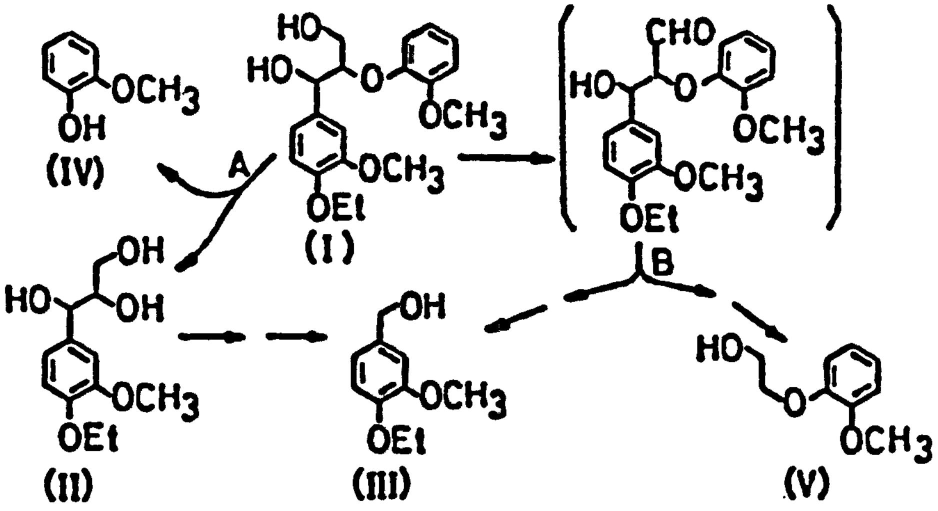


Figure 8-3a. Arylglycerol-β-aryl etherase

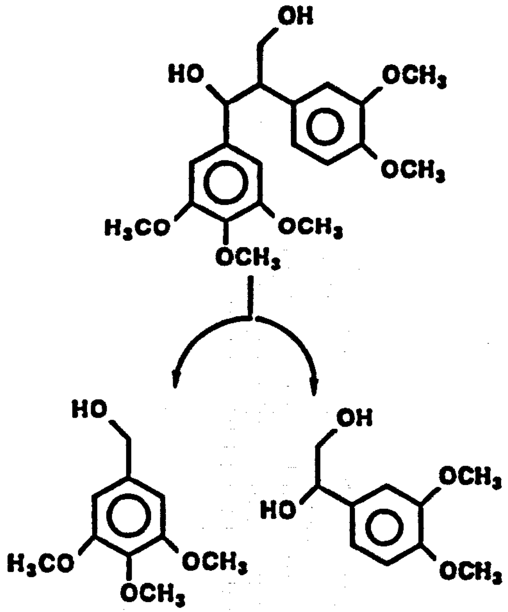


Figure 8-3b. 1-β and 4-β Ligninase Reactions

the severity of chemical reactions associated with microbial degradation of coal. At this point in this discussion, it is important to illustrate how versatile microorganisms can be when interacting with relatively inert materials such as wood.

8.3.1.2 Early Investigations

Suggestions that microbial action could occur on coal were reported in the early 1960's (11,12). However, these data were not pursued until quite recently when two groups of workers (4,13) almost simultaneously reported that filamentous fungi could produce coal-derived liquid materials. When the hyphae (fungi filaments) were viewed under a microscope, newly germinated hyphae were seen to have no affinity for coal. As the culture matured, greater and greater numbers of coal particles were observed attached to the hyphae. Furthermore, at the points of contact between the coal and the hyphae, the hyphae appeared dark or black. Additional work (14,15,16) followed these initial findings to confirm that organic-containing liquids were produced by numerous types of fungi when these fungi were grown in the presence of low-rank coals. Table 8-1 lists some of these organisms.

Based on the confirmation that organisms could live and grow on coal, research began to focus on how to enhance the observed action and to gain insight into what materials were being produced. When a range of coal types were examined for fungal activity, the greatest degree of activity was found to be associated with a lignite coal called leonardite (17). Comparison of the chemical compositions of the tested coals showed that the concentration of oxygen in the leonardite was considerably higher than that found for other types of coal. This finding led several groups (18,19) to investigate the impact of oxidative pretreatments on the coals in relation to microbial interaction.

The oxidative procedures that were evaluated ranged from heating the coal in air to chemical treatments, such as ozone, hydrogen peroxide, potassium permanganate, and nitric acid. Results showed that oxidative pretreatments improved biological degradation, but only for low-rank

Table 8-1. Fungal Types Examined for Solubilization Activity

- *Ascomycetes sp.*
- *Aspergillus sp.*
- *Candida sp.* (ML13,ACL-13)
- *Coprinus comatus*
- *Coriolus hirsutus*
- CP1 and CP2
- *Cunninghamella sp.* (YML-21)
- *Ganoderma lucidum*
- *Geosmithia argellacea*
- *Lentinus edodes*
- *Lenzites trabea*
- *Neurospora sitophila*
- *Paecilomyes TLi*
- *Penicillum sp.* (RML-5)
- *Penicillum waksmanii* (ML20)
- *Phanerochaete chrysosporium*
- *Pleurotus ostreatus*
- *Pleurotus sapidus*
- *Polyporus monticola*
- *Polyporus vericolor*
- *Rhizopus arrhizus*
- *Sporothix sp.*
- *Streptomyces flavovirens*
- *Strepotomyes setonii*
- *Streptomyces virdosporus*

coals. These findings also suggested that as the oxidative strength of the pretreatment increased, so did the extent of microbial degradation. The nitric acid pretreatment -- 8N nitric acid for 48 hours -- resulted in the lignite being almost completely solubilized (20,21). Pretreatment of the coal was also found to accelerate the onset of microbial action. When untreated coal was placed on an established fungal matte, the time required for the formation of black droplets could be as long as a week or more. A similar test performed on coal pretreated with 8N nitric acid began to produce black droplets within two hours after introduction of the coal to the fungal matte (22).

As the amount of biologically produced material increased from isolated drops to milliliters of material, researchers began to examine the material being produced by microbial action. The material was found to be highly polar and soluble in water up to greater than 20 weight percent (20). The solubility of the material was shown to be highly pH dependent, and a brown-to-black solid could be precipitated on acidification of the microbially produced liquid (17). Chemical analysis of this precipitate did not show a significant difference between the original lignite and the microbial product. However, the amounts of nitrogen and phosphorus in the microbial product were elevated. Spectroscopic analysis of the microbial product indicated an increase in oxygen functionalities. All analytical data combined to support the characterization of the microbial material as being a high-molecular-weight polycarboxylated aromatic polymer.

8.3.1.3 Recent Findings

Data now support the fact that the coal is not being directly converted to an organic liquid, but is, rather, being solubilized in water. (Hence, "biosolubilization" may be a more precise term for this process rather than "direct liquefaction.") This solubilization process is greatly enhanced by either using a weathered coal or performing an oxidative pretreatment on the coal. Coal types that are the most receptive to microbial solubilization tend to be low rank, such as lignites. Some subbituminus and bituminous coals have been shown to be partially solubilized. The water-soluble coal material appears to be large highly charged macromolecules. Current research activities are focusing on issues related to: (1) how pretreatment enhances or promotes microbial solubilization, (2) if microorganisms are secreting material that can react with the coal polymer to reduce its molecular weight, and (3) if enzyme systems isolated from lignin-degrading organisms can be used to degrade the coal polymer.

Early work investigating biological solubilization of coal determined that the amount of coal solubilized by microorganisms was dependent on coal rank and degree of oxidation. Many oxidative pretreatments were examined to improve the efficiency of microbial coal solubilization. The method which seemed to yield the greatest solubilization efficiencies was a pretreatment with 8N nitric acid for 48 hours.

When Texas lignite is exposed to 8N nitric acid, an exothermic reaction occurs. This reaction results in approximately 35 to 40 percent of the coal to be lost either during the reaction or during the coal washing needed to remove excess, unreacted acid. Comparison of Fourier Transform Infrared spectra for samples of treated and untreated Texas lignite indicates that nitric acid results in a significant amount of oxidation of the coal. There is also an indication that nitric acid also promotes nitration of the coal. Several researchers (16,19) have reported that the resulting acid-treated coal is extremely soluble in base. If the pretreated coal is washed with a series of buffer solutions of varying pH values, a comparison of the final extraction buffer pH and the cumulated weight of material lost suggests that acidic groups in the coal are being neutralized. Maximal coal solubilization always occurs when the final extraction buffer pH value ranges from 5.2 to 5.8. The resulting neutralization of coal acidic groups seems to result in increased water solubility. The resulting base- or buffer-solubilized coal can be reprecipitated using acid.

Since the culture pH value for many fungal and bacterial cultures which were effective in solubilizing acid-treated coal fell in the range of 5.0 to 6.0, researchers began to wonder if a similar effect of base-catalyzed solubilization could be responsible for microorganism-promoted solubilization of coal. To test this hypothesis a series of Streptococus sp. known to promote lignin degradation and coal solubilization were grown in liquid culture conditions (19). The pH of the culture was monitored prior to and at regular intervals following introduction of acid-pretreated coal to the culture. The culture pH was observed to initially decrease due to the residual acid in the coal and then gradually increase with time. A comparison of the extent of coal solubilization with the rise of the culture pH indicated that culture pH was correlated with coal solubilization. These data suggested that one mechanism responsible for Streptococal solubilization of acid-pretreated coal was related to the production of a material that increases the pH of the culture.

More recent results (20,23) indicated that the production of basic material(s) by fungi could also be related to the degree of coal solubilization. These findings suggested that one mechanism of initial coal solubilization was related to the release of an organic base produced by the organism. These organic bases were neutralizing the acid groups on the coal. This neutralization enhanced the hydrophilic nature of the coal, thereby increasing its water solubility.

Workers have also been interested in determining whether microorganisms are responsible for additional chemical degradation of the chemical structure of solubilized coal. Both fungi (21) and bacteria (19) have been examined for their ability to further degrade solubilized coal. Studies of bacteria using S. viridosporus, S. setonei, and S. flavovirens suggest that the solubilized coal is being altered due to microbial attack. This conclusion is based on changes observed in the ultraviolet spectra of culture solutions and on changes in the infrared spectrum of acid-precipitated material.

One organism (RWL-5) has been found to promote sufficient alteration in the solubilized coal that the polymer will not precipitate upon acidification. Results of studies using fungi indicate that fungi also have the ability to degrade solubilized coal (24). Studies have shown that products obtained from different fungi grown on the same coal are not exactly the same. HPLC chromatographs of the products show peaks which do not elute at the same retention times. These results suggest that microorganisms do have the ability to attack solubilized coal.

Researchers have also been examining the utility of using cell-free enzyme extracts to promote coal solubilization and degradation of the resulting solubilized polymer (20,24,25). These studies are still very preliminary and do not support a definitive conclusion. Several researchers report that certain laccases (26) and peroxidases (25) have the ability to enhance the rate of coal solubilization.

A recent study (25) of the effect of purified lignin peroxidase from *P. chrysosporium* on previously base-solubilized coal extracts prepared from North Dakota lignite and German subbituminous coal found significant decreases in the high-molecular-weight coal polymer peak using gel filtration. The decrease was dependent on the polymer-to-enzyme ratio. This decrease in the polymer peak was accompanied by the appearance of both higher- and lower-molecular-weight peaks. No peaks were observed for monomeric units. Additional research was suggested to ascertain whether the polymer was being degraded chemically or the enzyme was causing polymer subunits to be dispersed and reaggregated. The latter explanation could explain the appearance of higher-molecular-weight fragments. However, a similar reaggregation of chemically broken fragments could also be responsible for the observed results.

Additional research is required in the area of enzymatic interaction with solubilized coal before any conclusions concerning the production of low-molecular-weight fragments from coals can be made.

8.3.2 Current Research Agendas and Objectives

Current research activities in coal solubilization can be summarized as being concerned with four major topics: (1) microbial promotion of coal solubilization, (2) microbial degradation of the solubilized coal polymer, (3) chemical structure of the solubilized coal polymer, and (4) the implications of metal-ion binding to the coal macromolecule. Numerous research groups are currently trying to understand the mechanism by which the microorganism facilitates coal solubilization. Work is focusing on various issues, and the typical questions being addressed are:

- Does the presence of coal solids induce base production?
- What is the role of nitrogen additives in the medium in relation to the production of base?
- Does the microorganism produce other materials such as enzymes that also promote solubilization?
- Are microorganisms able to directly oxidize the coal structure without prior oxidative pretreatment?

Degradation of the solubilized coal polymer is also a very active area of research. Questions being investigated by this research include:

- Can microorganisms act to further degrade the solubilized coal polymer?
- What is the mechanism for this action?
- Can cell-free enzyme preparations be used to degrade the coal polymer?
- Do nonaqueous enzyme systems have any utility for degradation of the coal polymer?
- Are there anaerobic organisms that will metabolize the coal polymer to produce hydrocarbons, methane, or other types of materials?

Coal structure and the structure of the solubilized coal polymer are being studied to a lesser extent. Answers to these questions are currently being sought:

- What is the chemical composition of the coal polymer?
- What is the chemical structure of the polymer?
- What is the role of metal ions in holding the original coal structure together, and are metal ions holding the polymer subunits together?

Overall, the key research issues for coal solubilization are:

- Are microorganisms important for coal solubilization?
- Does microbial solubilization afford any advantage relative to conventional methods for coal liquefaction?

Research into microbial coal solubilization has only just begun to address these issues. Past research has been beneficial in providing insight and opportunities, but more effort is needed in all aspects of this research area.

Although several schematic systems for microbial coal solubilization processes have been proposed, the field is so embryonic that research findings are continually causing researchers to rethink what the eventual process may look like. It does not seem reasonable at this point to devote a great deal of effort to propose processes for microbial solubilization of coal, and the data and findings currently being reported do not support extensive technology development. They are, rather, very supportive of continued research into the phenomena and of expanded funding for a broad range of exploratory work related to coal solubilization.

8.3.3 Research and Development Needs

8.3.3.1 Biotechnology

For biosolubilization to become a significant processing scheme for the treatment and conversion of coal, a significant amount of research and development will be needed. Intense study of microbial systems for processing of coal has only occurred in the last four to five years. Most of this effort has focused on the phenomena of microbial interaction with coal. Reaction chemistry, kinetics, and process-related development still need to be performed. More extensive characterization of all classes of organisms needs to be undertaken.

Most studies have examined only a limited number of organisms. Higher plants and animals, such as algae and protozoa, have been ignored. These biosystems are extremely varied and complex. The complexity of these higher biosystems supports their potential of providing highly specific conversion and processing chemistries and of their being more amenable to coal bioconversion than lesser developed microorganisms. Most of the organisms that have been studied for processing of coal are not common to most academic studies. Therefore, very little is known about their physiology and genetics.

If bioconversion of coal is to be performed with organisms that have been genetically enhanced, more knowledge will be needed about the biochemistry involved in the desired process and the nature of the genetic control of this chemistry. Mechanisms will need to be developed to transfer and incorporate the genetic material into the organism.

8.3.3.2 Bioreactors

Once viable organisms are obtained, considerable development of bioreactors which can handle solid substrates will need to be performed. Due to the significant impact of the need for medical drugs, most bioreactors have been developed to treat substrates that are either suspended or soluble in water. Coal does not readily suspend in water and without pretreatment is not soluble in water. Limited studies using solid substrates in conventional bioreactors have shown that solids present various types of problems. These problems include reactor plugging by the biomass, solids settling, and decreased mass transport. Most bioprocesses require mass loading of less than 20 percent. Methods will be needed to cost-effectively remove this large amount of excess water, or new bioreactor designs based on minimal water content will need to be developed.

Various economic analyses suggest that product separation and dewatering could represent a cost as large as the cost of the actual bioprocess. These estimates suggest that significant advances in separation processes will need to be found to reduce process costs. At some point in time, funds will need to be made available to scaleup appropriate concepts.

8.3.3.3 Solubilization Studies

Continued study of coal solubilization is warranted by the interesting findings starting to be published. More effort needs to be focused on the examination of microbial systems which function in the absence of oxygen. Most of the current solubilization studies are using an oxidative organism to produce oxygenated products. Organisms which function in the absence of oxygen have the potential of producing products low in oxygen content and having reduced chemical natures. These products could be more soluble in nonpolar solvents, thus making them amenable to separation from water.

Current efforts to find cell-free enzymes should be continued. The scope of these studies should be broadened to include decarboxylases, dehydroxylases, and other such enzymes. To support these enzyme studies more emphasis needs to be given to understanding the structure of low-rank coals, such as lignite. Special attention needs to be given to the type of bonding which holds the three-dimensional structure together. If we understand how low-rank coals are held together, we may be able to select specific enzymes or microorganisms which can effectively degrade these chemical structures. More effort is needed to explore all the possible research avenues.

8.4 INDIRECT LIQUEFACTION

8.4.1 Historical Background

8.4.1.1 Overview

The use of coal-derived gases affords advantages for conversion of coal and coal gas to methane and other low-molecular-weight fuels. The gasification can be performed in situ, the reaction kinetics for coal degradation are accelerated, and the process is independent of coal type. Biological processes offer advantages for conversion of coal-derived gas to clean fuels in that the process can occur at ordinary temperatures and pressures. Biological conversions have the potential for very high conversion yields and very high product specificity. Biological processes will generally tolerate trace quantities of substances that will poison catalysts used in conventional chemical conversion schemes.

8.4.1.2 Early Investigations

All of the research related to indirect liquefaction using microorganisms has been performed by researchers at the University of Arkansas (27). The primary thrust of their early research in this area was to determine the feasibility of converting gas mixtures containing hydrogen, carbon monoxide, and carbon dioxide to methane. Initial studies employed samples of organisms collected from sewage treatment plants and various types of animal wastes. A mixed culture was obtained which was capable of converting approximately 95 percent of the carbon monoxide and hydrogen to products. The time required for conversion of the gases supplied to the culture was approximately two hours. The products obtained from the microbial conversion were analyzed and found to be primarily methane with a small amount of acetate.

Attempts to improve the biological pathway led the researchers to screen large numbers of organisms for their ability to convert carbon monoxide to methane. In the process two organisms were identified, Peptostreptococus productus (P. productus) and Acetobacterium woodii. P. productus converts carbon monoxide and water to acetate and carbon dioxide.

When a test gas composed of 65 percent carbon monoxide, 22 percent hydrogen, 11 percent carbon dioxide, and 2 percent methane was introduced to a previously acclimated culture of P. productus, approximately 90 percent of the carbon monoxide was converted to acetate in 0.7 hour. Analysis of the products also indicated small amounts of other organic acids and alcohols. The sensitivity of P. productus to hydrogen sulfide and carbon disulfide, common catalyst poisons, was also evaluated, and at concentration levels typical of coal gasification, these gases were found not to inhibit acetate production.

In an attempt to produce more acids and alcohols from the mixed cultures isolated from wastes, various types of methane formation blocking agents were investigated (28). The preliminary screening studies showed the ability to obtain small quantities of ethanol, butanol, and methanol, as well as acetate. Attempts to isolate a pure culture from this mixed consortium found one organism capable of producing only ethanol.

8.4.1.3 Recent Findings

The Arkansas group has continued to investigate the production of low- molecular-weight alcohols from both mixed and pure cultures grown in the presence of gasifier products (29). Their results indicate conclusively that various types of low-molecular-weight organic acids and alcohols can be produced when carbon monoxide is used as the carbon source. A pure isolate has been found which produces only acetate and ethanol. This culture requires that a small amount of yeast extract be incorporated in the growth medium, and conversion of carbon monoxide is enhanced when the medium is agitated. An ethanol concentration of approximately 4.3 grams per liter has been obtained. Attempts to identify this organism indicate that it is a bacterium of the Clostridium sp. classification.

8.4.2 Current Research Agendas and Objectives

The scope of research activities related to microbial indirect liquefaction is currently being defined by only two research groups. The research effort is being placed on conversion of biosolubilized coal to methane and on conversion of syngas to methane and various alcohols. Research related to production of liquid fuels is currently seeking answers to the following:

- Which types of cultures are best suited to the production of alcohols?
- How can biochemical systems associated with these organisms be controlled to cause the microorganisms to produce only a single product or the desired product?
- What type of bioreactor design is most suited for production of products when using gaseous substrates?

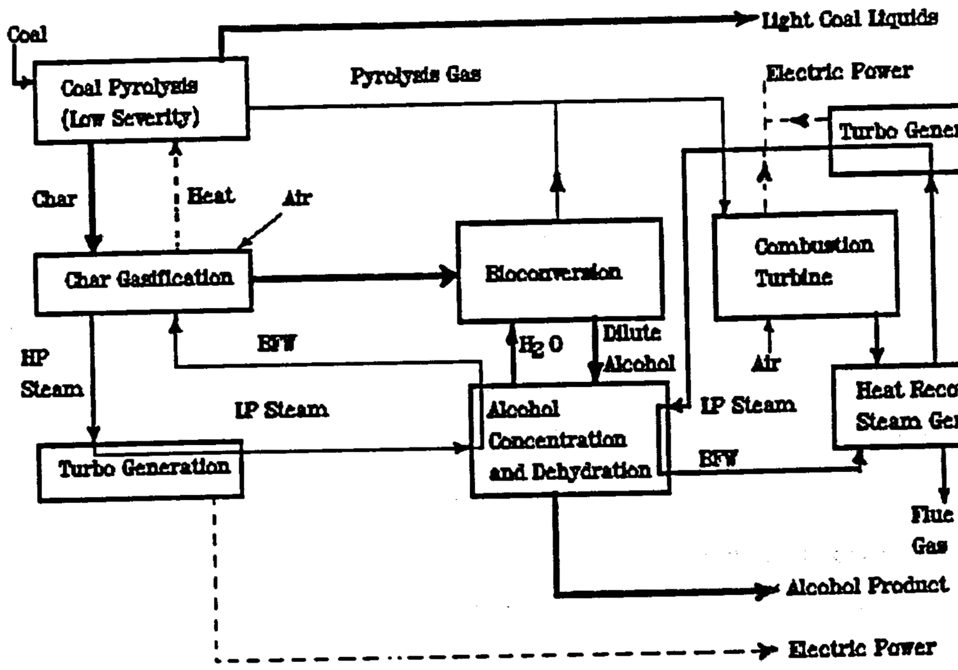
Studies examining the potential of microorganisms for conversion of solubilized coal polymers to methane are concerned with:

- What types of methane-producing organisms are also salt tolerant (halophiles)?

The key research issues associated with these types of investigations are:

- Can efficient conversion of carbon monoxide to ethanol be obtained using single organisms or collections of organisms?
- Can microorganisms which produce methane be found which can use solubilized coal as a substrate?

Two integrated gasification, bioconversion combined-cycle processes have been proposed for the conversion of syngas to alcohol (30). (See Figure 8-4.) These system schematics are based on a combination of existing combined-cycle gasification plants where the bioprocess is included at some point in the scheme. As yet, the specific unit operations associated with the bioprocessing element have not been fully defined. Bench-scale bioreactors have been constructed to evaluate the feasibility of matching a bioprocess to a gasifier. Larger-scale models of this reactor have not been constructed or tested.



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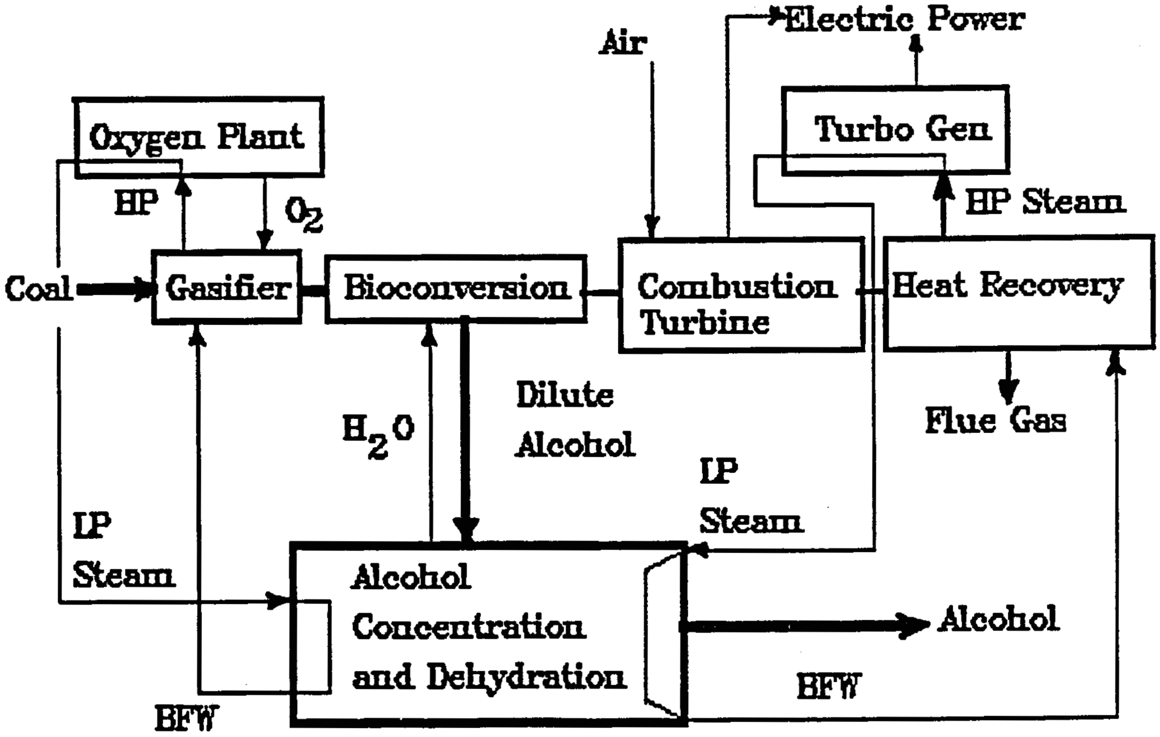

Figure 8-4. Integrated Gasification, Bioconversion Combined Cycle Processes

One large-scale process has been proposed for conversion of solubilized lignite coal to methane (31). (See Figure 8-5.) As a novel approach for a bioreactor, it is proposed to use a large salt dome as the reactor. Proposers suggest that due to the subsurface depth of the salt dome, the heating of the culture and the subsequent pressurization of the evolved gas will be provided by the geologic conditions. If a methane-producing extreme halophile can be identified and found to metabolize solubilized coal, this concept may be the first bioprocess demonstrated on a large scale.

One economic analysis has been published for the production of ethanol from syngas using a microbial conversion process (30). This analysis assumed that the syngas was cooled and partially purified. The alcohol was recovered from the organism growth medium suspension by distillation and prepared for gasoline blending by conventional concentration and dehydration. Two separate financing schemes were assessed, utility and private. The estimated cost per gallon of alcohol produced ranged from $0.78 for private financing to $0.58 for utility financing. These costs compare favorably with the current $1.06 per gallon cost of fuel grade alcohol. It should be noted that a significant cost return was realized for the power produced by the process, and this return significantly reduced the cost of the alcohol.

8.4.3 Research and Development Needs

The research and development needs for biosolubilization discussed above in Section 8.3.3.1 apply to bioconversion in indirect liquefaction as well. A greater variety of organisms need to be studied, including more extensive characterization. Reaction chemistry, kinetics, and process-related development need to be performed.

A significantly enhanced research program is needed in the area of syngas and biosolubilized coal conversion to liquid fuels. Based on the positive finding of a single research activity, the scope of the present

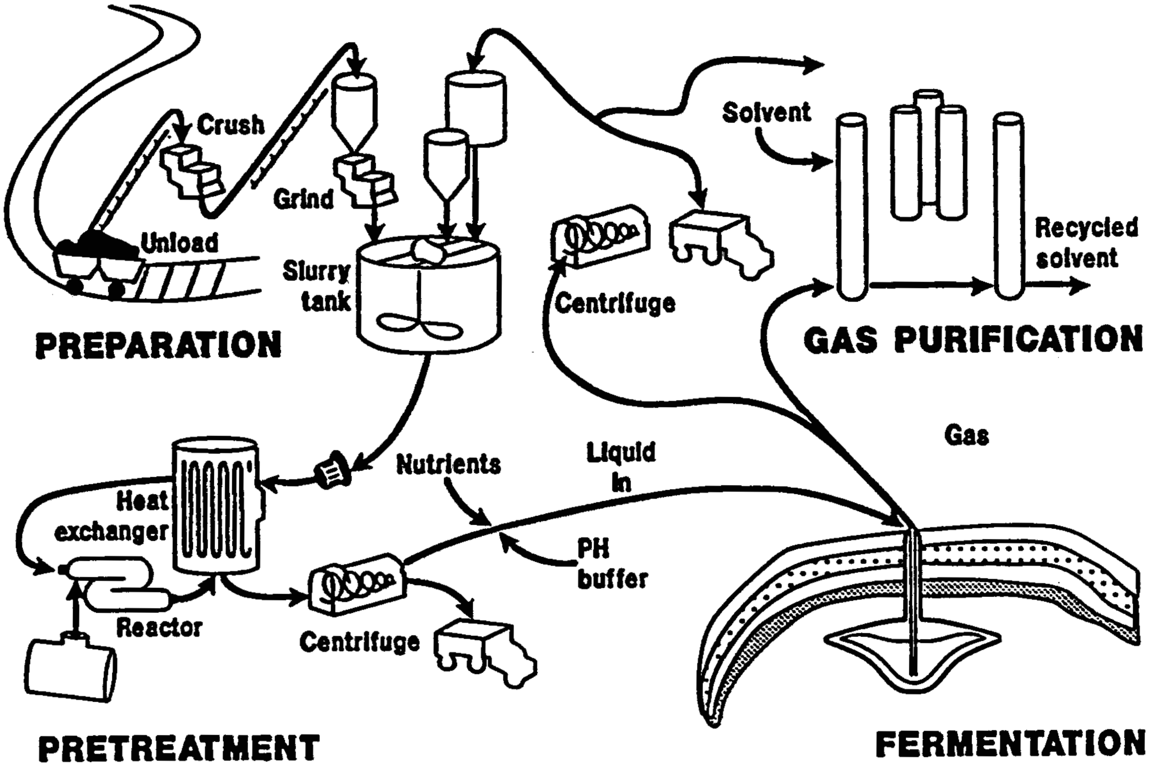

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Figure 8-5. Biosolubilized Coal to Methane Processing Plant research activity needs to be dramatically expanded. Since gaseous and liquid substrates are more convenient to introduce and to maintain in bioreactors, the problems associated with solids processing will not be experienced. Studies which examine a greater variety of anaerobes and facultative anaerobes should be undertaken. Organisms which convert acetate to higher-molecular-weight compounds should be examined. More emphasis should be given to conversion of biosolubilized coal to low-molecular-weight fuels, such as methane, acetate, and alcohols. In general, a greatly expanded program is required in all areas. Researchers should be encouraged to take a broader look at conversion of either biosolubilized or gasified coal.

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CHAPTER 9

LIQUEFACTION DEVELOPMENTS OUTSIDE THE U.S.[1]

9.1 INTRODUCTION AND SUMMARY

9.1.1 Introduction

A reliable energy supply is a prerequisite for the preservation and further development of the economic power of an industrialized country. Few industrialized countries have extensive petroleum reserves, but several have large coal reserves or, as in the case of Japan, have reliable foreign sources of coal. Consequently, coal conversion to liquid fuels is being pursued by several countries to ensure a continued supply of these fuels in the event of the disruption or reduced availability of imported oil supplies.

This chapter reviews the major liquefaction efforts in six other countries -- the Federal Republic of Germany (FRG), Japan, Canada, Great Britain, Italy, and the Peoples Republic of China. The three commercial Fischer-Tropsch plants in South Africa were discussed in Chapter 5. The New Zealand plant converts syngas to gasoline via the Mobil MTG process; however, the syngas is made from methane, not coal. Finally, the work in the Soviet Union cannot be reviewed because it has not been published, even though the government announced a few years ago that a commercial-sized liquefaction plant was to be built in the Urals.

As discussed in Chapter 5, commercial oxygenate plants are in operation worldwide. Fourteen plants are in operation, under construction, or being planned with plant capacities ranging from 55,000 to 1.6 million lb/yr of methanol production (1). Forty-two other plants make or will soon make alcohols other than methanol, with plant

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[1] This chapter was written by Harvey D. Schindler, Science Applications International Corporation.

capacities ranging from 20,000 to 950,000 lb/yr (1). These plants are based on a variety of processes, including CO/H_2 synthesis. However, few start from coal; natural gas is the major source of syngas.

9.1.2 Summary

Several industrial nations are continuing active development of coal liquefaction technology. Process conditions are determined by the particular needs and properties of the coals that pertain to each nation. For example, the coal resources in the People's Republic of China (PRC) are in the interior, while the population and industrial centers are along the coast. Consequently, a major objective of liquefaction in the PRC is to produce a more easily transportable fuel. The Brown Coal Process in Australia is designed for a specific, reactive coal, while German technology has been developed to liquefy older, less reactive coals.

Despite such differences direct liquefaction processes under development are surprisingly similar. All are based on high-pressure, high-temperature hydrogenation. Several differ from U.S. technology, principally in the use of cheap iron-based catalysts, as originally used in Germany, and the emphasis on fixed-bed instead of ebullated-bed reactors. Table 9-1 shows the similarity of the processes in the development. The German technology differs from the others in that the second reactor is a gas-phase hydrogenator of the coal liquids, which integrates liquefaction with refining.

Table 9-1. Direct Liquefaction Processes Under Development Outside the U.S.

Country	Process	Reactor Stage			
		First		Second	
		Catalyst	Configuration	Catalyst	Configuration
Germany	German Technology	Red Mud	Slurry Phase	N/A	Fixed Bed
	Pyrosol	Red Mud	Slurry Phase		Coker
	High-Pressure Hydrogenation	Red Mud	Slurry Phase		
	Coprocessing	Red Mud	Slurry Phase	N/A	Fixed Bed
Japan	Brown Coal	Iron-Based	Slurry Phase	NiMo	Fixed Bed
	Bituminous Coal	Iron-Based	Slurry Phase	NiMo	Fixed Bed
U.K.	Low-Severity Extraction		Thermal	NiMo	Ebullated Bed
Canada/[1]	ARC	Iron Sulfide	Slurry Phase	Iron Sulfide	Slurry Phase
	CANMET	Iron in Coal	Slurry Phase		
	OOFC	NiMo	Ebullated Bed	NiMo	Ebullated Bed
Italy		Sodium Carbonate			
PRC		Iron-Based	Slurry Phase	N/A	N/A

N/A = Information not available.
[1] Coprocessing

9.2 FEDERAL REPUBLIC OF GERMANY

The major effort in Germany is in direct liquefaction, with some work having started recently in coprocessing. Indirect liquefaction (Fischer-Tropsch) is considered less attractive for commercialization because it requires higher investment and has a lower energy efficiency. Three direct liquefaction processes and one coprocessing process are under development. Table 9-2 presents an overview of these projects (1).

9.2.1 German Technology

German liquefaction technology is basically an extension by Ruhrkohle AG of the Bergius-Pier process. It uses high pressure, high temperature, and an inexpensive iron catalyst, such as red mud. Typical operating conditions are shown in Table 9-3. This technology was demonstrated from 1981 to 1987 at Bottrup at a scale of 200 tons/day. Among the process advances made during this development period was the addition of a gas-phase hydrogenator (GPH) to produce a light product with low heteroatom content. The all-distillate recycle solvent is recovered from the GPH (see Figure 9-1).

The test operation with coal was terminated in 1987, and the unit is now being used to process petroleum vacuum resid.

9.2.2 Pyrosol Process

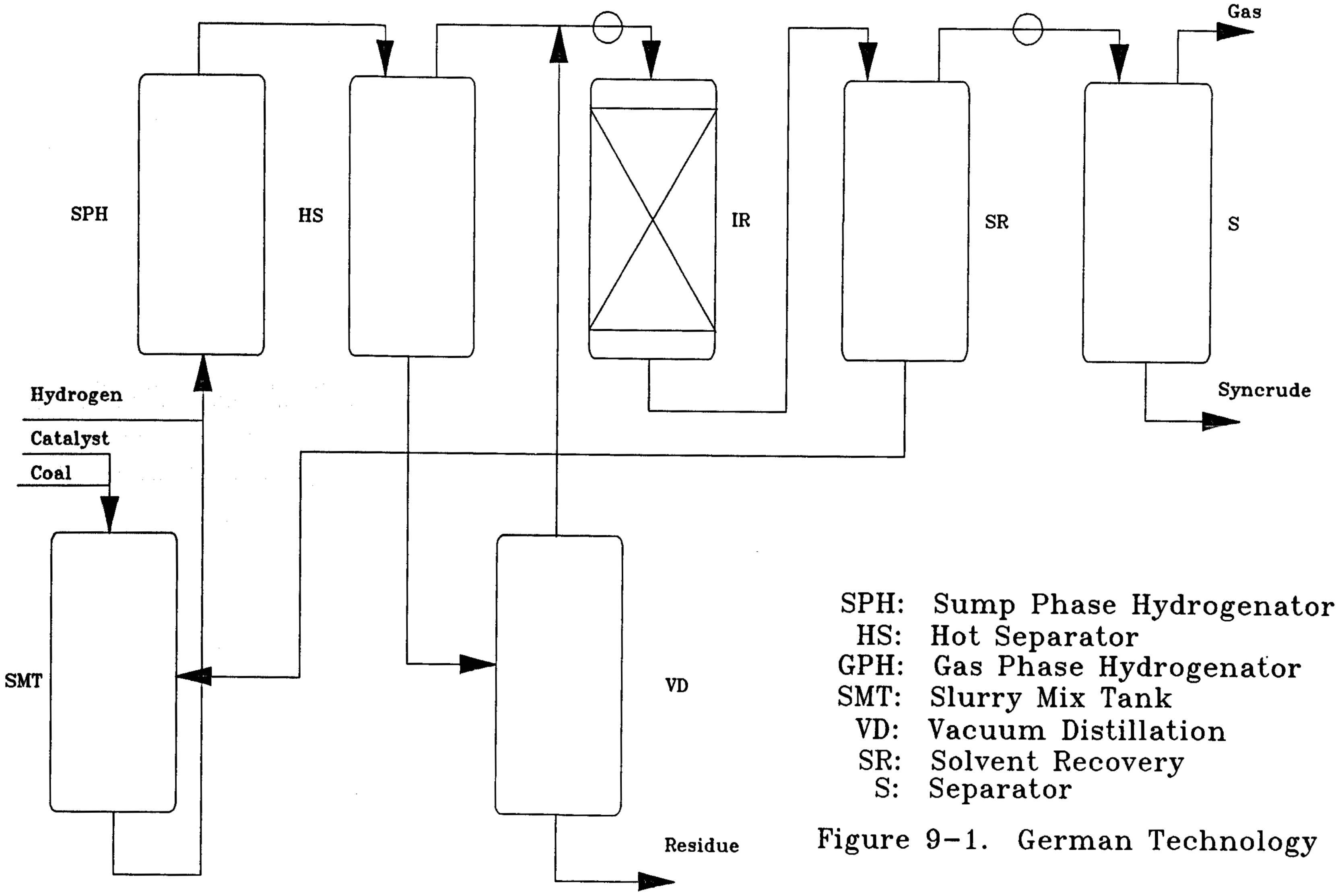
Saarbergwerke AG has been developing this process at a scale of 6 tons/day since 1985. Coal is hydrogenated at 3000 psi in the first stage. In the second stage the separated hydrogenated residue is coked under hydrogen pressure (see Figure 9-2). The coker distillate is recycled to slurry the coal feed. The major feature of this process is the low hydrogen consumption of 4 percent for a liquid yield of 57 percent.

Table 9-2. German Coal Liquefaction Projects

Process	Scale of Development Tons/day	Liquid Yield wt %
German Technology	200	66
Pyrosol	6	57
High-Pressure Hydrogenation	2	59
Coprocessing	0.05	>75

Table 9-3. German Technology (Ruhrkohle AG) Typical Operating Conditions

Pressure, psig	4500
Temperature, °F	890
Coal/Solvent, lb/lb	0.7
Type of Solvent	distillate
Catalyst	red mud
Type of Coal	Ruhr
Volatile Matter, % MAF	36-39
Reactor Volume, ft^3	390



SPH: Sump Phase Hydrogenator
HS: Hot Separator
GPH: Gas Phase Hydrogenator
SMT: Slurry Mix Tank
VD: Vacuum Distillation
SR: Solvent Recovery
S: Separator

Figure 9-1. German Technology

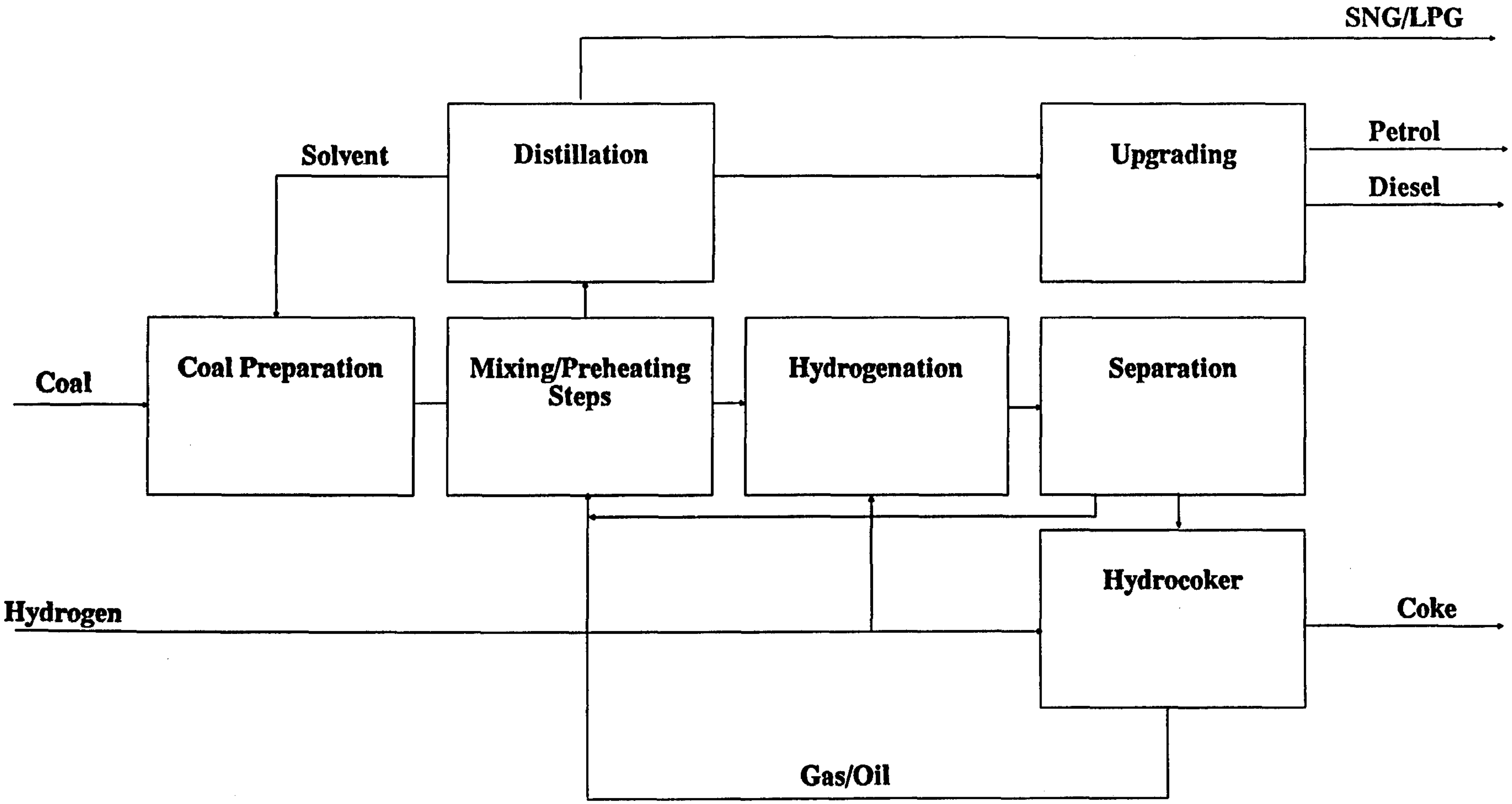


Figure 9-2. Pyrosol Process

9.2.3 High-Pressure Hydrogenation

This process, under development by Salzgitter AG, goes in a direction opposite to the trend of mild reaction conditions. The pressure is 10,000 - 22,000 psi, the temperature is 950°F, and the catalyst is red mud. The extreme process conditions are used to obtain high liquid yield at high reaction rates and short residence time. A test plant with a throughput of 2 tons/day has been operated since 1984. A simplified process flow diagram is shown in Figure 9-3.

The maximum oil yield is 59 percent with a hydrogen consumption of 6 percent.

9.2.4 Coprocessing

Veba Oil AG and Ruhrkohle AG have been developing coprocessing in a joint venture started in 1987. The process is the same as for the German liquefaction technology, except that the petroleum solvent is used on a once-through basis. Tests have been made at a scale of 100 lb/day. Oil yields have been reported to be above 75 weight percent.

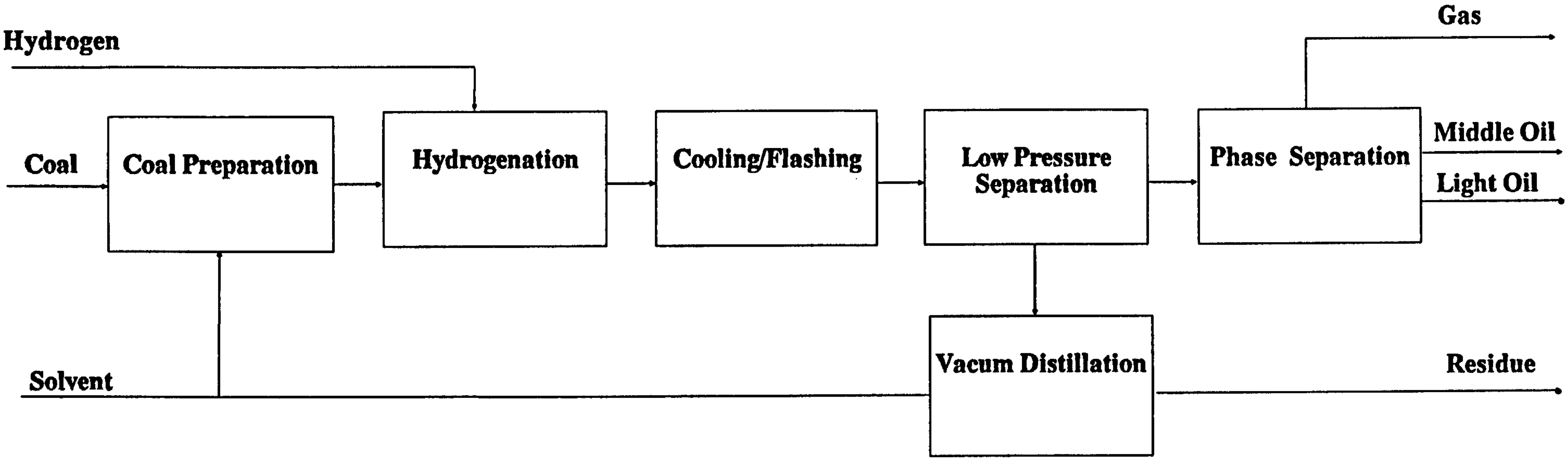


Figure 9-3. High - Pressure Hydrogenation

9.3 JAPAN

Japan's liquefaction program is the responsibility of NEDO, the New Energy Development Organization. Two direct liquefaction projects are being funded.

9.3.1 Brown Coal Liquefaction

The first project started was the Brown Coal Liquefaction (BCL) Project, which is designed specifically to liquefy high-moisture Victorian (Australia) brown coal. A 50-tons/day plant has been in operation in Mornsell, Victoria, since 1987 and is scheduled to operate through 1989. The BCL process consists of two-stage hydrogenation with deashing between stages. The first stage uses an inexpensive slurried iron-base catalyst on a once-through basis. The second stage uses a fixed bed of Ni-Mo catalyst. System pressure is 2200-3000 psig, and reaction temperatures are 800-840°F. The targeted liquid yield is 50 percent light and middle distillate. A special slurry drying system is being used because of the high (>60%) moisture content of this coal.

9.3.2 Bituminous Coal Liquefaction Project

Japan's liquefaction research effort started in 1974 with the development of three processes that are similar to U.S. processes-direct hydrogenation (H-Coal), solvolysis (ITSL), and solvent extraction (EDS). In 1984 these three processes were combined as the NEDOL process.

In the first stage the coal is liquefied, converted to naphtha, and distilled by catalytic hydrogenation and hydrogen transfer from the recycle solvents. After removal of net product, solids, and residue, the solvent is hydrogenated in a fixed bed reactor and recycled to slurry the coal. A schematic flow diagram of the one-ton/day PDU is shown in Figure 9-4. The NEDOL process will be scaled up to 150 tons/day starting in 1991. Operations are scheduled to begin in 1994. The operating conditions for the two reaction stages are:

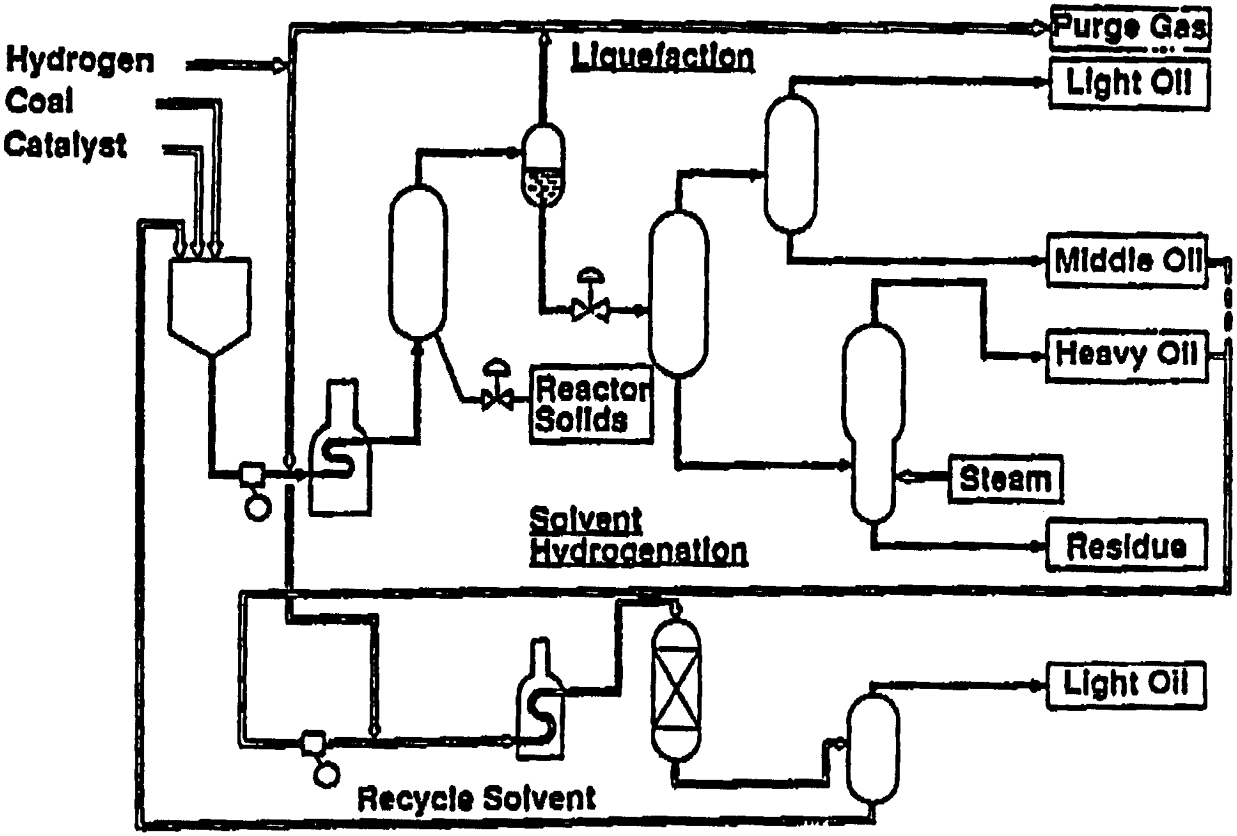


Figure 9-4. Schematic Flow Diagram of NEDOL Process PDU

Coal Liquefaction Unit

Temperature, °F	840
Pressure, psig	2400
Liquid Residence Time, min	60
Gas/Slurry Ratio, SCF/lb	55

Solvent Hydrotreating Unit

Temperature, °F	625-700
Pressure, psig	1400
LHSV, hr^{-1}	1.0
Gas/Solvent Ratio, SCF/lb	28
Catalyst	Ni-Mo/Al_2O_3

In addition to the large scale NEDOL plant, supporting research is being conducted to obtain process and engineering data necessary for its successful operation. The research is being performed in three units--a 0.1-ton/day bench unit, a 1-ton/day process development unit (PDU), and a newly completed 1-ton/day process supporting unit (PSU).

9.4 CANADA

Canada's emphasis in liquefaction is the coprocessing of the low rank coals and heavy crude oils which are in abundance in the west. The coprocessing effort actually started with the CANMET Hydrocracking Process, which was developed to hydrocrack heavy crudes, such as Cold Lake, Lloydminster, and Athabasca tar. In this process 2-5 percent coal is slurried as catalyst with the petroleum resid feed. A promoter, such as an iron salt, is coated on the coal to provide additional hydrogenation activity. Distillate yields of almost 100 volume percent have been reported (5). The development culminated in the construction of a 5000 barrel/day unit in Montreal that started up in 1985. Little information has been published about the operation of that unit.

From that hydrocracking process it was a relatively small leap to go to coprocessing. The reactor configuration was maintained, but the coal concentration was increased to 30-35 weight percent. Two independent, but similar, developments are in progress.

9.4.1 Alberta Research Council (ARC)

The Alberta Research Council operates a 100-lb/day continuous unit that contains two 3-liter stirred autoclaves in series (6). The operating parameters are:

Coal Concentration, wt% MAF	33-35
Preheater Temperatures, °F	575°F
Reactor Temperature, °F	770-825
Reactor Pressure, psig	2000-3000
Catalyst, wt% on feed	
Iron oxide	0.6
Dimethyl Disulfide	0.36

This work is exploring the effect of reaction conditions, using several combinations of Alberta coals and crude oils.

9.4.2 CANMET

The second Canadian development is being carried out by CANMET. The feedstocks that they have tested include coals from the U.S. and eastern Canada.

The CANMET process development uses a single one-liter back-mixed reactor with a capacity of 50 lb/day (see Figure 9-5). The catalytic promoter is apparently coated on the coal, as previously done in the CANMET Hydrocracking Process. Reaction temperature is about 840°F, and pressure is 2000 psig.

This work is still at a bench scale, testing reaction parameters on several coal/oil combinations. Although no scale-up plans have been announced, the hydrocracking unit would appear to be the obvious choice for a commercial demonstration.

9.4.3 Ontario-Ohio Clean Fuels (OOCF)

Despite the name all recent research and development has been performed in the U.S. OOCF received a DOE Clean Coal award for an 11,700 barrel/day coprocessing plant in Ohio. The feeds will be Ohio bituminous coals and Cold Lake reduced crude. This project was discussed in Chapter 7.

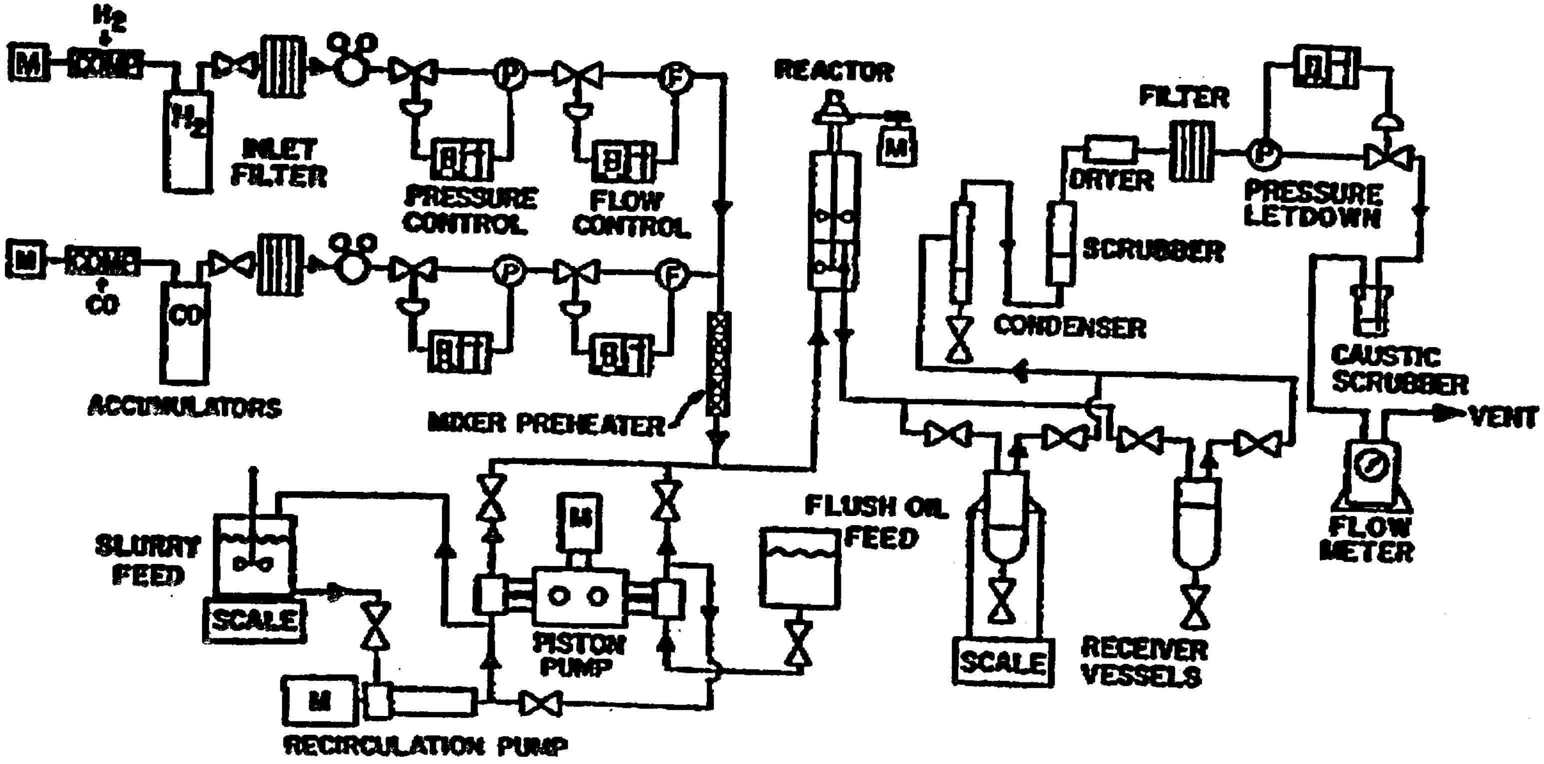


Figure 9-5. CANMET Continuous-Flow Coprocessing Unit

9.5 GREAT BRITAIN

9.5.1 Direct Liquefaction

The Coal Research Establishment is developing a two-stage process called Liquid Solvent Extraction (LSE). After extensive development in a 20-lb/day bench unit, LSE is being scaled up to 2.5 tons/day at Point of Ayr, North Wales (8). The first stage is a low-pressure thermal liquefaction, in which hydrogen is transferred from solvent to coal. The first-stage product is filtered to provide a clean feed to the second-stage hydrocracker. Initially, the LSE process used a fixed-bed hydrocracker, but recent interest is in an ebullated-bed reactor, which will probably be installed at Point of Ayr.

9.5.2 Indirect Liquefaction

A process for the manufacture of mixed alcohols, as a gasoline additive, from synthesis gas and methanol has been developed in a small unit (unspecified size). Experimental studies have concentrated on establishing optimum feed ratios of hydrogen, carbon monoxide, and methanol and optimum pressures (up to 3000 psi) to determine alcohol yields and quality of the products as gasoline additives.

9.5.3 Pyrolysis

The Coal Research Establishment continues to do research on a bench scale on hydropyrolysis and catalytic hydropyrolysis. The results of the catalytic hydropyrolysis research were reported in Chapter 6, Section 6.2.3. Their reported tar yield of 59 percent is by far the highest for any pyrolysis process, and based on this result, the assessment panel recommended that high priority be given to studies of catalytic hydropyrolysis.

9.6 ITALY

Several research efforts in the U.S. and abroad (9) are using carbon monoxide and water to generate hydrogen in situ in the hydroliquefying reactors. This process concept is the basis of work by Eniricerche (10). The tests are performed at 750°F for 60 minutes. The catalyst is sodium carbonate. Tests with Illinois No. 6 coal resulted in greater than 90 percent conversion to THF-solubles, with a carbon monoxide conversion of 60-80 percent. The calculated hydrogen consumption was 1.7 percent by weight of coal. Although promising, this work is in a very preliminary stage.

9.7 PEOPLES REPUBLIC OF CHINA (PRC)

9.7.1 Direct Liquefaction

PRC started its process development by buying three small units-one from Germany, which can be used to test the German technology; one from Japan, to test the NEDOL process; and a third from the U.S. to test H-Coal (11). They have now decided to pursue the German process and an unspecified Japanese process. The U.S.-made reactor is being used to upgrade the coal liquids.

A major consideration in China's decision to apply the German and Japanese processes to their coals is the use of cheap disposable catalyst. The U.S. processes use promoted alumina catalyst, which the Chinese believe is too expensive and requires foreign sources.

9.7.2 Indirect Liquefaction

Currently, PRC produces about thirty percent of its methanol from coal or coke (11). They anticipate a rapid increase in demand to supplement their motor fuel pool which now contains 15 percent methanol, and that their vast coal reserves will be used as the raw material.

Considerable research is being done on syngas clean-up, reactor design, and improved catalysts.

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APPENDIX

APPENDIX A

SUMMARY OF RECOMMENDATIONS FROM THE FERWG-II REPORT[1]

A.1 INTRODUCTION

The starting point for the present assessment of coal liquefaction research needs was the report on Assessment of Long-Term Research Needs for Coal-Liquefaction Technologies prepared by the Fossil Energy Research Working Group in March 1980 (the FERWG-II report). This report contains a number of general and specific recommendations which were developed as a result of evaluating the status of the technologies being developed at that time.

As background for evaluating the results of the present assessment, it may be useful to refer to these FERWG-II recommendations, and many reviewers of the present report will want to do this. By comparing the present recommendations with the results of the FERWG-II study, it should be possible to obtain an understanding of how coal liquefaction technologies and their needs are evolving.

A.2 EXECUTIVE SUMMARY OF FERWG-II

Reproduced in this section is the Executive Summary of the FERWG-II Report. This summary contains what FERWG believed to be their most important recommendations, although no ranking or prioritization methodology was apparently used to arrive at this list. All references are, of course, to parts of the FERWG report.

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[1] Fossil Energy Research Working Group (S.S. Penner, Chairman), "Assessment of Long-term Research Needs for Coal Liquefaction Technologies," Report for DOE Contract No. DE-AC01-79ER10007, March 1980.

(From the FERWG-II Report (1))

EXECUTIVE SUMMARY

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

We identify below important R&D areas, each of which we believe requires substantial additional funding (i.e., more than $\$10^6$/year) and the first three of which we regard as especially urgent:

1. Research is needed on each of the following topics: the basic physics and chemistry, structure, composition, and thermochemistry of coals and of model compounds; volatilization; kinetics and mechanisms of bond scission; subsequent free radical and ionic reactions, including reaction steps involving unstable intermediates; transport properties and fluid mechanics of multiphase flows (see Section 2. 1).

2. Major opportunities exist for improving direct and indirect coal liquefaction through research in homogeneous and heterogeneous catalysis, using either recoverable or disposable catalysts. Fundamental research should concentrate on mechanisms, kinetics and surface chemistry (see Sections 2. 1 and 2. 2).

3. Bottoms processing is likely to limit commercialization of direct coal liquefaction processes (see Sections 2. 6 and 2. 7). An integrated program of R&D is needed, using bench-scale tests and pilot plants processing up to 100 tons of coal per day. These tests should be used to study gasification, combustion, and coking of residues (see Sections 2. 4 and 2. 5).

4. Scale-up and optimization of coal-liquefaction processes require improved understanding of processing steps, including two- and three-phase flows with heat and mass transfer and chemical reactions (see Section 2.7).

5. A review of environmental and health effects has not been performed by FERWG. We are aware of work in this field. We recognize the need for careful studies on methods of analysis and toxicology in order to assure the definition of adequate environmental and health standards. The emphasis should be on determining health effects of the finished products (see Sections 2.1, 2.8, and 2.9) in parallel with development.

6. Improved instruments must be developed for the measurement and control of all phases of the coal-liquefaction technologies, including the characterization and control of effluents (see Section 2.6).

7. An augmented and integrated effort must be made to solve, control, or avoid the many physical and chemical materials problems that have been encountered in the development of a variety of coal-liquefaction technologies (see Appendix C).

8. Additional research is needed on the characterization of a wide range of individual coals for different coal-liquefaction processes and for optimizing the designs of coal-liquefaction processes for particular coals (see Section 2.1 and Appendix C). These studies will require the creation of a carefully selected coal-sample bank.

9. Research on rapid pyrolysis of coal (at low and high pressures) and on coke utilization may lead to attractive alternative routes to coal liquids (see Chapter 3). Fundamental research is needed on the escape of pyrolysis products from a coal particle and on their subsequent chemical reactions, both within the particle and in the vapor phase (see Section 2.1 and Chapter 3).

10. Basic research is needed on mechanisms to control regressive reactions that lead to high viscosity of vacuum bottoms and to formation of sticky reactor residues. These studies are needed to assure system operability, good product recovery, and long catalyst life (see Section 2.3).

11. Fundamental and applied research should be pursued on separations of liquid streams and solids from the reaction products formed during coal liquefaction. These studies are needed in order to improve recycle systems to reduce processing costs. Vapor/liquid equilibria should be better defined, especially in regions near the critical points (see Sections 2.3, 2.4, and 2.5 as well as Appendix C).

12. Down-stream refining facilities should be leased or built for experimental refining of coal-derived oils to produce commercially usable liquids for engine development and also for use in turbines and boilers (see Section 2.9 and Appendix C).

A.3 DISPOSITION OF FERWG-II RECOMMENDATIONS

The Executive Summary of the FERWG-II Report (1) contains twelve high-priority recommendations, which, for the most part, are directed toward general areas of interest in liquefaction. Recommendation No. 9 is specific for pyrolysis, No. 3 is specific for direct liquefaction, and No. 2 for direct and indirect liquefaction. The recommendations are to do research in the following areas:

- Coal structure and coal chemistry
- Catalysis
- Bottoms processing
- Multi-phase flow
- Environmental concerns
- Coal characterization
- Retrograde reactions
- Product recovery
- Product refining

A number of other recommendations appear throughout the report. These are more process- or technology-specific, although only one other is for indirect liquefaction because the FERWG-II report emphasized pyrolysis and direct liquefaction.

In reviewing these recommendations, the reader must keep in mind that the largest liquefaction plant in operation at the time of FERWG-II was the 50 ton-per-day SRC-I and SRC-II pilot plant in Fort Lewis, Washington. A major concern was the need for larger-scale integrated operations to provide the information needed for reliable scale-up and design of commercial plants. This is seen in Recommendations 3, 4, 6, and 7.

Since that time, two 100-200 tons-per-day direct liquefaction pilot plants have been operated, a 200 ton-per-day plant was operated in Bottrup, Germany, and a 150 ton-per-day bituminous coal pilot plant is being designed and will be built in Japan. Many of the larger-scale tests have, therefore, been performed. Of greater significance is that the Great Plains Gasification Plant in Beulah, North Dakota, produces 137 million cubic feet per day of synthetic natural gas from 14,000 tons of lignite. Although the final product is natural gas, most of the operations are identical to those of an indirect liquefaction plant. In the planning stage is a coprocessing plant that will produce 11,700 barrels per day of distillable liquids from 800 tons per day of Ohio bituminous coal and 8000 barrels per day of Cold Lake reduced crude. Despite the relatively small coal feed rate, the large petroleum feed will require that this plant contain one train of a commercial-sized plant.

Although each process and each plant design will have its particular scale-up problems, these two commercial plants will resolve many of the scale-up and design uncertainties addressed by these FERWG-II recommendations.

Recommendation No. 5 is for the study of the toxicity of finished products. This work was performed by Battelle Pacific Northwest Laboratory, which concluded that coal liquids with a boiling point below 650°F and with a H/C atomic ratio of at least 1.5 has a toxicity no greater than petroleum liquids (Section 4.3.5). Thus, product toxicity is no longer a major research concern.

Recommendation No. 12 is for downstream refining of coal liquids. The tests by Chevron that concluded in 1985 (Section 4.3.3) showed that coal liquids can be refined by conventional refinery processes and catalysts. Thus, this is another liquefaction concern that has been resolved.

Some of the FERWG-II recommendations are still applicable today. Recommendation No. 1 on coal structure and chemistry is reiterated in direct liquefaction recommendations 1.1.2, 1.1.4, 1.3.4, and 1.3.5 (see Table F-2 in Appendix F). Sections 4.2.1 and 4.2.2 show that we know more about coal structure and chemistry. However, more research is needed to develop the desired coal structure-reactivity relationship that will lead to more efficient liquefaction processing.

Catalysis (FERWG Recommendation No. 2) continues to be an area of research interest for both direct liquefaction (1.8.1 and 1.8.2) and indirect liquefaction (1.1.2, 1.1.1, 1.4.1, 1.5.1, 1.2.1), although the process improvements that can be attributed to catalyst development have been modest.

Recommendation No. 3 was to test liquefaction bottoms as a feed to gasification, combustion, and coking. This has been done, most extensively by Exxon's fluid coking tests. These operations are not considered to be problems for commercialization, although performance depends on the bottoms properties, which will vary with each process.

Finally, Recommendation No. 2 is for a study of the control of regressive reactions. This recommendation refers to the stability of liquid products in reactors, and during product recovery and distillation. The stability of these products has improved considerably as the result of more extensive catalytic hydrogenation in the liquefaction reactors (Section 4.3.2) and product stability during processing is no longer considered to be a major problem.

APPENDIX B

OXIDATIVE COUPLING OF METHANE -- REVIEW

George Marcelin
University of Pittsburgh
Pittsburgh, Pennsylvania

B.1 INTRODUCTION

Most indirect coal liquefaction processes produce a significant portion of the product as light hydrocarbons, mostly methane, both in the gasification and the synthesis steps. For example, in the only large-scale commercial process involving the conversion of coal to transportation fuels, Lurgi gasification followed by the Synthol process in South Africa, over 20 weight percent of the direct product yield is light (C_1-C_2) hydrocarbons (1). Furthermore, significant amounts of methane exist worldwide, and recent discoveries in remote areas suggest that abundant supplies will be available for decades. Traditional exploitation of these carbon resources is not always a viable option because of process complexity and transportation problems, and flaring of the gas is a wasteful alternative. Consequently, the ability to convert these light hydrocarbons, most importantly methane, into easily transportable liquids can have a great impact on the energy health of the U.S.

Approaches to methane conversion can be conveniently grouped according to the method of activation, and whether another reactant is present. Methane can be activated by either thermal or surface-assisted techniques. The CH_3-H bond dissociation energy is 103 kcal/mole, which is significantly greater than that found in the higher alkanes, and emphasizes the unique problems associated with direct methane conversion.

Thermal activation leading to methane pyrolysis has been known for decades and is the basis for the commercial process for making acetylene (2). The endothermic deydrodimerization reactions to form acetylene and hydrogen are generally conducted above 1400°C. Aromatics can be obtained at somewhat lower temperatures (ca. 1200°C), although such processes have not been commercialized (3, 4). Autothermic or controlled flame processes have also been developed in which sub-stoichiometric quantities of O_2 are mixed with the methane feed.

The main drawback of thermal processes is the extremely high temperatures required for useful conversion, resulting in extremely high energy costs. Additionally, such processes typically exhibit less than optimum selectivity to the desired products and a significant amount of coke formation.

There is currently great interest in developing new technologies for the direct conversion of methane to more useful products. This interest reflects the commercial importance of any such technology. Recent workshops in the U.S. and Canada have addressed this topic (5, 6), and many of the major oil companies, as well as many other industries, are actively conducting or funding research in the direct conversion of methane.

One avenue that offers great promise for directly converting methane to useful products without the extensive energy consumption needed in thermal processes is catalytic oligomerization. Although there are many possible routes, including homogeneously catalyzed schemes, electrocatalysis, and photocatalysis, one specific route that has received considerable attention in recent years is the oxidative coupling route. This route has shown promising results and can potentially result in a process that is highly selective to liquid hydrocarbons.

B.2 OXIDATIVE COUPLING

B.2.1 Partial Oxidation -- Current Commercial Processes.

Partial oxidation reactions are currently one of the most widely applied processes in the petrochemical industry, consuming large amounts of energy in the process. These reactions are difficult to control due to the inevitable competing reactions leading to complete oxidation of both reactants and products to CO or CO_2 and H_2O. Some of the partial oxidations most commonly practiced by the chemical industry are listed below (7):

1. partial oxidation of propylene to acrolein.
2. ammoxidation or propylene to acrylonitrile.
3. methanol to formaldehyde.
4. benzene or butane to maleic anhydride.
5. naphthalene or o-xylene to phthalic anhydride.
6. ethylene to ethylene oxide.

All these reactions are carried out commercially using complex multioxide catalysts which are typically proprietary and are designed to operate with high selectivity only within a narrow range of operating conditions. Process parameters like reactor type, temperature, pressure, and reactant mix can have a profound effect on the efficiency of the reaction. Even small deviations from the design conditions can cause a dramatic increase in selectivity to the undesired "burning" products, resulting in wasted energy consumption during production and separation.

Mechanisms of oxidation reactions have been extensively studied for a variety of reactions and catalysts (8 - 10). In general, it has been concluded that the conversion takes place through reaction of the hydrocarbon species with the lattice oxygen of the oxide catalyst, followed by reaction of the reduced oxide with O_2 to give back the original active form (7). An effective catalyst is one which makes available only a limited amount of active oxygen to the hydrocarbon reactant, thereby preventing complete "burning" to CO_x.

B.2.2 Oxidative Coupling of Methane

The direct coupling of methane is a thermodynamically prohibited process at temperatures and pressures of interest. If an oxidizing agent is present, however, oxidative coupling can take place. Recent work at Union Carbide (11), Atlantic Richfield (12 - 16), and others (17) has shown the feasibility of converting methane to higher homologs by reacting it with a metal oxide, thereby coupling the methane through the abstraction of the lattice oxygen and the formation of water, i.e.:

$$x\ CH_4 + x\text{-}1\ MO \dashrightarrow C_xH_{2x+2} + x\text{-}1\ H_2O + x\text{-}1\ M$$

In addition to oxidative coupling to form, for example, ethane, the oxidation of methane by metal oxides can result in complete oxidation, leading to CO_2. This complete oxidation can be in fact the predominant reaction, accounting for over 50 weight percent of the products in most reported instances. The free energy change for the reduction of various metal oxides to either of the likely products, however, is approximately equal. This indicates that this reaction is controlled by kinetics rather than thermodynamics and it is possible to selectively produce higher hydrocarbons directly from methane.

It has been well established that the oxidation of hydrocarbons (alkanes, alkenes, or aromatics) over oxide catalysts occurs via hydrogen abstraction by an oxygen ion to form a neutral surface radical (18 - 20). Lunsford and co-workers have shown evidence that over MgO and Li-promoted Mgo the resulting surface radical desorbs into the gas phase where it can react with other methyl radicals to form ethane (and subsequently ethylene, through dehydrogenation) (21). Although most reports dealing with oxidative coupling have concentrated in the first coupling, i.e., to ethane, there is ample evidence that higher hydrocarbons are also obtained.

Sofranko and co-workers have shown further evidence for the gas phase radical reaction over a variety of oxide catalysts, including a typical free radical product distribution. As expected, such a distribution included measurable amounts of higher paraffinic and olefinic homologs and some aromatic compounds, such as benzene and toluene (22,23). Their reports, however, only show data obtained under a limited set of conditions and do not include any discussion relating to the optimization of product distribution.

A considerable amount of work has appeared in the literature the past few years dealing with active and selective catalysts for the oxidative coupling of methane. The majority of this work has consisted of screening a large sampling of materials for their potential as coupling catalysts, with emphasis placed on metal oxides.

Pioneering work by Keller and Bhasin at Union Carbide reported in the early 1980's involved the screening for activity and selectivity of 26 metal oxides for the selective coupling of methane at atmospheric pressures and 800°-1000°C (7). The most active catalysts for C_2 formation were the oxides of Sn, Pb, Bi, Tl, Cd and Mn, where selectivities of approximately 50 percent and conversions of 10 percent were reported. Other workers followed with similar studies (24 - 25) and similar results were obtained.

Lunsford has studied the conversion using both nitrous oxide and oxygen as the oxidant (26 - 30). He has proposed that centers of the type $[M^+O^-]$ with M^+ being a substitutional alkali metal ion are responsible for the first H-abstraction step. Both Li/MgO and Na/CaO were found to be active and selective for higher hydrocarbon formation.

The role of surface oxygen has been studied by Hutchings (31) who found that O^- can have two distinct roles in the oxidation of methane. At high temperatures (>720°C) it acts as a non-selective oxidant enhancing the formation of CO_2 and H_2O, whereas at low temperature it acts via hydrogen abstraction to form ethane selectively.

Kaliaguine (32) has found surface O^- to be involved in the formation of the surface alkoxide species CH_3O-, which was quite stable and decomposed only upon heating. Marcelin (33) has also found evidence for methoxy species during methane oxidation. In a series of reaction-quench-measure experiments, they observed via ^{13}C-NMR stable methoxy species during the oxidation of CH_3I as a model for methane oxidation. A molecular orbital study of O^- and O_2^- centers on the surface of MoO_3 suggested that methyl radicals will be mobile over O_2^- sites but will bind as methoxy over O^- (34).

Other studies indicate that the active oxygen species responsible for the activation of methane is not a monoatomic one but a diatomic, O_2^{2-} (35, 36). These researchers found that on the surface of Sm_2O_3, Na_2O_2, BaO_2, and SrO_2, the number of oxygen atoms needed to synthesize C_2 hydrocarbons was 9 times greater than the number of surface atoms. Thus, it was concluded that O_2^{2-} species on the surface contributed to the reaction.

There have been some questions as to the role of the gas phase in the reaction, to the extent that some researchers have suggested that the role of the catalyst is simply to concentrate molecular oxygen so that gas-phase free radical reactions can take place (37). Indeed, in some cases the role of the homogeneous gas-phase reaction can be very significant considering the high temperatures at which this reaction takes place (38). However, many of these problems can be overcome by operating at low partial pressures and by using tapered reactors to minimize gas-phase holdup of the products (39).

Obviously, we are far from achieving the ultimate commercial process for oxidative coupling. However, there is much potential for success which will be realizable once we develop a clear picture of the nature of a highly selective catalyst. Work in this area has grown rapidly in the past few years and, based on the current literature, continues to grow.

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APPENDIX C

MEMBERS OF THE EXPERT PANEL

In keeping with the changed environment for DOE-sponsored R&D in coal liquefaction, SAIC selected a panel made up of experts who are knowledgeable about the recently developed basic information and oriented towards the basic and applied research in coal liquefaction. However, the panel members' experience does span the scientific, technical, economic, environmental, and application areas of coal liquefaction. The experts on SAIC's panel are all currently active in coal liquefaction R&D and have demonstrated up-to-date technical competency and expertise directly related to coal liquefaction. Dr. Harvey Schindler of SAIC, the Principal Investigator, was also a member of the panel.

The members of the panel and their addresses are listed in Table C-1.

The technical qualifications and the experience of the panel members are summarized below.

Dr. Francis P. Burke is the director of Applied Research at Consolidation Coal Company (Consol). His principal research activities are in oil agglomeration for fine coal recovery, coal liquefaction product deashing, coal liquefaction process development, coal liquefaction process oil characterization, retrograde reactions in coal liquefaction, coal weathering and oxidation, coal mineralogy, retrofit processes for SO_2 abatement, and methanol reforming. He was the principal investigator for a DOE subcontract on retrograde reactions in SRC-I liquefaction and for a DOE contract on coal liquefaction process solvent quality characterization and evaluation, and has served as a panel member for several workshops on coal conversion and liquefaction.

Table C-1. Names and Addresses of COLIRN Panel Members

Dr. Francis Burke
Consolidation Coal Company R&D
4000 Brownsville Road
Library, PA 15129
(412) 854-6676

Dr. K.C. Chao
School of Chemical Engineering
Chemical & Metallurgical Eng. Bldg.
Purdue University
West Lafayette, IN 47907
(317) 494-4088

Dr. Burtron Davis
Kentucky Energy Cabinet Laboratory
Box 13015
Lexington, KY 40512-3015
(606) 257-0251

Dr. Martin Gorbaty
Exxon R&D
Clinton Township
Route 22 East
Annandale, NJ 08801
(201) 730-3012

Dr. Kamil Klier
Department of Chemistry
Lehigh University
Bethlehem, PA 18015
(215) 758-3577

Dr. Carl W. Kruse
Illinois State Geological Survey
615 East Peabody Drive
Champaign, IL 61820
(217) 333-5161

Dr. John Larsen
Department of Chemistry
Lehigh University
Bethlehem, PA 18015
(215) 758-3489

Dr. Robert Lumpkin
Amoco Corporation
200 East Randolph Drive
Chicago, IL 60601
(312) 856-2839

Dr. Michael E. McIlwain
Idaho National Engineering Laboratory
P.O. Box 1625
2151 North Blvd.
Idaho Flls, ID 83415
(208) 526-8130

Dr. Harvey Schindler
SAIC
One Sears Drive
Paramus, NJ 07652
(201) 599-0100

Mr. Norman Stewart
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94303
(415) 855-2508

Dr. Irving Wender
University of Pittsburgh
1261 Denniston Ave.
Pittsburgh, PA 15217
(412) 624-9644

coal liquefaction process development, coal liquefaction process oil characterization, retrograde reactions in coal liquefaction, coal weathering and oxidation, coal mineralogy, retrofit processes for SO_2 abatement, and methanol reforming. He was the principal investigator for a DOE subcontract on retrograde reactions in SRC-I liquefaction and for a DOE contract on coal liquefaction process solvent quality characterization and evaluation, and has served as a panel member for several workshops on coal conversion and liquefaction.

Dr. Kwang-Chu Chao, a professor of chemical engineering at Purdue University, is experienced in the fundamentals of process engineering, especially energy-related processes. His most recent work involves coal liquefaction processes, kinetics, and super-critical fluid extraction. He has also made numerous significant contributions to thermodynamics and fluid phase equilibrium. Dr. Chao is widely published on a variety of chemical engineering topics and has co-written several books on thermodynamics and equations of state.

Dr. Burtron H. Davis is the program director for coal liquefaction at the Kentucky Energy Cabinet Laboratory. His most recent assignment has involved developing a comprehensive direct coal liquefaction program. During the past 10 years, Dr. Davis has developed a comprehensive research program in direct coal liquefaction. This extensive program includes studies of conversion characteristics in small-scale reactors, detailed analyses of products from in-house liquefaction studies and large U.S. pilot plants, studies of catalyst aging in coal liquefaction, studies of corrosion and materials failures in large U.S. direct coal liquefaction pilot plants, and operation of a bench-scale 10-lb coal/hour fully integrated direct coal liquefaction pilot plant.

Dr. Martin Gorbaty is a senior staff advisor for Corporate Research Science Laboratories of Exxon Research and Engineering Company. He has 15 years of research experience in organic chemistry and coal science. He was the director of the Heavy Hydrocarbon Sciences Laboratory at Exxon, where he directed and oversaw various heavy hydrocarbon research programs, including coal liquefaction processes. In 1984 Dr. Gorbaty served as a DOE AR&TD panel member to assess coal liquefaction research needs. His current research interests include coal physical structures and temperature effects in coal hydropyrolysis. Dr. Gorbaty has published numerous technical papers on organic chemistry and coal science; he has also edited several technical books on synthetic crudes and coal sciences.

Dr. Kamil Klier is a University Distinguished Professor of chemistry at Lehigh University and the director of the Catalysis laboratory at the Zettlemoyer Center for Surface Studies. He has published extensively in the fields of solid state and physical chemistry of surfaces, and has made major contributions to the understanding of the molecular basis of sorption and catalysis. These contributions were in the areas of molecular structure and dynamics of water at surfaces and interfaces, electronic structure of intrazeolitic transition-metal ion complexes, and comprehensive catalyst and mechanistic studies of oxygenates, mainly alcohol, synthesized from CO/H_2. Dr. Klier has chaired ACS and MRS symposia, and has been on editorial boards of the Journal of Colloid and Interface Science, the Journal of C^1 Chemistry, and Materials Letters.

Dr. Carl W. Kruse is with the Illinois State Geological Survey. His experience includes 15 years of industrial petrochemicals research and 10 years of coal research. In his 10 years at the Illinois State Geological Survey, he has developed a coal desulfurization program funded through contracts. He has pursued two lines of research -- physical cleaning of very fine coal and production of crude liquid fuel and residual solid fuel by pyrolysis of coal. His current responsibilities include managing a contract with the Electric Power Research Institute to look at pretreating coal to improve its pyrolysis performance by improving either the yield of liquids or their quality.

Dr. John W. Larsen is a professor of chemistry at Lehigh University, a non-regular employee of the Exxon Research and Engineering Company, and the editor of the ACS journal Energy & Fuels. At Lehigh his research areas are coal chemistry (specifically coal structure and reactivity), new ionic hydrogenation reactions, and organic chemistry in molten salts. At Exxon his research deals with the macromolecular structure of coals, non-covalent interactions in coals, and coal conversion. He has chaired the American Chemical Society's Division of Fuel Chemistry and has served on numerous public and private sector advisory boards and panels.

Dr. Robert E. Lumpkin, director of Coal Utilization Projects in the Synthetic Fuel Development Department of Amoco Corporation, has 20 years of experience in managing, developing, and analyzing chemical engineering technologies. As Amoco's representative on the Wilsonville direct coal liquefaction project, he focused the experimental program on making those improvements most likely to reduce commercial costs, such as using Amocat catalysts, operating at higher space velocities, and recycling heavy liquids to extinction. He organized and directed an evaluation of two-stage direct coal liquefaction commercial economics.

Dr. Michael McIlwain is the fossil energy program manager at the Idaho National Engineering Laboratory. He has more than 12 years of experience in various aspects of fossil energy applications and advanced research. He is responsible for a major program at the Idaho National Engineering Laboratory concerned with studying the use of microorganisms to clean and process coal. Dr. McIlwain currently advises the Office of Fossil Energy on current developments in the area of biotechnology and its energy applications.

Mr. Norman C. Stewart is the project manager of the Coal Liquefaction Program in the Advanced Power Systems Division of the Electric Power Research Institute (EPRI). His work involves H-Coal, EDS, and SRC-I processes, as well as support to the Wilsonville facility. Other projects deal with indirect liquefaction (liquid phase methanol). Before joining EPRI in 1974, Mr. Stewart spent 12 years with Cities' Service Oil Company as a process engineer and as a manager of a product development facility in Lake Charles, Louisiana. Previously, Mr. Stewart worked at Callery Chemical Company as a process engineer, with Celanese Chemical

Company as a manufacturing engineer, and Monsanto Chemical Company as a plant engineer.

Dr. Irving Wender, a research professor for the Chemical and Petroleum Engineering Department of the University of Pittsburgh, has more than 30 years of research experience in a variety of fields, including fossil energy, coal and petroleum chemistry, and certain aspects of organic chemistry. He has also researched the reactions of synthesis gas catalyzed by transition metals. As director of the Office of Advanced Research and Technology in the Office of Fossil Energy of DOE, Dr. Wender was responsible for all advanced research programs and technology activities in the fossil energy area. He was a research director at the Pittsburgh Energy Research Center from 1972 to 1978, and at PETC from 1978 to 1979. In November 1988 Dr. Wender received DOE's Homer H. Lowry Memorial Award for Meritorious Contributions in Fossil Energy Science and Technology.

APPENDIX D

PANEL MEETING REPORTS

An important element of the methodology used in conducting this assessment of coal liquefaction research needs was holding two formal meetings of the entire expert panel. The initial two-day meeting at the beginning of the project was held to conduct a preliminary evaluation of R&D needs assessment. The second full panel meeting was held to finalize the recommendations of the study. The panel meetings, which were run by the principal investigator, were structured to give the experts the primary role in making R&D recommendations and guiding study efforts.

This appendix contains brief reports of the activities of the two panel meetings, which were held as follows:

First Panel Meeting:	Pittsburgh, PA January 5-6, 1988
Second Panel Meeting:	McLean, VA July 13-14, 1988

D.1 REPORT ON FIRST PANEL MEETING

D.1.1 Overview

The twelve-man expert panel selected for the Assessment of Coal Liquefaction Research Needs project held its first meeting, at the Hotel Sheraton South Hills in Pittsburgh, on January 5-6, 1988. This meeting was followed by a one-day site visit to the Pittsburgh Energy Technology Center (PETC), where DOE personnel reviewed in-house research on coal liquefaction.

The two-day meeting and the PETC site visit were attended by all twelve panel members. A number of people from DOE Headquarters, PETC, and METC attended the meeting as ex-officio members, and several SAIC staff participated in the meeting to assist the panel's discussion. A complete list of attendees is as follows:

Panel Members

Dr. Francis Burke
Dr. K. C. Chao
Dr. Burtron Davis
Dr. Martin Gorbaty
Dr. Kamil Klier
Dr. Carl W. Kruse
Dr. John Larsen
Dr. Robert Lumpkin
Dr. Michael E. McIlwain
Mr. Norman Stewart
Dr. Irving Wender

Ex-Officio Members

Dr. George Jordy, DOE
Dr. Gilbert S. Jackson, DOE
Dr. Paul C. Scott, DOE
Dr. Robert Hamilton, DOE
Dr. Lloyd Lorenzi, PETC
Dr. Malvina Farcasiu, PETC
Dr. Madhav Ghate, METC

SAIC

Dr. Edward Wan
Dr. Harvey Schindler
Dr. Malcolm Fraser
Dr. Isaac Kwarteng
Mr. William R. King

The meeting was broken down into four sessions. The first session was a general meeting of all attendees. After introductions and introductory remarks, presentations were made to review project objectives and the development status of the three main coal liquefaction technology areas--direct liquefaction (H. Schindler), indirect liquefaction (K. Klier) and pyrolysis (C. Kruse).

Following the technology status reviews, the panel was divided into three subpanels--one for each technology area. Simultaneous sessions of the three subpanels were held to discuss research recommendations and to try to develop preliminary rankings of the ideas.

After presentations of research priorities by the subpanels to the full panel, plans for future information-gathering, suggested ranking criteria, and potential site visits were discussed.

The third day of the meeting was devoted to a site visit to PETC.

D.1.2 Meeting Accomplishments

A comprehensive meeting agenda was planned in advance in detail to try to accomplish certain objectives. Some of these objectives were met while others were completed via follow-up actions such as mailings and phone calls.

During the initial general discussion, the background, objectives, and expected product of the assessment were reviewed so that all panel members would have a common understanding of them. An emphasis was placed in several presentations on the need to set research priorities. The technology status and the potential new developments of the three liquefaction technology areas were reviewed.

Over one hundred research recommendations were generated and discussed by the subpanels. A preliminary ranking procedure was proposed and used for selecting 30 to 40 of the more important recommendations. A final ranking procedure was not agreed upon at the meeting because panel members had different opinions regarding evaluation criteria selection and a weighting procedure.

The information and the supporting rationale developed for these research recommendations were necessarily incomplete, to be expanded later to serve as the basis for the final ranking.

Sites for visits were discussed. The second panel meeting was scheduled for June 15-17 in McLean, Virginia.

D.1.3 Subpanel Meetings

After the initial general meeting of the panel members and other attendees, the meeting was divided into meetings of three subpanels organized by technology area: direct liquefaction, indirect liquefaction, and pyrolysis. Panel members and the others were assigned to one of the subpanels, although moving from one subpanel to another was encouraged, depending on the person's interests and the topics being discussed.

The subpanel meetings were devoted to several types of discussions:

- Problem areas
- Research recommendations
- Technology status
- Recommendation evaluation.

Much of the discussion in each subpanel was of a general and freewheeling nature with little specific information becoming available as conclusions.

The most important specific information generated within each subpanel meeting was an initial list of research recommendations--topic areas as well as specific projects. This initial list in each of the three technology areas was a preliminary list which was pruned, condensed, added to, and organized during the course of the project.

This initial list of research recommendations for each technology area was discussed and the ideas evaluated within each subpanel. Ranking methodologies discussed in the general meeting were then applied to a sample of the recommendations to illustrate the use of a ranking procedure to develop research priorities.

The results of the deliberations of each subpanel were then summarized and reviewed by the entire panel in another general meeting.

D.2 REPORT ON SECOND PANEL MEETING

D.2.1. Overview

The twelve-man expert panel for the assessment of Coal Liquefaction Research Needs held its second full meeting at facilities at the SAIC main building in McLean, Virginia on July 13-14, 1988. This two-day meeting was attended by all twelve panel members and Dr. Gilbert Jackson from DOE. SAIC staff (Dr. Edward Wan and Dr. Malcolm Fraser) also participated in the meeting to assist the panel's discussions.

As background to the prioritization effort, which was the main concern of the meeting, the initial discussion was concerned with a review of the background to the project, the project objectives, and the emphasis of the DOE coal liquefaction programs. Following these introductory discussions, the main work of the meeting was concerned with discussing, ranking, and prioritizing the research recommendations generated and collected during the site visits. Rankings and prioritization were finally determined by compiling lists of what the panel members thought were the most important research needs and projects in each technology area.

In direct liquefaction, out of a total of 19 general research categories, 13 were mentioned by panel members as being important enough to be ranked and prioritized. In addition, 42 specific recommendations for research projects were rated. In general, the panel emphasized the need for fundamental work to discover new approaches with more potential than existing processes.

Coprocessing was considered to be part of direct liquefaction, but recommendations specific to this technology area were considered separately by the panel. The result was that four recommendations were rated by the panel in this area.

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.

The future of pyrolysis was discussed by the panel. In particular, there is a need for novel approaches, to increase the amount of liquid produced and to decrease the amount of co-product char or to utilize all of the char within the process. The categories of recommended research (4) and the specific projects rated (8) all emphasized fundamental work and the relatively new process of catalytic hydropyrolysis rather than further development of other existing processes.

In indirect liquefaction the panel made some changes in the list of recommendations, combining some and adding new ones. A total of six general research needs were rated, as well as nine specific recommendations, in both areas of syngas to hydrocarbons and syngas to oxygenates.

With respect to direct conversion of methane, the sixth and last technology area discussed, 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 information and the recommendations gathered by the panel will be included in the report, but the recommendations will not be ranked or prioritized.

After the technology areas were discussed and the research recommendations ranked and prioritized, the outline of the final report was discussed, and the list of possible contributors of the technology status sections was reviewed. The panel members then discussed the selection of a peer review committee. A number of possible reviewers were proposed by panel members.

The schedule for the preparation of the final report was reviewed. The schedules of the panel members were also reviewed for their availability for the remainder of the project.

D.2.2 Discussion of Individual Technology Areas

D.2.2.1 Direct Liquefaction

This technology has undergone significant process modifications in recent years, but the cost of the liquid product is still considerably higher than that for petroleum liquids. The 76 research recommendations that had been generated in this technology area spanned all steps of direct liquefaction from break-up of coal bonds to refining of coal liquids. The emphasis was on obtaining a greater understanding of liquefaction chemistry, from which new processes may be developed.

At the start of the discussion, the panel agreed that research on coal structure and reactivity cross-cut several technologies and should not be confined to direct liquefaction. A comment was made that alternative chemistries were not adequately represented in the recommendations that had been compiled. This may be a result of the DOE solicitation procedure (see discussion in Section D.2.3).

The panel members were asked to each select their three top categories. Ratings were based on a score of five for first choice, three for second, and one for third. Twelve of the nineteen categories were selected by at least one panel member; coal structure, preconversion chemistry, hydrogen production, and catalysis were the most highly rated categories or research needs.

The panel members then picked the top 10 research recommendations (out of a total of 76). Ratings were based on a score of 10 for the first choice, down to one for the tenth choice. Forty-two recommendations were selected by at least one panel member. Fundamental research needs ranked higher than applied needs and followed the scoring trend pattern of the categories--research in coal structure, preconversion chemistry, and catalysis received strong support. The single highest score, however, was for operation of a large-scale pilot plant. As originally proposed at the first panel meeting, this recommendation referred to a scale of 50-100 tons per day, but as currently worded, it could also mean the Wilsonville PDU.

D.2.2.2 Coprocessing

This technology is an outgrowth of direct liquefaction which has received strong support from DOE. Originally, coprocessing was included in this assessment under direct liquefaction. This may have limited the number of recommendations that specifically addressed the co-conversion of coal and petroleum.

The panel members were asked to select their top three research categories/recommendations. All 13 categories/recommendations received support from at least one panel member. Not surprisingly, one category (1.1) was the first choice of nine members. This category is the study of the chemistry of coal/oil reactions. Other research areas of importance were the study of hydrogen-donor chemistry in coprocessing, process studies, and development of catalysts specifically for coprocessing.

A recommendation that was not scored highly was 2.5.1-Design, construct, and test a small-scale, continuous-flow unit. However, the discussion during the second day indicated that some panel members had second thoughts, because without such a unit, new process concepts cannot be scaled up, unless the leap is made from laboratory to Wilsonville PDU.

D.2.2.3 Bioliquefaction

The panel found that bioliquefaction is in such an embryonic stage of development that little background information and data are available upon which to base research recommendations. The panel members did not rank specific project recommendations in this area but rather endorsed the list of recommendations, with an indication of the relative importance of the general research needs. In general, the type of research needed should be termed "scoping studies," as it is too early to determine what the specific needs are in either fundamental or applied research.

D.2.2.4 Pyrolysis

Pyrolysis is the oldest of the liquefaction technologies, but it has received little attention recently because of the low yields of liquid that have been demonstrated in past process developments.

The consensus of the panel was that pyrolysis will not be a viable commercial technology unless the liquid yield is increased substantially, and this increase in liquid yield can be achieved only with a new approach. Therefore, none of the recommendations that seek to make improvements on current processes was scored highly.

The panel members were each asked to select the three top categories; ranking was based on a score of five for first, three for second, and one for third. Eight of the 11 categories received support from at least one panel member, but category 1.4 (study the chemistry and the mechanism of catalytic hydropyrolysis) was selected first by six panel members. This scoring may not have been an endorsement of this particular pyrolysis procedure, as much as a rejection of most of the other categories.

In the scoring of recommendations in which each panel member selected his top six, category 1.4 was again the clear choice, receiving first- or second-place scoring from 11 panel members. The second highest score was for the study of coal functional groups and their relationship to pyrolysis reactivity.

D.2.2.5 Indirect Liquefaction

The DOE research program in indirect liquefaction starts with syngas as the feedstock. Thus, indirect liquefaction in the coal liquefaction program is not directly concerned with the properties of coal or the technology of producing synthesis gas, but only with the conversion of the syngas itself. This constraint limited the scope of the research needs to be considered for indirect liquefaction, and the list of recommendations proposed by the panel reflects this limitation. The DOE program of surface coal gasification does include coal gasification research for the production of syngas. (The reader is referred to the 1987 COGARN report for research needs for the production of syngas.)

Indirect liquefaction does include two distinct areas within the broad area of syngas reactions: conversion of syngas to hydrocarbons and conversion of syngas to oxygenates, such as alcohols or ethers. The types of research recommendations proposed and considered by the panel are a reflection of this status and the important concerns within this technology area.

The panel first recommended some changes in the list of recommendations. Two general categories were added, with two specific recommendations in each category, in the area of syngas to oxygenates. Some minor changes in the wording of some recommendations were also proposed.

The panel members were then asked to each pick their top three categories. Points were awarded to each category mentioned (five for a first place mention, three for a second place, and one for a third). The panel appeared to consider alcohol and ether syntheses to be more important than hydrocarbon (F-T) syntheses. Fundamental needs ranked higher than applied.

To rank specific recommendations the panel members were asked to each pick their top six. Most of the prioritized recommendations are in the fundamental area.

D.2.2.6 Direct Conversion of Methane

Direct conversion of methane is a technology which was not originally considered within the scope of this research needs assessment. This technology was first discussed at the site visit to PETC where research is currently being conducted in this area. Additional presentations were made on this technology at the meetings at Naperville and Newtown Square.

This technology is considered by some to be of potential interest to the coal liquefaction community because it may be a useful way of dealing with the methane produced as a byproduct from coal gasification (depending on the type of gasifier, particularly Lurgi) or from Fischer-Tropsch synthesis reactions.

However, the panel discussed whether this technology should properly be included within the area of coal liquefaction. What would be the source of the methane, which should be derived from coal to be of interest to coal liquefaction researchers? It was suggested that a number of research recommendations in indirect liquefaction would lead process design and operation in the direction of minimizing the production of methane as a byproduct. It is improbable that anyone would purposely produce methane from coal as a feedstock for this technology; any methane produced from coal is expensive compared to alternative sources.

The consensus of the panel was to include consideration of this technology in the report, but as a separate technology in an appendix. The recommendations are to be submitted but will not be ranked and prioritized. Direct conversion of methane is not properly to be considered a part of coal liquefaction. There may be a great incentive to work in this area, but only because of the large amount of remote natural gas. Funding for research on direct conversion of methane should be sought from sources other than the budget for coal liquefaction.

D.2.3 Comments and Recommendations on DOE Programs and Policy

Part of the afternoon of the second day was devoted to a discussion of DOE programs and policy in the coal liquefaction area. From the comments that were made in this discussion, several recommendations and concerns were voiced.

First, the panel recommended that open-ended solicitations are needed to ask for research proposals on fundamentally new chemistries to liquefy coal. It was also recommended that more funds be set aside to fund unsolicited proposals. The current system of putting all research funds into restricted RFPs channels research money in specific directions and has the unintended result of stifling new ideas which don't fit preconceived programs. New ideas are thought by the panel to be particularly important with respect to coal liquefaction because new approaches are needed.

Second, one panel member noted that DOE university programs are currently very small. Universities have no participation in larger programs. Academic participation should be solicited. He therefore recommended that all DOE-sponsored contracts with industrial contractors require a certain amount of participation (perhaps 20 percent as a minimum) by universities. For example, universities could do analyses and bench/autoclave tests.

The justification would be that universities could then attract and professionally train graduate students interested in industrial careers. This program would lead to an integrated and interdisciplinary approach to research. Guidance would be available for professors and graduate students, as well as industrial staff. The panel member suggested that this type of program is necessary because there is currently a lack of academic-industrial funding by the NSF.

As a related issue to this recommendation, it was noted by another panel member that organizations allied with universities and staffed with non-teaching researchers are for the most part shut out of programs, which are frequently directed at either university teaching professors or industrial organizations.

A third comment brought up the opinion that currently no mechanism exists for getting new ideas resulting from fundamental work into process development. Industrial organizations seem to be spending their effort on their old, known, or proprietary processes.

APPENDIX E

DEVELOPMENT OF RESEARCH RECOMMENDATION DATABASE

E.1 GENERATION OF COAL LIQUEFACTION RESEARCH NEEDS

A preliminary list of research needs for each technology area was generated by the panel during the first panel meeting. Additional research recommendations were developed through the following sources:

- Technology overview reports and papers
- DOE coal liquefaction contractors' reports
- IEA/International trip reports
- Personal communications between panel members and other experts
- Technical presentations during site visits.

An updated list of research recommendations was prepared by SAIC staff, disseminated, and passed to panel members during site visits. Panel members reviewed the research needs list and provided additional suggestions and ideas during the course of site visit discussions.

E.2 CATEGORIZATION AND DATABASE DEVELOPMENT

A comprehensive detailed list of research recommendations was generated during this research needs assessment as a result of the site visits and presentations made to the panel and the other activities described above. This list contained recommendations which were both general needs as well as specific projects. A number of the specific projects overlapped one another or were redundant, etc. To make this list of recommendations manageable, it was revised and categorized, and six specific technology areas were defined so that smaller areas would not be overlooked and lost compared to the more dominant technologies. The six technology areas so defined are direct liquefaction, coprocessing, bioliquefaction, pyrolysis, indirect liquefaction, and direct conversion of methane. The recommendations for each area are shown in a separate list.

The research recommendations for each technology were categorized and put into a research breakdown structure and database. This breakdown structure starts with the basic research types of Fundamental and Applied. Each research type has a number of appropriate research categories or general research needs. Specific research recommendations are then listed within each general category as examples of specific projects which can be carried out to fulfill the general research need. The utility of this approach for DOE is that the general research needs or categories can be used to define parts of an overall program while specific recommendations embody specific ideas of work to be carried out. Each general category is given a two-digit number for easy reference within the database, and each specific recommendation has a three-digit number.

As the result of this effort, a total 178 research recommendations in 57 general categories were prepared in this manner to comprise the database, which is shown in Table E-1.

Table E-1.

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- DIRECT LIQUEFACTION

Type	Category	No.	Description of Research Need
1.0 FUNDAMENTAL			
	1.1		Characterize coal structure, properties, and reactivity as applied to direct liquefaction.
		1.1.1	Study ways of separating coal macerals, and their chemical properties.
D5*		1.1.2	Develop a coal structure-reactivity model based on analytical and behavioral phenomena.
		1.1.3	Investigate the role of coal porosity in liquefaction.
D9		1.1.4	Determine role of mineral matter in initial reactions of coal.
		1.1.5	Determine the inherent limitations of maceral liquefaction.
		1.1.6	Classify U.S. coals according to liquefaction potential by correlating liquefaction performance with coal structure, properties, and reactivity and develop liquefaction database.
D1		1.1.7	Identify the structures that are responsible for retrograde reactions and study their reactivity and their kinetics.
	1.2		Study preconversion chemistry of coal feedstock including pretreatment.
		1.2.1	Study free-radical formation during heating of coal with or without a solvent.
		1.2.2	Study the interaction of mineral matter and coal macerals as it pertains to coal beneficiation.
D3		1.2.3	Test pretreatments, such as low-temperature catalytic pretreatment, to enhance coal reactivity and otherwise improve the overall process.
		1.2.4	Study effects of handling procedures on chemical and physical properties , and reactivity of coal feedstocks.
		1.2.5	Study application of coal cleaning the feedstock for liquefaction.
	1.3		Study the chemistry and the mechanisms of coal dissolution.
		1.3.1	Study the multicomponent catalytic dissolution of coal.
		1.3.2	Conduct model polymer studies of liquefaction chemistry.
		1.3.3	Investigate effect of solvent mediation in thermal and catalytic processes.
D7		1.3.4	Develop kinetic models of liquefaction based on coal structure.
D10		1.3.5	Develop intrinsic quantitative rate expressions for conversions of individual components and ensembles of components as a basis for understanding initial reaction paths during coal dissolution.
		1.3.6	Explore the role of electron transfer and oxygen functional groups in coal liquefaction.
	1.4		Investigate the chemistry involved in the conversion of resid and distillate.
		1.4.1	Study relationship between chemical composition and reactivity of resids, including reaction kinetics.
		1.4.2	Conduct a quantitative investigation of the reactivities of various coal liquids in catalytic hydroprocessing with emphasis on competitive reactions and inhibition effects (high-pressure, high-temperature reaction networks, kinetics, modeling).
		1.4.3	Conduct a quantitative investigation of the reactivities of asphaltenes and compounds representative of asphaltene functional groups in catalytic hydroprocessing.
		1.4.4	Study product quality as a function of conversion and reaction conditions.

*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE   TECHNOLOGY AREA -- DIRECT LIQUEFACTION

Type	Category	No.	Description of Research Need
	1.5		Explore the use of novel conditions for coal dissolution.
		1.5.1	Study the potential use of chemically directed selective reactions (non-thermal) for direct liquefaction.
	1.6		Study the fundamentals of hydrogen-transfer chemistry.
		1.6.1	Study in detail the hydrogen transfer mechanism.
		1.6.2	Investigate new classes of hydrogen-donor solvents.
		1.6.3	Extract the process implications of competing H-transfer reactions in bond scission and formation.
	1.7		Study the chemistry and the catalysis involved in upgrading coal liquids.
		1.7.1	Develop new catalysts/processes for upgrading coal liquids.
		1.7.2	Evaluate methods of refining coal liquids.
	1.8		Investigate new and novel catalysts for direct liquefaction.
D11*		1.8.1	Develop new catalysts for liquefaction (conventional metal on solids).
D6		1.8.2	Investigate potential homogeneous catalysts for liquefaction.
		1.8.3	Develop methods for the recovery/recycle of catalysts (emphasis on dispersed).
		1.8.4	Study soluble bifunctional (hydrogenation/acid cracking) liquefaction catalysts.
	1.9		Study the fundamentals of catalysis in direct liquefaction.
		1.9.1	Determine the effects of catalytic deactivation on the reactivities of various coal liquids and mixtures in catalytic hydroprocessing.
D12		1.9.2	Study the mechanism of catalytic hydrogenation and cracking functions to establish their interaction and to determine the effects of thermal reactions on these functions.
		1.9.3	Determine why iron is catalytic for low-rank coals.
		1.9.4	Study catalyst deactivation with the objective of learning how to reduce it or to maintain catalyst activity.
		1.9.5	Study the effect of H2S, added or generated in situ, on coal liquefaction reactions.
		1.9.6	Develop in-situ instrumental methods to study catalyst-substrate interactions.
	1.10		Analyze coal liquids and determine their physical and chemical characteristics.
		1.10.1	Develop analytical procedures for characterizing and analyzing resid.
		1.10.2	Characterize liquefaction products in a chemically significant way.
		1.10.3	Conduct a detailed analytical comparison of products from diverse liquefaction processes and contact times, including characterization of liquid products and well-defined fractions in terms of compound classes (functional groups)(NMR, MS, GC-MS...).
		1.10.4	Develop new instrumental techniques for conversion analysis.
		1.10.5	Develop empirical methods necessary for process monitoring that are simple, fast, and cheap and can work in a plant environment.
		1.10.6	Develop standardized method of reporting product quality and yields.
		1.10.7	Develop methods for meaningful characterization of coal resids related to resid reactivity.
		1.10.8	Develop methods to identify species and quantify O and S functional groups in coal and coal resids.
		1.10.9	Develop methods to analyze for trace elements in liquefaction streams and products.

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*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- DIRECT LIQUEFACTION

Type	Category	No.	Description of Research Need
		1.10.10	Develop chemmometric IR analysis for process monitoring and performance prediction.
	1.11		Study the fundamentals of liquid/solid separation.
		1.11.1	Study the fundamentals of solids agglomeration as it pertains to liquid/solids separation.
2.0 APPLIED			
	2.1		Conduct process research studies for further development of direct liquefaction processes.
		2.1.1	Investigate ways of separating aromatic/aliphatic mixtures.
D8*		2.1.2	Develop new approaches to solubilize coal, building on new information on coal chemistry.
		2.1.3	Develop low-severity first-stage reactor for multi-stage process.
		2.1.4	Investigate novel ways of removing heteroatoms, particularly nitrogen.
		2.1.5	Expand the study of using lower-rank coals as liquefaction feedstocks.
		2.1.6	Study the use of coal mixtures as liquefaction feedstocks.
		2.1.7	Study the effects of using lower-ash coals as liquefaction feedstocks.
	2.2		Conduct economic studies of direct liquefaction processes and products.
		2.2.1	Assess values of coal liquids as finished products and evaluate their upgradability.
		2.2.2	Conduct periodic economics studies both for well-developed processes and emerging concepts.
		2.2.3	Develop an economic-impact guidance tool.
		2.2.4	Investigate ways of making higher-value products via coal liquefaction.
	2.3		Develop materials, components, and instrumentation for direct liquefaction processes.
		2.3.1	Develop new on-line instrumentation for direct liquefaction processes.
		2.3.2	Develop more reliable high-pressure coal slurry feed pumps.
		2.3.3	Study the metallurgy of process equipment under liquefaction conditions.
	2.4		Assess the environmental considerations of direct liquefaction processes.
		2.4.1	Investigate environmental problems such as toxicity of products and disposal of mineral matter.
		2.4.2	Prepare a comprehensive updated report on the carcinogenic properties of coal liquids.
	2.5		Conduct pilot-plant and scale-up studies for further development of direct liquefaction processes.
		2.5.1	Design, construct, and test a small-scale continuous-flow unit.
D2		2.5.2	Operate large-scale pilot plant to test engineering concepts, including PDU-scale studies of effects of reaction parameters (temperature, H2 pressure, solvent quality, etc.), and to supply samples for other research.
		2.5.3	Investigate alternative deashing methods, bottoms processing schemes, and process configurations for possible development.
	2.6		Formulate new catalysts for process studies.
		2.6.1	Develop improved physical characteristics for ebullation catalyst at Wilsonville.
	2.7		Find new applications for coal liquids.
		2.7.1	Conduct research to build engines capable of combusting low-H/C liquids.

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*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- DIRECT LIQUEFACTION

Type	Category	No.	Description of Research Need
04*	2.8		Investigate new methods and processes for producing and recovering hydrogen.
		2.8.1	Find new catalysts for low-temperature steam gasification of carbonaceous materials.
		2.8.2	Find catalysts for steam gasification of residual materials for producing H2 and CO2.
		2.8.3	Investigate the mechanism of steam gasification catalysis.
		2.8.4	Study the interaction of ash components and catalysts in catalytic gasification.

*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- INDIRECT LIQUEFACTION

Type	Category	No.	Description of Research Need
A. NON-SYNTHESIS-SPECIFIC FUNDAMENTAL CATALYSIS RESEARCH			
I2*	1.1		Analyze structure, reactivity, function, role of supported organometallic complexes to elucidate the mechanisms of heterogeneous (as well as homogeneous) catalysts.
I1	1.2		Develop novel catalyst supports, co-precipitated catalyst precursors, novel ways of surface doping, chemical vapor deposition, plasma doping, and analyze catalyst structures.
B. SYNGAS TO HYDROCARBONS			
1.0 FUNDAMENTAL			
	1.1		Perform basic studies of F-T syntheses, including catalysis, and reaction chemistry and mechanisms.
		1.1.1	Characterize in-situ the surface of F-T catalyst.
		1.1.2	Study the liquid-phase F-T synthesis using ultra-fine iron particles as catalyst.
I8		1.1.3	Investigate the carbon form leading to deactivation of F-T catalyst.
I9		1.1.4	In F-T and related syntheses use probe molecules to 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.
		1.1.5	Study the reaction kinetics and mechanisms of F-T reactions including carbon chain growth, chain branching, and the formation of paraffins, olefins, aldehydes, or alcohols.
		1.1.6	Measure the rate-determining step in F-T synthesis under commercial conditions.
	1.2		Study the fundamentals of chemical reactor engineering as applied to F-T syntheses.
		1.2.1	Investigate the fundamentals of hydrodynamics in 3-phase reactors.
2.0 APPLIED			
	2.1		Develop improved catalysts for F-T syntheses.
		2.1.1	Improve the stability of iron F-T catalysts.
		2.1.2	Improve the specific activity of ruthenium catalyst for F-T.
		2.1.3	Study the production of light olefins from synthesis gas catalyzed by ruthenium on rare earth oxides.
	2.2		Conduct process development studies for F-T processes.
		2.2.1	Develop the fixed fluidized-bed and the slurry-phase reactor systems.
		2.2.2	Conduct research leading to improved reactor design for 3-phase reactors and scale-up.
		2.2.3	Study the oligomerization of lower olefins to octane enhancers and distillate-range olefins by nickel-based homogeneous and supported catalysts.
		2.2.4	Investigate ways to get lower light-ends production with Co catalyst in F-T.
I5		2.2.5	Investigate maximizing middle distillate yield from syngas.
		2.2.6	Study combining sequential slurry-phase F-T and ZSM-5 catalysis to maximize aromatics, isoparaffins, and olefins and to minimize methane yield.

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*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- INDIRECT LIQUEFACTION

Type	Category	No.	Description of Research Need
	2.3		Characterize F-T products and develop applications.
		2.3.1	Develop diesel and jet fuels via F-T, methanol-nitrate mixtures, and other novel routes.
	2.4		Conduct economic studies and assessments.
		2.4.1	Perform computer simulation studies of indirect liquefaction processes.
		2.4.2	Determine relative importance of catalyst life, activity, and product selectivity on F-T economics.
		2.4.3	Investigate coproduction of energy, fuels, and chemicals.
C. SYNGAS TO OXYGENATES			
1.0 FUNDAMENTAL			
	1.1		Perform basic studies of alcohol syntheses, including catalysis, and reaction chemistry and mechanisms.
I7*		1.1.1	Study the reaction kinetics and alternative catalysts for methanol syntheses.
		1.1.2	Conduct isotopic and mechanistic studies of methanol conversion.
		1.1.3	Determine chemical reaction mechanisms in methanol conversion to gasoline and distillates.
		1.1.4	Study the process of converting methanol to olefins.
	1.2		Study the fundamentals of chemical reactor engineering as applied to alcohol syntheses.
		1.2.1	Investigate the fundamentals of hydrodynamics in 3-phase reactors.
	1.3		Find new paths to produce octane-enhancing ethers from syngas and its oxygenated products.
I4		1.3.1	Find catalyzed paths to produce octane-enhancing ethers from alcohols.
		1.3.2	Find high-temperature (>200 C) catalysts for producing octane-enhancing ethers from alcohols.
	1.4		Find new low-temperature catalysts for the water gas shift reaction which are more sulfur tolerant.
I6		1.4.1	Develop sulfur-tolerant low-temperature water gas shift catalysts.
		1.4.2	Improve the activity of existing Cu-based shift catalysts by means of chemical promoters.
2.0 APPLIED			
	2.1		Conduct process development studies for alcohol syntheses.
		2.1.1	Develop the fixed fluidized-bed and the slurry-phase reactor systems.
		2.1.2	Conduct research leading to improved reactor design for 3-phase reactors and scale-up.
I3		2.1.3	For the conversion of synthesis gas to C1-C5 alcohols, develop syntheses with high ethanol selectivity, minimizing the hydrocarbons made.
		2.1.4	Improve the slurry-phase production of methanol from syngas.
		2.1.5	Study plant simplification and integration of the MTG process (TIGAS).
		2.1.6	Develop the fluidized-bed process for producing olefins and aromatic hydrocarbons from methanol.
	2.2		Conduct economic studies and assessments of alcohol syntheses.
		2.2.1	Perform computer simulation studies of alcohol synthesis processes.
		2.2.2	Investigate coproduction of energy, fuels, and chemicals.

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*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE   TECHNOLOGY AREA -- PYROLYSIS

Type	Category	No.	Description of Research Need
1.0 FUNDAMENTAL			
	1.1		Characterize coal structure and reactivity as applied to pyrolysis.
P2*		1.1.1	Characterize coal functional groups and their relationship to pyrolysis reactivity.
		1.1.2	Study the mechanisms of oxidative weathering of coal.
		1.1.3	Study the effects of oxidized components on pyrolysis reactions.
		1.1.4	Correlate product properties with coal feedstock properties.
		1.1.5	Determine coal devolatilization rates as a function of coal type.
		1.1.6	Study the effects of inherently present inorganic constituents on product quality and quantity, and process conditions.
		1.1.7	Study possible role of inherently present mineral matter or externally added inorganics on the thermoplastic properties of coal.
	1.2		Study the mechanisms and the kinetics of pyrolysis reactions.
P6		1.2.1	Study the chemistry and the mechanisms of pyrolysis reactions to learn where products come from and to minimize unwanted secondary reactions.
		1.2.2	Conduct systematic studies to learn: a) effects of particle size, b) effects of surfaces on nature of secondary reactions, and c) roles of free radicals.
		1.2.3	Determine reaction kinetics of pyrolysis by defining the time and temperature history of coal particles.
P7		1.2.4	Define the chemistry and the mechanisms of steam-enhanced pyrolysis, under both subcritical and supercritical conditions for steam.
P3		1.2.5	Compare products and yields of pyrolysis with and without reactive atmospheres (CO, CO2, H2O, H2), to understand the roles of these gases in the devolatilization of coal.
		1.2.6	Develop models to interpret coal devolatilization data.
	1.3		Determine the effects of pretreating the coal feedstock.
P8		1.3.1	Study the effects of moisture in coal and physicochemical changes that occur during drying or rewetting of coal.
		1.3.2	Study steam pretreatment of coal, especially the effect on carbon conversion and liquid yields.
		1.3.3	Study effects of feedstock comminution method on product properties and yields.
		1.3.4	Study effects of alkali addition to coal feedstock on reactions and processes.
P1	1.4		Study the chemistry and the mechanisms of catalytic hydropyrolysis.
	1.5		Characterize the liquid products of pyrolysis processes and their properties.
		1.5.1	Characterize pyrolysis products for cleaned coals.
		1.5.2	Investigate the combustion characteristics of pyrolysis liquids.
		1.5.3	Define the potential toxicological and carcinogenicity problems with pyrolysis liquids.
	1.6		Characterize pyrolysis char and its properties.
		1.6.1	Work on methods for characterizing reactivity of char for combustion and gasification.
		1.6.2	Study the fundamental aspects of combustion of char and char-coal mixtures (e.g., ignition flammability, flame stability, and slagging characteristics.

*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- PYROLYSIS

Type	Category	No.	Description of Research Need
		1.6.3	Define the relationship between the devolatilization conditions of the coal and the reactivity of the resulting char.
		1.6.4	Study the slagging characteristics of char (and the nature of the corresponding coal).
2.0 APPLIED			
	2.1		Conduct process studies for further development of pyrolysis processes.
		2.1.1	Investigate the separation of fine suspended solids from liquid products.
		2.1.2	Study possible use of low-cost inorganic additives as scavengers for sulfur or nitrogen.
P5*		2.1.3	Study staged catalytic hydropyrolysis.
		2.1.4	Determine distributions of heteroatoms/pollutants as a function of process conditions and coal type.
		2.1.5	Identify factors controlling product selectivity.
		2.1.6	Determine effects of reactor design and make design improvements.
		2.1.7	Assess early low-temperature pyrolysis processes with a view of mitigating their negative attributes by varying process conditions.
		2.1.8	Study the sensitivity of system performance as a function of process variables.
	2.2		Investigate novel pyrolysis processes.
		2.2.1	Investigate the use of high-energy fields, such as corona discharge, laser techniques, microwaves, to decompose heavier tar fractions, activate H2O molecules, etc.
		2.2.2	Investigate radio frequency (RF) or microwave volumetric heating as a potentially useful technique.
	2.3		Conduct economics studies of pyrolysis processes.
P4		2.3.1	Conduct systems analysis of pyrolysis and hydropyrolysis coupled with gasification/combustion.
		2.3.2	Assess the sensitivity of process economics (e.g., to changes in the prices of fuels or product compositions).
		2.3.3	Perform a systems study on the transport, effluents, and handling of pyrolysis liquids, keeping in mind the potential for liberating carcinogens into the environment.
	2.4		Conduct char utilization and upgrading studies.
		2.4.1	Examine alternative uses of char, such as its combustion in fluidized-bed combustors.
		2.4.2	Investigate methods and systems for handling hot fresh char.
		2.4.3	Study how to create multi-phase, high-density fuels with micronized char.
		2.4.4	Study the treatment of char to remove heteroatoms and mineral matter.
	2.5		Develop methods for upgrading pyrolysis liquids into useful products.
		2.5.1	Develop low-cost novel poison- and coke-resistant catalyst systems for reducing N and S compounds in coal liquids.

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*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- COPROCESSING

Type	Category	No.	Description of Research Need
1.0 FUNDAMENTAL			
C1*	1.1		Study the fundamental chemistry of coal/oil reactions for coprocessing.
		1.1.1	Study the interaction of alicyclic petroleum-type molecules and coal-type compounds.
	1.2		Study the fundamentals of hydrogen-donor chemistry in coprocessing.
		1.2.1	Study the effects of hydrogen donors in coprocessing.
	1.3		Develop methods for analyzing coprocessing products.
		1.3.1	Develop analytical methods to determine the contribution of coal/oil to coprocessing products.
2.0 APPLIED			
	2.1		Investigate scale-up methods for coal/oil coprocesses.
		2.1.1	Investigate scale-up procedures, problems, and opportunities for combining coal with non-coal-derived heavy organic solvents.
C2	2.2		Conduct process studies to develop coprocessing.
		2.2.1	Study the effects of different feeds on reactivity and product quality.
		2.2.2	Study the influence of residua and coal composition.
	2.3		Develop coprocessing catalysts.
		2.3.1	Optimize the catalyst used for coprocessing.

*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE TECHNOLOGY AREA -- BIOLIQUEFACTION

Type	Area	No.	Description of Research Need
2.0 APPLIED			
B1*	2.1		Identify useful microoganisms and enzyme systems.
		2.1.1	Identify nonaqueous enzyme systems to degrade three-dimensional structure (by enhancing solubility and swelling).
		2.1.2	Identify optimal organisms for bioconversion of syngas to ethanol.
		2.1.3	Investigate potential of microorganisms and biomaterials to decompose nitrogen and sulfur compounds and to clean (pyrolysis) liquid products.
	2.2		Conduct process studies to develop bioreactor systems.
		2.2.1	Develop design of bioreactors to handle solids as feeds.
		2.2.2	Optimize reactor design for mass transfer, heat removal, and product preparation.
	2.3		Conduct assessment and economic studies of bioprocesses.
		2.3.1	Develop reactor and total system design for economic optimization.

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*Identifies a high-priority recommendation.

Table E-1. (Continued)

RESEARCH BREAKDOWN STRUCTURE DIRECT CONVERSION OF METHANE

Type	Category	No.	Description of Research Need
1.0 FUNDAMENTAL			
	1.1		Study the reaction chemistry, mechanisms, and catalysis of the partial oxidation of methane to H2/CO, C2+ hydrocarbons, methanol, and formaldehyde with emphasis on novel approaches to achieve high selectivity.
		1.1.1	Study the oxidation of methane to heteropoly oxometalates.
		1.1.2	Investigate new low-temperature routes to direct conversion of methane to oxygenates.
	1.2		Study the reaction chemistry, mechanism, and catalysis for the synthesis of ethylene via the catalytic oxidative coupling of methane with emphasis on approaches to achieve high selectivity.
		1.2.1	Study the oxidative coupling of methane over promoted magnesium oxide catalyst.
		1.2.2	Study the conversion reactions of methanol and methane over zeolites and aluminophosphates (ALPOs).
		1.2.3	Investigate promoted oxidative coupling of methane (including halogen-promoted).
		1.2.4	Study the oligomerization of lower olefins to octane enhancers and distillate-range olefins by nickel-based homogeneous and supported catalysts.
		1.2.5	Investigate new low-temperature routes to direct conversion of methane to C2+ hydrocarbons.
2.0 APPLIED			
	2.1		Conduct process development studies to develop oxidative coupling processes.
		2.1.1	Conduct R&D on fluidized-bed process for oxidative coupling of methane, including high-density fluid beds.
		2.1.2	Assess the engineering aspects of alternative routes for the conversion of natural gas.
		2.1.3	Evaluate materials of construction to minimize halogen corrosion in direct conversion of methane.
	2.2		Conduct economic studies to assess processes for the direct conversion of methane.
		2.2.1	Perform computer process simulation studies of direct conversion processes.
		2.2.2	Investigate coproduction of energy, fuels, and chemicals.

APPENDIX F

PEER REVIEWERS' COMMENTS

A draft final version of this report was sent to ten outside reviewers. The reviewers were chosen for their experience and background in coal liquefaction research and development. The following people served as peer reviewers of this report:

1. Mr. Seymour Alpert, Electric Power Research Institute
2. Dr. Raymond Anderson, National Institute for Petroleum and Energy Research
3. Dr. David Gray, MITRE Corporation
4. Dr. Gerald Huffman, University of Kentucky
5. Dr. Alex Mills, University of Delaware
6. Mr. Eric Reichl, Consultant
7. Dr. George Roberts, Air Products and Chemicals
8. Dr. David Schmalzer, Argonne National Laboratory
9. Dr. Howard Stephens, Sandia National Laboratory
10. Dr. Duayne Whitehurst, Mobil Oil

In most instances peer reviewers' comments were incorporated within this report, particularly those which dealt with corrections or specific changes. Policy recommendations, opposing viewpoints, and comments which may be of general interest are reproduced in this appendix.

F.1 COMMENTS FROM SEYMOUR ALPERT (FEBRUARY 2, 1989)

I have completed the review of the report on "Assessment of Coal Liquefaction Research Needs" that was sent to me on January 6, 1989. I find the report authoritative and thorough. The detailed Chapters 4 to 9 are well prepared and show an important recent body of work. The report competently summarizes the research work performed over the last decade or so. When the report is completed, I would like a copy for my files.

Enclosed are detailed comments on Chapter 3 which draws on the detailed treatment in the next Chapters 4 to 9. I agree with the panel's recommendations and priorities and the broad conclusions of the panel.

I have read each of the detailed chapters, which are well done. The subject of bioconversion is a difficult one. It is a research topic and will require a long duration program with uncertain outcome. I found that section of the report realistic in its appraisal and not too optimistic. The rest of the sections also seem to present a balanced perspective.

F.2 COMMENTS FROM ERIC REICHL (JANUARY 19, 1989)

I appreciate the opportunity to review this exceptionally fine report and hope you will find my comments helpful.

I. General Comment

This is an outstanding report. The high quality of the report is, of course, a reflection of the excellent choice of panel members; their wide experience and competence assured that the total status of the synfuel enterprise was exhaustively reviewed and the major advances of recent years were described in a clear manner; this includes particularly the reasoning underlying individual developments. This is true of all sections of the report, especially Chapters 4 through 8.

II. Comments on Direct Liquefaction

When IG-Farben decided in 1923 to proceed with the commercial development of the Bergius process, the ratio of gasoline to coal price, in terms of $/BTU, was 8:1. Today, 65 years and billions of $'s later, the ratio still is 6:1 (see Table 4-21); all this in spite of the great improvements which have been achieved, such as:

- o reduction of pressure from 10,000 PSI to 2500 PSI;
- o cutting H_2 - requirement in half (6 vs. 12%)
- o improving the yield pattern (selectivity)
- o lowering cost of hydrogen by pressure gasification

Evidently the processing of solids is inherently a forbidding, expensive task, and there is doubt whether the pace of improvement we have seen in the last 8 years, from EDS to H-Coal to ITSL to CTSL, can be maintained by further pursuit of the current path; specifically the 2-stage, thermal/catalytic process using the Co/Ni/Mo catalysts which dominate petroleum processing.

The cost of direct liquefaction, as currently perceived, is embedded in the basic need for processing coal at 2500 PSI with about 6% H_2 addition. Even if the catalytic reactors were completely eliminated, the cost of product would not drop very much. To make further advances implies the discovery of some new approach which might allow operation in the 250-500 PSI range. This would require new insights in coal chemistry, possibly a slight retreat from depth of conversion, and probably some new type of catalysis. In this context it remains unexplained why the unique results obtained 10 years ago with molten $ZnCl_2$ have not aroused more interest in the R&D community. There was a totally different homogenous catalyst with great activity and specificity; it certainly deserves another look with the benefit of the greatly improved diagnostic systems which have since come on line (see also Chapter 6; Reference 70 & 71 and Chapter 4; Reference 97). Quite generally, R&D needs to be more "exploratory" and less "programmatic", and particularly the university laboratories should be encouraged in this direction.

The key conclusion re direct liquefaction, as of 1989, is the remarkable advance made since EDS/H-Coal. Given the actual operating experiences from these earlier 200-T/D plants and the extensive use of catalytic hydrocracking in the oil industry, the current state of the art as described in the report makes the $35/bbl present cost very credible. The same range, incidentally, is evident from the latest operation of F-T indirect conversation at SASOL and Great Plains.

A firm and credible CAP is thus set on the price of petroleum, which is, of course, well below the $35/bbl figure since the world oil price must be kept well below the synfuel cost, lest it trigger the production of this alternate in quantity. In fact, the nation has been well rewarded for its synfuel efforts during the last 2 decades, all comments by the many detractors notwithstanding.

III. Comments on Indirect Liquefaction

Here again the report is an excellent comprehensive review of the present state of the art. However, the subject covered has relatively little to do with coal liquefaction. It is narrowly limited to the conversion of CO/H_2 mixtures to marketable liquid fuels. As is well known, this part of the total path from coal to liquids is very highly developed and well covered by R&D in the private sector. As matters stand, further efforts along the suggested lines of R&D will do little to improve the economics of indirect coal liquefaction.

The two major reasons for this are: first, the fact that in indirect liquefaction the cost of preparing clean synthesis gas from coal under pressure represents probably 4/5 of the total cost, and second, the fact that CO/H_2 conversion is already so efficient and specific that further improvements are destined to be irrelevant.

Finally, one may add, that CO/H_2 mixtures are much more economically produced from natural gas; the large and often remote resources of gas have led the oil and chemical industry towards a concentrated R&D effort in the catalytic CO/H_2 conversion area. There is no need for DOE to interfere with these private-sector efforts.

I realize that DOE has established a sharp programmatic distinction between "gasification" and "liquefaction" of coal; hence the MAIN issue of R&D in indirect liquefaction, i.e., the gasification/gas clean-up segment, was arbitrarily left out of the COLIRN report. This is most unfortunate, because the reader is misled about the subjects which are important in indirect liquefaction; they are gasification and gas clean-up.

Actually the field of gasification is very adequately covered in the U.S. and abroad, by government and by private-industry R&D. It is thus not likely that increased gasification R&D will lead to significant improvements unless here, too, the program is directed towards more exploratory, non-orthodox concepts. An example (listed unfortunately under pyrolysis) is the catalytic gasification of char at relative low temperatures, admittedly a long shot.

Next to gasification proper, the extensive clean-up of syngas, particularly desulfurizing to <1 ppm H_2S, is one of the large cost items in indirect liquefaction. Virtually all classic CO/H_2 conversion catalysts are exquisitely sulfur sensitive. Any advance which would allow a less costly desulfurizing step is thus an exciting breakthrough. Apparently this has occurred; see Chapter 7, p. 76: DOW-HAS Process.

A more extensive evaluation of indirect liquefaction based on sulfur-resistant catalysts in the CO/H_2 conversion step should be recommended.

A somewhat more uncertain reduction in the cost of synthesis gas might be found in the use of air in lieu of oxygen. Here the potential advantage will be strongly affected by the required level of desulfurization. To permit liquid synthesis from air-blown synthesis gas (approx. 40-50% N2) would call for extremely active catalysts, of the type claimed, for example, by Brookhaven N.L. (Chapter 5, References 64, 65, 66).

To sum up: the hope of significant reductions in the cost of indirect coal liquefaction would most likely be found in CO/H_2 conversion systems which will allow use of lower-cost synthesis gas; this means higher sulfur content and, possibly, air-blown gas. This point needs to be highlighted in the COLIRN R&D Recommendations; it is not mentioned there.

IV. Comments on Pyrolysis

Here again the draft report constitutes an exhaustive review of the subject with emphasis on the last 2 decades. Of course pyrolysis has a much longer history, and it should be remembered that at the high point of synthetic fuel production, during the 1940's in Germany, the largest block of coal-based gasoline was produced by pyrolysis (of low-rank coal) followed by high-pressure catalytic hydrogenation of the resulting tar. A major reason for this preference of tar over coal as hydrofeedstock was the much higher synfuel capacity resulting from a given volume of high-pressure hydrogenation reactors if tar is fed in lieu of coal. It was thus possible to rapidly increase output, because pyrolysis units could be built more rapidly than high-pressure hydro stalls.

The panel recommends no "push" toward pyrolysis because it correctly notes that no significant improvements are to be expected from R&D in this most exhaustively tested of all coal processing schemes. I will therefore simply express complete agreement with this conclusion. No attempt to unravel the chemistry of this complex thermal degradation of coal will open the door to any more economic pyrolysis. This is so even if there may be a few selected instances where it can succeed.

The report did not draw particular attention to one very important issue, usually the major operating problem which arises when coal is pyrolyzed at optimum tar-forming temperature (800-1000° F). A very large part of U.S. coals exhibit this "caking" property, which has dominated process technology. Various means to live with this property have been developed, but all ultimately result in higher cost plant per ton of throughput.

The swelling or "caking" tendency is enormously increased by any hydrogen treatment, however applied. Coal simply fuses as hydrogen begins to react with coal; as expected, this tendency is less with lower-rank coal. The obvious answer to this problem, first recognized by Bergius, is of course operation in liquid phase; this breakthrough remains as valid today as it was in 1912.

I am therefore not optimistic about the potential of hydropyrolysis, which is recommended by the COLIRN Panel. This is particularly so, if the "pyrolysis" is to be carried out under > 2000 PSI of hydrogen. If coal is to be processed with high-pressure hydrogen, it should be done in liquid phase along the line of direct liquefaction, say CTSL. A "dry" coal reactor with 2000 PSI hydrogen would be inoperable due to swelling of the coal. Besides, in the absence of catalysts, the use of hydrogen would be very inefficient, much of it going to CH4; it would be a major step backward.

This leaves the potential of "catalytic hydropyrolysis"; this is of course just another word for "direct hydrogenation in dry phase" as I understand the proposed thrust. In chemical terms there is little difference between testing coal with 2000 PSI hydrogen in a "dry" system or a liquid system; if it works, it will not stay "dry" very long.

This comment is not intended to deny the interest in the low-pressure hydrogenation of Utah and Montana coals with $ZnCl_2$ catalyst (see Fig. 6-3). This work was probably done on a small laboratory scale, and the correct technology for carrying out this reaction on large scale may very well be liquid (slurry) phase, just to keep control of runaway temperatures, which are the key concern with large-scale hydrogenation systems treating coal.

In other words: catalytic hydropyrolysis may simply be a new buzzword and should really be treated as part of the wider subject of "innovative catalysts for hydrogenation at lower pressures." This is certainly a proper target for R&D.

F.3 COMMENTS FROM DAVID SCHMALZER (JANUARY 30, 1989)

The subject draft report is generally well written by knowledgeable individuals, and I would concur in most of the recommendations. I believe, however, that process development and large pilot-plant activities must receive substantially greater resources than DOE has provided in recent years if there is to be any substantial likelihood of commercially deployable, U.S.-based technology available in the foreseeable future.

There are fundamental problems in the current DOE programs that virtually assure the failure of advances from basic research finding their way into process development, and also of processes being developed to the point that technical and economic risks become consistent with commercial deployment. Absent adequate resources at the process development and demonstration level, basic work will tend to dead end. In this environment, fundamental findings are likely to provide interesting and valuable scientific literature; however, their economic value is much more likely to be exploited in Japan or Germany than in the United States. I believe, therefore, that the panel's recommendations over-emphasize the need for and value of basic research on liquefaction given the inadequate resources provided for meaningful utilization of the products of basic research.

Some other advisory groups, notably the Energy Research Advisory Board (ERAB), have placed much greater emphasis on the need for pilot- and demonstration-scale activities if synfuel technologies are truly expected to be commercialized.

Direct liquefaction well illustrates two concerns expressed by the panel: the seeming inability to transfer basic research findings into the process development sphere and the seeming inability to move liquefaction technology from the process development phase to demonstration-scale or commercial-scale plants. The termination of DOE funding of bench-scale continuous flow process exploration and initial process development units has created a major barrier to the transfer of chemistry findings to the process development sphere, as process development work has virtually stopped in the United States. In a similar vein, the termination of the large pilot-plant and demonstration-plant programs leaves U.S. process developers with no vehicle for moving partially developed processes to the point of readiness for commercial deployment.

The recent Union Oil shale retorting plant has graphically illustrated that technological risk cannot be ignored in pioneer plants employing new technology at substantial scale. Similarly, the Great Plains Gasification Plant has shown that even for a facility where the technology of the major process elements is relatively mature, environmental issues and product price shifts can make a multi-billion dollar plant uneconomic.

In indirect liquefaction, the report devoted great attention to the potential for improvement in well-developed catalyst systems and chemistry for the production of methanol and higher alcohols from synthesis gas, but said little regarding the technology or economics of the production, purification, and shifting of synthesis gas derived from coal. As production, purification, and shifting represent a substantial, possibly dominant, fraction of the costs in a coal-based facility, greater research attention to those aspects of the process could have greater economic impact than minor improvements in well-developed catalyst systems.

The usability and value of char produced in coal pyrolysis is critical to process economics, and I feel the panel is accurate in indicating that conventional pyrolysis approaches are unlikely to produce major improvements in yields or economics.

Coal-petroleum coprocessing can be viewed as a special case of direct liquefaction, and any substantial scale coprocessing or other special applications of direct liquefaction should be encouraged as their experience will be valuable in reducing the technical risk of subsequent direct liquefaction facilities.

I appreciate the opportunity to comment on this draft report and hope that you and the panel will find the comments constructive. I would like to receive a copy of the final report when it issues.

The following are specific comments on the subject report keyed to the page numbering on the draft.

Page 3-14 - Paragraph 1
An additional need for the operation of an integrated pilot plant is a development of meaningful environmental, safety, and health information. Worker health and safety and the potential environmental impact of such facilities on local areas are highly sensitive issues are potentially critical to the permitting, construction, and operation of demonstration or commercial scale liquefaction facilities. These issues will exist notwithstanding any election to limit net plant product to 650° F minus streams which appear to have toxicological properties similar to their petroleum counterparts.

Page 3-49 - Figure 3-2
Under coprocessing it indicates DOE seeks transitional technology having potential for near-term production of coal liquids using, to a large extent, existing petroleum refining facilities and technology. If one assumes that existing ebullated-bed hydrocracking units could coprocess petroleum and meaningful quantities of coal without major rework, an assumption that is likely unwarranted, the number and capacity of ebullated-bed units in the United States is very small. It is exceedingly difficult to envision the utilization of fixed-bed hydrocracking/hydrotreating units for coal oil processing without major rework of such units.

Page 4-50 - Paragraph 3
The paragraph asserts that U.S. industries and processes have usually employed high-area supported catalysts operating at lower pressures and accepted higher catalysts costs than European (e.g., German) developers. This is inconsistent with the facts. Of the processes reaching large pilot plant-scale of development, EDS, SRC I, and SRC II employed native coal minerals or throw-away materials as liquefaction catalysts, and only H-Coal used a supported catalyst. EDS employed catalytic hydrotreating of coal derived distillates in its pilot plant, and SRC II had developed and patented a variant of the SRC II process that employed catalytic hydrotreatment of reactor effluent high-pressure separator overhead (distillate) materials.

Page 4-73 - Paragraph 4
As discussed earlier, environmental, safety, and health issues have the potential for being major impediments to commercialization. Any DOE program that envisions ultimate commercial deployment of the technology would be well advised to implement supporting activity that will provide a firm basis for "regulatory agency and public perception concerns."

Page 4-164 - Paragraph 2
While Wilsonville has been and remains a useful facility it is more a large PDU or small pilot plant than a large pilot plant, and has neither the scale of equipment nor level of process integration necessary for commercial process confirmation. Should DOE have the resources, some combination of a few bench-scale continuous recycle units for process screening and process parameter studies and at least one integrated pilot plant of 100 to 200 tons per day capacity would be desirable. A PDU-scale unit, perhaps with 0.5 to 2.0 tons per day of capacity, and the design and instrumentation capable of highly accurate material balances and yield determinations would also be desirable.

Page 5-41 - Bullets 1 through 6
Given that the heterogeneous methanol catalysts have high activity, excellent selectivity, relatively low cost, and three-four year lifespans

there seems to be little economic incentive in those areas for developing homogeneous liquid-phase catalysts. If a homogeneously catalyzed system has economic merit over existing systems it will likely be from improved heat transfer, allowing higher per-pass conversation. That reaction kinetics are simpler and intermediates more easily characterized in a homogeneous system seems unlikely to motivate a change in industrial practice. Methanol synthesis reactor design is generally limited by heat transfer from the highly exothermic reaction, not by catalyst activity or selectivity.

Page 8-10 - Paragraph 2
If the mature cheese industry typically loses 3% of its batches due to biological contamination, similar problems could exist in a much less mature coal conversion process, though the scale of the batches would tend to be much larger. The environmental consequences of contaminated bioprocess batches should be explored.

Page A-3 - Paragraph 6
The FERWG-II recommendation regarding measurement and control instrumentation and devices was well taken and deserves consideration in the present assessment.

F.4 COMMENTS FROM G. ALEX MILLS (JANUARY 28, 1989)

The draft report "COAL LIQUEFACTION: A RESEARCH AND DEVELOPMENT NEEDS ASSESSMENT" has been reviewed as requested. My comments are presented below.

This report provides a comprehensive and authoritative review of the status of coal liquefaction science and technology. In general I am in agreement with the recommendations. Many of the sections are excellent.

This report does not bring out the surge in technology and commercialization for oxygenate fuels made from syngas. Fundamental to their success is the new evaluation of fuels based on their high performance as octane enhancers, made critically significant with phase-out of lead. Pertinent information is the phenomenal success of MTBE (synthetic methanol makes up 36% of MTBE), the scale of M-85 (85% methanol) in California and of premium gasoline containing mixed alcohols in Italy, new capabilities for use of methanol in flexicars and diesel engines, and the recent requirements for use of fuels containing oxygenates in Colorado to assist in protecting the environment. I think that DOE is not giving sufficient support to indirect liquefaction and particularly for research on synthesis of the oxygenates.

I believe that there should be more importance given to innovative research. Emphasis is given to fundamental research. This can be fruitful in a practical sense if it leads to inventive ideas. Thus the encouragement of fundamental research should be matched by support of inventive research. The Japanese program stresses exploratory .innovative research.

I would like to add emphasis to the recommendation for coal gasification research, a subject not discussed at length in this report. It did receive a fairly high rating as Item D 4.
Chapter 4. Review of Direct Liquefaction.

This chapter is particularly useful in that it is so comprehensive, including as it does research, development, and economics. The interrelationships of the various processes and their evolution is very helpful, as well as a clear account of the advances achieved by utilizing the close-coupled two-stage concept, configurations which include new solvent separation techniques, and the production of a liquid of < 650° F boiling point. I have two particular concerns and some comments.

1. Liquid Yields. The yield of liquids, either in terms of % or Bpt, is presented in a manner which is incomplete or indeed misleading. Table 4-11 makes it appear that the distillate yield has increased from 41 to 78 wt% in the period 1982 to 1987. (2.4 to 5.0 Bpt). Likewise Table 4-9 gives the impression that 5.0 Bpt of coal are obtained, although careful reading does show that there is the requirement for chemical hydrogen. I believe that the amount of coal needed to produce the hydrogen should be shown and the net Bpt of liquid produced.

2. This chapter calls repeatedly for innovation but does little to point the way. Certainly in the right direction is the statement on page 4-26 that "research is needed to develop catalysts which will positively affect the initial coal conversion". But there is little presentation of innovative ideas.

3. In regard to reference to foreign technology, it seems to me an overstatement that they have adopted the two-stage concept. The Japanese have just made a commitment to build a large pilot plant based primarily on the U.S. EDS process. The Germans' process is a continuation of their WWI Bergius process using red mud. Incidentally, it might be worth noting as a footnote to Table 4-42 that the German process can operate successfully on U.S. coals at 200 atm pressure although German coals require 300 atm.

4. There is an environmental issue of importance which is not addressed. This is the restrictions of the aromatic contents of

gasoline. California is proposing 0.8% benzene, and Europe has a benzene limit of 5% effective in 1989.

5. Boiler Fuel. As a somewhat historical note, it can recalled in connection with p. 4-81, -85, that coal liquefaction received its major push in the 1970's to produce a clean boiler fuel. This need has been met by effective stack - gas scrubbers using technology which was not available then nor was it obvious that economical processes could be developed.

Chapter 5. Review of Indirect Liquefaction.
This chapter presents both an excellent overview and a critical summary of the catalytic chemistry involved. There are several comments and a few minor suggestions.

1. MTBE. The report could bring out more strongly that there has emerged a new criterion for determining the value of synthetic oxygenate fuels. This is based on their high performance in use, particularly their ability for octane-enhancement, made more significant with phase-out of lead in gasoline. This comment is particularly true for the ethers but also applies for the alcohols.

The statement that the volume of MTBE is limited by the availability of isobutylene, page 5-115, is misleading. Butanes are available in large supply and can be converted by isomerization and dehydrogenation to isobutylene. This is being done commercially in a Texas plant and in the largest MTBE plant in Saudi Arabia mentioned on page 5-116.

Page 5-115 states that MTBE relies on petroleum at least to 80-83%. However, methanol, mw 32, provides 36.4% of the weight of MTBE, mw 88.

The pioneering commercialization of MTBE and its phenomenal growth in Europe is particularly well described in "European Oxygenates Experience," F. Morandi, R. Trotto, G. Pecci and M. Sposini, Energy Progress, 8, no. 1, p. 1-15 (1988).

2. Methanol. Many are convinced that neat or near-neat methanol will be a major fuel of the future. While the technology for methanol manufacture is old, there have been recent technical advances, for example - Macnaughron, Pinto and Rogerson, Energy Progress, 4, no. 4, p. 232 (1984) and Dybyjaer and Hansen, Chem. Ec. and Eng. Rev., 17, no. 5 (1985).

3. Dual-Site Catalysis and Catalyst Design. The establishment and delineation of the essential dual-site mechanism of syngas hydrogenation seems to me to be a major breakthrough. This appears in various places in the report, p. 5-54 and 55, 5-105 and 5-107. It could be emphasized more, particularly in the sense that this provides the opportunity to design superior catalysts in which each site is optimized and including the knowledge that the site for hydrogen activation should be one which is not poisoned by CO.

4. Mobil Slurry FT. Reference is made to the processing of FT products using catalysts containing ZSM-5 molecular sieve. However, the research conducted at Mobil goes beyond that. By use of a slurry FT synthesis technique and followed by processing with ZSM-5, it was possible to obtain high yields of wax and of 92-octane gasoline. (Ref. 1 of Chapter 5).

5. It may be pointed out that the information given relating to group VIII metal catalysts is very abbreviated relative to the major research activity in this field. Table 5-16 is particularly abbreviated.

Chapter 9. Liquefaction Development Outside the U.S.
This chapter provides a concise and comprehensive account of foreign developments in direct coal liquefaction. However, a similar account would be desirable for indirect liquefaction. The following or similar information is suggested.

Federal Republic of Germany.

The Winkler process has been improved by developing technology for operation at high temperature, 950° C, and elevated pressure, 1 MPa. Rheinische Braunkohle constructed and operated a large demonstration plant, which converts 30 t/h German brown coal to syngas which is used to produce about 14 t/h of methanol. Some of the methanol is used to operate demonstration VW autos fueled by a mixture of 85% methanol-15% hydrocarbons.

Japan.

An intensive R&D effort is underway to convert syngas to mixed alcohols for motor fuel use. This is sponsored (1) in universities by the Ministry of Education, Science and Culture, (2) in industry by the RAPAD program -- Research Association for Petroleum Alternative Development -- and (3) in extensive research in the National Institute for Chemical Research for Industry. There is emphasis on innovation, with the particular objective to produce alcohol mixtures with relatively large amounts of ethanol.

Using technology developed by the French Institut du Petrol and in Japan, a 7,000-BPY plant producing mixed alcohols has been constructed and operated by Idemitsu Kosan.

Italy.

Italy has been a pioneer in the establishment of technology and commercial manufacture of MTBE and also of mixed alcohols from syngas for transportation fuels. The SEHT process, described in Chapter 5 of this report, was operated at a 15,000-TPY plant for the production of higher alcohols during the period 1982-87. The alcohols were blended at the 4.3% level in gasoline and marketed as SUPER E.

Italy was also the pioneer in the commercialization of MTBE, building a 100,000-TPY plant in 1973. Production of MTBE was expanded greatly and reached 1,150,000 TPY in western Europe by 1988.

The above information and relevant references are provided in the report G.A. Mills, "Catalysis for Fuels from Syngas, New Directions for Research", IEACR/09, 1988, [NTIS # IEACR 8901].

F.5 COMMENTS FROM G.P. HUFFMAN (FEBRUARY 1, 1989)

I have completed my review of the COLIRN report, "Coal Liquefaction -- A Research and Development Needs Assessment." I found it to be well-written and informative and I congratulate the panel on a thorough, well-done job. Specific comments are given below.

Chapter 3.

Section 3.2.1, p. 3-12. Priority 1, Retrograde Reactions.

It would be of interest to investigate the coke/char formed by various coals under identical liquefaction conditions by petrographic, chemical and physical techniques. The recommendation does not specifically call for such research, although it is implied.

Generally speaking, I agree with the rankings in Section 3.2, but would have rated Coal Structure-Reactivity and Homogeneous Catalysts higher.

Section 3.4.2--Pyrolysis

Since the large amount of char produced seems to be the major problem, I would have thought studies of char gasification, perhaps coupled with indirect liquefaction of the syngas, might have been a high-priority topic.

Section 3.9, p. 3-56

I agree that many DOE RFP's are unnecessarily constrictive. This causes fewer responses because potential proposal writers feel that the RFP is directed towards a particular group, laboratory or process. RFPs should be more generic.

Chapter 4

Section 4.2.1.3 p. 4-10

The need for adsorptivity measurements using appropriate solvents should be noted.

p. 4-15--New methods ought to be tried for determining M i.e. M_c, e.g., small angle synchrotron radiation scattering and atomic force microscopy (AFM) are possibilities.

p. 4-18--An additional reference to XAFS studies or organic sulfur in coal should be added: G.. Huffman, F.E. Huggins, S. Mitra, N. Shah, R.J. Pugmire, B. Davis, F.W. Lytle and R.B. Greegor, "Investigation of the Molecular Structure of Organic Sulfur in Coal by XAFS Spectroscopy," Energy & Fuels, in press.

p. 4-21--The paragraph on magnetic resonance should contain references to some excellent recent work by Pugmire et al. using the techniques of variable angle sample spinning (VASS) and depolar dephasing. Some excellent recent in situ ESR work by Seehra which determined the free radical concentration as a function of temperature during pyrolysis should also be mentioned. The references are:

> Sethi, N.K.; Pugmire, R.J.; Facellie, J.C.; and Grant, D.M., Anal. Chem., 60, 1574 (1988).
>
> Pugmire, R.J.; Sethi, N.K.; Solum, M.S.; Facelli, J.C.; and Grant, D. M., "The Use of Variable Angle Sample Spinning 13C-NMR Spectroscopy to Assess the Aromatic Cluster Size in Coals, Coal Chars, and Carbonaceous Materials," Carbon '88 Proc., University of Newcastle Upon Tyne, U.K. 18-23 September 1988, p. 349.
>
> M.S. Seehra, B. Ghosh and S.E. Mullins, Fuel, 65, 1315 (1986).41.5

p. 4-22--Low-temperature ashing followed by X-ray diffraction or FTIR is not a good way to study mineral matter. Computer-controlled scanning electron microscopy (CCSEM), coupled with element-specific spectroscopic methods like Mossbauer and XAFS spectroscopy, is preferable. These methods all investigate the whole coal directly. Typical references are:

> F.E. Huggins, G.P. Huffman, and R.J. Lee, in: Coal and Coal Products: Analytical Characterization Techniques, ACS Symposium Series, 205, ed. E.L. Fuller, Jr., pp. 239-258, Amer. Chem. Society, 1982.
>
> G.P. Huffman, F.E. Huggins, N. Shah, D. Bhattacharyya, R.J. Pugmire, B. Davis, F.W. Lytle, and R.B. Greegor, in: "Processing and

Utilization of High Sulfur Coals II," eds. Y.P. Chough and R.D. Caudle, pp. 3-12, Elsevier, 1987.

Sections 4.2.2 and 4.2.3 were both well written and informative. However, there was little discussion of catalyst structure versus catalyst performance. This would seem to be an area where more work is needed.

Section 4.3--Direct Liquefaction Process Development. An excellent review of pilot plant activities in this country. Sections 4.3.4 and 4.3.5 are good, brief summaries of the economic and environmental aspects of coal liquefaction.

Chapter 5

Section 5.3--A very thorough, informative review. The discussion of the various types of catalysts used in oxygenate technology was excellent. The models of alkali promotion mechanisms were summarized particularly well.

Chapter 6.

Sections 6.2.1 and 6.2.2 would have been clearer and easier to read with the additions of a few figures displaying pyrolysis behavior as a function of time, temperature, coal rank, etc.

The outstanding pyrolysis/mass spectrometry work by Meuzelaar et. al. should be referenced. Two recent papers are:

T. Chakravarty, H.L.C. Meuzelaar, P.R. Jones, and R. Khan, ACS Div. of Fuel Chem. Preprints, 33(2), 235-41 (1988).

B.L. Hoesterey, W. Windig, H.L.C. Meuzelaar, ACS Div. of Fuel Chem. Preprints, 32(2), 195-203 (1987).

p. 6-25--Catalytic hydropyrolysis sounds promising relative to other pyrolysis techniques, but isn't it essentially a low-pressure direct liquefaction process?

Chapter 7

The review of coprocessing was well done and identified most of the major research needs in that area. I would suggest two small additions, however. On p. 7-19, where demetallation of the oil is discussed, the following could be added: Recent work by Wender's group indicates that vanadium is present as a porphyrin in the crude oil and retains that same basic structure during incorporation into mesophase preceding coke formation (48).

48. T.J. Miller, S.V. Panvelker, I. Wender, J.W. Tierney, Y.T. Shah, and G.P. Huffman, ACS Division of Fuel Chem. Preprints, 33(3), 202-210 (1988).

In the discussion of small pilot scale coprocessing operations, recent work on tar sand coprocessing and isotope abundance studies at the Kentucky Center for Applied Energy Research should be mentioned.

Chapters 8 and 9 presented good summaries of bioconversion research and developments in other countries.

F.6 COMMENTS FROM R. P. ANDERSON (FEBRUARY 10, 1989)

Overall, I believe you have assembled an excellent panel and the study was well done. In general, I found the reviews of each of the five research areas well done. These reviews perhaps point out another research need; i.e., the need for a systematic complete review of everything we know about the liquefaction process to date. It is obvious that some of the work being performed has been done previously but may be published in obscure government reports, or obscure journals or in a foreign language.

Although it may have been difficult to reach a consensus, I believe that some relative weighting should have been assigned to each of the five research areas. There is perhaps an implicit ranking by the order in which the five areas are presented. I would agree with this ranking but would include coprocessing as a subtopic of coal liquefaction. For my own ranking of the level of effort for each area (based on my personal bias of where the most progress toward an economic process will be made), I would give very unequal ratings; e.g., direct liquefaction including coprocessing, 100; indirect liquefaction, 10; pyrolysis, 1; bioconversion, 0.1. I won't attempt a justification for this rating beyond the following. Significant improvements are being made in direct liquefaction. As for indirect liquefaction, we know that it works but the cost will surely be higher than for direct liquefaction. Attempts to beat the Anderson-Schultz-Flory distribution continue to fall short. It is doubtful that pyrolysis should be considered a liquefaction process, and char doesn't appear to be a very attractive primary product. Some effort on bioconversion may be justified, but for meeting any real energy needs I can't help believing bioconversion will remain pie in the sky.

I would have found references useful in the Executive Summary and/or Section 3. There are a number of assertions made which might be questioned. References to support such assertions would be useful. As an example, it is stated that coal liquids are suitable for processing in a refinery. I presume this is based on the Chevron work. I personally have no quarrel with the Chevron hydrotreating studies, but that work notwithstanding, I doubt that many refiners are going to welcome coal liquids into their refineries. Similarly, there are comments regarding retrogressive reactions without reference. Some leading references to this area would be useful. This is not a significant drawback to the report as copious references are provided in the following sections.

According to the report, a stated major objective of the DOE coal liquefaction program is to develop a data base that industry can use to commercialize coal liquefaction technology when needed. One area where data is needed which is recognized in the research reviews but is not addressed in the research needs is data required for engineering design and process scale-up. The absence and need for such data was recognized in the design efforts for the SRC-I and SRC-II demonstration plants, which led to overdesign and higher projected costs to compensate for the deficiencies.

In a recent engineering evaluation of the nonintegrated two-stage liquefaction (NITSL) process for coal prepared by Sterns Catalytic Corporation for the Electric Power Research Institute, the lack of thermodynamic data was highlighted in the section on critical areas of design and reliability.

There is no mention anywhere in the research needs report of the need for or use of thermodynamics. Physical chemistry is made up of two branches: thermodynamics and kinetics. The former tells you what can be done and the latter how fast you can accomplish it if it can be done. In the absence of thermodynamic data in the development of all stages of a process, the research is working in the dark. He/she is not able to know if the process is operating near equilibrium conditions, what effect changes in the conditions of operation will have, or if a change in catalyst will effect increased reaction. In the absence of accurate thermodynamic data, what could be done by calculation usually requires expensive and time-consuming experimentation.

F.7 COMMENTS FROM DAVID GRAY (FEBRUARY 21, 1989)

The size of the report is indicative of the enormous amount of effort that has been devoted to its preparation. The real meat of the matter is contained in the executive summary and the first three chapters. It is here that the research needs are identified and prioritized. The remainder of the report contains sometimes extensive overviews of the various technologies. My main criticism is that the research needs are not well justified by sound supporting material. For example, it should be possible for the reader to concur with the major recommendation in the direct liquefaction section that retrograde reactions should be minimized. However, there is no evidence provided that supports the supposition that these retrograde reactions are actually occurring or on how important they may be to the performance of the system. I suggest that a synopsis of the evidence supporting the R and D recommendations be included in Chapter 3. I think it should be specifically stated that the high capital costs of these plants is in large part due to the high severity of the current process conditions required to produce liquids. Thus the goal should be to reduce this severity without compromising the excellent yields that have been demonstrated at Wilsonville. Possible ways of accomplishing this may be through coal pretreatment, preconversion techniques or by more optimal temperature/time processing.

The same lack of scientific rationale exists in the recommendations for indirect liquefaction where the major recommendation is for improvements in catalysts. Current F-T catalysts at Sasol could be improved with respect to selectivity, but the major problem is heat removal from the highly exothermic F-T reaction. This is a problem of reactor design, not improved catalyst activity. It is well known that the greatest cost item in indirect liquefaction is the cost of preparing the clean synthesis gas; the effect of improved catalysts on the overall economics is not likely to be great. Catalyst R and D should be conducted for specific reactor systems since the requirements for fixed-bed and slurry systems will be different. As far as the DOE program is concerned, apart from a few precipitated iron catalysts that have been made in bench-scale amounts, there is no standard F-T catalyst on which to conduct reproducible R and D. Thus, a more down-to-earth goal of developing a working F-T catalyst that could be produced in a reproducible manner in sufficient quantities to be used by several contractors and in a larger PDU may be more appropriate. I do not understand the recommendation to develop sulfur-resistant water gas shift catalysts; these are already available commercially. A far better R and D goal would be to try and develop sulfur-resistant F-T or alcohol catalysts to minimize the complex and extensive gas clean-up currently required to protect catalysts.

There is no mention in the report of environmental aspects of these technologies that seek to use coal (a dirty word these days) to replace conventional petroleum. I think it would be wise to at least try and preempt criticism by emphasizing the positive aspects of these potential technologies with respect to their ability to produce clean products that are essentially sulfur free. Also, since the implicit goal of all this R and D is to improve overall efficiency, adverse environmental effects will be minimized.

With pyrolysis, the key question is always what is the point of pyrolysing coal when all I get are dirty gas, dirty liquids, and tar and a char that has considerably less value than the coal. Even if the liquids can be refined, at some considerable expense, there aren't enough of them to offset the large char yield. The major recommendation is for R and D on catalytic hydropyrolysis, which implies the panel does not think that thermal pyrolysis alone has any potential. In Chapter 6 there is some evidence to support the contention that catalyzed hydropyrolysis increases the liquid yield, as well it should considering the additional severity and expense this approach involves. A major problem not addressed in this area is that of reactor design. It is notoriously difficult to feed dry coal, especially high-volatile bituminous, under pressure into hot hydropyrolysis reactors. That is one reason slurry oils are used as in direct liquefaction. The other problem is removal of particulates in any pyrolysis process. When all these problems are taken into account and combined with the lower yields, it is difficult to imagine catalytic hydropyrolysis being economically competitive with direct coal liquefaction.

One aspect that could be mentioned is the complementary nature of the two processes of direct and indirect liquefaction. They are complementary in both the nature of the products that are produced (good gasoline from direct and good diesel from F-T) and also in many of their common process steps (gasification, product refining). There is thus the potential for hybrid plants in the future. I suggest a recommendation to study conceptual hybrid plants that utilize the best of both technologies as a potential way of reducing the costs of these technologies.

F.8 COMMENTS BY HOWARD STEPHENS, FRANCES STOHL, AND ARTHUR LYNCH (FEBRUARY 16, 1989)

We recognize that a review of the status of research and development efforts for coal liquefaction since the last similar report of the FERWG committee in 1980 was an immense task and that the COLIRN committee has made a commendable effort toward providing recommendations to effectively guide future research. From our perspective, we agree, in general, with the high-priority recommendations made for future R&D in coal liquefaction. Although we would add a few recommendations, reorganize them, and ladder rank the importance of the recommendations somewhat differently, we emphasize that, for the most part, <u>they are sound recommendations made by persons with extensive experience</u> in various aspects of research and development for coal liquefaction. We hope the following comments will make the report an even more effective document for planning future coal liquefaction research and development.

1. The body of the report is divided into two basic sections: coal liquefaction R&D Recommendations (Chapter 3) and a review of the status of the various liquefaction R&D technologies (Chapters 4 through 8). The bridge connecting the recommendations to the review of the status of R&D is the rationale or basis for formulating the recommendations. We found this rationale, as given in Chapter 3, to be weak, nonspecific and, in some instances, contradictory to other portions of the report. The rationale should directly link the specific needs identified in the review chapters to the recommendations given in Chapter 3 in order to demonstrate the need for the recommended research. The following are examples of weak or contradictory rationale.

    Pg. 3-17. Recommendation (Section) 3.2.2.8. "Develop new chemical techniques to solubilize coal." Again, the rationale needs to be clearly defined. It is stated that "nearly complete conversion of coal is achieved by alkylation with methanol." Conversion to products soluble in solvents such as THF or toluene (but not liquid themselves) does not necessarily lead to higher yields of liquid products.

Pg. 3-18. Recommendation (Section) 3.2.2.10. "Develop intrinsic rate expressions for initial coal dissolution reactions." Not only is this recommendation a subelement of Recommendation (Section) 3.2.2.7 -- develop kinetic models of direct liquefaction and 3.2.2.5 -- develop a coal structure-reactivity model, but there is no clear rationale given. One would assume that kinetic models of direct liquefaction would include the kinetics of the dissolution step, and that coal structure-reactivity models for coal liquefaction would include the kinetics of the reactions involved.

Pg. 3-24. Recommendation (Section) 3.3.2.1. "Apply new advances in materials science to catalyst preparation for F-T and alcohol synthesis." We agree with this recommendation, but the need for this approach needs to be clearly stated.

2. We note some inconsistencies between Section 4.2.3 "Catalysis of Direct Liquefaction" and the recommendations for direct liquefaction, specifically D6, D11 and D12. These recommendations address use of homogeneous catalysts, development of new catalysts, and studies of catalytic hydrogenation and cracking mechanisms. Although D6 recommends the evaluation of metal carbonyls for coal liquefaction, the basis for this is not mentioned in Section 4.2.3. In addition, the descriptions of promising new catalyst systems need to be augmented, and a discussion of the functions of catalysts in direct coal liquefaction needs to be included.

   In our judgement, <u>recommendations for augmenting catalyst R&D in support of direct liquefaction processes should rank as one of the highest-priority items</u>. This judgement is supported by the IEA Coal Research Report, "Catalysis in Direct Liquefaction: New Directions for Research," by Dr. Frank Derbyshire (COLIRN report, Chapter 4, reference 225). It is stated in this IEA report that "The supported catalysts now applied to liquefaction are plainly unsuitable for hydroprocessing high-boiling liquids due to their rapid deactivation."

We therefore recommend addition of the following as a high-priority need for coal liquefaction R&D:
Identify the mechanisms of catalyst deactivation in direct liquefaction processes and develop techniques to prevent or mitigate the effects of catalyst deactivation. The basis for this recommendation is clearly identified in Section 4.2.3, pages 4-57 through 4-63. Catalyst deactivation is an enormous problem for direct liquefaction. Catalysts used in Wilsonville runs lose up to 90% of their activity within the first few days of processing. To make up for this activity loss, Wilsonville is currently adding about 5 pounds of catalyst per ton of coal. For a full-scale commercial plant this would amount to approximately 200,000 pounds of catalyst per day, creating substantial additional expense due to the cost of the fresh catalyst addition and disposal of the spent catalyst. Approaches must be developed to prevent or mitigate deactivation, prepare catalysts resistant to deactivation, or alternatively, to regenerate spent catalysts.

3. For indirect liquefaction R&D we offer the following as another high-priority R&D need:
Investigate the fluid dynamics and reaction kinetics of slurry-phase catalystic reactors for indirect liquefaction and develop computational models to allow scale-up of these reactors.
Experience with bench and pilot-scale slurry-phase reactors for Fischer-Tropsch and methanol synthesis has demonstrated several advantages: 1) isothermal operation, 2) excellent heat exchange, and 3) use of small catalyst particles. However, the rates of reaction in certain slurry reactors appear to be limited by mass transport in the fluid phase. Additional studies of the fluid dynamics are required in order to develop models to predict requirements for scale-up to commercially-sized plants.

4. Division of the report into sections for review of the various technologies separately has artificially eliminated consideration of potential benefits derived from combining two or more processing technologies into one processing complex. For example, could combination of direct and indirect technologies into a single process lead to a more cost-effective approach? Perhaps an additional chapter on integrated technologies is warranted. Only one recommendation, (Section) 3.4.2.4 for pyrolysis, considers a systems analysis approach.

5. On page 4-3 it is noted that "There seems to be a gap between fundamental research and process development contractors, which must be bridged if we are to test and apply the fundamental work in the context of a liquefaction process." This COLIRN report should provide a bridge for that gap. Promising approaches for liquefying coal which have emerged from basic and applied research programs should be clearly identified, and recommendations for development of processes based on these advanced approaches should be made.

6. In our opinion the COLIRN report should not contain numerical ratings for the high-priority recommendations listed in the report. Such ratings are based on subjective judgements and the makeup or the committee with respect to fields of expertise, and may not be representative of the coal liquefaction research community as a whole. Furthermore, the method used to rate the recommendations does not allow comparison between categories of recommendations, for example, direct liquefaction with 12 high-priority recommendations and bioliquefaction with only one.

F.9 COMMENTS FROM D.D. WHITEHURST (FEBRUARY 17, 1989)

In general, the report is very well written, and I agree with most of the recommendations proposed by the panel. There are a few comments I would like to make regarding the report, however. I will address general features first, then go on to specific areas.

I object to the inference that the commonly accepted mechanisms for the conversion of coal are being "challenged" by new thinking. The proposed new mechanisms are like many in past proposals for additional chemistry that could help answer some questions on observed phenomena. Generally, such proposals have been made by researchers deeply involved in academic exercises using exclusively model compounds. It would be wise to recommend that new theory be tested with real coals and solvents under actual coal liquefaction conditions. If the new mechanism can predict a new approach to that derived empirically, it is extremely useful. If, however, it provides no means for process improvement, it should not be overly emphasized.

Let's put the chemistry involved in perspective. First, there should be a clear definition of what is meant by "coal conversion". It is commonly accepted that conversion means a change in form or composition of a starting material. It was clearly established by many groups over 10 years ago that under typical liquefaction conditions the reactive macerals of coal are converted completely to freely soluble products in 1 to 5 minutes, depending on the rank of the coal. During this conversion about 0.3 to 1% hydrogen is consumed by the conversion of the coal independent of the source of that hydrogen.

Consider what this means on a molecular level, using a typical bituminous coal. The coal will contain 77% C dmmf, and about 70% of that carbon is found in aromatic rings predominantly no larger than 3 condensed rings. Simple stoichiometry predicts that a pound of raw coal contains 116 moles of carbon bonds. About 12% of those are associated with heteroatoms. In converting that coal to soluble species, only about

2.5% of those bonds have to be broken. The products are still far from the compositions desired for conventional fuels; they have an average molecular weight of about 1000 and thus cannot be distilled even with high vacuum. At this size, even though they are soluble species, they have little access to the interior of conventional heterogeneous catalysts. In addition, they contain about 8 heteroatoms per molecule, 4 of which are phenolic. In upgrading these materials farther another 1% of the original carbon bonds in the original structure must be broken to produce distillable material (450 molecular weight), and the phenolic functionality must also be removed.

At this stage, all of the easy conversions are over. Fortunately, at this molecular size, catalysts with pore sizes of around 100 A can begin to alter the structures as access is less diffusionally restricted.

If there is a need for new chemistry, it is after this point, and here some of the arguments of thermal cleavage limitations are valid. Thermal reactions are very slow, and acceleration is needed for improved processes. Of the hydrogen consumed about 5% is needed to lower the molecular weight to 450, 30% to remove heteroatoms, and the other 65% is needed to convert the products to gasoline and diesel fuel. The predominant hydrogen consumption is for ring-opening reactions, and it is at this point where gas formation becomes problematic. There is essentially no difference between breaking an aliphatic ring fused to an aromatic and dealkylation of a short chain on an aromatic ring.

As far as the "theoretical" prediction that regression does not occur through benzylic radical coupling, there is ample evidence that even methyl naphthalene condenses and dehydrogenates to form 5-membered polycyclic ring systems when adequate H-donors are not available during coal liquefaction. Pyrene when present in liquefaction solvents can be substituted with as much as 1 out of 80 carbons from the original coal (found as methyl substituents on pyrene). This observation is strongly suggestive of benzylic coal radical addition and further cleavage of the coal fragment. It should also be recalled that any attempt to follow where H adds to coal with deuterated reagents is completely confused by very rapid scrambling of D throughout the product spectrum, which implies that radical addition and elimination is a rapid dynamic process.

As far as the "need" for a great deal of solid state characterization of catalysts with new sophisticated techniques, I have reservations. I am not aware of any new catalyst development that has come from such studies. Results so far have only confirmed what we already know from well-conducted reactions.

I wholeheartedly agree that a very important recommendation for the future use of coal in the U.S. is to maintain operation of Wilsonville. If funding limitations require restrictions of other recommendations, so be it!

Recommendations for increased understanding of structure and reactivity are also very worthwhile.

Recommendations to study pretreatment of coal could be quite important in view of recent Wilsonville results. However, such pretreatments are best directed to ash etc. removal, not to coal structure modification. Coal liquefaction reagents such as hydrogen are expensive enough. Why make things more expensive.

INDIRECT LIQUEFACTION

In general, the recommendations appear sound, but there is an overemphasis in expectation from surface science studies. More will be learned by actual experiments.

The need to improve MeOH synthesis is questionable. The process is already 75% thermally efficient. How much can this be improved, and how much will this improvement cost?

Conversion of syngas to oxygenates probably makes more sense than liquid hydrocarbon fuels, as the panel concluded.

PYROLYSIS

The main concern with this area will be char disposal. This will be increasingly of more concern in the future as environmental issues will limit direct combustion.

Reference to pyrolysis as a second-order process has no meaning. Getting two solid species together to form products as if they are freely diffusing soluble species makes no sense.

There was a whole body of information completely ignored in this section. It is contained in a book "Coal" by Wilfred Francis. This reference should be included in fairness to the readers.

I agree in general with the recommendations for more fundamental studies in this area and the need for higher yields of liquid before getting too excited.

COPROCESSING

In my view this will be the evolutionary entry of coal liquefaction into the commercial market. Product specifications will have to be met before coal liquids can be consumed in large quantity, and to produce them in an integrated facility where environmental issues can be addressed will be more efficient than separate plants.

The review was well done and though slightly biased was generally fair to all researchers in the field. One deficiency in this section is the lack of consideration of disposal of unconverted coal and resid. Gasification of such liquid slurries via Texaco type processes should be encouraged, e.g., proposed for funding. It is highly likely that even more synergisms will be found in partial oxidations than in liquefaction.

BIOPROCESSING

In my opinion this area has little hope for fuel production applications. Nature is inherently inefficient, and if researchers were to make a balance of Btu of nutrients consumed/Btu of fuel produced, it would clearly show a net consumption of energy. This is because organisms must perform a lot of very specialized tasks to metabolize their food. Thus most of the metabolism is concerned with CO_2 generation to provide the energy needed to perform the other transformations they wish to do. I would not encourage research in this area.

There is a need for biological processes in environmental control. Wilsonville is even now using special phenol-consuming bacteria for water cleanup. It would be well worth investigating the use of the newly discovered deep-sea microorganisms, which thrive at high pressure and temperature and which can tolerate and perhaps even consume H_2S. Perhaps new routes to H_2S scrubbing could be discovered.

CLOSING COMMENT

I enjoyed reading this report and feel it will be a valuable contribution to the literature as well as an aid to DOE personnel.

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

A	Angstrom (10^{-10} meter)
amu	atomic mass unit
ANL	Argonne National Laboratory
APCI	Air Products and Chemicals, Inc.
API	American Petroleum Institute, gravity
AR&TD	Advanced Research and Technology Development (Program)
ASDA	Antisolvent Deashing (Process)
ASF	Anderson-Schulz-Flory
ATB	atmospheric tower bottoms
atm	atmosphere
bbl	barrel
BCL	Brown Coal Liquefaction (Process)
BN	binaphthyl
BPD	barrels per day
BPSD	barrels per stream day
BRSC	Burns and Roe Services Corporation
Btu	British thermal unit
BTX	benzene, toluene, and xylene
^{o}C	degrees Celsius
CANMET	Canada Centre for Mineral and Energy Technology
CC-ITSL	Close-Coupled Integrated Two-Stage Liquefaction
C-E	Combustion Engineering
cf	cubic foot
CH	carbon-hydrogen
cm	centimeter
COED	Char, Oil, and Energy Development (Process)
COGARN	Coal Gasification Advanced Research Needs (Panel)
COIL	HRI coprocessing process
COLIRN	Coal Liquefaction Research Needs (Panel)
Consol	Consolidation Coal Company
CSD	Critical Solvent Deashing (Process)
CSF	Consol Synthetic Fuel (Process)
CTSL	Catalytic Two-stage Liquefaction
d	day
DHP	dihydrophenanthrene
DIBE	di-isobutyl ether
DITSL	Doubly Integrated Two-Stage Liquefaction
DMF	dimethyl ether
DMMF	dry, mineral-matter-free
DNM	dinaphthyl methane
DOE	Department of Energy
ECLP	Exxon Coal Liquefaction Plant
EDS	Exxon Donor Solvent (Process)
EI	evaporative index
EP	end point

EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
°F	degrees Fahrenheit
FBR	fluidized-bed reactor
FCC	fluidized-bed catalytic cracker
FERWG	Fossil Energy Research Working Group
FIMS	field-ionization mass spectrometry
FL	fluoranthene
FRG	Federal Republic of Germany
ft	foot
FT	Fischer-Tropsch
FTIR	Fourier-transform infrared spectroscopy
FTS	Fischer-Tropsch Synthesis
g	gram
ΔG	Gibbs free energy
gal	gallon
GC	gas chromatography
GHSV	gas hourly space velocity
GPH	gas phase hydrogenator
GSSTFR	gas-solid-solid trickle flow reactor
ΔH	enthalpy of reaction
HAS	higher-alcohol synthesis
HBR	hanging-basket reactor
H/C	hydrogen-to-carbon ratio
HD	heavy distillate
HDN	hydrodenitrogenation
HDS	hydrodesulphurization
HHV	higher heating value
HPLC	high-performance liquid chromatography
hr	hour
HR	hydrotreated resid
HRI	Hydrogen Research, Inc.
HTR	hydrotreater
hv	high volatile
ICC	International Congress of Catalysis
ICI	Imperial Chemical Industries
IEA	International Energy Agency
IFP	Institut Francais du Petrol
IGCC	integrated coal gasification combined cycle
in	inch
IR	infrared
ITSL	Integrated Two-Stage Liquefaction
J	Joule

°K	degrees Kelvin
l	liter
lb	pound
LCI	Lummus Crest, Inc.
LHSV	liquid hourly space velocity
LPG	liquefied petroleum gases
LR	Lurgi Ruhrgas
LTR	light thermal resid
LU	Lehigh University
LV	liquid volume
m	meter
MAF	moisture ash-free
MAS	metanolo piu alcoli superiori
M_c	average molecular weight between cross-links
METC	Morgantown Energy Technology Center
MIBE	methyl isobutyl ether
min	minute
MS	mass spectrometry
MTBE	methyl tertiary-butyl ether
MTG	methanol-to-gasoline
NEDO	New Energy Development Organization (Japan)
NMR	nuclear magnetic resonance
NTSL	Non-integrated Two-Stage Liquefaction
OER	Office of Energy Research
OFE	Office of Fossil Energy
OOCF	Ohio-Ontario Clean Fuels, Inc.
OPA	Office of Program Analysis
ORC	Occidental Research Corporation
p	pressure
Pa	Pascal
PCAH	polycyclic aromatic hydrocarbons
PCT	physical, chemical, and thermal (properties)
PDU	process development unit
PETC	Pittsburgh Energy Technology Center
PNA	polynuclear aromatics
PNL	Pacific Northwest Laboratory
POC	proof of concept
PONA	paraffins, olefines, naphthenes, and aromatics
POX	partial oxidation
ppm	parts per million
PRC	Peoples Republic of China
psi(g)	pounds per square inch (gauge)
R&D	research and development
RHT	radical hydrogen transfer
RITSL	Reconfigured Integrated Two-Stage Liquefaction
ROM	run of mine

s	second
SAIC	Science Applications International Corporation
SCF	standard cubic foot
SCFD	standard cubic feet per day
SCS	Southern Company Services
SCT	short contact time
SEHT	Snamprogetti, Enichem, and Haldor Topsoe
SG	synthetic gas
SMDS	Shell Middle Distillate Synthesis
SRC	Solvent Refined Coal (Process)
STY	space time yield
T	temperature
TAME	tertiary-amyl butyl ether
TBA	tertiary-butyl alcohol
THF	tetrahydrofuran
THFL	tetrahydrofluoranthene
THQ	tetrahydroquinoline
TIGAS	Topsoe Integrated Gasoline Synthesis Process
TLU	thermal liquefaction unit
TPD	tons per day
TPSD	tons per stream day
TR	thermal resid
TSL	Two-Stage Liquefaction
TSP	total suspended particulate
UCC	Union Carbide Corporation
U.K.	United Kingdom
UP&L	Utah Power and Light
U.S.	United States
UV	ultraviolet
VGO	vacuum gas oil
WGS	water gas shift
WHSV	weight hourly space velocity
wt	weight
x	probability of chain growth
XANES	X-ray absorption near edge structure
yr	year
ZSM-5	zeolite catalyst

PREFIXES

k	kilo (10^3)
m	milli (10^{-3})
MM	Mega (10^6)

μ	micro (10^{-6})
N	normal
n	nano (10^{-9})
p	pico (10^{-12})