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

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Progress Report No. 7
(Covering the period April 1 - June 30, 1994)

Wendell H. Wiser, Principal Investigator
Alex G. Oblad, Co-Principal Investigator

Department of Chemical and Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

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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

Chung-Hsi Tsai, Post Doctoral, part time

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

TASK A

A flow diagram of the reactor system was presented in Progress Report No. 5. A detailed description of the intended operation of the system was presented in the prior report No. 6.

Work is continuing on installation of the remaining components of the system. As previously described, the reactor tube assembly consists of ten-foot straight sections of stainless steel tubing, one-half inch inside diameter. These sections are joined in a hairpin configuration. With the feed entering at one end of the system, and product removal at the opposite end, it becomes possible to operate with reactor tube lengths of about 10 feet, 30 feet, 50 feet, 70 feet and 90 feet, as presently accommodated by the fluidized bed.

In order to obtain a maximum particle heat-up rate, with hot hydrogen gas as the heat-transfer medium, the system will be operated with the coal particles and hydrogen gas moving through the tubes in turbulent flow. This will result in residence times of about two seconds per pass in a ten-foot section. Residence times will then be varied from about two seconds when using a single ten-foot reactor tube, to six seconds in a 30-foot reactor, and so on to a maximum residence time of about 18 seconds for the 90-foot system. Prior work with both the microreactor and the small-diameter continuous-flow system indicated that the optimum residence time will lie somewhere between these two limits.

The prior work indicated that, for maximum ratios of liquids/hydrocarbon (HC) gases, a residence time not greater than about 10 seconds is desirable. The microreactor yielded results of ratios of liquids/HC gases as high as 30/1, with conversions greater than 80 percent by weight liquids, in operation in a mode to simulate recycle of unreacted solids. For this reason, the first installation of the tubular reactor contains three 10-foot sections, or a total length of about 30 feet.

The hydrogen preheater consists of a bundle of 3/16 inch diameter tubes, located in a separate section of the fluidized bath, inasmuch as the hydrogen must be preheated to a considerably higher temperature than the reactor itself. This preheater has also been installed and is ready for operation.

Referring to the flow diagram found in Progress Report No. 5, system start-up will be achieved by feeding hydrogen gas with the finely-divided coal particles. As system operation progresses, the gases separated from the liquids and solids, being mostly hydrogen, will be recycled, and will become the principal gas used for transporting the coal particles, with hydrogen makeup. The plumbing for this hydrogen and product gas system has been installed, designed to operate at pressures up to 2000 psig.

The gas recycle system includes several back-pressure regulators for maintaining the desired system pressure, as well as pressure sensors and digital mass flow meters. This part of the system has now been fully installed.

The sand bath has been loaded with alpha-alumina powder, with about 4000 pounds being required to bring the sand to a level for operation. As mentioned previously, the alumina powder contained a small fraction of very fine dust which escaped from the top of the bed when fluidized. A plastic cover was placed over the bed, with vents to two exhaust fans, and operated at room temperature for about 30 hours, to remove the fine dust particles. A permanent canopy, fabricated from galvanized sheet metal, has now been installed to channel the hot air rising from the bed during fluidization of the bed. This hot air from the bed, together with any bed fines carried out of the bed, will be exhausted from the building.

The console for the computer has now been installed. The computer components are being used in preparation of the program for process control and data logging for the reactor system. The components are ready for installation.

TASK B

Methylnaphthalene was selected as the first model compound representative of aromatic compounds which may be found in coal-derived liquids. In the previous progress report (No. 6), data were presented for conversion of methylnaphthalene using several well-known catalysts, most of which exhibited both hydrogenation and cracking activities. Based upon prior work involving compounds of this nature, it is to be expected that methyl decalins would be an important intermediate compound enroute to isoparaffins. None of the catalysts yielded any isoparaffins in

three hours. It may be noted that the temperatures employed were rather low for cracking of the hydrogenated intermediates to form isoparaffins. However, a nickel-moly catalyst supported on titania-alumina produced yields of decalins in excess of 90% by weight of the starting methylnaphthalene.

In an effort to be conservative on expenditures, an autoclave was borrowed from one of my companion projects for the experiments for conversion of aromatics to isoparaffins. The autoclave system, with minor modifications, is suitable for these experiments. A gas-sampling manifold built for use with the autoclave was temporarily in use in some other experiments. The first experiments reported below, therefore, did not provide for analysis of the HC gases produced. However, the gas sampling manifold has now been installed on this equipment, and will be in use for future experiments. But the data presented below report product yields as weight percents of the liquids (and any solids) produced, not including conversions to HC gases.

Experiments have been conducted with the decalins formed in the prior experiments as feed material. Various catalysts exhibiting both hydrogenation and cracking activities have been used. The prior work indicated that a temperature higher than 400 °C would probably be necessary to crack the saturated rings in the decalins. However, since the desired end product is isoparaffins, it is desirable to avoid cracking the side chains formed in ring opening to yield short-chain hydrocarbons. A temperature of 450 °C was therefore selected. Again, a time of

three hours was selected for the residence times in all but one of the experiments. The results are presented in Table 1.

Of the catalysts examined, a commercially-available catalyst consisting of nickel-tungsten supported on silica-alumina yielded much higher conversions (about 75%) of the feed material (methyl decalins) than any of the other catalysts. Further, about one-fourth of the liquids in the product were isoparaffins, the only catalyst producing significant yields of isoparaffins.

The last entry in the table presents data when additional silica-alumina catalyst was added, to see if additional cracking activity would produce any effect upon the yield of isoparaffins. It was observed that any effect was negligible.

It should be mentioned that the data presented in Table 1 are very preliminary. The results are from single experiments only for each set of conditions. The amounts of HC gases produced during the conversions were not measured, as explained above. However, since these are the first experiments wherein significant amounts of isoparaffins are produced, it was believed to be of interest to show that progress is being made toward the end objective of the Task. All future experiments will provide a material balance over the whole product stream, including gases.

The last column in the table, labeled "other", contained a very broad mixture, consisting of alkyl benzenes, alkyl cycloparaffins, indanes, tetralins, and some methylnaphthalenes. In future experiments, these compounds will also be analyzed. It is expected that recycle of these liquids will yield more isoparaffins.

Table 1: Product Distribution from Methyl Decalins

Catalyst	Reaction Temperature °C	Reaction Pressure, psig	Reaction Time, minutes	Products		
				Methyl Decalins wt.% liq	Isoparaffins wt.% liq	Other liq
NiMo/TiO ₂ -Al ₂ O ₃	400	2100	180	96.63	-	3.37
NiMo/TiO ₂ -Al ₂ O ₃	450	1920	180	63.44	1.15	35.41
NiMo/SiO ₂ -Al ₂ O ₃	450	2100	50	69.33	-	30.67
NiMo/SiO ₂ -Al ₂ O ₃	450	2100	180	51.37	1.41	47.22
ZrO ₂ /Sulfated	450	1400	180	71.77	5.58	22.65
NiW/SiO ₂ -Al ₂ O ₃	450	1700	180	28.18	24.47	47.35
NiW/SiO ₂ -Al ₂ O ₃ ⁺ SiO ₂ -Al ₂ O ₃ (3:1, w/w)	450	1770	180	26.38	21.36	52.26

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