V

TECHNICAL EVALUATION OF PROCESSES

A. GENERAL

As discussed in Chapter IV, coal liquefaction processes may be grouped into four general classifications: pyrolysis and hydrocarbonization, solvent extraction, catalytic liquefaction, and indirect liquefaction. Pyrolysis is carried out in absence of externally added hydrogen; heating in the presence of hydrogen without added catalyst is called hydrocarboniza- tion. Solvent extraction may be accompanied by indirect hydrogenation (i.e., hydrogenation of the solvent in a reactor in which no coal is present). Catalytic liquefaction includes only those processes in which the coal comes in direct contact with the added catalyst. Indirect liquefaction includes those processes in which the coal is converted to a gas and the gas, in turn, is converted to a liquid.

1. Unit Size

Experimental work has been carried out on a variety of unit sizes, and the term "pilot plant," as used in the industry, describes the ob- jective of the work--i.e., to test all of the major process steps in an integrated operation--usually using the smallest size equipment in which this can be done. To be consistent with terminology used by the Office of Coal Research (now ERDA), however, the term "bench scale" will be used to describe experimental work up to several hundred pounds of coal per day, "process-development scale" will refer to work carried out at 0.5 to 10 tons per day, and "pilot-plant scale" will refer to operations with 25 to 600 tons per day.

Bench-scale work typically involves expenditures for equipment up to about $300,000, with a yearly operating budget of about the same magnitude. Process-development units (PDU), on the other hand, may cost $5 million to $15 million to construct, with a yearly operating budget of as much as $5 million. Pilot plants may cost as much as $300 million to construct, with a yearly operating budget of about $50 million.

Up to now, ERDA has described "demonstration" plants as involving feed rates of 1,000 to 3,500 tons of coal per day while "commercial" plants are in the range of 10,000 tons per day and higher. It is the

opinion of the Panel that if a demonstration plant is too small to be economical for continued commercial operation after the demonstration period, it should not be built. Instead, the pilot plant should be carefully designed and operated so that the data obtained can be used in the design of at least a single train of a commercial plant.[1]

Eliminating the demonstration plant step and carrying out the demonstration in a "pioneer" plant that can later be operated commercially might save as much as five years and hundreds of millions of dollars in the overall program. Admittedly, it would increase the risk, but the saving in time would make it worthwhile.[2]

While catalytic liquefaction was commercialized abroad before and during World War II, indirect liquefaction is the only process that has been operated on a commercial scale since that time. Solvent extraction and pyrolysis have been carried out on a pilot-plant scale while improved catalytic liquefaction and solvent extraction processes are in the development stage. In view of the high costs of construction and operation, it would appear advisable to limit pilot-plant operation to those processes that show high potential.

2. Physical Variables

Because of the uncertainties of scale-up, demonstration in a pilot plant is required to prove operability and to provide an estimate of capital and operating costs. For example, it is often impossible to reproduce in a small-scale plant all of the physical variables that will be encountered in the commercial unit, and impurities encountered commercially may not be found in laboratory testing or vice versa.[3] Specific operations that might cause problems in scale-up of coal conversion processes are:

a. Dry feeding of pulverized coal to a pressurized system

b. Handling of caking coals at elevated temperatures

c. Transporting and preheating coal-oil slurries

d. Separating solids from the liquid products

e. Fouling of heat transfer surfaces (slurry preheaters and product coolers)

f. Pressure reducing, particularly in the presence of solids

g. Handling and utilization of new products

Dry feeding of pulverized coal to an atmospheric pressure system is a fairly straightforward operation. Feeding at higher pressures generally involves the use of lock hoppers that, while operable on a small scale, have not been demonstrated on a large scale. The larger the valves, the more chance there is for leakage and the more unwieldy the system becomes.

With the exception of the Lurgi process for gasification of coal, which has been operated in relatively small modules because of restrictions in reactor diameter and only at pressures less than 500 psi, the use of lock hoppers in this type of service has not been demonstrated on a larger commercial scale. This is perhaps one of the reasons that processes for coal liquefaction use slurry-type feeding. For processes feeding dry coal in large tonnages, viable feeding systems remain to be developed.

Feeding of caking coals to systems at temperatures above approximately 300 °C presents problems because the coal swells as temperature is raised, becomes sticky, and forms agglomerates that are difficult to handle. Slurry feeding mitigates these problems. Other methods that have been investigated for dry handling of caking coals at elevated temperatures are preoxidation, char recirculation, heating in stages, chemical treatment, and mechanical mixing. Although preoxidation has been widely used, it has the disadvantage of lowering gas and liquid yields, increasing hydrogen consumption, and producing water, which represents as much as a 10 to 15 percent energy loss. Other methods have been applied with some success in certain cases, but there is no single treatment that can work for all processes; the problem must be handled on a case-by-case basis.

Transport of coal-oil slurries causes erosion. As a result, positive displacement pumps have been substituted for centrifugals in the solvent-refined coal pilot plant, but this has brought with it the problem of keeping check valves and plunger packings in operation.

Separation of solids from a liquid product is perhaps the most difficult problem to solve in coal liquefaction processes.[4] Batchelor and Shin recently reported that consideration was given to vacuum distillation, solvent precipitation, filtration, and centrifugation. Of these, only vacuum distillation has been sufficiently well demonstrated to be a practical solution for large plants, and this is applicable only when coupled with a liquefaction process yielding a product that is largely distillable. Filtration does not appear to be an economically practical solution at the present time (e.g., Batchelor has calculated that a solvent-refined coal plant designed for 25,000 tons of coal feed per day would require 94 rotary precoat filters, each containing 500 square feet of surface, or 60 pressure leaf filters, each containing 1,100 square feet of surface; if centrifuges were used, 199 units would be required).

Solvent precipitation appears to be more attractive than filtration since it would eliminate rotary mechanical equipment, which is costly and difficult to maintain. Solvent deashing processes have been under development in at least three different laboratories. C-E Lummus uses an anti-solvent in the kerosene boiling range and claims that the ash content of a coal liquid topped to remove components boiling below 315 °C can be reduced to less than 0.01 percent, with a solvent-to-liquid ratio of the order of 0.5:1.[5] However, the data presented indicate that residence times of 2 to as much as 8 hours are required, and shorter residence times would be necessary for most practical applications. Kerr-McGee uses a light coal-derived deashing solvent near its critical temperature and pressure.

Advantages claimed for this procedure applied to vacuum bottoms from a catalytic or noncatalytic conversion are the low density and viscosity of the solvent, resulting in rapid gravity settling of the ash.[6-8] With a ratio of solvent to liquid of at least 2:1 and temperatures of about 205 °C, the deashed coal is claimed to have less than 0.16 percent ash.

Conoco Coal Development Company also has carried out work on solvent deashing, generally in connection with solvent extraction of coal. Its results indicate that it is not always necessary to add an anti-solvent; in one series of runs with Pittsburgh seam coal, deashing was accomplished simply by cooling the effluent from the extraction from 400 °C to 315 °C. A product containing 0.16 percent ash was obtained.[9] With Utah sub-bituminous coal, on the other hand, it was necessary to add up to 0.3 parts of n-decane to 1 part of extraction solvent in order to remove 98 percent of the ash. In general, the work by Conoco indicates that solvent precipitation is a very complicated operation that depends on the nature of the coal, the conditions under which the conversion is carried out, settling temperature, the particle size of the ash, the settling velocity, etc.[10]

Although solvent deashing has the advantages of eliminating mechanical equipment, it must be tailored to the particular feedstock to be handled. Furthermore, it requires very efficient recovery of the solvent, which can be expensive. Nevertheless, next to vacuum distillation, solvent precipitation would appear to be the most promising means of ash removal for catalytic liquefaction or solvent extraction processes.

In the case of pyrolysis processes, the problem of solids separation from the product is much simpler if it is possible to make a clean separation of the solids when the products are in the vapor phase. This requires several stages of cyclones, and there may still be a small amount of solids in the condensed liquid product; however, in this case, a final clarification step may well prove practical.

Fouling of heat-transfer surfaces is a problem that has been particularly acute in the solvent-refined coal process and indicates that considerable investigation is needed in any process in which tubular heaters or coolers are employed. A possible solution—for example, in the Synthoil process—might be to supply the heat by means of the recycle hydrogen. This method has been used to overcome a similar problem in heating residual petroleum stocks for the H-Oil process. In a somewhat similar fashion, the problem of fouled condensing surfaces was eliminated in the H-Oil process by a vapor-liquid separation at reactor temperatures followed by separate cooling of the two streams. Without the vapor-liquid separation, the condensed naphtha caused precipitation of asphalts. In the case of coal conversion, the same problems would be encountered but, in addition, carry-over of fine particles into the vapor stream also might cause difficulties.

When operating at pressures of 1,000 psi or higher, pressure reduction becomes a problem because of valve wear, particularly when particles of char or ash are present to cause erosive action. The problem is being

approached in several ways, including improved valve design and development of more erosion-resistant materials.

Product handling presents no unusual difficulties for coal conversion processes that yield a product similar to petroleum products. However, when the product is a solid at room temperature and has a high melting point, as in the case with solvent-refined coal, new handling methods are required. Whether or not a solid product (e.g., briquettes or prills) can be produced that has sufficient mechanical strength for subsequent handling and is not sticky or friable remains to be seen. Shipment as a solid in tank cars with steam coils might not be practical if the temperatures required for melting are too high. It is possible that the only solution in this case would be to upgrade the material to improve its handling characteristics (e.g., to hydrocrack the material as in the CSF process).

3. Recovery and Regeneration of Catalysts

If catalysts are used, provision must be made for replacement or regeneration when activity level has dropped to some predetermined value. Whether or not the catalyst is regenerated or a process is used to recover the active ingredients depends on the technical problems involved and the economics.

Because catalysts are used in indirect liquefaction and in some of the solvent extraction processes, these applications have been studied for many years and the techniques and economics of replacement and regeneration are well known. On the other hand, in catalytic liquefaction, where the catalysts come in direct contact with the coal and its impurities, the problems are relatively new and require much study.

Perhaps the most challenging problem involves those processes in which the coal is impregnated with the catalyst. In the Bergius process, for example, the catalyst is used on a once-through basis, and so far no catalyst recovery scheme has been found practical for the recovery of tin or molybdenum.[11] This has greatly restricted the type and amount of catalyst that can be used in the process. More recently, investigation at the University of Utah on gas-solid catalytic liquefaction has included work on recovery of the zinc catalyst that has been found to be superior in this process.[12]

In those processes in which coal is suspended in a heavy oil to form a slurry and is then passed through a bed of pelleted or extruded catalyst, the metals in the ash tend to accumulate on the surface of the catalyst and gradually reduce its activity. In this case, however, the rate of deactivation may be acceptable, but this depends on the amount of ash present in the original coal, the rate at which the metals in the ash accumulate on the catalyst, and the tolerance of the catalyst for these metals. In the H-Coal process, for example, continuous replacement of the catalyst is possible because it is present in an ebullating bed. In the case of

pelleted or extruded catalysts, regeneration and reuse may be possible, or it may prove more worthwhile to send the catalysts to a chemical plant for reclamation of the important constitutents.

4. Materials of Construction

Limited data available from coal conversion programs on the process-development and pilot-plant scales indicate that selection of construction materials cannot be based entirely on corrosion experience developed in the petroleum industry. The complex corrosive/erosive environments associated with coal conversion processes most likely will require the development of new corrosion/erosion rate data on common construction materials and, additionally, may require the application of new, more resistant materials of construction.[13]

Areas of primary concern include high-pressure and high-temperature furnace tubes, reactors, and vessels and the associated mechanical equipment. Recent stress-chloride cracking failures reported in the 316 stainless steel preheater coils of the solvent-refined lignite PDU at the University of North Dakota support these concerns.[14] The coils, as well as the downstream dissolvers and interconnecting piping, have been replaced with equipment constructed from Incoloy-800 materials. In addition, the original carbon steel separator vessels have been replaced with cast 316 stainless steel vessels containing 2 to 15 percent ferrite, which reportedly retards stress-chloride cracking.

Conventional weld overlaid hydrocracker/hydrodesulfurizer-type reactors used in the petroleum industry are constructed from 2.25 percent chrome alloy steel with Type 304L weld overlay. If the corrosive behavior of the sulfur present in coal liquids is no more severe than that observed in Middle East crudes and erosion is not excessive, liquefaction reactors could be similarly constructed. However, current applications of heavy-wall vessels generally are limited to approximately 7 or 8 inches in wall thickness. Based on a 12-foot vessel diameter, this permits reactor design conditions of 2,000 psi pressure and 450 °C temperature. For this type of construction design, higher pressures would require thicker reactor walls, and higher design temperatures would require refractory vessel linings or specially designed hot wall construction. With wall thicknesses in excess of 4 inches, cold-weather impact problems must be considered. This is not a factor for multi-layer or centrifugally cast vessels. Recent advances in reformer tube construction, such as Manoir Pompey's Manaurite 36X, could significantly increase the temperature limits for liquefaction reactor operations.[15]

Several material programs currently are being sponsored by the Fossil Energy Research Division of ERDA. In addition, the National Association of Corrosion Engineers is organizing a Technical Practices Committee (T-12A) for coal conversion and utilization processes. This committee conceivably could monitor the numerous ongoing programs and provide the guidance to ensure that proper materials of construction are specified for coal liquefaction plants.

B. PYROLYSIS AND HYDROCARBONIZATION PROCESSES

1. Types of Processes

Compared to slurry-phase hydrogenation processes, pyrolysis and hydro-carbonization processes are less complex and generally operate at conditions of lower severity. Many pyrolysis processes do not use hydrogen or steam. Hydrocarbonization processes, on the other hand, do employ hydrogen and also may use steam to gasify char for subsequent hydrogen generation. Operating pressures for conventional pyrolysis processes are normally below 100 psig and usually between 5 and 25 psi. Hydrocarbonization processes operate between 300 and 1,000 psi. Operating temperatures in both categories of processes are between 500 and 600 °C.

These operating conditions are substantially below the 1,000 to 5,000 psi and 450 and 550 °C required in slurry-phase hydrogenation. The penalties on the pyrolysis processes are reduction in quantity, especially of liquid products, and lower quality products compared to hydrocarbonization.

2. Pyrolysis Reactors

Three types of pyrolysis reactors are of commercial interest: mechanically agitated, entrained-flow, and fluidized-bed reactors. Agitated reactors such as in the Toscoal process are mechanically complex. Wear and erosion lead to high maintenance and may create fine char particles that require special downstream processing using filters or electrostatic precipitators.

Entrained-flow reactors such as those used in the Occidental process[16] have several advantages, including either upflow or downflow operation. In the PDU program it was found that downflow operation reduced the tendency toward reactor plugging with agglomerating coals. In either operation, the entrained flow reactor provides short residence time. In addition, fine particles (50 to 60 microns) can be heated very rapidly, contributing to high liquid yields that may exceed the volatile content of the coal as determined by proximate analysis. The short residence time results in high coal throughput and smaller reactors.

The fluidized-bed reactor is the most common type employed in pyrolysis and hydrocarbonization processes such as the Clean Coke,[17] COED,[18] CSIRO, and Coalcon.[19] The U.S. Steel Clean Coke process utilizes a hydrocarbonization section that recycles a hot hydrogen-rich gas stream to provide heat for the reaction and to convert the sulfur to H_2S.

Fluidized-bed pyrolysis reactors have been used successfully to process noncaking coals in PDU units in the COED and Coalcon programs as well as in a 20-foot-diameter commercial reactor during the CSIRO work. With the exception of the multiple-staged temperature-fluidized reactor system used in the COED process, problems may be encountered in processing caking coals in fluidized beds.

3. Pyrolysis of Caking Coals

Major problems with agglomeration may be encountered when strongly caking coals are fed to pyrolysis reactors. There is some evidence that even weakly caking coals tend to agglomerate if heated at rates greater than 75 °C per minute in a fluidized bed operating above 500 °C. Methods for the prevention of agglomeration include bed recirculation, feed preoxidation, staged preheating, feed dilution, and stirred-bed operations. Of these methods, the last is built into the Lurgi-Ruhrgas process. Bed recirculation appears to be most promising for fluidized systems. In entrained-flow reactor systems agglomeration problems have been experienced with caking coals. These are frequently eliminated by changing to downflow operation.

4. Product Qualities and Disposition

Liquids recovered from pyrolysis processes normally contain less hydrogen than those produced by slurry-phase hydrogenation. Consequently, the viscosities, boiling points, and sulfur contents are higher. Desulfurization of these liquids will be mandatory for most uses, including boiler fuels. Hydrotreating can remove 95 percent of the sulfur.[20] Nitrogen removal is more difficult and requires hydrogenation under conditions that generally produce syncrudes as well as No. 4 fuel oil.

Much of the sulfur originally in the coal remains in the char and is substantially increased in concentration. Desulfurization of the char to acceptable levels is possible by a combination of coal-feed beneficiation, removal of H_2S from the gases recycled to the hydrocarbonizer, and treatment of the char. If the char is to be used for hydrogen production, desulfurization may not be necessary since H_2S can be removed effectively from the gas stream.

C. SOLVENT EXTRACTION

As indicated in Chapter IV, solvent extraction of coal in the presence of a hydrogen-donor solvent has been developed in three different process configurations: extraction in the absence of hydrogen with a hydrogenated solvent, extraction in the presence of hydrogen with a recycle material that has not been hydrogenated, and extraction in the presence of hydrogen using a solvent that has been hydrogenated in a separate step. While it would appear obvious that the last of these schemes would give the highest quality product, it also is the most expensive, so an overall comparison of the processes must balance the technical and economic advantages.

1. Extraction in the Absence of Hydrogen with a Hydrogenated Solvent

This is the Consolidation CSF process, originally built as a 20-ton-per-day pilot plant at Cresap, West Virginia, and called Project Gasoline. Many technical and operational problems were encountered that caused the plant to be shut down. However, the problems were no greater than those

that appear to have been solved on a pilot scale in the solvent-refined coal process, and their lack of resolution may be attributed to lack of experience on the part of the companies responsible for the design, construction, and operation of the plant and of inadequate coordination and management attention.[21] General comments on the technical feasibility and operability are thus identical to those for the solvent-refined coal process. It is of interest, however, that Exxon's data[22] appear to indicate that conversion of coal in the absence of hydrogen can be just as complete as in the presence of hydrogen if the "solvent quality index" is sufficiently high and pressure is maintained at an adequate level.

The Fluor Corporation was awarded a contract to refurbish the pilot plant at Cresap, West Virginia, so that it could be operated to demonstrate the CSF process for producing a low-sulfur boiler fuel. Provision also is being made to use the pilot plant for testing various types of equipment (e.g., various methods of solids separation).

2. Extraction in the Presence of Hydrogen with a Recycle Material that Has Not Been Hydrogenated

The solvent-refined coal (SRC) process, developed by Pittsburgh and Midway Mining Company, employs hydrogen pressure in the extraction step but recycles the solvent without further treatment. Two units are currently in operation--a 50-ton-per-day plant at Fort Lewis, Washington, and a 6-ton-per day plant at Wilsonville, Alabama. Both plants have demonstrated operability, and the most recent report on the larger unit shows an on-stream operating factor of 80 to 90 percent.[23] However, the report identifies the problems mentioned previously in transport of coal-oil slurries, in fouling of heat-transfer surfaces, and in separation of solids. The information presented in Section A illustrating the problems in filtration was based on data obtained on these units. Thus, it appears that either a better filtration scheme or an economic solvent precipitation scheme is necessary to make this process feasible on a large scale.

The solvent-refined lignite (SRL) process, developed by the Engineering Experiment Station at the University of North Dakota, is very similar to the SRC process except that it includes a solvent precipitation step instead of filtration for deashing.[24] In contrast to the CE-Lummus and Conoco schemes that use paraffinic anti-solvents, this process uses benzene or toluene, further supporting the previous conclusion that the deashing schemes are strongly dependent on the nature of the materials to be treated. Another feature of the SRL process is the use of synthesis gas (H_2 + CO) instead of hydrogen; presumably the large amount of moisture in this low-rank coal supplies enough steam for in-situ production of hydrogen.

The Costeam process is very similar to the SRL in that synthesis gas (H_2 + CO) is used instead of hydrogen and the most successful demonstration of the process has been on North Dakota lignite.[25] Thus, the successful use of synthesis gas seems to require coals with high reactivities and high moisture contents.

In a presentation to the Panel, reference was made to a modification of the SRC process, SRC-II, in which solids are recycled to the dissolver and changes are made in the recycle solvents, with the result that hydrocracking is increased and the separation of product from solids is accomplished by vacuum distillation. While it is possible that this scheme might work with some very reactive coals or coals containing an unusual type of ash, other tests have shown that, for most coals, the ash would not have sufficient catalytic activity to accomplish the necessary conversion.

3. Extraction in the Presence of Hydrogen with a Hydrogenated Solvent

Exxon's donor solvent process fits in this category, having been described in a recent paper.[22] The importance of controlling the composition of the recycle solvent was emphasized, and a parameter called "solvent quality index" has been developed that has an important effect on the degree to which the coal can be converted. An interesting point is the indication that the use of molecular hydrogen in the extraction step is helpful only below a certain "solvent quality index." Above that point, the addition of molecular hydrogen does not increase conversion.

Plans are being made for a 250-ton-per-day pilot plant to produce large quantities of products for evaluation and to provide the data necessary for scale-up to a commercial-size plant of approximately 50,000 barrels per day. Aside from the pumping of slurries and the fouling of heat-transfer surfaces, there are no other obvious problems of operability in this process, the key feature being the use of vacuum distillation to separate the converted liquid from the unconverted coal and ash.

D. CATALYTIC LIQUEFACTION

Processes for direct catalytic conversion of coal to liquids can be divided into two broad categories: processes in which coal is impregnated with catalysts prior to liquefaction and processes in which the coal is dispersed and brought into close contact with the catalyst. Catalytic liquefaction processes generally operate at higher pressures than the other types of liquefaction processes and therefore are made prone to high-pressure slurry pumping and pressure reduction problems. Conversely, the products from catalytic processes are generally of a higher quality (i.e., lower boiling and less viscous), and this improves operations in subsequent solids separation and product-handling steps and could reduce the requirements for further product upgrading.

By definition, all catalytic liquefaction processes employ catalysts that come directly in contact with the coal. Therefore, the recovery and recycling of impregnated or dispersed catalysts and/or the maintenance of catalyst activity and operability in catalytic-bed reactors are important areas.

1. Liquefaction of Coal Impregnated with Catalysts

Processes in this category of catalytic liquefaction include those that feed a catalyst-impregnated coal as a finely pulverized solid, usually in a continuous liquid reactor system. The paste feeding of catalyst-impregnated coal feeds was successfully used first by the German Bergius process before and during World War II.

Coal liquefaction in a continuous gas phase is a relatively recent development that has been studied by Schroeder[26] and the University of Utah.[27] Typically, catalysts such as zinc, stannous chloride, or ammonium molybdate are used to impregnate coal prior to liquefaction. Recent results obtained from the University of Utah program indicate that finely ground (smaller than minus 40 mesh) dry coal and zinc chloride can be uniformly mixed together and liquefied to provide equally satisfactory yields.

A major advantage of these processes is the absence of the recycle solvent or pasting oil used in other catalytic and solvent extraction processes. In place of using a slurry feed, the pulverized solid coal from a lock hopper is entrained and rapidly heated in a fast-moving stream of preheated hydrogen. The residence time of the entrained coal in the reactor system at 2,000 psig and 500 °C usually is less than 20 seconds. Acceptable conversion levels have been achieved in small bench-unit equipment at reactor-specific feed rates of 500 pounds of coal per hour per cubic foot for processes that employ recycle solvents or pasting oils. Shorter coal residence times and higher temperatures may result in even greater conversion incentives.

Catalytic coal liquefaction in a continuous gas phase appears to share the advantages and problems of the hydrocarbonization pyrolysis process: (a) solids separation can be effected between the solid and vapor phases with multiple cyclones; (b) the problems associated with feeding a solid into a high pressure system are magnified as the operating pressure increases; and (c) the volume of hydrogen gas recycled may be larger than required in some of the liquid phase processes.

Because of the similarity to the hydrocarbonization pyrolysis, some of the potential problems may be investigated during existing development programs. However, a complete process evaluation demonstrating liquid yields and qualities, catalyst recovery, and overall operability can be achieved only from an independent PDU program.

Catalyst impregnation of coal feed in liquefaction processes and feeding of pastes or slurries has been accomplished in several ways. The Bergius process impregnated the coal feed with ferrous sulfate by soaking in a water solution. The subsequent Bureau of Mines development program at Louisiana, Missouri, in the early 1950s added dry copperas ($FeSO_4 \cdot 7H_2O$) catalyst to the coal before the primary crushing step. This procedure, using a high-moisture coal, provided the necessary 0.8 weight percent iron concentration in the finely ground coal feed before paste preparation.

101

From this work, it was concluded that actual impregnation of the coal before paste preparation was not necessary for effective hydrogenation. A homogeneous, well-agitated mixture of oil, coal, and <100 mesh copperas was sufficient and was used in a subsequent study design for a commercial coal hydrogenation plant.

2. Liquefaction of Coal in Catalytic-Bed Reactors

Processes in this second broad category include those that use liquid-fluidized, liquid-entrained, molten-bed reactors and fixed-bed reactors.

Currently the H-Coal process developed by Hydrocarbon Research, Inc.,[28] is the only ebullating-liquid-bed process under investigation. The reactor and catalyst are identical to those in the H-Oil process that has operated for many years on a commercial scale. The main difference is the presence of finely divided coal in the feed slurry and ash in the recycle liquid stream. This direct exposure of catalyst to heavy coal liquids and ash is the major source of catalyst deactivation. In the H-Oil reactor, catalyst activity is controlled by semicontinuous removal of spent catalyst and addition of fresh catalyst. A similar approach is proposed for the H-Coal reactor. Because of problems associated with small-scale operations, removal and addition of catalyst has not yet been demonstrated on the 3-ton-per-day PDU; however, by observing the loss in catalyst activity of a single catalyst charge during a 34-day operation period, it was estimated that 1 pound of fresh catalyst should be added per ton of coal processed (this would add $0.30 to $0.50 per barrel of oil). Based on this estimate, it seems highly desirable to experimentally confirm the actual catalyst requirement necessary to maintain constant catalyst-bed activity. It would appear that operations in the 3-ton-per-day PDU should resolve the catalyst deactivation problem before entering into the 600-ton-per-day pilot-plant program.

Solids separation techniques used in the H-Coal process depend on the mode of operation. For the highly severe, syncrude production mode, vacuum distillation is used. The alternative low-sulfur fuel oil production mode results in a product that is not entirely distillable, and the product must be treated by filtration, centrifuging, or solvent precipitation. Currently solvent precipitation appears better than filters or centrifuges.

The liquid-entrained catalytic-bed reactors employ a solid-phase catalyst such as molybdenum, tin, cobalt, or iron that is blended with the coal-oil slurries in concentrations ranging from less than 0.1 weight percent to about 1.0 weight percent on the coal. This method of applying the catalyst was used in the early Bergius coal hydrogenation plants. In this application, a finely divided iron oxide disposable catalyst was used with subsequent catalytic liquefaction taking place at temperatures of 450 to 500 °C and pressures of 3,000 to 10,000 psig.

During the 1950s, Union Carbide applied the Bergius technology to production of low-ash pitch and chemicals from coal. The development

program included a 300-ton-per-day coal feed unit that was successfully operated from 1952 through 1956. The severity of operations was not substantially reduced from the conditions used in the early German work since the catalyst used was iron oxide.

Union Carbide was successful in advancing coal liquefaction technology in several areas. These include control of reactor temperatures with water injection, successful application of filters to obtain a low-ash product, and a method of feeding slurries containing 65 to 75 weight percent coal. This latter accomplishment involved the separate preheating of coal and pasting oil to temperatures that would result in a paste temperature between 320 and 400 °C. Consequently, the critical high-viscosity gelation zone was not encountered and a semicolloidal solution was directly formed.

ERDA (PERC) currently is again reviewing the Bergius approach to coal liquefaction, including producing heavier products, using better catalysts, and improving reactor designs to reduce the processing severity that has thus far limited the commercial application of the process.

A molten zinc chloride process for liquefaction of either coal slurry or coal extract currently is being developed by Conoco Coal Development Company and Shell Oil under ERDA sponsorship. Conoco has demonstrated that coal extracts can be successfully converted, primarily to gasoline. Current efforts are directed toward production of distillate fuel and recovery of the zinc chloride catalyst by hydrolysis and reaction with coal ash. The conversion studies will be conducted initially in a 2-pound-per-hour bench unit and subsequently in a 100-pound-per-hour PDU. This latter unit will be an attempt to demonstrate continuous operation of the integrated molten pool reactor and the fluidized-bed combustion system used for catalyst regeneration.

Fixed-bed catalytic reactors are used in several direct liquefaction processes such as the Synthoil and Gulf CCL processes. In the Synthoil process,[29,30] a slurry of coal and oil is forced through a fixed bed of catalyst with a high-velocity stream of hydrogen (with the objective of maintaining catalyst activity and preventing bed plugging). However, this approach has thus far not been successful in maintaining catalyst activity in a 0.2-ton-per-day coal feed program. Standard cobalt-molybdenum catalyst life from fresh to completely inactive was on the order of 300 hours, which would require 4 pounds of catalyst per ton of coal processed. This quantity of catalyst is a factor of 4 greater than that estimated for the H-Coal process. Efforts to identify the actual mechanisms of deactivation and develop improved catalysts and regeneration techniques currently are under way at ERDA's Sandia Laboratories.

Another area of critical concern, reactor bed plugging, also has been investigated in the 0.2-ton-per-day unit. Results indicate that a steady-state reactor pressure drop of 100 psig is reached after approximately 100 hours of operation. This corresponds to about 10 psi per foot of reactor length and adds $0.07 to $0.10 per barrel to the overall processing cost.

Still another area of concern is that the Synthoil process requires 15 to 20 minutes of turbulent preheating prior to the 2-minute catalytic step to obtain satisfactory liquid yields. This preheating time is not considered to be economically practical. The observed preheating effects and requirements are currently being studied at ERDA's Argonne and Pittsburgh Laboratories.

Product slurry from the Synthoil process is centrifuged in batches at 80 °C and 15 psi, and after two stages of centrifuging, the liquids contain less than 0.1 percent fines, which is adequate for boiler fuels. Improved separation efficiencies may be required to produce products for turbine fuels application.

The Lummus Clean Fuel from Coal process contacts the coal with a catalyst in a manner that has not been described and uses a solvent precipitation technique for solids separation that has successfully deashed the solvent-refined coal to less than 0.1 percent ash. This method of solids separation currently is being studied by Kerr-McGee, Lummus, Conoco, Hydrocarbon Research Institute, and Fluor Corporation.

The major application of fixed-bed catalytic liquefaction technology is in the Gulf CCL process,[31] in which the catalyst is placed in baskets that are stacked vertically in a high-pressure containment vessel. The catalyst is arranged in each basket in pie-shaped wedges with alternate slices containing inert noncatalytic packing. The flow in each basket is radially outward and upward. Solids distribution through the catalyst baskets and basket orientations are reported to be very important to successful operations.

Gulf initially used standard hydrogen-donor solvent (HDS) catalyst in this reactor but has since adopted a new type of catalyst specifically designed for use with coal. Reported loss of catalyst activity over 700 to 800 hours of operation in the 1-ton-per-day PDU was minor. A major expense is associated with the complicated reactor designs. Gulf is continuing to work on the development of catalysts and supports that are resistant to titanium and iron poisons.

E. INDIRECT LIQUEFACTION

As indicated previously, indirect liquefaction can be carried out to produce hydrocarbons in the gasoline range as a major product (Fischer-Tropsch) or to produce methanol. The processes involve coal gasification, shift conversion, and gas purification to produce a hydrogen-carbon monoxide mixture and a catalytic reaction to produce gasoline or methanol. Advantages of this approach are that: (1) variations in the quality of the coal are eliminated in the gasification step so that the feed to the liquefaction step can be maintained at the desired purity and ratio of hydrogen to carbon monoxide, (2) a clean product results, and (3) there is the possibility that the products of in-situ gasification can be used. Furthermore, processes involving the use of hydrogen and carbon monoxide from other sources (e.g., from oil or natural gas) can be directly applied.

1. Fischer-Tropsch Process

Of the four methods of coal liquefaction that are discussed, only indirect liquefaction as carried out in the Fischer-Tropsch process is currently in commercial operation. The SASOL plant in South Africa has continued in operation since it was built in 1956, and construction is under way on a second, much larger, plant.

The SASOL process uses an entrained-bed synthesis reactor since the fixed-bed reactor cannot be scaled up to larger sizes and multiple units would be less economical. Future applications of this process also might consider the fixed-fluid-bed or slurry reactor.

During the 20 years since the SASOL plant was started up, much work has been carried out in studying the mechanism of the Fischer-Tropsch reaction.[32-35] Catalyst promoters and new supports have been studied.[34-36] Comparisons of fixed-bed and slurry reactors have been made. About 150 literature articles and 130 patents have been published during this period. Therefore, in spite of the fact that the process has already been commercialized, it would be very desirable before building additional plants to study this literature and carry out further work with a view toward improving the process by increasing its thermal efficiency and lowering the capital costs.

2. Methanol Process

As indicated in Section E of Chapter IV, methanol synthesis processes are already well developed and may be considered off-the-shelf technology. However, work has recently been carried out on a liquid-phase process that simplifies the problem of heat removal and reduces the size of the equipment required.[36] This process should be considered for possible future methanol installations.

REFERENCES

1. C. J. Gauthier, oral presentation on fossil programs to ERDA's Task Force on Demonstration Projects as a Commercialization Incentive, February 24, 1976.

2. W. T. Slick, Jr., "Commercialization of New Energy Technology," in *Proceedings of the Third Energy Technology Conference* (Washington, D.C.: Government Institutes, Inc., 1976).

3. A. L. Conn, "How Much Experimentation Before Commercialization," *Chem. Eng. Progress* 67 (June 1971):22-7.

4. J. D. Batchelor and Christopher Shin, "Solid-Liquid Separation in Coal Liquefaction Processes," paper presented at American Institute of Chemical Engineers 68th Annual Meeting, Los Angeles, California November 18, 1975.

5. M. C. Sze and G. S. Snell, "A New Process for Removing Ash from Coal Liquefied by Hydrogenation," paper presented at the American Power Conference, Chicago, Illinois, April 21-23, 1975.

6. J. W. Roach, U.S. Patent 3,607,716, September 21, 1971.

7. J. W. Roach, U.S. Patent 3,607,717, September 21, 1971.

8. W. M. Leaders, and Jack W. Roach, U.S. Patent 3,607,718, September 21, 1971.

9. E. Gorin, C. J. Kulik, and H. E. Lebowitz, "Deashing of Coal Liquefaction Products via Partial Deasphalting I-Hydrogen-Donor Extraction Effluents," paper presented at the Division of Fuel Chemistry, American Chemical Society, Philadelphia, Pennsylvania, April 6-11, 1975.

10. E. Gorin, C. J. Kulik, and H. E. Lebowitz, "Deashing of Coal Liquefaction Products via Partial Deasphalting II-Hydrogenation and Hydroextraction Effluents," paper presented to the Division of Fuel Chemistry, American Chemical Society, Philadelphia, Pennsylvania, April 6-11, 1975.

11. Kirk-Othmer, *Chemistry of Coal Utilization* (New York: John Wiley and Sons, Inc., 1963):1050.

12. R. E. Wood and W. H. Wiser, "Coal Liquefaction in Coiled Tube Reactors," *Ind. Eng. Chem., Process Des. Dev.,* 15 (January 1976): 144-9.

13. Bill Han, "Overview of Materials Problems in Current Pilot Plant Operation," presentation to NACE T-12A Technical Practices Committee Meeting on Coal Conversion and Utilization, Houston, Texas, March 26, 1976.

14. Donald E. Severson, *Project Lignite Monthly Technical Progress Report No. 44,* FE124-50 (Oak Ridge, Tennessee: Oak Ridge Technical Information Center, 1975).

15. M. Pompey, "Centrifugally Cast Reformer Tubes," *Hydrocarbon Processing* (March 1975):12.

16. A. Sass, "The GR&D Coal Pyrolysis Process—A Status Report," paper presented at Clean Energy from Coal Session, American Institute of Chemical Engineers 67th Annual Meeting, Washington, D.C., December 3, 1974.

17. U.S. Steel Engineers and Consultants, Inc., *Clean Coke Process,* Annual Report for Period July 1, 1974-June 30, 1975, ERDA Contract No. E(49-18) 1220 (Washington, D.C.: U.S. Energy Research and Development Administration, 1975).

18. R. C. Merrill, L. J. Scotti, L. Ford, and D. J. Domina, "Clean Fuels from Eastern Coals by COED, in *Coal Processing Technology,* Vol. 2, p. 88 (New York: American Institute of Chemical Engineers, 1975).

19. W. D. Morgan, "Coalcon's Clean Boiler Fuels from Coal Demonstration Plant," paper presented at the 68th Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, California, November 16-20, 1975.

20. D. B. Anthony and J. B. Howard, "Coal Devolatilization and Hydrogasifications," *AIChE Journal* 22 (1976):625-56.

21. W. C. Schroeder, A. L. Conn, and R. W. Hiteshire, *Evaluation and Recommendations Concerning the Design, Construction, and Operation of Consol Synthetic Liquid Fuel Pilot Plant,* R&D Report No. 50 (Washington, D.C.: U.S. Department of the Interior, Office of Coal Research, 1969).

22. L. E. Furlong, E. Effron, L. W. Vernon, and E. L. Wilson, "Coal Liquefaction by the Exxon Donor Solvent Process," paper presented at the 68th Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, California, November 18, 1975.

23. G. H. Pastor, "Operations of the SRC Pilot Plant," paper presented at the 68th Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, California, November 18, 1975.

24. D.E. Severson and A. M. Souby, *Process Development for SRL Design of Continuous 50 lb/hr Process Development Unit* (Oak Ridge, Tennessee: Oak Ridge Technical Information Center, 1974).

25. E. Del Bel, S. Friedman, P. M. Yavorsky, and I. Wender, "The Liquefaction of Lignite by the COSTEAM Process," paper presented at the National Meeting of the American Institute of Chemical Engineers, Houston, Texas, March 18, 1975.

26. W. C. Schroeder, "Solid Phase Hydrogenation Cuts Cost," *Hydrocarbon Processing* 55 (January 1976):131-3.

27. R. E. Wood and W. H. Wiser, "Coal Liquefaction in Coiled Tube Reactors," *Ind. Eng. Chem. Proc. Des. Dev.* 15 (1976):144.

28. C. A. Johnson, M. D. Chervenak, A. G. Comolli, E. S. Johanson, C. C. Kang, and W. Volk, "H-Coal Process Development," paper presented at the 68th Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, California, November 16-20, 1975.

29. P. M. Yavorsky, "ERDA Coal Liquefaction Programs for Synthetic Fuel-Oil Development," paper presented at the Symposium on Air Quality Management in the Electric Power Industry, Austin, Texas, January 28-30, 1976.

30. Sayeed Akhtar, N. J. Mazzocco, M. Weintraub, and P. M. Yavorsky, "Synthoil Process for Converting Coal to Nonpolluting Fuel Oil," paper presented at the 4th Synthetic Fuels from Coal Conference, Oklahoma State University, Stillwater, Oklahoma, May 6-7, 1974.

31. A. A. Simone, "Clean Fuel From Coal Process," *Combustion* 47 (May 1976):15-19.

32. D. L. Katz, D. E. Briggs, E. R. Lady, J. E. Powers, M. R. Tek, B. Williams, and W. E. Lobo, *Evaluation of Coal Conversion Processes to Provide Clean Fuels*, Part 2, NTIS PB-234203 (Springfield, Virginia: National Technical Information Service, 1974):275-81.

33. D. Hanus and H. Koelbel, "The Reaction Mechanism of the Fischer-Tropsch Synthesis, *Chemie Ingeninur Technik* 46 (December 1974): 1042-3.

34. M. V. C. Sastri, R. B. Gupta, and B. Ziswanathan, "Mechanism of the Fischer-Tropsch Synthesis on Cobalt Catalysts," *J. Indian Chem. Soc.* 51 (1974):140-4.

35. M. A. Vannice, and R. L. Gartern, "CO-H_2 Reactions over Supported PtFe Catalysts: Kinetic Chemisorption and Mossbauer Spectroscopic Studies," paper presented at the 67th Annual Meeting of the American Institute of Chemical Engineers, Washington, D.C., December 1-5, 1975.

36. M. B. Sherwin and D. Blum "Methanol Synthesis in a Three Phase Reactor," paper presented at the National Meeting of the American Chemical Society, Chicago, Illinois, August 24-29, 1975.