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

Progress Report No. 10
(Covering the period January 1 - March 31, 1995)

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

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

We have no objection from a patent standpoint to the publication or dissemination of this material.

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MASTER

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 form coal with satisfactory octane rating but low in aromatic content.

ACTIVITY FOR THE REPORTING PERIOD

TASK A

Shake-down tests on the continuous reactor system have continued throughout this reporting period. It was expected that various components in the system may require adjustments or modifications.

When fluidization of the reactor bed was first examined, it was believed that what appeared to the eye to be a fairly uniform fluidization, had been achieved. However, when the full system was tested together, with the heaters operating at or near the design capacity, such uniformity as required for satisfactory operation did not exist. The heaters were designed to operate at 90% of capacity when the air flow through the bed would provide for 50% above minimum fluidization velocity. However, in order that each and every section of the bed would achieve minimum fluidization velocity, some sections were operating at air velocities considerably higher than 1.5 times minimum fluidization velocity. When the bed was operated in that manner, the total volumetric air flow through the bed was so great that a practical heat-up rate could not be achieved by the heat flux from the heaters, even operating at full duty cycle in the computer program. As a consequence, the heat-up rate of the bed was extremely slow, and it is not certain whether the desired bed temperature could be achieved, and maintained during operation.

The distributor plate at the bottom of the bed, as originally designed, was fabricated with uniform hole size and spacing. Following observation of the bed operation, calculations were made and a change in hole diameter and spacing determined for various sections of the bed which could eliminate the variable air flow and provide uniform fluidization. A new distributor plate was fabricated based upon these calculations, and installed. A significant improvement was realized with the new plate, but operation still was not satisfactory.

The original design of the fluidized-bed chamber provided for entry of the fluidizing air at one end of the bed. A manifold has been installed along the outside of the chamber, running the full length of the bed. Air is admitted to the chamber, below the distribution place, at five locations in the chamber. Each entry port contains a valve such that the rate of air flow into the bed can be adjusted for each entry port. This installation aided further in equalizing the air flow through the bed, but it still was not uniform enough to permit operation of the bed at some velocity near the minimum fluidizing velocity. Baffles have now been installed midway between each pair of entry ports, effectively dividing the chamber below the distributor plate into five chambers. It is now believed that, following sealing the distributor plate to the support grating, the volumetric air flow can be controlled such as to operate near the minimum fluidizing velocity throughout the bed.

A coal feed hopper, previously fabricated for use in an earlier coal research contract, was known to be available at the time of preparation of the proposal, and was selected for use in this reactor system as an economy measure. The shaft seal and bearing required rebuilding. This has been completed and the hopper installed. A digital motor controller has been installed for controlling the coal feed rate, and can be precisely operated at velocities from 3 to 600 rpm. For each rotation of the feeder mechanism the hopper feeds 1.5 grams of coal at a pressure of 1500 psia, when feeding coal screened to pass through a 65 mesh screen and retained on a 100 mesh screen (Standard Tyler Screen Series). The coal feed rate can thus be precisely controlled in this feed range. The coal feed system has been pressure tested as part of the tubular reactor system, and operates in a satisfactory and leak-free manner, following minor modifications.

The complete tubular reactor system is now being tested for heat-up rate, including the hydrogen pre-heater tube bank, which operates in a separate fluidizing chamber of the fluidized bed.

TASK B

Experimental work is continuing toward the objective of producing from coal-derived liquids a transportation fuel exhibiting a satisfactory octane rating but low in aromatics. Inasmuch as coal-derived liquids are high in aromatics, the work has first focussed on conversion of aromatic compounds to isoparaffins, which are observed to exhibit high octane numbers. The studies were initiated using 1-methylnaphthalene as a model compound, which compound is somewhat representative of aromatic compounds found in coal-derived liquids.

Tables 1, 2, and 3 present data with 1-methylnaphthalene as feed. The data in Table 1 were obtained with a reaction time of three hours. A total of 11 catalysts have been examined with this feed material. All of the catalysts exhibit hydrogenation activity, and several are hydrocracking catalysts. Included in the experiments reported in the Tables are:

NiMo/SiO_2-Al_2O_3, sulfided
NiMo/TiO_2-Al_2O_3, sulfided
PtMo/SiO_2-Al_2O_3, sulfided
RhMo/SiO_2-Al_2O_3, sulfided
C-344 (CoMo/Al_2O_3)
C-344: SiO_2-Al_2O_3.
NiW/SiO_2-Al_2O_3 (sulfided
HT-400 (CoMo/Al_2O_3)
Pt (0.5%)/Al_2O_3
Ni-4301 (NiW/SiO_2-Al_2O_3)
Mobil Proprietary Catalyst

Six temperatures have been investigated, ranging from 450 ^{0}C to 200 ^{0}C. Referring to Table 1, at 450 ^{0}C, in a time of three hours, only a small amount of hydrogenation to tetralins occurred, and formation of isoparaffins (branched alkanes) was negligible. Most of the starting material (other aromatics in the table) remained unreacted. A temperature of 450 ^{0}C favors dehydrogenation, and is too high for hydrogenation unless the hydrogenated product is withdrawn from the system.

At the opposite end of the temperature range, at 275 ^{0}C most of the aromatic feed was hydrogenated to tetralins, but with no formation of methyldecalins or isoparaffins. At 200 ^{0}C essentially no hydrogenation occurred even at the high pressures of 1800 psig, and with a strong hydrogenation catalyst.

Formation of decalins is of interest as a possible intermediate on the pathway to isoparaffins. Several experiments were conducted at 400 ^{0}C, as a possible temperature compromise between a temperature low enough to accomodate hydrogenation to decalins and a temperature high enough to accomodate ring opening of the decalins formed. Of these experiments at 400 ^{0}C, several of the catalysts yielded tetralins in amounts greater than 50%, with significant amounts of decalins, up to about 30%, but essentially no production of isoparaffins, these yields in a time of three hours.

In Table 2, the times were increased to 8 to 10 hours, and the temperature decreased to 325 ^{0}C. Hydrogenation to decalins was nearly complete with several of the hydrocracking catalysts, but production of isoparaffins was negligible. However, with one specialized Harshaw catalyst, nearly one-half of the product is single-ring saturated compounds (the other cyclanes column). In this one case 5.60% of the liquid product is isoparaffins.

To examine the potential for conversion of the decalins to isoparaffins, several experiments have been conducted using methyldecalins as feed. These results are presented in Table 4. Several temperatures were utilized, ranging from 300 to 450 ^{0}C. The highest yield of isoparaffins was achieved with the proprietary Mobil catalyst, at a temperature of 450 ^{0}C (Runs number 79 and 80). In Run No. 79, 10.64% by weight of the liquids appeared as isoparaffins. From Table 5, the liquids from Run No. 79 were about 25/40, or about 63% of the methyldecalin feed. Therefore the isoparaffins, as a percent of the feed, is

0.63 x 10.64, or about 6.7% by weight of the methyldecalins converted to isoparaffins, not a very encouraging conversion per pass to isoparaffins. It is noted that the highest conversions to isoparaffins, occurring at 450 ^{0}C, were accompanied by large-scale dehydrogenation of the decalins to aromatics (about 60% by weight of the liquids), principally naphthalenes.

Attention is next focussed on the data of Table 5, relative to the gaseous products from experiments with decalins as feed and the Proprietary Mobil catalyst, all with reaction times of one hour. Of particular interest in the gases are the butanes and pentanes, with the thought in mind that these materials may be alkylated or polymerized to form isoparaffins in the gasoline boiling range. Applying a little bit of arithmetic to the data in Tables 4 and 5, one obtains the values presented in Table 6.

When this work was initiated, a possibility was entertained that it may be possible to identify, or develop, a hydrocracking catalyst with sufficient cracking activity to provide the necessary ring opening to yield substantial amounts of isoparaffins, at a temperature low enough to accomodate hydrogenation of the aromatics. Such a catalyst has not been identified, and results to date do not indicate a high probability of developing such a catalyst. However, that chapter of the investigation has not been totally closed.

Of substantial interest is the production of substituted single-ring alkanes in the hydrogenation of 1-methylnaphthalene, shown in Table 2, Run No. 23-b, listed in the "Other Cyclanes" column of the table, with the Harshaw catalyst. Experiments are now being conducted to determine the amounts of substituted cyclohexanes and substituted cyclopentanes in this product, and the optimum conditions for maximizing the yield of these products. Production of these compounds directly from condensed aromatics will be of great value, because these compounds exhibit high octane ratings. The results of this work will be included in the next report.

The overall results achieved to date, considering the yields of isoparaffins, the yields of iso-butanes and iso-pentanes for possible alkylation to gasoline-size isoparaffin molecules, and the yields of substituted cycloalkanes now indicated from reaction of methylnaphthalene, show genuine promise of a single-stage system to reduce the aromatic content of coal-derived liquids to very low values, while yielding a gasoline product of octane number of 85 or higher. Such an octane rating projection is based upon the substituted cycloalkanes and isoparaffins, both produced directly fron the aromatics, and with alkylation of the isobutanes and isopentanes to follow. Work is continuing to learn whether one catalyst, operating at some intermediate temperature, can accomplish the first two of these things to a satisfactory, cumulative degree.

Table 1 : Product distribution for the hydrocracking of 1-methylnapthalene by using several catalysts.

			Product Distribution, wt. %								
			Cyclanes			Alkanes				Aromatics	
Run	**Catalyst**	**T, °C**	**Methyl-decalins**	**Others**	**Cyclenes**	**Branched**	**Normal**	**Alkenes**	**Alkynes**	**Methyl-tetralins**	**Others**
7	PtMo/$SiO_2Al_2O_3$ (sulfided)	450	0.13	--	--	--	--	--	--	16.85	83.02
19	NiMo/$TiO_2Al_2O_3$ (sulfided)	450	1.20	0.94	--	0.47	0.19	--	--	12.56	84.65
17	NiMo/$SiO_2Al_2O_3$ (sulfided)	400	17.77	0.52	--	--	--	--	--	59.52	22.19
5	PtMo/$SiO_2Al_2O_3$ (sulfided)	400	8.99	0.16	--	--	--	--	--	71.03	19.82
6	RhMo/$SiO_2Al_2O_3$ (sulfided)	400	15.76	0.60	--	--	--	--	--	64.25	19.39
8	NiMo/$TiO_2Al_2O_3$ (sulfided)	400	29.47	0.82	--	--	--	--	--	54.55	15.15
14	C-344(1)	400	--	--	--	--	--	--	--	52.40	47.59
15	C-344:$SiO_2Al_2O_3$ (4:1 w:w)	400	--	--	--	--	--	--	--	48.53	51.56
16	Pt(0.5%)/Al_2O_3(2)	400	16.57	--	--	--	--	--	--	67.50	15.92
18	NiW/$SiO_2Al_2O_3$(2) (sulfided)	400	5.35	4.37	0.37	0.31	0.10	--	--	45.86	43.63
21	HT-400(3) (sulfided)	400	20.72	--	--	--	--	--	--	62.31	16.97
20	NiMo/$TiO_2Al_2O_3$ (sulfided)	350	33.32	--	--	--	--	--	--	64.39	2.28

Reaction Conditions : Feed = 1-methylnapthalene ; Initial H_2 pressure = 1000 psig ; Reaction time = 3 hours. All MMo catalysts were prepared by incipient wetness impregnation and contain 25 mmol of M and 77 mmol of Mo/100 g $SiO_2Al_2O_3$ or 77 mmol of Mo/100 g $TiO_2Al_2O_3$.

(1) C-344 : CoMo/Al_2O_3 from Criterion Catalysts

(2) from Strem Chemicals

(3) HT-400 : CoMo/Al_2O_3 from Harshaw Catalysts

Table 2 : Product distribution for the hydrogenation of 1-methylnapthalene by using several catalysts.

					Product Distribution, wt. %								
					Cyclanes			Alkanes				Aromatics	
Run	Catalyst	P_{H_2},(initial) psig	t, h	Catalyst/ Feed, w/w	Methyl-decalins	Others	Cyclenes	Branched	Normal	Alkenes	Alkynes	Methyl-tetralins	Others
22	NiMo/$TiO_2Al_2O_3$	1000	10	10/1	95.05	--	--	--	--	--	--	4.95	--
24	NiMo/$TiO_2Al_2O_3$	1000	10	10/1	97.22	1.99	--	--	--	--	--	0.79	--
39	NiMo/$TiO_2Al_2O_3$	1500	10	10/1	98.59	0.46	--	--	--	--	--	0.95	--
54	NiMo/$TiO_2Al_2O_3$	1000	10	5/1	99.46	0.54	--	--	--	--	--	--	--
56	NiMo/$TiO_2Al_2O_3$	1520	8	5/1	92.48	0.74	--	--	--	--	--	6.78	--
58	NiMo/$TiO_2Al_2O_3$	1500	8	4/1	96.10	0.85	--	--	--	--	--	3.05	--
23a	Ni-4301(1)	1000	5	10/1	22.49	4.85	0.32	--	0.18	0.16	--	39.52	31.48
23b	Ni-4301(1)	1000	10	10/1	34.21	45.96	5.87	5.60	0.28	3.53	0.73	0.86	2.95
27	Pt(0.5%)/Al_2O_3(2)	800	5	10/1	--	0.63	--	--	--	--	--	15.73	83.64
	Pt/REX(3)	1000	10	10/1									
	Pd/REX(3)	1000	10	10/1									

Reaction were performed at 325°C. All MMo catalysts were prepared by incipient wetness impregnation and contain 25 mmol of M and 77 mmol of Mo/100 g $SiO_2Al_2O_3$ or 77 mmol of Mo/100 g $TiO_2Al_2O_3$. Catalysts were sulfided prior to use.

(1) Ni-4301 : ~~Ni/Al2O3 from [illegible] Catalyst, sulfided prior to use~~ NiW/SiO_2-Al_2O_3, Harshaw, sulfided prior to use.

(2) from Strem Chemicals

(3) from Mobil

Table 3 : Product distribution for the hydrogenation of 1-methylnapthalene by using platinium catalyst.

					Product Distribution, wt. %								
					Cyclanes			Alkanes				Aromatics	
Run	Catalyst	P_{H_2},(initial) psig	T, °C	t, h	Methyl-decalins	Others	Cyclenes	Branched	Normal	Alkenes	Alkynes	Methyl-tetralins	Others
10	Pt(0.5%)/Al_2O_3	1000	275	2	--	--	--	--	--	--	--	72.65	27.35
11	Pt(0.5%)/Al_2O_3	1800	200	4	--	--	--	--	--	--	--	1.33	98.67
12	Pt(0.5%)/Al_2O_3	1800	200	4	--	--	--	--	--	--	--	0.62	99.28
26	Pt(0.5%)/Al_2O_3(1)	800	200	5	--	--	--	--	--	--	--	--	100.00

(1) It was activated prior to use.

Table 4 : Liquid product distribution for the hydrocracking of methyldecalins by using several catalysts.

					Product Distribution, wt. %								
					Cyclanes		Cyclenes	Alkanes		Alkenes	Alkynes	Aromatics	
Run	Catalyst	P_{H_2}(initial) psig	T, °C	t, h	Methyl-decalins	Others		Branched	Normal			Methyl-tetralins	Others
25	NiMo/$TiO_2Al_2O_3$ (sulfided)	1000	380	3	91.35	3.27	--	--	--	--	--	1.25	4.13
40	HPC-G416(1) (sulfided)	1200	400	3	83.46	4.32	--	--	--	--	--	3.37	8.84
41	NiMo/$SiO_2Al_2O_3$(2) (sulfided)	600	450	0.8	58.34	6.22	--	0.17	0.13	--	--	10.18	24.96
42	NiMo/$SiO_2Al_2O_3$(2) (sulfided)	600	450	3	40.17	9.92	--	0.98	0.38	0.44	--	19.15	28.95
45	NiMo/$TiO_2Al_2O_3$ (sulfided)	600	450	3	49.42	9.00	--	0.58	0.40	--	--	14.83	25.78
44	ZrO_2/SO_4^{-2}	600	450	3	54.28	15.39	--	2.26	0.31	--	--	1.09	26.66
46	NiW/$SiO_2Al_2O_3$(3) (sulfided)	600	450	3									
47	NiW/$SiO_2Al_2O_3$(3) : $SiO_2Al_2O_3$ (3:1 w:w) (sulfided)	600	450	3									
48	NiW/$SiO_2Al_2O_3$(4) (sulfided)	600	450	3									
59	Pt/REX(5)	700	300	1	33.08	54.55	6.99	1.88	0.16	3.34	--	--	--
60	Pt/REX(5)	700	350	1	6.24	54.84	3.52	7.66	1.98	5.48	--	1.80	18.48
62	Pt/REX(5)	700	400	1	0.22	35.68	0.22	8.30	1.55	4.52	1.02	1.22	47.27
79	Pt/REX(5)	700	450	1	--	21.55	--	10.64	3.19	0.77	1.70	0.79	61.36
74	Pd/REX(5)	700	300	1	60.03	31.64	5.67	0.71	0.11	1.84	--	--	--
75	Pd/REX(5)	700	350	1	5.12	54.02	3.76	5.88	1.40	5.54	--	1.17	23.10
76	Pd/REX(5)	700	400	1	0.29	35.01	0.45	8.17	1.65	3.25	0.48	1.05	49.65
80	Pd/REX(5)	700	450	1	0.29	23.59	0.17	9.45	2.99	2.11	0.85	0.67	59.88

All MMo catalysts were prepared by incipient wetness impregnation and contain 25 mmol of M and 77 mmol of Mo/100 g $SiO_2Al_2O_3$ or 77 mmol of Mo/100 g $TiO_2Al_2O_3$.
(1) NiMo/$TiO_2Al_2O_3$ from Engelhard Catalysts (2) 16.3% MoO_3, 3.6% NiO ; from Engelhard (3) from Strem Chemicals??? (4) .,....?
(5) from Mobil

Table 5 : Gas product distribution for the hydrocracking of methyldecalins by using Pt/REX and Pd/REX catalysts(1).

			weight of(2), g		Gas Product Distribution, wt %											
Run	Catalyst	T, °C	Gas, g	Liquid, g	CH_4	C_2H_6	C_3H_8	C_3H_6(3)	i-C_4H_{10}	n-C_4H_{10}	i-C_5H_{12}	n-C_5H_{12}	i-C_6H_{14}	C_6H_{12}(4)	C_7H_{14}(5)	C_7H_{14}(6)
59	Pt/REX	300	4.92	35.04	0.37	0.67	12.44	--	66.12	4.12	10.34	0.37	0.29	2.11	1.90	1.27
60	Pt/REX	350	5.78	34.21	0.53	2.50	20.38	--	55.23	7.40	8.44	0.86	0.29	1.55	2.06	0.76
62	Pt/REX	400	7.06	32.74	3.45	9.45	32.96	--	33.32	11.41	5.88	1.58	0.29	0.91	0.75	--
79	Pt/REX	450	14.38	25.34	8.64	17.36	35.22	--	20.61	11.35	4.34	1.66	0.37	0.46	--	--
74	Pd/REX	300	4.14	35.33	--	--	10.82	1.15	55.12	12.01	14.93	1.87	0.57	1.71	1.81	--
75	Pd/REX	350	6.23	33.72	0.53	2.76	20.10	--	55.48	7.03	8.85	0.67	0.40	1.57	1.58	1.04
76	Pd/REX	400	8.84	30.47	2.94	9.13	30.06	--	36.48	10.24	7.81	0.58	0.45	0.75	1.13	0.42
80	Pd/REX	450	14.08	25.74	7.84	17.79	35.18	--	24.20	9.63	4.30	0.57	0.11	0.22	0.17	--

Reaction Conditions : Feed = Methyldecalins ; Initial H_2 pressure = 700 psig ; Reaction time = 1 hours.

(1) from Mobil (2) for 40 g of feed (3) Methylcyclopropane (4) Methylcyclopentane (5) Dimethylcyclopentane (6) Methylcyclohexane

Table 6

Weight Percents of Butanes and Pentanes in Gas Product, as Percentages of Methyldecalins Fed

Run No.	Temp. °C	wt. % Liquid	wt. % Gases	wt. % of feed as butanes	wt. % of feed as pentanes	wt. % butanes plus pentanes	wt. % isoparaffins, Table 4
59	300	87.6	12.4	8.64	1.32	9.96	1.65
74	300	89.6	10.4	6.98	1.75	8.73	0.63
60	350	85.6	14.4	9.02	1.34	10.36	6.55
75	350	84.4	15.6	9.75	1.49	11.24	4.96
62	400	82.4	17.6	7.87	1.31	9.18	6.79
76	400	77.9	22.1	10.33	1.85	12.18	6.22
79	450	64.0	36.0	11.51	2.16	13.67	6.73
80	450	64.8	35.2	11.91	1.71	13.62	6.08

In the above table, the butanes are mostly iso-butanes, and the pentanes are mostly iso-pentanes. For each pair of temperatures, the catalyst used in the first experiment at the temperature contained platinum as the metal, while the catalyst in the second experiment at the temperature contained palladium as the metal.