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MECHANISMS AND KINETICS OF COAL HYDROGENATION
Quarterly Progress Report for the Period January—March 1981

By
R. M. Baldwin
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by

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Colorado School of Mines

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ABSTRACT

Colorado School of Mines is engaged in an experimental program for the Department of Energy to develop comprehensive models for the effects of coal composition upon the kinetics and mechanisms of coal hydrogenation, for the effects of mineral matter additives (disposable catalysts) upon kinetics and mechanisms of coal hydrogenation, and for the kinetics and mechanisms of the hydrogenation of coal derived products such as preasphaltenes, and asphaltenes.

During this quarter experimental work was completed on a suite of bituminous coals, thus completing the initial phase of the coal reactivity study. Eleven of the 14 coals of the suite were successfully run in duplicate. Conversion to THF solubles was correlated well by pseudo-second order kinetics. The resulting kinetic rate constants correlated with H/C ratio, mean-max vitrinite reflectance, and a specially-defined "fraction of reactive macerals". The data did not correlate well with O/C ratios of the parent coals. Computer-derived statistical fits of various kinetic models of the series reaction type:

were shown to be limited in their effectiveness at fitting the experimental data.

Experimental work on the first phase of the disposable catalyst studies was completed in this period. Statistical significance testing of the experimental data showed:

- Fractional conversion and yield of light hydrocarbon products increased with time
- Mineral properties of the additives were more significant in increasing overall conversion than the additive surface areas

- The relative magnitudes of the additives effects were shown to be:

Effect on increase of overall conversion:

$\text{FeS}_2 > \text{FeS}_2/\text{Fe}_{0.9}\text{S} > \text{Fe}_{0.93}\text{S}, \text{FeS}(\text{tech}), \text{moly ore}$

Effect on increase of THF-insoluble H/C ratios:

$\text{FeS}_2 > \text{moly ore}, \text{FeS}_2/\text{Fe}_{0.9}\text{S}, \text{FeS}(\text{tech})$

Effect on increase of preasphaltene H/C ratios:

$\text{FeS}_2 > \text{moly ore} > \text{FeS}_2/\text{Fe}_{0.9}\text{S}, \text{Fe}_{0.93}\text{S}, \text{FeS}(\text{tech})$

- An indication of a synergistic effect on the activity of iron sulfide catalysts in the system with total sulfur content of the coal was found.

OBJECTIVE AND SCOPE OF WORK

Colorado School of Mines is conducting coal hydrogenation research with the following objectives and scope of work:

1. Comparison of the rates of coal hydrogenation in continuous flow stirred tank and tube flow reactors using pure hydrogen, catalyzed CO-STEAM, and syngas processing conditions.

2. Investigation of the influence of coal properties on the rate of hydrogenation of coal to preasphaltenes, asphaltenes, and oil in batch reactors.

3. Evaluation in a CSTR of the effect of operating conditions (temperature, added catalysts, and pressure) on the rate of hydrogenation of coal-derived preasphaltenes and asphaltenes.

4. Determination of the effect of selected disposable catalysts on the rate of batch hydrogenation of selected bituminous coals. Testing and evaluation of promising catalyst systems in the continuous processing units.

5. Formulation of a unified kinetic/mechanistic model for coal liquefaction taking into account petrography of the feed coal and hydrocarbon lumps in the product oil.

Task I Milestone Chart

ix

Summary of Technical Progress

Task I - Continuous Coal Processing Studies

The objective of this task is to utilize the continuous-flow bench-scale coal liquefaction reactor system at CSM to investigate the rate of reaction of different coals at different processing conditions. Particularly, reaction rates at short residence times are to be measured in a Continuous Flow Stirred Tank Reactor (CSTR), and this information used to model reactions in the Plug Flow Reactor (PFR) section of the unit.

Figure 1 presents a schematic diagram of the continuous processing system. The unit consists of the following components: (1) feed and mixing tanks, (2) slurry feed pump, (3) tube-flow preheater, (4) tube-flow reactor, (5) stirred-tank reactor, (6) two high pressure gas-liquid separators, (7) one low pressure gas-liquid separator, (8) gas compressor and gas delivery system, (9) gas measurement and sampling system, (10) liquid sampling system, and (11) associated pressure and temperature control systems. The unit has been designed for maximum flexibility with respect to reactor type, both stirred tank and tubular flow reactor configurations; and with respect to gas-liquid contact times, either premixing of gas and slurry before preheating or mixing of gas and liquid in the reactor. The scale of the unit is indicated by the stirred tank reactor which has an effective liquid phase volume of 0.5 liters, the separators which are 2 liters in volume, and the tube flow reactor which has a volume of 0.366 liters. The system is designed for a maximum coal treatment rate of 36 lb/day.

The experimental plan consists of the following phases:

1. Modification of the unit to allow operation at short residence times (5-10 minutes). Tune-up of the unit as necessary.

Figure 1

Continuous Processing Unit Schematic

Figure 2

Symbol Key for Continuous Processing Unit Schematic

	Compressor	GC	Gas Cylinder
	Feed Pump	He	Helium Gas
	Recycle Pump	FM	Flow Meter
	Rupture Disc	SC	Sample Cylinder
	Manual Valve	AV	Air Valve
	Check Valve	CV	Control Valve
	Metering Valve	GH	Gas Holding
	Heat Exchanger	LK	Liquid Knock-out
	Line Filter	LH	Liquid Holding
	Inline Thermocouple	PM	Pressure Measuring Device
	Surface Thermocouple	PIC	Pressure Indicating Controller
	Fluidized Bed Preheater	PR	Pressure Recorder
	Pressure Switch	P	Pressure Gauge
	Magnetic Stirrer	DC	Dessicant Column
	Stirrer	CS	Caustic Scrubber
	Heater	AGS	Acid Gas Scrubber
	Regulator Valve	TIC	Temperature Indicating Controller
		TF	Tube Flow Heater Section
		STR	Stirred Tank Reactor
		HPS	High Pressure Separator
		LPS	Low Pressure Separator

2. Measurements of thermal hydrogenation rate data. These data will be baseline data for the remainder of the project. A fixed gas treatment rate, fixed solvent to coal ratio, and a fixed pressure will be used for this study.

3. Measurements of thermal CO-Steam rate data for comparison with baseline data using the same gas treatment rate, solvent-to-coal ratio, and operating pressure.

4. Measurements of catalytic CO-Steam data following the work of Chour, Stenberg, Appel, and others.

5. Measurements of catalytic hydrogenation data using the results of a parallel batch reactor study in this laboratory.

No further progress was made on this Task during this reporting period. During the upcoming quarter collection of the baseline data will be completed and measurement of thermal rate data will begin.

Task II

A. Coal Reactivity Study

The objective of this study is to determine the effect of physical and chemical properties of coal upon the rate of coal hydrogenation to products such as preasphaltenes, asphaltenes, and oils. The rates of conversion to these products and interconversion between them will be used to gauge reactivity. Models will be developed incorporating coal petrographic and physical-chemical composition as well as gross hydrocarbon lumps present in the liquefaction products.

The experimental portion of this study is being performed using a one-liter batch reactor manufactured by Autoclave Engineers, Inc. The experimental system shown in Figure 3 is designed to permit rapid injection of coal into the reactor, and to allow withdrawal of small slurry samples from the reactor during the course of an experimental run.

During this reporting period the final two coals in the suite PSOC 577, an unnamed Texas hvB bituminous coal and PSOC 737, a West Virginia Upper Kittanning hvA bituminous coal were run. Additionally, a run of the Colorado Energy coal (the feedstock for the disposable catalyst study, Task II,C) was accomplished at 360°C to provide temperature-rate data. Correlations between kinetic reactivity and several coal properties, reported previously (79ET 14881-4), were revised to include the new data. Further computer modeling was accomplished to check the degree of model complexity necessary to fit the mass fraction data.

Experimental Results

Two coals, PSOC 577 and PSOC 737, were run at the established reaction

Figure 3

Coal Reactivity Reactor System Schematic

conditions to complete experimental work on this suite of coals. The results of these runs, reduced by the constant weight ratio (CWR) method, are reported in Table 1.

Table 2 lists a 360°C temperature run of the Colorado Energy, disposable catalyst study feedstock coal. Also in Table 2 are the data from three other runs of this coal, two at 400°C and the third at 380°C. These data were reported previously (79ET 14881-3).

Table 3 lists the pseudo-second order reaction rate constants for the five runs (three coals) discussed above. The constants were evaluated by a least squares linear fit of the equation:

$$\frac{1}{x} = \frac{1}{ka^2} \frac{1}{t} + \frac{1}{a}$$

which is the integrated form of the pseudo-second order kinetic expression:

$$\frac{dx}{dt} = k (a-x)^2$$

where

x = fractional conversion of coal to THF solubles

k = pseudo-second order rate constant (min.fract.)⁻¹

a = pseudo equilibrium conversion

t = time (minutes)

In addition to these current data, the pseudo-second order fits for all 11 coals of the experimental suite and the comparable, 400°C data from the Colorado Energy and Fies Mine #9 coals are summarized in Table 4.

In a previous report (79ET 14881-3) the pseudo-second order rate constant was defined and described as a "kinetically-defined reactivity".

Table 1: Experimental Results for Two Coals

Run Number:		45	46	47	48
	Sample Time (minutes)				
% Conversion	5	32.5	28.5	42.2	41.7
	10	44.2	37.7	55.9	54.4
	30	58.0	53.9	69.5	68.9
	60	70.6	65.8	77.2	76.6
% Unreacted Coal	5	67.5	71.5	57.8	58.3
	10	55.8	62.3	44.1	45.6
	30	42.0	46.1	30.5	31.1
	60	29.4	34.2	22.8	23.4
% Preasphaltenes	5	14.6	12.6	24.2	24.0
	10	19.2	15.9	28.3	28.5
	30	24.1	20.9	28.8	28.7
	60	27.1	24.6	26.9	25.4
% Asphaltenes	5	15.0	14.8	15.9	16.7
	10	18.1	18.6	21.2	20.6
	30	23.4	23.7	26.9	26.8
	60	28.0	28.6	31.3	30.9
% Oil + Gas	5	2.9	1.1	2.1	1.1
	10	6.8	3.3	6.4	5.3
	30	10.5	9.3	13.8	13.4
	60	15.5	12.6	19.0	20.3
% Ash (Calculated)	5	6.7	7.7	22.8	23.1
	10	6.4	7.1	23.0	23.3
	30	6.3	6.3	23.5	23.4
	60	6.0	6.3	23.6	22.8
% Coal:		9.72	9.55	8.89	9.18
% Ash in Coal:		7.35		23.29	
Coal (PSOC #):		737		577	

Table 2: Experimental Results for Colorado Energy Coal

Run Number:		29	30	31	44
	Sample Time (minutes)				
% Conversion	5	36.4	39.5	--	22.0
	10	50.2	53.6	38.5	31.3
	30	67.8	71.1	52.3	42.4
	60	77.6	80.8	62.9	51.4
% Unreacted Coal	5	63.6	60.5	--	78.0
	10	49.8	46.4	61.5	68.7
	30	32.2	28.9	47.7	57.6
	60	22.4	19.2	37.1	48.6
% Preasphaltenes	5	16.4	16.2	--	6.4
	10	21.4	20.9	13.2	12.8
	30	23.8	23.8	18.4	18.1
	60	23.2	23.6	20.6	20.8
% Asphaltenes	5	14.8	13.7	--	9.6
	10	19.7	17.6	15.2	11.4
	30	26.6	23.4	20.3	14.5
	60	31.8	27.9	25.3	17.6
% Oil + Gas	5	5.3	9.7	--	6.1
	10	9.2	15.0	10.1	7.1
	30	17.5	24.0	13.5	9.8
	60	22.7	29.5	17.1	13.0
% Ash (Calculated)	5	4.9	5.1	--	5.2
	10	5.4	5.0	4.8	5.1
	30	5.0	4.7	4.9	4.9
	60	4.9	4.4	5.0	5.0
% Coal:		9.56	9.56	9.58	9.50
% Ash in Parent Coal:		5.45	5.63	5.63	5.38
Reaction Temperature ($^{\circ}\text{C}$):		400	400	380	360

Table 3: Pseudo-Second Order Rate Data

<u>Coal PSOC #</u>	<u>K</u>	<u>1/a</u>	<u>r²</u>	<u>a</u>	<u>k</u>
737	9.61	1.41	0.942	0.709	0.207
577	5.80	1.23	0.997	0.814	0.260
Colo. Energy (360°C)	13.76	1.81	0.996	0.553	0.237

Table 4: Summary of Pseudo-Second Order Fits

<u>Coal PSOC #</u>	<u>K</u>	<u>1/a</u>	<u>r²</u>	<u>a</u>	<u>k</u>
001	12.310	1.225	0.961	0.816	0.122
056	4.700	1.183	0.979	0.845	0.298
071	5.002	1.166	0.963	0.858	0.233
107	10.990	1.074	0.990	0.931	0.105
151	4.612	1.208	0.989	0.828	0.316
370	12.085	1.121	0.980	0.892	0.104
437	4.213	1.126	0.980	0.888	0.301
444	9.068	1.033	0.932	0.968	0.118
456	3.749	1.112	0.980	0.899	0.330
577	5.802	1.228	0.997	0.814	0.260
737	9.610	1.410	0.942	0.709	0.207
Fies Mine	5.680	1.048	0.964	0.954	0.193
CO Energy	7.412	1.171	0.983	0.854	0.185

Other researchers have used the term "reactivity" to apply to conversion of coal to soluble products in a given solvent at one point in time at set reaction conditions. Generally, the conversion measured after a fairly long reaction period (60 minutes) was used to define "reactivity". After long periods of reaction an equilibrium conversion ("a" by the pseudo-second order kinetics) is approached. That kinetically-defined reactivity values are more appropriate for correlation purposes than single-time conversion or equilibrium conversion values is aptly illustrated in Figure 4.

Figure 4 shows the pseudo-second order fits for the THF soluble conversion data from PSOC 444 and PSOC 456 plotted against time. This figure clearly illustrates the differences between a kinetically-defined reactivity and a single time conversion point definition. The pseudo-second order rate constants for PSOC 444 and PSOC 456 are $0.118 \text{ (min-mass fraction)}^{-1}$ and 0.330 , respectively. Thus, by a kinetic definition, PSOC 456 would be deemed substantially more reactive than PSOC 444. However, at 60 minutes, both coals have a fractional conversion of approximately 0.80. If data at this time only were taken the coals would be deemed equal in reactivity. Comparison of the pseudo-equilibrium conversions of the two coals ("a" values) would indicate that PSOC 444 is the more reactive ($a = 0.97$ versus 0.90 for PSOC 456). Thus, depending on the definition chosen for "reactivity" three separate conclusions could be obtained regarding the relative liquefaction characteristics of these two coals. Of the three approaches, the rate constant definition, k , is the only one which implies no time constraints on the resulting relative values of "reactivity" for two coals. This implies

Figure 4: Conversion Versus Time, PSOC 444 and PSOC 456

a more general applicability of this definition as the only constraints on the value are the reaction conditions and not the run time. It should be noted, however, that the pseudo-equilibrium conversion value, "a", becomes significant at longer reaction times. As the conversion approaches the equilibrium value, the rate constant, k, becomes less significant than the difference between x and a.

Correlations Between Coal Properties and Reactivities

The correlations between kinetically-defined reactivity (k for the pseudo-second order expression) and parent coal properties reported in the previous report (79ET 14881-4) have been modified to include data from the last two coals of the suite and to exclude data from the Fies Mine coal and the Colorado Energy coal. The exclusion of these coals was deemed advisable, as they were run only as tests of the reactor system integrity and were not part of the experimental coal suite.

These changes in the correlation base adversely affected the correlation coefficients (r^2) of the correlations of reactivity with the mean-max vitrinite reflectances, R_o (Figure 5) and the atomic H/C ratios (Figure 6). In the former case the r^2 value is 0.59 and in the latter, 0.31. However, the fits are improved very substantially by eliminating one "outlier" from each plot. In the case of the H/C ratio, if PSOC 444 is not considered in the correlation the r^2 value becomes 0.658. As discussed in the previous report (79ET 14881-4), the reactivity may show a substantial drop off at higher H/C ratios. This raises an important point. Fitting straight lines to these reactivity coal property correlations are only a first effort, and there is no fundamental indication that these fits should be correct. Future efforts will be directed

Figure 5: Reactivity, k , Versus R_0 of Coal

Figure 6: Reactivity, k , Versus H/C Ratio of Coal

toward expanding the data base such that non-linear relationships may be examined along with linear.

The mean-max reflectance correlation (Figure 5) is improved ($r^2 = 0.79$) by eliminating PSOC 737 from the correlation. That this should be the case is understandable when examining the maceral distribution of this coal relative to the other coals of the suite. PSOC 737 has a very low vitrinoid content, 53.3%, relative to the rest of the suite (average vitrinoid content, 81.4%). The reflectance of vitrinite should have the greatest influence on coals with high vitrinite contents. Since PSOC 737 was of low vitrinite content its elimination from the correlation was substantially justified.

Other researchers have shown correlations between the oxygen to carbon (O/C) ratio of coals and their conversions at a fixed time. Correlation of "k" and the O/C ratios of the coals was attempted for this suite. The resulting correlation is very poor ($r^2 = 0.299$). Figure 7 shows a plot of "k" versus O/C with the "best fit" correlation. A second regression line is given in Figure 7 with PSOC 444 and PSOC 737 eliminated from the calculations. The fit is still not good ($r^2 = 0.578$) and no justification for exclusion of these data exists.

The fraction of reactive macerals, defined as:

$$\frac{(\% \text{ vitrinite} \leq V6 \text{ reflectance}) + \% \text{ liptinites} - \% \text{ sporinites}}{100 - \% \text{ inertinites}}$$

is plotted against kinetic reactivity, k, in Figure 8. This correlation fits all 11 coals with an r^2 value of 0.70. Once again, PSOC 444 and PSOC 737 are the most significant outliers, although the fit is still good even with their inclusion in the correlation.

Figure 7: Reactivity, k , Versus O/C Ratio of Coal

Figure 8: Reactivity, k , Versus Fraction of Reactive Macerals

Computer Modeling

As reported previously (79ET 14881-4), a non-linear parameter estimation program coupled with a Runge Kutta-plotting routine is being used to examine various models for coal product interactions. A complex seven-parameter model was reported in the previous report and the similarity of its parameters with the pseudo-second order models discussed. A less complex (fewer parameters) model was sought. To this end, several "series" reaction models were explored. These models were tested by running two coals which had shown markedly different rate constants in the seven-parameter model (PSOC 071 and PSOC 370), and markedly different rates of pentane-soluble oil formation.

The first model examined was the simple series model:

The resulting fits to the data for PSOC 071 and 370 are shown in Figures 9 and 10. The number of parameters was increased by adding pseudo-second order terms to the coal reactions, so that:

$$\frac{dc}{dt} = -k_1 (C - \alpha)^2$$

where α was defined as the fraction of dry mineral matter free coal which was unreactive at the given reaction conditions. This improved the fits somewhat, as illustrated in Figures 11 and 12. The "unreacted coal" fraction was substantially improved, as would be expected.

It should be noted that the "dmmr" value on the plots was given by the NLPE program as the "determinant of the moment matrix of residuals",

Figure 9: First Order Series Model
3 Parameter - PSOC 071

Figure 10: First Order Series Model
3 Parameter - PSOC 370

Figure 11: Series Model; Second Order in Coal
4 Parameter - PSOC 071

Figure 12: Series Model; Second Order in Coal
4 Parameter - PSOC 370

the "residuals" being the differences between the experimental values for each of the component concentrations and the model-predicted value for the variable. The closer the value of this determinant is to zero, the better the fit of the model to the experimental data. The values of this variable for each of the fits is given on the appropriate plot as the "dmmr" value. For a fit to be good by empirical (visual) evaluation, a value of the dmmr less than 10^{-9} is required for the coals for which two runs were made. The dmmr value is usually higher when more runs had been made on a given coal.

A five-parameter series model was generated by adding "reversibility" to the asphaltenes to oils reaction (Figures 13 and 14) and a six-parameter model by allowing reversibility of the preasphaltenes to asphaltenes reaction (Figures 15 and 16). Addition of these parameters causes the models to become gradually better fits to the data.

The "series" models, though, were felt to be unrealistic in the constraints that they implicitly placed on the actual mechanisms of coal liquefaction. The series-parallel model which was discussed in the last report did not, for example, limit the reaction of coal to preasphaltene formation only. Although the exact mechanisms of the coal reactions are not known with any precision, it is quite feasible for coal to react initially to asphaltenes or oils as well as preasphaltenes. The series models place an artificial restraint on the mechanisms of coal liquefaction by disallowing such reactions. Until the true reaction pathways can be determined, none of the proposed models can be expected to have a fundamental physical meaning and the "reaction rate constants" represent only statistical "best fits" and not true physical parameters.

Figure 13: Series Model; 2nd Order $C \rightarrow P, A \rightarrow O$ Reversible
5 Parameter - PSOC 071

Figure 14: Series Model; 2nd Order C → P, A → O Reversible
5 Parameter - PSOC 370

Figure 15: Series Model; 2nd Order C → P, P → A → O Reversible
6 Parameter - PSOC 071

Figure 16: Series Model; 2nd Order $C \rightarrow P$, $P \rightarrow A \rightarrow O$ Reversible
6 Parameter - PSOC 370

Tetralin Consumption

As a cross check for the solvent-donor effect of the tetralin to naphthalene solvent reaction, gas chromatographs of the pentane soluble fractions at each time (5,10,30, and 60 minutes of reaction) were run. The chromatograph was equipped with a 12 meter x 0.2 mm ID fused silica capillary column coated with a liquid phase of methyl silica oil (SP-2100) on deactivated carbowax 20M. The system was calibrated with known tetralin-naphthalene samples so that the weight ratio of naphthalene to tetralin could be calculated for each time sample. The results of these analyses are illustrated by Figure 17 which shows the naphthalene/tetralin weight ratio plotted as a function of time for Run #40 of PSOC 456. This figure clearly illustrates the hydrogen donor effect.

Future Work

Submission of publications of this work are currently underway and should be completed shortly. In the upcoming reporting period refinement of the coal property-reactivity correlations will be engaged and further examination of the data base will continue to ascertain the most efficient approach to continued experimental work. Correlation of kinetic reactivities with coal properties as determined by pyrolysis-mass spectrometry and NMR will be examined. In subsequent reporting periods selection and experimental runs on other coal suites than bituminous coals will be initiated.

Figure 17: Naphthalene to Tetralin Mass Ratio
Versus Time of Sample

B. Hydrogenation of Preasphaltenes and Asphaltenes Study

The objective of this study is to determine the reaction sequence and analyze the kinetics of the following reactions:

1. The conversion of asphaltenes to preasphaltenes and oils
2. The conversion of preasphaltenes to asphaltenes and oils.

The overall reaction scheme to be studied is shown below:

This project will study these reactions using a donor solvent as well as gaseous hydrogen at high temperature and pressure.

The equipment to be used in this study is a continuous stirred tank reaction system. The overall unit consists of the following sub-systems:

1. Gas flow control system
2. Liquid feed system
3. Reactor system
4. Temperature control system
5. Liquid-gas separation system
6. Pressure reduction system
7. Gas sampling and clean-up system
8. Liquid product collection system.

A flow diagram and symbol key is shown by Figures 18 and 19.

During the past reporting period, calibration of the gas flow system was completed, and safety modifications on the reactor system were completed by the construction of a Lexan safety shield around the external liquid sampling system.

Figure 18

Flow Micro-reactor System Diagram

Figure 19

Key to Symbols for Flow Micro-reactor Systems

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B	Buret		Pump
D	Demister	NV	Metering valve
Three way valve		Liquid recovery
Check valve	PC	Pressure controller
Compressor	SC	Sample gas cylinder
Control valve/Regulator	M	Drive motor
Filter	MC	Motor control
FC	Flow controller		Valve
Gas cylinder	CSTR	Continuous stirred tank reactor
HPS	High pressure separator	T	Transducer
LC	Level controller	WTM	Wet test meter
LPS	Low pressure separator
Knock-out flask
Pressure guage (mounted)
Pressure guage (unmounted)		

Future Work

During the forthcoming reporting period tests of a model compound in the experimental system will be finished, and experimental work on the thermal rate of hydrogenation of asphaltenes will begin.

C. Disposable Catalysts Study

The objective of this study is to determine the influence of disposable catalysts and coal mineral matter upon the rate of hydrogenation of selected coals. The initial investigation in this area is a series of screening tests using disposable catalysts and a selected bituminous coal. Responses to be measured will be the rates of formation of preasphaltenes, asphaltenes, and oil and the rate of disappearance of unreacted coal. During the past reporting period, effort has been directed towards developing the proper experimental procedure for testing the effects of the catalysts. In doing so, ten- and sixty-minute baseline runs, along with the initial testing of selected catalysts, have been completed.

The experimental apparatus is shown in Figure 20. The reactor is a 300 cc batch, stirred tank reactor manufactured by Autoclave Engineers. The system has been designed to allow a small amount of concentrated coal slurry to be rapidly injected into the reactor from a sample vessel using high pressure hydrogen.

Experimental work on this phase of the disposable catalyst study and statistical analyses of the data have now been completed.

A two-way analysis of variance with unequal replicates was carried out on the data. Dunnett's method of comparison against a control enabled

Figure 20

identification of those additives which showed significant effects (Steele and Torrie, Principles and Procedures of Statistics:, New York, McGraw-Hill, pp 111-112(1960)). Table 5 gives a summary of the results of the study upon which the analyses were based. The effects of time and additives on the following responses were measured:

1. overall conversion
2. oil yield
3. asphaltene yield
4. preasphaltene yield
5. H/C ratio of asphaltenes
6. H/C ratio of preasphaltenes.

These results are discussed below.

Effect of Time

At a 95% significance level, an increase in residence time from 10 to 60 minutes increased overall conversion, oil, asphaltene, and preasphaltene yields, and effected the preasphaltene hydrogen-to-carbon ratios. Overall conversion increased from 32% for the 10 minute run to 61% for the 60 minute run with no additives present. Similar effects were seen with each of the additives tested, with total conversion increasing with increased residence time. These results are shown graphically in Figure 21. All runs (base and with additives) also resulted in increases in yields of oils, asphaltenes, and preasphaltenes as time increased from 10 to 60 minutes, as shown in Figures 22, 23, and 24.

These results are as expected. The greatest effect of time was seen in the yield of preasphaltenes, which accounted for the largest fraction

Table 5

Summary of Results of Disposable Catalyst Tests

<u>Time (minutes)</u>	<u>Additive</u>	<u>% Conversion</u>	<u>% Pre- asphaltenes</u>	<u>% Asphaltenes</u>	<u>% Oil</u>	<u>Preasphaltene H/C ratio</u>	<u>Asphaltene H/C ratio</u>
10	None	31.8	10.2	13.3	8.4	0.91	0.77
10	FeS ₂	39.4	20.5	8.5	10.4	0.91	0.78
10	FeS ₂ /Fe ₉ S	36.0	16.6	10.9	8.5	0.90	0.78
10	Fe ₉₃ S	31.0	12.4	7.8	10.8	0.94	0.77
10	FeS (tech)	30.8	16.9	4.1	9.8	0.92	0.77
10	moly ore	28.0	11.9	9.1	7.0	0.92	0.75
60	none	60.5	25.1	15.8	19.6	0.89	0.75
60	FeS ₂	70.6	37.1	19.9	13.6	1.25	0.95
60	FeS ₂ /Fe ₉ S	69.6	32.5	18.1	19.0	0.92	0.76
60	Fe ₉₃ S	61.6	30.1	13.1	18.4	0.86	0.74
60	FeS (tech)	61.8	30.8	11.4	19.5	0.88	0.72
60	moly ore	62.5	32.0	14.8	15.8	1.17	0.74

Figure 21. Effect of Time and Additives on Conversion

Figure 22. Effect of Time and Additives on Oil Yields

Figure 23. Effect of Time and Additives on Asphaltene Yields

Figure 24. Effect of Time and Additives on Preasphaltene Yields

of the observed increase in overall conversion with time. Oil and asphaltene yields were influenced to a lesser degree. These results are merely presented to substantiate the use of this coal for the catalyst screening study. Obviously, the coal is very refractory towards direct hydrogenation, and serves as a rigorous test of the ability of the additives tested to catalyze hydrogenation reactions. These results also emphasize the importance of the preasphaltenes in coal hydrogenation. Catalysts capable of hydrogenating the preasphaltene fraction will be required to effectively alter the thermal yield structure of this coal, as most of the increased conversion with increased time goes into this fraction. Thus, the chemistry of the preasphaltene fraction must be examined closely for evidence of apparent catalytic activity.

Effect of Additives

Analysis of variance of the data indicated that additives had a significant effect (95% confidence level) on overall conversion (10 and 60 minutes), preasphaltene yields (10 and 60 minutes), hydrogen-to-carbon ratios for the preasphaltenes (60 minutes) and THF-insolubles (60 minutes). Dunnett's method for comparison against a control identified FeS_2 and the mixture of $\text{FeS}_2/\text{Fe}_9\text{S}$ as having had significant effects on overall conversion at 60 minutes residence time, while only FeS_2 was significant at 10 minutes (Figure 21). None of the additives could be identified as responsible for the increased preasphaltene yield (Figure 24), while FeS_2 was found to be responsible for the observed increase in THF-insoluble hydrogen-to-carbon ratios at 60 minutes (Figure 25). Both pyrite (FeS_2) and moly ore exhibited significant effects on preasphaltene hydrogen-to-carbon ratios, as shown in Figure 26.

Figure 25. Effect of Time and Additives on THF-Insoluble H/C Ratios

Figure 26. Effect of Time and Additives on Preasphaltene H/C Ratios

Pyrite appeared to be the active form of iron sulfide responsible for increasing the rate of hydrogenation in this study. As shown previously (Reports 79ET 14881-3, -4) added pyrite was rapidly converted in high yield (80%) to pyrrhotite during reaction, with little incremental conversion occurring past 10 minutes. However, the enhancement of coal conversion obtained with added pyrite could not be reproduced when pyrrhotite derived from the pyrite was substituted as the additive. This result is contrary to the findings of other researchers who report pyrrhotite to be the active iron-sulfide compound. Looking more closely at the previous studies revealed some possible explanations for this discrepancy.

Wright and Severson (ACS Div. Fuel Chem. Prepr., 16 (2), 69 (1972)) found FeS to exhibit catalytic properties in the hydrogenation of coal. Using raw anthracene oil as the solvent, they tested washed coal insolubles from a Kentucky No. 11 HVb bituminous coal for catalytic activity towards hydrogenation. The washed coal insolubles contained the following percentages of sulfur: 0.5% sulfate, 0.1% pyritic, 1.9% organic, and 3.0% sulfide sulfur. Granoff et al. (U.S.D.O.E., Liq. Div. Coal Conv. Conf., Albuquerque (1978)) found chemical grade pyrrhotite to give an 8% increase in conversion when using an Illinois No. 6 coal. The coal contained 1.25% pyritic sulfur and 2.15% organic sulfur. Guin et al. (I.E.C., Proc. Des. and Dev., 18 (3), 371 (1979)) demineralized a Kentucky 9/14 blend coal and an Illinois No. 6 coal and reacted these coals with mineral additives. They found reduced pyrites to show significant catalytic activity for the hydrogenation and dehydrogenation of solvent, the ultimate direction of the reaction depending

upon the initial hydrogen partial pressure. The Kentucky 9/14 blend contained 2.69% sulfur, while the Illinois No. 6 coal contained 2.7% sulfur.

All of the coals tested in these studies contained between 2.69% and 5.5% sulfur in various forms. The coal used in this study contained only 0.56% sulfur, 85% less than the coals used in the previous studies. Therefore, it seems that a small but significant amount of sulfur, either in pyritic or organic form, may be necessary to activate FeS or reduced pyrite to show catalytic activity towards hydrogenation. These results suggest that small amounts of H_2S are responsible for maintaining the active iron sulfide species in the reactor. H_2S is formed upon the reduction of pyrite and organic sulfur moieties in the coal, which would have occurred when the coals used in the previous studies were tested.

In an attempt to verify this hypothesis regarding the effect of additional sulfur/ H_2S in the reaction mixture, one additional 60 minute run was performed. For this run, two grams of dibenzothiophene were added to the reactor during heat-up, thus raising the total sulfur level of the coal (after injection) to approximately 2.25%. Two grams of the coal-derived pyrrhotite ($Fe_{.93}S$) were used as the additive.

Overall conversion was raised to 66.75% over the 60.54% conversion of the base runs. This figure lies between the 61.56% conversion obtained using the $Fe_{.93}S$ additive without the dibenzothiophene and the 70.60% which resulted from using FeS_2 as the additive. The oil yield increased to 18.90% for this run, compared to 18.37% for the run with the $Fe_{.93}S$ additive without added sulfur, 13.60% for the run with the FeS_2 , and 19.62% for the base runs. The asphaltene yield was 17.93% for this run, 19.94%

for the FeS_2 run, 13.05% for the $\text{Fe}_{.93}\text{S}$ run without the added sulfur, and 15.82% for the base runs. Preasphaltene yield was 29.92% compared to 37.07% for the FeS_2 run, 30.14% for the $\text{Fe}_{.93}\text{S}$ without added sulfur, and 25.09% for the base runs.

Gas analysis indicated no H_2S in the reaction gas atmosphere following the run, and Mossbauer spectroscopy of the THF-insolubles following the run showed the additive to be essentially still 100% pyrrhotite after reaction. Comparison of the overall conversion and fractional yields obtained from this additional run to the results from the pyrite and pyrrhotite (without added sulfur) runs, indicates that a synergistic effect exists between the total sulfur level of the reaction mixture and the effectiveness of the sulfide additive. It is well known that elemental sulfur was blended with certain German coals hydrogenated in the 2-stage Bergius process during the 1930's (Wu and Storch, U.S.B.M. Bull. 633 (1968)). This result indicates the potential need for added sulfur as well as disposable catalysts in processes designed for the hydrogenation of certain unreactive U.S. coals with low inherent sulfur content.

Effect of Additives on THF-insoluble Hydrogen-to-Carbon Ratio

At the 60 minute residence time, FeS_2 was the only additive to have a significant effect on the THF-insoluble H/C ratio. The THF-insoluble ratio resulting from using the FeS_2 was 0.95, compared to 0.75 for the base runs. This was not a surprising result since the FeS_2 showed catalytic activity towards increasing the overall conversion for the 60 minute runs.

No additives were found to exhibit any significant effects on the THF-insolubles hydrogen-to-carbon ratio at the 10 minute residence time.

The experimental results are shown graphically in Figure 23.

Effect of Additives on the Preasphaltene Hydrogen to Carbon H/C Ratio

Only coal-derived pyrite and the moly ore showed significant effects on the preasphaltene H/C ratio at the 60 minute residence time. These results are shown in Figure 26.

The catalytic effects of Co/Mo and Co/Mo/Al in coal liquefaction have been documented (Tarrer et al., Div. Fuel Chem. Prepr., 16 (2), 68 (1976), Granoff et al. (1978)). These results have indicated possible catalytic properties for molybdenum. The small percentage of molybdenum present during the moly ore runs appeared to have little effect on overall conversion and product yields. However, at a 60 minute residence time, it was found to have increased the H/C ratio to 1.17. This increase may indicate the possibility of the moly ore having catalytic activity towards hydrogenation. The amount of ore, and therefore molybdenum, may not have been large enough to have had more substantial effects.

Effect of Additive Surface Area on Overall Conversion

The BET Gas Adsorption Method was used to determine the surface area of the parent coal and the additives used in this study. All of the samples were outgassed at 110°C for 16 hours prior to the surface area determination. Results of the analysis are given in Table 6.

Table 6

Surface Area of the
Parent Coal and Additives

<u>Sample</u>	<u>Surface Area (m^2/g)</u>
Parent Coal	10.9
FeS_2	1.3
$\text{FeS}_2/\text{Fe}_{.9}\text{S}$	2.1
$\text{Fe}_{.93}\text{S}$	4.1
FeS (tech)	0.9
Moly Ore	1.2

A linear regression was attempted to correlate surface area with conversion. The r^2 factor was equal to 0.05 for the 60 minute runs and 0.01 for the 10 minute runs, indicating no correlation between additive surface area and conversion.

Conclusions

The following conclusions were drawn from the results of this study:

- 1) An increase in residence time resulted in an increase in overall conversion and fractional yields of light hydrocarbon products.
- 2) Pyrrhotite does not appear to be the active form of iron sulfide responsible for increasing conversion and product quality. Evidence exists to indicate the necessity of having added sulfur and/or H_2S available to maintain the catalytically active iron sulfide form.
- 3) The mineral properties of the additives were more important in increasing overall conversion than the physical state (i.e. surface area).
- 4) The tested additives had the following relative magnitudes of effects:

Catalytic activity for increasing overall conversion:

$FeS_2 > FeS_2/Fe_{.9}S > Fe_{.93}S, FeS \text{ (tech), moly ore}$

Catalytic activity for increasing THF-insoluble H/C ratios:

$FeS_2 > \text{moly ore, } FeS_2/Fe_{.9}S, Fe_{.93}S, FeS \text{ (tech)}$

Catalytic activity for increasing preasphaltene H/D ratios:

$FeS_2 > \text{moly ore} > FeS_2/Fe_{.9}S, Fe_{.93}S, FeS \text{ (tech)}$

Future Work

This study will be extended during the upcoming quarter to further investigate the effect of added sulfur/ H_2S on iron sulfide activity. Various pyrite impregnation techniques, including vacuum vapor deposition will also be examined.