CONTRACT TITLE AND NUMBER:
Exploratory Research on Novel Coal Liquefaction Concept
DOE Contract No. DE-AC22-95PC95050

CONTRACTOR NAME:
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Research & Development
4000 Brownsville Road
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ANTICIPATED COMPLETION DATE: May 23, 1998

CONTRACT OBJECTIVES

CONSOL Inc., the University of Kentucky/Center for Applied Energy Research (CAER), and LDP Associates are conducting a three-year research program to explore the technical and economic feasibility of a novel direct coal liquefaction concept. The purpose of this research program is to explore a new approach to direct coal liquefaction in which the primary coal dissolution step is effected by chemical rather than thermal cleavage of bonds in the coal. This is done at a temperature which is significantly lower than that typically used in conventional coal liquefaction. Reaction at this low temperature results in high conversion of the coal to a solubilized form, with little hydrocarbon gas make, and avoids the thermally induced retrograde reactions which are unavoidable in conventional thermal processes. In addition, for low-rank coals, a substantial portion of the oxygen in the coal is removed as CO and CO₂ during the dissolution. The higher selectivity to liquid products and rejection of oxygen as carbon oxides should result in improved hydrogen utilization. The basis of the novel concept is the discovery made by CONSOL R&D that certain hydride transfer agents are very active for coal dissolution at temperatures in the range of 350 °C.

Because of the exploratory nature of the research, the project is divided into sequential tasks that are designed to first evaluate key elements of the process.
concept and then to evaluate their integration. Task 2 will include a parametric study of low-temperature liquefaction, an evaluation of filtration and solvent separation to deash the liquefaction product, evaluation and selection of catalysts, and a literature and engineering study of hydride ion regeneration. The results of Task 2 will be used to define the reaction steps and establish a conceptual flow sheet and design for partially integrated testing, Task 3. In Task 3, experimental work will be done to combine the solubilization and solids separation steps, and to evaluate catalytic conversion options pertinent to a second-stage design. This information will be used to finalize an integrated flow sheet, which will be tested experimentally in Task 4. The goal of Task 4 is to test the combined reaction steps experimentally as a basis for the engineering and economic analysis. The initiation of Task 4 is contingent on the feasibility of this concept, as determined by a concurrent engineering and economic analysis under Task 5. The Engineering and Economic Study (Task 5) will be conducted throughout the project to establish economic feasibility and to provide guidance at key decision points at the completion of project Tasks.

SUMMARY OF TECHNICAL PROGRESS

Contraacting

The subcontract with the University of Kentucky Center for Applied Energy Research was initiated on June 2 and the subcontract with LDP Associates was initiated on May 30.

Task 1 - Management Plan

The Management Plan, which includes detailed experimental planning for Task 2, was drafted, issued for review to project participants, revised, and delivered to DOE/PETC on August 25. This completes Task 1.

Task 2 - Evaluation of Process Steps

NEPA approval to begin the experimental program was received on August 15.

A 33 lb pound sample of 4" x 0" ROM Freedom Mine North Dakota lignite was received from Coteau Properties. Half was stored as received in a triple-layer bag. The remainder was ground to -1", and a suite of coal analyses was obtained. Approximately 2.5 kg of the ground lignite was air dried and pulverized and 15 g aliquots were sealed in triple-layer bags. The moisture and ash contents of the air-dried sample were determined by TGA to be 26.8 wt % and 6.3 wt % (MF), respectively. A new sealed package is used for each microautoclave test. The moisture and ash contents of the individual sample used for each microautoclave test is determined by TGA. If it is determined that the samples are homogeneous enough, individual analyses will not be necessary. This procedure both preserves the coal and allows TGA determination of the moisture and ash contents of the individual coal samples used for each test.

Wilsonville Run 262E V1074 solvent was distilled to a 910 °F equivalent end point to produce the solvent for the microautoclave work. The distillate yield was about 73 wt %. Fifty grams each of the whole V1074 and of the distillate were sent to UK/CAER.

The microautoclave tests were begun. The principal variables in these runs are temperature, residence time, reagent to coal ratio, solvent type and solvent to coal ratio. The main purpose of these runs is to scope operating conditions and
develop work-up procedures to obtain mass and elemental balances for autoclave runs. In the initial scheme tested, the reaction products, after venting the gases, were distilled directly from the autoclave reactor body and the distillation residue was extracted with THF to determine coal conversion. The distillation produced a light aqueous fraction and a higher boiling solvent fraction. Coal conversions were lower than expected and filtration rates were very slow, perhaps because of over-heating during the distillation. Coal conversions and filtration rates both improved when the reactor products were extracted with THF prior to distillation or when only the light aqueous phase was distilled before THF extraction. Nine microautoclave tests were completed with the work-up scheme in which the products are extracted with THF but not distilled. This limits the determined results to coal conversion and gas yield. Coal conversions as great as 92% MAF were achieved, although the required reaction temperature was somewhat higher than expected. The 12 runs originally planned as Phase I, plus additional runs to expand the range of variables, will be completed early in the next quarter. Next quarter, microautoclave tests will be completed in which the work-up scheme includes distillations and complete material balances.

H-NMR and gas chromatographic methods were developed to analyze the light aqueous distillate fraction of the microautoclave runs. The two methods appear to give consistent results. A gas chromatograph was set up for analysis of the product gases.

A 1L Autoclave Engineers stirred autoclave will be used in this project. It is constructed of 316 SS, rated for operation at 5800 psi at 650 °F, and equipped with a magnetic stirrer drive and numerous inlets/outlets. The vessel was hydrostatically tested and thoroughly inspected. The site was prepared for installation of the IL autoclave.

Preparations were made at the CAER for experiments related to Task 2. These experiments are classified into two major areas: filtration and hydrotreating. For both studies, products from CONSOL’s first-stage coal conversion step will be investigated. Filtration studies will be performed on samples that are generated at CONSOL in either micro or stirred autoclaves. The filtered first-stage products will then be the subject of hydrotreating studies in microautoclaves using dispersed and supported catalysts.

Major equipment for the filtration study was obtained, including a viscometer and stainless steel tubing fittings for the fabrication of the micro-filtration rig(s). Upon notification from CONSOL regarding the sample size to be expected from the first-stage microautoclave studies (approximately 10 g), the design of the rig for the micro-filtration studies was initiated. This filtration system is expected to be completed before CONSOL begins sending first-stage samples to the CAER in October. Outline designs of larger filters for later stages of the project have been made, but detailed specification will depend upon results obtained with the micro-filter.

A microautoclave for the second-stage hydrotreating studies was designed, fabricated and successfully hydrotested to 3500 psig. Two additional microautoclaves are also being fabricated. The agitation (dashing) system used in previous coal liquefaction studies with this type of autoclave was modified to accept the newly designed reactor. The reactor system includes instrumentation to continuously measure and record the temperature and pressure within the reactor during operation. The calibration of the pressure transducer was checked against a 400 psig test gage and a hydrotest gage at 2500 psig. A major change in the
original design of the reactor involves the use of a tubing coil to replace the braided flexible tubing for connection to the pressure transducer. Only one valve is used at the end of the coiled tubing for charging and venting the reactor, thereby minimizing dead volume and eliminating the former angle valve (potential leak source) used for support in the older style.

In order to test the operability of the new reactor system, a trial hydrotreating run using 3 g of Wilsonville Run 262E de-ashed resid and 1000 ppm Mo was completed, while continuously logging the temperature and pressure. The new apparatus performed without problem. The reactor was quenched with cold water, replacing the cold sandbath used previously. The 1000 psig cold H₂ charge customarily used in previous work produced only 1600 psig at temperature due to the cold reactor volume above the sandbath; therefore, a higher charge pressure will be used in future runs to increase the pressure at temperature. The liquid products of the test were not distilled because the operation of the reactor was of most interest, but the operability of the micro-distillation apparatus was confirmed during separate testing. The gas sampling and gas analysis procedures were tested as part of this hydrotreating test, however. The gas, when cool, was expanded into a calibrated 10-liter acrylic syringe for volume measurement and for storage prior to analysis. The gas was then pumped through a multiport sampling valve for injection into the gas chromatograph. All major gas species were identified at the anticipated levels.

Akzo A060 was chosen as the supported catalyst for second-stage upgrading studies. It is an experimental Ni/Moextrudate that HTI has been using in their studies. The CAER has received 350 g of this catalyst from HTI. Catalyst sulfiding will be performed with 3% H₂S in H₂. A literature search for Mo sulfiding kinetics was initiated. Over 500 titles were examined from Chemical Abstracts, and copies of 28 articles have been requested. Most have been received.

The boiling curves of the hydrotreated products will be determined by simulated distillation. The process of identifying suitable simulated-distillation equipment for purchase was initiated. One bid was received for an instrument that is capable of extended ASTM D2887 (up to C₁₂₀) using capillary gas chromatography. The possibility of utilizing supercritical fluid chromatography in a simulated-distillation application was also explored. A literature search of simulated distillation of coal-derived liquids in the Chem Abstracts database was performed. Twelve pertinent references were identified. Samples of V-1074 and V-131B materials were sent to two vendors for evaluation, but no results of these tests were made available during the reporting period. A recommendation for purchase of simulated distillation equipment will be made during the next quarterly reporting period.

**Task 5 - Engineering and Economic Study**

A speculative overall, elementally balanced material balance for the proposed process concept was prepared based on prior CONSOL experimental data for the first-stage reaction and estimates for the downstream units (see Table). The results of this study indicated that the proposed process appears to be very hydrogen efficient, although the distillate yield is lower than state-of-the-art liquefaction processes due to its higher CO₂ yield. Based on this study, recommendations were made for the type of first-stage experimental data which would be useful for future technical and economic assessments of the proposed process.
A review of the literature pertaining to the synthesis and commercial production of hydride reagents was begun with an electronic literature search. Numerous references were located, and the more promising of these publications were obtained for further review. Additional references will be requested as they are identified in those articles that were obtained in the initial search. Fifteen publications pertaining to either hydride ion liquefaction or to the production of hydride ion sources were sent to LDP. The first edition of the annotated bibliography of the review literature was completed. Fifty-one additional articles, including 26 patents, are on order. Five confidential CONSOL internal reports were sent to LDP.

Task 6 - Reporting

A meeting was held with UK/CAER and LDP Assoc. at CONSOL on June 7 to begin detailed planning of the project, including planning the Management Plan, the literature search, and quarterly technical meetings. The kick-off meeting with DOE was held at CONSOL on July 21. A project overview and the proprietary nature of the prior data were discussed. A record of the meeting was issued. A project review meeting was held in Library on August 28 with representatives from CONSOL, UK/CAER, LDP Associates and DOE. A meeting report was issued. The scheduled quarterly conference call between CONSOL and the DOE contracting officer's representative was held on September 27 and a report documenting the call was issued.

Bi-monthly conference calls among CONSOL, UK/CAER and LDP were scheduled for the first and third Wednesday of each month to keep the project work closely coordinated. The scheduled conference calls were made and reports describing the highlights of the calls were issued.

The contract initiation reports (Notice of Energy RD&D, Cost Management Plan, etc.) were submitted.

DISCLAIMER

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<th>TABLE</th>
<th>CONSOL NOVEL COAL LIQUEFACTION CONCEPT SPECULATIVE MATERIAL BALANCE OVERALL YIELDS</th>
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**INPUTS:**

- MF COAL: 100.00
- COAL MOISTURE: 50.36
- NET HYDROGEN CONSUMED: 1.55
- NET CO CONSUMED: 5.34

Total = 157.25

**OUTPUTS:**

- WATER: 39.33
- HYDROGEN SULFIDE: 0.58
- AMMONIA: 0.87
- CARBON DIOXIDE: 43.86
- C1 to C3: 5.83
- C4+ DISTILLATE: 43.85
- FILTER CAKE: 17.22*
- UNCONVERTED 535°C: 5.71*

Total = 157.25

Lb C4+ Distillate/Lb Hydrogen Equivalent Consumed = 22.7