1 of 1

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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. 3
(Covering the period April 1 - June 30, 1993)

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yes

PERSONNEL

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

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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

When the proposal was prepared for this work, it was anticipated that approximately one year would be required for the combined activities of circulation of invitations to bid in the appropriate media, as required by law, allowing time for interested persons to prepare and submit bids, evaluation of the bids and selection of the successful bidder, and the design, construction and installation of the reactor system. It was expected that most of this time would be consumed in the design and construction of the system. Actually, the engineering firm selected for the design and construction essentially completed that phase of the work in about six months. It had been expected that the reactor system would be installed in the same laboratory space previously utilized by us for the previous work with a small, continuous-flow reactor. We therefore believed we would be able to commence experimental work with the new continuous-flow system ahead of the schedule presented in the proposal.

The interpretations of the safety requirements for work of the nature of this work have become much more demanding than were utilized when the earlier system had been installed, some 15 or more years ago. Also the significant increase in reactor size, with the large increase in quantities of hydrogen to be present in the reactor environment, led to the imposition of more rigid requirements in the laboratory space itself. The safety personnel in the University thereby directed that the reactor

system must be installed in other space prepared for high-pressure research. The air circulation capability in that laboratory required upgrading, and enlarged capacity, in order to accomodate this system in a completely safe manner. In addition, additional electric power capacity in the new space was required, because of the size of the system and the power demands.

We have been advised that the design work required for preparation of the space has been completed, and invitations to potential bidders for selected portions of that work are now to be circulated. It is hoped the installation of the reactor system for Task A can be completed within the time frame of the July to September reporting period, and that actual experimental work on this task will commence reasonably near to the timetable included in the proposal.

TASK B

In the previous report (No. 2) free energies were presented for formation of various isoparaffin products from several aromatic compound types expected to be found in the liquid products formed in the reactor system of Task A. Examination of the free energy values reveals that if conversion of these aromatic compound types to isoparaffins is to occur in a single stage, that stage must operate at a temperature not higher than about 400 °C, if a satisfactory yield of the isoparaffins is to be obtained, even with recycle.

In the experimental work performed in a microreactor under a prior contract, liquid products were analyzed, obtained at 82%

conversion in 5 seconds, with a liquid/hydrocarbon gas ratio of 26/1, by weight. Inasmuch as a high proportion of the liquid products formed consists of molecules containing two aromatic or hydroaromatic rings in a condensed configuration, work of conversion of aromatics to isoparaffins has commenced with the use of a naphthalene derivative as the beginning compound. The first model compound utilized as a starting material is methylnaphthalene.

The conversion of a multi-ring aromatic compound to an isoparaffin incorporates several steps in sequence. It is clear that a catalyst must be used in at least one of the steps of the sequence, if a satisfactory rate is to be realized. A decision was made to first examine the formation of isoparaffins from aromatics in a single stage.

The conversion process must be initiated by hydrogenation of at least one of the aromatic rings, unless the starting molecule already contains a saturated ring. For this initial step the catalyst employed must contain a strong hydrogenation function or capability, if the hydrogenation is to occur at an acceptable rate at a temperature where the free energy is favorable for formation of an isoparaffin molecule. Following hydrogenation, if cracking of the hydroaromatic molecule is to occur in the same stage as hydrogenation, then a second function must be present in the catalyst, namely a cracking function, in order to open the saturated ring at a temperature low enough to accomodate the hydrogenation function.

The experiments for this portion of the study were conducted in a 50-ml batch autoclave, each experiment utilizing 50 minutes reaction time at temperature. To initiate the study, four dual-functional catalysts were selected known to exhibit the functionalities believed to be of importance in these conversions. The catalysts selected are Nickel-Molybdenum supported on Silica-Alumina, Rhodium-Molybdenum supported on Silica-Alumina, Platinum-Molybdenum supported on Silica-Alumina, and Nickel-Molybdenum supported on Titania-Alumina. As indicated by the values of free energies, a temperature of 400 °C was selected as the probable maximum temperature which would permit the necessary degree of hydrogenation of the aromatics for high conversions. The results are presented in Table 1. All conditions remained the same for all experiments, changing only the catalyst, except for the fifth row of data in the table, where the temperature was changed for one catalyst.

The highest conversions, as revealed by the amounts of the starting material, methylnaphthalene, remaining at the end of the 50-minute reaction time, were achieved with the nickel-moly catalyst, both with the silica-alumina support and the titania-alumina support. However, at 400 °C, the differences in total conversion were small.

In all cases, the product present in the largest quantity, by a large margin, was the tetralins, both with the methyl group still attached and without the methyl group. This is to be expected in the time frame of the experiments, because the

reactions for conversion are initiated by hydrogenation of one of the rings in the naphthalene. The catalyst containing platinum produced the highest yield of methyltetralins, as well as the highest overall yield of all tetralins. This observation is a reflection of the very strong hydrogenation capability of platinum.

The end objective of this portion of the research is the production of isoparaffins, which requires the ultimate hydrogenation of both rings of the starting compound. Three of the compounds in the product reflect hydrogenation of both rings of the naphthalene. The highest yield of all three of these compounds combined was produced by the nickel-moly supported on titania-alumina. The nickel-moly catalysts, both with the silica-alumina support and the titania-alumina support, led to considerably higher yields of the compounds with the second ring hydrogenated than is observed with the platinum catalyst. It appears that while the platinum catalyst hydrogenates the first ring more rapidly, or at least to a larger extent, the nickel catalyst is more effective in hydrogenating the second ring. However, when one compares the yields of the sum of all tetralins plus compounds with the second ring hydrogenated, the totals for the nickel catalyst and the platinum catalyst, on the same support (silica-alumina), are essentially the same. The change of support to titania-alumina increased the total yield of tetralins plus second ring hydrogenation (combined) in favor of the nickel catalyst.

The objectives in this work not only include the reduction of aromatic compounds to low levels, but also the production of other compounds as replacements for the aromatics which will impart a high octane number to the fuel. The three compounds in the products in Table 1 which reflect hydrogenation of both rings of the parent compound exhibit low octane numbers, and would not be useful in gasoline for the intended purpose. Most of the product which reflects hydrogenation of both rings is methyldecalin, which exhibits a low octane number (lower than 50). Cyclohexane, without side chains, exhibits an octane number near 100, but as alkyl groups are added of increasing length, the octane number rapidly decreases, reaching a value of only 34 for butylcyclohexane. Therefore, following hydrogenation the saturated rings need to be opened (both rings).

The percentages of the products of conversion (excluding the methylnaphthalene in the products) represented by ring opening in the products ranges from about 17% to about 22%. The highest yield of products with ring opening was achieved with the platinum catalyst. In the time frame of 50 minutes, at a temperature of 400 °C, there was no opening of the second ring to produce isoparaffins, even when products with ring opening in one ring reached values as high as 22% of the products.

Using the platinum catalyst, the temperature was increased to 450 °C, to observe whether opening of the second ring could be achieved at the higher temperature, being more favorable to the cracking operation. The data in the bottom line of Table 1

illustrate the products at 450 °C. At the higher temperature, the sum of tetralins plus fully-hydrogenated compounds was reduced from about 67% of the feed to about 47% of the feed, due to reduced hydrogenation, which proceeds less readily as the temperature is increased. Inasmuch as hydrogenation of at least one of the naphthalene rings initiates the conversion process, the overall conversion of the methylnaphthalene was significantly reduced, from about 89% to about 75%. Even at this higher temperature, there still was no opening of the second ring to yield isoparaffins.

It is clear that if conversion of aromatics to isoparaffins is to be successfully conducted in a single stage, the cracking function in the dual-functional catalyst must be significantly stronger. A search of the recent literature is now in progress by the graduate student, to learn of any recent application of cracking catalysts in work which may relate to the present work. Also, work will be conducted in two stages, with hydrogenation at a temperature most suitable for that operation, to be followed by hydrocracking at a higher temperature most suited to that operation.

Table 1

Catalytic Hydrocracking of Methylnaphthalene

Catalyst	Reaction Temp. °C	Methyl-Naphthalene	Methyl-Tetralins	Methyl-Decalin	Tetralin	Methyl-Butyl-Benzene	Pentyl-Benzene	Methyl-Butyl-Cyclo-Hexane	Butyl-Cyclo-Hexane	Alkyl-Benzenes
NiMo/SiO ₂ -Al ₂ O ₃	400	8.36	41.27	15.81	7.06	3.08	9.37	2.25	1.29	-
RhMo/SiO ₂ -Al ₂ O ₃	400	9.85	47.42	13.57	5.89	3.58	10.45	2.47	0.96	-
PtMo/SiO ₂ -Al ₂ O ₃	400	10.75	55.92	8.86	-	3.85	13.31	2.31	-	-
NiMo/TiO ₂ -Al ₂ O ₃	400	7.77	40.01	20.39	8.67	2.80	10.96	2.46	1.13	-
PtMo/SiO ₂ -Al ₂ O ₃	450	24.50	33.19	3.93	6.06	7.29	-	4.70	-	10.23

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