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**HIGH CONVERSION OF COAL TO TRANSPORTATION FUELS
FOR THE FUTURE WITH LOW HC GAS PRODUCTION**

Progress Report No. 13
(Covering the period October 1 - December 31, 1995)

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PERSONNEL

In addition to the Principal Investigators, research personnel participating in this project during the reporting period are:

Belma Demirel, Graduate Student

Jiazhi Pu, Graduate Student

OBJECTIVES AND SCOPE OF THE RESEARCH PROJECT

An announced objective of the Department of Energy in funding this work, and other current research in coal liquefaction, is to produce a synthetic crude from coal at a cost lower than \$30.00 per barrel (Task A). A second objective, reflecting a recent change in direction in the synthetic fuels effort of DOE, is to produce a fuel which is low in aromatics, yet of sufficiently high octane number for use in the gasoline-burning transportation vehicles of today. To meet this second objective, research was proposed, and funding awarded, for conversion of the highly-aromatic liquid product from coal conversion to a product high in isoparaffins, which compounds in the gasoline range exhibit a high octane number (Task B).

Experimental coal liquefaction studies conducted in a batch microreactor in our laboratory have demonstrated potential for high conversions of coal to liquids with low yields of hydrocarbon (HC) gases, hence small consumption of hydrogen in the primary liquefaction step. Ratios of liquids/HC gases as high as 30/1, at liquid yields as high as 82% of the coal by weight, have been achieved. The principal objective of this work is to examine how nearly we may approach these results in a

continuous-flow system, at a size sufficient to evaluate the process concept for production of transportation fuels from coal.

A continuous-flow reactor system (1/2 inch inside diameter) is to be designed, constructed and operated. The system is to be computer-operated for process control and data logging, and is to be fully instrumented. The primary liquid products will be characterized by GC, FTIR, and GC/MS, to determine the types and quantities of the principal components produced under conditions of high liquids production with high ratios of liquids/HC gases. From these analyses, together with GC analyses of the HC gases, hydrogen consumption for the conversion to primary liquids will be calculated. Conversion of the aromatics of this liquid product to isoparaffins will be investigated, to examine the potential for producing a transportation fuel from coal with satisfactory octane rating but low in aromatic content.

ACTIVITY FOR THE REPORTING PERIOD

A no-cost extension was requested, and has been granted, to extend this Grant to September 28, 1996. The principal purpose in seeking the extension was to allow for completion of the research being performed by the Graduate Student (Belma Demirel) and the writing of her thesis for the Ph.D. Degree. A second purpose was to provide time and funding within the Grant for preparation of the Final Report, including payment from the Grant for the costs of printing the report, and some time of the P.I. in the preparation. The funds remaining in the budget when the time extension commenced were not sufficient to provide for continuing experimental work in the main reactor system.

TASK A

The work completed to date has established the viability of a new approach to production of transportation fuels from coal which presents promise for substantially reducing the cost of production of such fuels. The most important accomplishments, which aid in establishing the viability of the technology with a promise of improved economics, are:

1. A microreactor has been designed, constructed and operated which provided for precise control of reaction variables, particularly temperature and time, to permit determination of the maximum yields of liquids obtainable from coal under optimum values of reaction parameters, and to begin to identify those optimum values. In experiments conducted in the microreactor, at a pressure of 1500 psig, conversions to liquids in the amount of 60 weight percent in a single pass, and 82

weight percent in a mode to simulate recycle of unreacted solids, were achieved in residence times of 3 seconds. At these conversions and times, the ratio of liquids to hydrocarbon (HC) gases was 30/1, corresponding to a yield of HC gases of only about 3 weight percent. These low values of HC-gas yields contrast with values of 15 wt. percent or higher in other, advanced technologies.

2. A continuous-flow reactor system was constructed and operated, with a one-half inch inside diameter (ID) tube as the reaction vessel, to investigate whether conversions and reaction times, and ratios of liquids/HC gases, could be achieved in a continuous system which would approach those obtained in the batch microreactor. Because of the operating features of the continuous system, constructed within the space limitations as imposed by University facilities, it was anticipated that conversions may be lower than those observed in the microreactor, perhaps by as much as 25% lower, with ratios of liquids/HC gases of the order of 15/1. The results have exceeded our expectations. At a pressure of 1200 psig, in a single pass at a residence time in the hot zone of 6 seconds, conversion was 54% by weight liquids, with a ratio of liquids/HC gases of 18/1. Operation to simulate recycle of unreacted solids yielded a conversion of 70% by weight liquids, with a ratio of liquids/HC gases of 19/1. The continuous reactor system was designed and constructed at such size as to provide a realistic evaluation of what may be expected in a larger system.

3. Experiments have been conducted in the microreactor at pressures down to 250 psig. At a pressure of 500 psig, a conversion of 46% by weight was achieved in a single pass, with ratio of liquids/HC gases of 26/1, and a conversion of 66% by weight in a recycle mode, with ratio of liquids/HC gases of 22. It is noted that the recycle compressor purchased for the continuous-flow reactor system, which maintained the hydrogen pressure in the system, was purchased to provide for turbulent flow at pressures of 1500 psig. Experiments at 500 psig in the continuous-flow system were well below the turbulent flow regime. When the components were being purchased for the reactor system, it was not even imagined that high conversions accompanied by high ratios of liquids/HC gases, as now observed, might be possible at pressures below 1500 psig. All previous technologies require pressures of 2000 psig or higher. It is expected that, when a compressor is acquired which can maintain turbulent flow at 500 psig, the results in the continuous-flow system will be near those from the microreactor, both as to conversions and ratios of liquids/HC gases.

4. The work with the EDS process of Exxon, as reported by them, indicates that for a completely self-sustained process primary liquid yields greater than the range 46-55 weight percent of the coal should not be expected. The conversions reported above for a single pass lie within that range, even at pressures as low as 500 psig, and it is anticipated that recycle of unreacted coal may not be necessary with this technology.

5. The above results have been obtained with the use of iron-based catalysts, which will be relatively inexpensive in preparation and/or replacement. Examples of catalysts providing yields and high ratios of liquids/HC gases, as presented above, are ferric chloride hexahydrate, sulfated iron oxide, and ferric sulfate pentahydrate.

6. At least three factors have been identified in the experimental work of this project which show promise of a substantial reduction in cost of producing liquids from coal:

(a) Low hydrogen consumption, resulting from low production of HC gases, about 3% by weight in this work, as compared with 15% or greater in other advanced technologies.

(b) Much smaller reactor system for a given throughput, resulting from the short residence time of 3-5 seconds, compared with generally 15 minutes or longer in other advanced technologies.

(c) Lower construction costs for a vessel which can operate at pressures of 500 psig, or perhaps lower, compared with pressures greater than 2000 psig in other advanced technologies.

Analysis of these results leads to a conclusion that the chemistry of conversion at the short times involved in this technology proceeds in two distinct regimes, with the liquids being produced at short times of 5 seconds or less by means of bond rupture of the bonds between clusters in the coal, with HC gases being produced mostly by reactions occurring within the clusters, at times longer than 15 seconds. It thus becomes possible to separate these two time regimes and remove the

products from the hot zone before the reactions for production of gases become significant, thereby obtaining both high conversions to liquids and high ratios of liquids/HC gases.

The reality of this separation of the chemistry into two time regimes, and the nature of the chemistry involved, need to be investigated and confirmed. Proposals have been submitted to DOE, through the University Coal Research Program, to do this work. It is hoped that funding can be provided to perform this important work, needed before industrial organizations can be attracted to carry the work forward to commercial reality.

TASK B

During the time period of this report, the graduate student, Belma Demirel, has analyzed the data obtained under this task, organized it, and has proceeded to write her thesis for the Ph.D. degree. She is nearing completion of the writing. It is important, indeed necessary, that the student presents her thesis before her graduate committee, and defends it, before the P.I. writes and submits the final report covering the work performed by the student. It is anticipated that she will complete all work on her thesis, including its defense before her graduate committee, during the next reporting period. The final report will then be prepared during the remaining months of the Grant, with the report to be submitted by the end of September, 1996, when the period of funding expires.

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