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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. 6
(Covering the period January 1 - March 31, 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

Prepared for the United States Department of Energy
under Contract No. DE-AC22-92PC92121

April, 1994

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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

Quiping Yang, 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.

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ACTIVITY FOR THE REPORTING PERIOD

TASK A

In a prior project, it was demonstrated that, when feeding a sub-bituminous coal, conversion to liquids as high as 82% by weight, dry, mineral-matter-free basis (dmmf), can be achieved in residence times as short as three seconds, with hydrocarbon (HC) gas yields as low as three percent by weight of the coal, at pressures of 1500 psi. These yields represent a ratio of liquids/HC gases of 30/1, compared with values of the order of 4/1 in current advanced technologies.

In a prior report in this project, experimental data were presented which demonstrate that at a pressure of 500 psi, liquid yields as high as 66% by weight of the coal can be achieved in a residence time of five seconds, with ratios of liquids/HC gases as high as 22/1. It has been further demonstrated that at a pressure of 250 psi, liquid yields of 58% by weight of the coal can be achieved in a residence time of five seconds, with a ratio of liquids/HC gases as high as 14/1. These results were obtained in a batch microreactor.

The microreactor was designed and constructed to provide for maximum control of all parameters, in an effort to discern the most favorable theoretical combination of conversion to liquids and ratio of liquids/HC gases. A small continuous reactor was also operated, but due to limitations in that reactor system, it was not possible to optimize all of the operating parameters, in particular turbulent flow for maximum heat-up rates. An objective of this task, in this project, is to construct and

operate a continuous reactor system in which all reaction parameters may be adjusted to optimum values, and to learn what those optimum values are for production of liquids in high yields while limiting production of HC gases. A second objective is to construct such a system at a size large enough to give some valid indication of what one may achieve in a scaled-up reactor, e.g. of the size of a small pilot plant. A complete description of the system designed with these objectives in mind was presented in the prior report (No. 5).

The reactor itself is a stainless steel tube of one-half inch inside diameter. Each straight section of the tube is 10 feet long, followed by a hair pin turn of about 12 inches radius. The reactor length can thus be varied from one ten-foot section to as many as 10 sections, for a reactor length ranging from 10 feet to 100 feet or more. By thus varying the reactor-tube length, it is possible to operate at various residence times, while maintaining turbulent-flow conditions in the tubular reactor.

The bank of tubes is immersed in a fluidized bed of alpha alumina particles, fluidized by preheated air. The hydrogen preheater is immersed in a separate compartment of the fluidized bed, thus enabling preheating the hydrogen to a higher temperature than set for operation of the reactor. Inasmuch as the hot hydrogen gas is to be used for heating the coal in the reactor, it must be at a substantially higher temperature. Alpha alumina was selected for use in the bed because of its combination of physical properties in relation to the function of

the tubular reactor and the high-temperature operation of the hydrogen pre-heater. The alumina particles have a mean diameter of about 140 microns, in a particle mix specially prepared by the manufacturer for use in a fluidized bed.

The fluidized bed has been operated at room temperature in several tests, for several hours each. When operating in the desired gas velocity range, the bed fluidized uniformly throughout its length, without placing any baffles in the bed. It was found that the alumina contains a substantial amount of fines which were carried from the bed with the fluidizing air. Inasmuch as the space provided for installation of the reactor is in a high-pressure laboratory which also houses several other experimental operations, the scattering of the fines in the laboratory is unacceptable. It therefore became necessary to attempt to trap the fines, or to exhaust the air from the fluidized bed to the atmosphere.

A canopy was installed above the bed, with two exit lines to feed the exiting air to two exhaust fans, one near each end of the bed. This air containing the fines from the bed was exhausted from the laboratory. After about 20 hours of operation at room temperature, the fines in the exhaust air have been reduced to very low concentrations. It is not known whether small amounts of fines will be produced in the bed due to attrition of the particles during fluidization of the bed at operating temperature. However, since the fluidization velocity is low for particles of the size in the bed, it is expected that production of fines will not be a continuing problem.

The fluidized bed vessel has been insulated and is ready for high-temperature operation. The heating elements have been installed in the bottom of the bed, for heating of the fluidizing air. Three elements of 2500 watts each are located in the compartment which will heat the hydrogen. Twelve elements, also of 2500 watts each, are located in the main section of the vessel which will heat the reactor tubes. These elements are fully wired and ready for operation. In this connection, when the decision was made by University Officials that this reactor system should be located in the high-pressure laboratory, it was recognized that the electric power supply to the building was far too small to accomodate the heating requirements for this system. Additional power had to be brought into the building, a cause of some delay in the initial stages of preparation of space.

The manifold for supplying the recycled gas and make-up hydrogen to the reactor has been installed, and hook-up completed. The manifold accomodates eight gas cylinders -- now visualised to consist of four hydrogen cylinders, two nitrogen cylinders, and two cylinders of recycled gas products. The recycle gases pass from the gas collection section of the product recovery system to a recycle compressor, which is able to receive the gases at a pressure about 100 psi below the required delivery pressure. By this manifold and recycle system, we will be able to maintain a gas flow in the reactor tubes well into the turbulent range, for the required particle heat-up rates. This part of the system is now ready for operation.

The product collection system consists of four one-gallon high-pressure vessels. Two of the vessels will serve as solids-liquids separators, and the remaining two vessels as liquid collection vessels. The liquid collection vessels are water cooled. These vessels have been installed and pressure tested. This portion of the system is now ready for operation.

All of the elements of the overall system, identified above, work as anticipated, and we are confident that the system will function to obtain the data specified in the proposal. No problems have appeared to date which were not anticipated and provided for, except the dust problem in the fluidized bed at start-up of that bed. We had thought the alumina would be of a narrow size range, without fines. However, it is not anticipated an ongoing problem will exist from the dust.

TASK B

In the prior Progress Report (No. 5), it was observed that proceeding from aromatic compounds of two or more condensed rings to isoparaffins in a single stage does not appear to be possible to any significant extent using catalysts which are available to us in the market. At a temperature low enough to accomplish the necessary degree of hydrogenation, cracking is insufficient, and no iso-paraffins are produced. When the temperature in the single stage reactor is increased to a high enough level to provide for cracking to yield iso-paraffins, hydrogenation to the necessary intermediates is insufficient, all using catalysts available in the market. The decision was then made to conduct

the hydrogenation at a temperature suitable for that function, then conduct the cracking in a second stage at a temperature high enough for that function.

To commence this portion of the experimental work, 1-methylnaphthalene was previously selected, and its use is continued. Six catalysts known to exhibit strong hydrogenation activity when feeding aromatic compounds have been investigated. There is a large volume of work reported in the literature relative to hydrogenation of single-ring aromatic compounds, but very little work on aromatic compounds of two or more rings in a condensed configuration. The results are presented in Table I. All results were obtained in a batch autoclave at pressures of 1500 psig.

It is expected that in an atmosphere of hydrogen at 1500 psi, most of the cracking to yield isoparaffins will occur from methyldecalins. The hydrogenation effort therefore focussed on production of decalins as a measure of the effectiveness of the catalysts. Product analyses were carried out using a gas chromatograph, with some of the analyses also using a GC/MS instrument.

Some work has been reported in the literature for hydrogenation of methyl-naphthalene at 200 °C, using 0.5% platinum supported on alumina as catalyst. Conversions greater than 90% were reported, but a time was not specified. An experiment was conducted for hydrogenation of methyl-naphthalene, using 0.5% platinum supported on alumina, at 200 °C for 4 hours (Exp. No. 2). Total conversion was less than 2%. Considering

the work reported in the literature, we wondered whether our catalyst may have become deactivated to a degree. The catalyst was activated at 400 °C, then the experiment repeated (Exp. No. 3). There was no increase in conversion. We are unable to duplicate the work at 200 °C reported in the literature.

Another experiment was conducted with the same catalyst, at 275 °C for 2 hours (Exp. No. 1). Conversion to methyl tetralins reached 73%, but the hydrogenation stopped there. No products were detected reflecting cracking of any of the units. Another experiment with the same catalyst, but with the temperature increased to 400 °C, for 3 hours, was conducted (Exp. No. 6). Overall conversion increased to nearly 85%, and small amounts of various compounds appeared, including about 8% methyl decalins.

Experiments were conducted with catalysts containing also a cracking function. Sulfided nickel-tungsten supported on silica-alumina yielded 9% methyl-decalins; nickel moly on a silica-alumina support yielded 12% methyl-decalins. Cobalt-moly on a γ -alumina support, with no cracking function, yielded 13% methyl-decalins.

The best catalyst for yielding methyl-decalins was nickel-moly supported on titania alumina, the support synthesized in our laboratory. Results of these experiments are presented in Table I as follows: Exp. No. 7, 450 °C, 3 hours, 3% methyl-decalins; Exp. No. 8, 350 °C, 3 hours, 21% methyl-decalins; Exp. No. 11, 325 °C, 5 hours, three duplicate experiments, with methyl-decalins ranging from 27% to 50%; Exp. No. 12, 325 °C, 10 hours, three duplicate experiments, with methyl-decalins ranging

from 81% to 99%. The wide range of yields of methyl-decalins in the duplicate experiments of No. 11 seems to arise from the difficulty of heating the reactor at the same rate. Zero time was taken as the time when the reactor reached the set temperature, hence a slow-heating experiment gave a higher yield, because of reactions occurring during heat-up.

Since methyl-decalins are considered to be an important intermediate in the reaction pathway, an experiment was conducted with methyl-decalin as the feed material, with the same catalyst which produced the high yields of methyl-decalin, to see if further cracking could occur with that catalyst (Exp. No. 13). Even at 380 °C, there was no cracking of the methyl-decalin. A different, stronger cracking catalyst will be needed, at a higher temperature, to produce isoparaffins.

TABLE I

Product Distribution, %

Exp No.	Catalyst	Reaction temp and time	1-methyl-naphthalene (feed)	Methyl-tetra-lins							Alkyl-Benzenes
1	Pt(0.5%)/Al ₂ O ₃	275 ⁰ C 2 hr	26.86	73.14							
2	Pt(0.5%)/Al ₂ O ₃	200 ⁰ C 4 hr	98.43	1.57							
3	Pt(0.5%)/Al ₂ O ₃ activated, 400 ⁰ C	200 ⁰ C 4 hr	98.93	0.94		-	-	-	0.13	-	-
4	Criterion C-344	400 ⁰ C 3 hr	42.32	54.10	0.37	1.71	0.53	-	-	-	-
5	C-344: SiO ₂ -Al ₂ O ₃ 4 : 1	400 ⁰ C 3 hr	38.80	53.78	-	3.87	1.43	-	-	-	-
6	Pt(0.5%)/Al ₂ O ₃	400 ⁰ C 3 hr	15.79	63.63	0.84	1.12	7.50	2.97	8.16	-	-
7	Ni-Mo/TiO ₂ -Al ₂ O ₃ (Sulfided)	450 ⁰ C 3 hr	28.44	37.6	5.49	11.39	-	6.40	3.25	-	5.64
8	Ni-Mo/TiO ₂ -Al ₂ O ₃ (Sulfided)	350 ⁰ C 3 hr	1.63	59.12	-	-	8.32	9.28	21.44	-	-
9	NiW/SiO ₂ -Al ₂ O ₃ (Sulfided)	400 ⁰ C 3 hr	3.28				12.66		9.10	-	4.14
10	Co-Mo/γ-Al ₂ O ₃ (Sulfided)	400 ⁰ C 3 hr	13.13	52.94	0.58	1.25	9.58	4.16	13.37	1.57	-

TABLE I, (cont.)

Product Distribution, %

Exp No.	Catalyst	Reaction temp and time	1-methyl-naphthalene (feed)	Methyl-tetra-lins							Alkyl-Benzenes
11	Ni-Mo/TiO ₂ -Al ₂ O ₃ (Sulfided)	325 ⁰ C 5 hr	0.24 - 0.38	49.18 52.18 70.34	-	-	-	-	50.58 46.90 27.27	-	- 0.92 2.00
12	Ni-Mo/TiO ₂ -Al ₂ O ₃ (Sulfided)	325 ⁰ C 10 hr	- - -	4.95 - 18.42	-	-	-	-	95.05 99.24 80.98	-	- 0.76 0.62
13	Ni-Mo/TiO ₂ -Al ₂ O ₃ (Sulfided)	380 ⁰ C 3 hr	Feed: Methyl Decalins						98.75		
14	Pt(0.5%)/Al ₂ O ₃	200 ⁰ C 5 hr 1000 psi	No Conv- version		-	-					
15	Pt(0.5%)/Al ₂ O ₃ (Sulfided)	325 ⁰ C 5 hr	76.65	21.31	-	-	-	-	-	-	2.04
16	Ni-Mo/SiO ₂ -Al ₂ O ₃	400 ⁰ C	13.19	55.73	1.56	2.03	9.67	4.68	12.18	-	-

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