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

Progress Report No. 2
(Covering the period January 1 - March 31, 1993)

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MASTER

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

Experimental coal liquefaction studies conducted in a batch microreactor in my 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

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).

TASK A

The high ratio of liquids/HC gases as high as 30/1 achieved in my laboratory in the microreactor of the previous work, coupled with conversions to liquids in excess of 80% by weight of the coal, possibly represents near the ultimate in achieving high liquid yield combined with low HC gas yield. That level of success was made possible by virtue of heating the small coal particles to reaction temperature in one or two seconds, and following reaction removing the liquids from the hot zone in times as short as one second or less. It may not be possible for one to achieve these values of both of these operational parameters, simultaneously, in a continuous-flow reactor. However it is expected that one may be able to approach these values of operational parameters.

The reactor system designed for this work task has been designed to approach those values of particle heat-up and product quench as nearly as possible. Construction of the reactor system is nearing completion.

However a delay has been encountered in the installation of the equipment. In recent years regulations imposed by government have become more stringent. The high pressure laboratory at the University, where this research is to be conducted, was constructed several years ago, incorporating the necessary safety features required at that time and considered to be completely adequate for this type of research. Following receipt of the award for this research, we were informed that certain features of the research space required "upgrading" in order to meet current standards imposed by government.

The work of upgrading of the space is in progress, but not yet completed. It was necessary, operating within a State University, to obtain bids on part of the work, and the total process is just "slow". As soon as the work of upgrading the space is completed, the reactor system will be installed and the work of this task will proceed.

It is of value to note that delays of this nature were anticipated to a degree when the timetable for the work was placed in the proposal. It was estimated at that time that one year would be required for the design, construction and installation of the reactor system. We are still confident we will be on schedule when the installation of the equipment is completed and it is ready for operation.

TASK B

Analysis of the liquid products from the prior work, as mentioned above, reveals that most of the product consists of ring-type molecules, both aromatic and hydroaromatic, containing one, two or three rings, with various types of functional groups attached. Several compounds have been selected, expected to be present in significant quantities in the liquid products from the rapid liquefaction process of the work to be performed in Task A, as revealed by the analyses from the prior work. Free energies have been calculated at three temperatures, namely 227 °C, 327 °C and 427 °C, for proceeding from the compound to various product molecules. The calculated values of free energies are presented in Table 1. One observes that at 227 °C (500 °K), the free energy values are negative, and in most cases with rather large negative values, indicating that at equilibrium large concentrations of the product compounds could be formed. However it may be difficult to identify a catalyst which could provide a sufficiently high reaction rate to have practical value. At 327 °C (600 °K), some of the free energy values are negative, with a few exhibiting moderate negative values. It is possible that an appropriate catalyst may be identified which can provide a satisfactory reaction rate, such that, with some measure of recycle, a good product yield may be obtained. At a temperature of 427 °C (700 °K), all of the free energy values are positive, and mostly with rather large positive values. Even at equilibrium, the yields of product would be very small. Further, even with product removal and recycle of unreacted feed, it may

not be practical to achieve a satisfactory yield of the desired product.

It does appear likely, however, based upon values of free energy, that with an appropriate degree of recycle it may be possible to obtain satisfactory yields of isoparaffin products from a significant number of the compounds expected to occur in the raw liquid product, when operating at temperatures of the order of 300 to 350 °C. Obviously high catalytic activity will be essential in order to obtain both a satisfactory reaction rate and acceptable conversion per pass. This is the challenge to be addressed in the work which is to follow.

Values of equilibrium constants for each of the reactions presented in Table 1, at each of the three temperatures, are presented in Table 2.

DISCLAIMER

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Table 1 : Gibbs Free Energy at 500, 600, and 700K.

Reaction		ΔG , kJ/mol		
From :	To :	Temperature, K		
		500	600	700
Toluene	2-Methylhexane	-30.17	14.78	60.09
Toluene	3-Methylhexane	-31.01	13.40	58.17
Toluene	2,3-Dimethylpentane	-33.10	12.36	58.30
Toluene	Methylcyclohexane	-18.00	21.23	60.64
m-Xylene	2-Methylheptane	-18.09	26.66	71.71
m-Xylene	3-Methylheptane	-18.44	25.82	70.37
m-Xylene	4-Methylheptane	-13.75	31.43	76.94
m-Xylene	2,3-Dimethylhexane	-11.49	34.19	80.12
m-Xylene	2,4-Dimethylhexane	-17.41	28.41	74.59
m-Xylene	2,5-Dimethylhexane	-17.40	29.21	76.14
m-Xylene	2,2,4-Trimethylpentane	-12.08	35.86	84.05
m-Xylene	2,3,4-Trimethylpentane	-8.45	38.79	86.27
Napthalene	2(n-Pentane)	-96.84	-22.58	52.82
Napthalene	2(Iso-pentane)	-107.55	-32.03	44.19
Napthalene	2(Neo-pentane)	-94.17	-11.78	71.56
Napthalene	4,5-Dimethylcyclohexane	-37.04	40.47	118.85
Napthalene	4-Isopropylheptane	-36.04	41.97	119.55
Napthalene	2-Methyl-3-ethylheptane	-39.74	65.36	114.45
Napthalene	3,5-Dimethylcyclohexane	-44.04	32.67	110.45
Tetralyne	4,5-Dimethylcyclohexane	-27.25	26.04	79.94
Tetralyne	3,5-Dimethylcyclohexane	-34.25	18.24	71.54
Tetralyne	4-Isopropylheptane	-26.25	27.54	80.64
Tetralyne	2-Methyl-3-ethylheptane	-29.95	22.94	76.04
Tetralyne	2 mole(Isopentane)	-95.93	-44.52	7.36
Tetralyne	2 mole(Neopentane)	-85.99	-27.36	32.06
Anthracene	3-Methyltridecane	-61.19	45.56	153.20
Anthracene	2,2-Dimethyldodecane	-57.49	52.06	162.80
Anthracene	2,3-Dimethyldodecane	-57.11	50.86	160.13
Anthracene	2,4-Dimethyldodecane	-59.33	48.77	158.04
Anthracene	2 mole(2-Methylhexane)	-116.59	-9.94	98.6
Anthracene	2 mole(3-Ethylpentane)	-115.59	-9.94	97.4
Anthracene	2-Methylhexane + n-Heptane	-113.59	-7.54	100.3
Anthracene	2-Methylhexane + 3-Ethylpentane	-116.09	-9.94	98.00
Anthracene	2-Methylhexane + 2,3-Dimethylpentane	-114.76	-5.15	106.15
Anthracene	n-Hexane + 3-Methylheptane	-113.39	-7.66	99.48
Anthracene	n-Hexane + 3-Ethylhexane	-107.91	-1.59	106.09
Phenanthrene	3-Methyltridecane	-36.10	71.70	180.40
Phenanthrene	2,2-Dimethyldodecane	-32.40	78.20	190.00
Phenanthrene	2,3-Dimethyldodecane	-32.02	77.00	187.33
Phenanthrene	2,4-Dimethyldodecane	-34.24	74.91	185.24
Phenanthrene	2 mole(2-Methylhexane)	-91.50	16.20	125.80
Phenanthrene	2 mole(3-Ethylpentane)	-90.50	16.20	124.60
Phenanthrene	2-Methylhexane + n-Heptane	-88.50	18.60	127.50
Phenanthrene	2-Methylhexane + 3-Ethylpentane	-91.00	16.20	125.20
Phenanthrene	2-Methylhexane + 2,3-Dimethylpentane	-89.67	20.99	133.35
Phenanthrene	n-Hexane + 3-Methylheptane	-88.30	18.49	126.68
Phenanthrene	n-Hexane + 3-Ethylhexane	-82.82	24.56	133.29

Table 2 : Equilibrium constants at 500, 600, and 700K.

Reaction		K Temperature,K		
From :	To :	500	600	700
Toluene	2-Methylhexane	1419	.052	3.27e-05
Toluene	3-Methylhexane	1737	.068	4.56e-05
Toluene	2,3-Dimethylpentane	2871	.084	4.46e-05
Toluene	Methylcyclohexane	75.95	.014	2.98e-05
m-Xylene	2-Methylheptane	77.61	4.78e-03	4.40e-06
m-Xylene	3-Methylheptane	84.43	5.65e-03	5.60e-06
m-Xylene	4-Methylheptane	27.32	1.84e-03	1.80e-06
m-Xylene	2,3-Dimethylhexane	15.86	1.06e-03	1.00e-06
m-Xylene	2,4-Dimethylhexane	65.90	3.36e-03	2.70e-06
m-Xylene	2,5-Dimethylhexane	65.74	2.86e-03	2.00e-06
m-Xylene	2,2,4-Trimethylpentane	18.28	7.55e-04	5.00e-07
m-Xylene	2,3,4-Trimethylpentane	7.64	4.20e-04	3.00e-07
Napthalene	2(n-Pentane)	1.31e+10	92.44	1.14e-04
Napthalene	2(Iso-pentane)	1.72e+11	614.55	5.04e-04
Napthalene	2(Neo-pentane)	6.89e+09	10.61	4.50e-06
Napthalene	4,5-Dimethylcyclohexane	7408	2.99e-04	1.35e-09
Napthalene	4-Isopropylheptane	5824	2.22e-04	1.20e-09
Napthalene	2-Methyl-3-ethylheptane	14183	2.00e-06	2.64e-09
Napthalene	3,5-Dimethylcyclohexane	39902	1.43e-03	5.73e-09
Tetralyne	4,5-Dimethylcyclohexane	702.99	5.41e-03	1.00e-06
Tetralyne	3,5-Dimethylcyclohexane	3786	0.026	4.50e-06
Tetralyne	4-Isopropylheptane	552.61	4.00e-03	9.00e-07
Tetralyne	2-Methyl-3-ethylheptane	14918	.010	2.10e-06
Tetralyne	2 mole(Isopentane)	1.05e+10	7515	0.282
Tetralyne	2 mole(Neopen tane)	9.63e+08	240.98	2.33e-05
Anthracene	3-Methyltridecane	2.47e+06	1.08e-04	3.69e-12
Anthracene	2,2-Dimethyltridecane	1.01e+06	2.93e-05	7.10e-13
Anthracene	2,3-Dimethyltridecane	9.26e+05	3.73e-05	1.12e-12
Anthracene	2,4-Dimethyltridecane	1.58e+06	5.67e-05	1.61e-12
Anthracene	2 mole(2-Methylhexane)	1.52e+12	7.34	4.39e-08
Anthracene	2 mole(3-Ethylpentane)	1.19e+12	7.34	5.39e-08
Anthracene	2-Methylhexane + n-Heptane	7.36e+11	4.53	3.28e-08
Anthracene	2-Methylhexane + 3-Ethylpentane	1.34e+12	7.34	4.86e-08
Anthracene	2-Methylhexane + 2,3-Dimethylpentane	9.76e+11	2.81	1.19e-08
Anthracene	n-Hexane + 3-Methylheptane	7.02e+11	4.64	3.77e-08
Anthracene	n-Hexane + 3-Ethylhexane	1.88e+11	1.38	1.21e-08
Phenanthrene	3-Methyltridecane	5909	5.00e-07	3.45e-14
Phenanthrene	2,2-Dimethyltridecane	2426	1.00e-07	6.63e-15
Phenanthrene	2,3-Dimethyltridecane	2214	1.00e-07	1.05e-14
Phenanthrene	2,4-Dimethyltridecane	3777	3.00e-07	1.50e-14
Phenanthrene	2 mole(2-Methylhexane)	3.62e+09	0.039	4.09e-10
Phenanthrene	2 mole(3-Ethylpentane)	2.85e+09	0.039	5.03e-10
Phenanthrene	2-Methylhexane + n-Heptane	1.76e+09	0.024	3.05e-10
Phenanthrene	2-Methylhexane + 3-Ethylpentane	3.21e+09	0.039	4.54e-10
Phenanthrene	2-Methylhexane + 2,3-Dimethylpentane	2.33e+09	0.015	1.12e-10
Phenanthrene	n-Hexane + 3-Methylheptane	1.68e+09	0.025	3.52e-10
Phenanthrene	n-Hexane + 3-Ethylhexane	4.49e+08	0.007	1.13e-10

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