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MECHANISMS AND KINETICS OF COAL HYDROGENATION

Quarterly Progress Report for Period October—December 1980

By
J. H. Gary
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January 1981
Date Published

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Colorado School of Mines
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U. S. DEPARTMENT OF ENERGY

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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 safety modifications to the CSM continuous processing unit were completed to shield the control room from the gas and liquid-solid product sampling systems. A mass balance analysis of sample representability was begun.

All but two of sixteen coals in the suite of coal reactivity study coals have been run. Computer modelling of proposed reaction networks was started. Initial efforts at coal property versus reactivity correlations were begun.

Feed material preparation for the asphaltene hydrogenation study was completed, and preliminary testing of the reactor system was begun.

The experimental portion of the disposable catalyst study screening program was completed. Conclusions are pending statistical analyses of the data.

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 unit.

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

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 varied processing conditions. In particular, 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. To provide an idea of the scale of the unit the stirred tank reactor has an effective liquid phase volume of 0.5 liters, the separators are 2 liters in volume, and the tube flow reactor has a volume variable between 0.031 and 0.366 liters. The system is designed for a maximum coal processing rate of 20 lb/hr-ft³.

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 Chou, Stenberg, Appel, and others.

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

During this reporting period a sampling enclosure was constructed from 3/8 inch Lexan. The purpose of this structure was to contain any spills which inadvertently occur when sampling product liquids during pressurized operation of the system. Vapors which enter the enclosure are vented back through the reactor room rather than into the control room as had previously been the case.

The caustic wash system, part of the gas sampling system, has also been modified. Formerly, the caustic (NaOH) was placed in a two-liter side arm flask on an open lab bench. The revamped system is contained in a 3/8 inch Lexan liquid-tight enclosure. In the event of a system overpressurization, containment of a spill would be assured by the Lexan shield.

In the last report (79ET14881-3) it was indicated that the values for preasphaltene and asphaltene contents obtained in the reproducibility runs

were questionable. The data indicated a problem in obtaining representative samples. On the assumption that settling of solids in the system was causing this sampling problem, a mass balance on the continuous unit has been undertaken. The purpose of this mass balance is to determine whether all of the solid material being charged to the system is recoverable through the sampling system during operation of the unit. The mass balance is being conducted at ambient temperature and at a pressure between 1000 and 2000 psi of nitrogen. A slurry composed of tetralin and coal in a 4:1 weight ratio is being used to simulate normal operating conditions. Samples are taken at fifteen minute intervals as per normal running procedures, however, the method of sampling is being alternated between two techniques. Half of the samples are taken with a brief line flush prior to draining of the two 500 milliliter sample holding tanks as was done during previous runs on the system. The other half of the samples are taken directly, with no line flush, to determine whether solids settling in the holding tanks may have been the cause of the nonrepresentative samples. The feed tank, plug flow reactor sections, and the stirred tank reactor are drained after the test run is complete. A test run has been completed but sample analysis is pending.

In the upcoming period the mass balance test will be completed and measurement of baseline hydrogenation yields will be continued.

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 is being 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.

At last reporting, six coals from the suite selected from the Penn State coal bank had been run and the data were reported on those and on a Kentucky, Fies Mine #9 coal and the Colorado Energy Mine #1 coal used in the disposable catalyst tests (see Task #IIC).

During the current reporting period six more of the PSOC coals have been run, one PSOC coal reported on earlier was run again, initial attempts were made at modeling the overall reaction network, and correlations between coal properties and pseudo-second order rate constants for total coal conversion were begun.

Experimental Results

Six more PSU sample bank coals were run during the past quarter. PSOC 130, a West Virginia, Pocahontas #3, medium volatile bituminous coal, PSOC 056, an Arizona #2, hvCb coal, PSOC 001, a Kentucky, Upper Elkhorn #3, hvAb coal, PSOC 236, a Colorado Basin B medium volatile bituminous coal, and PSOC 456, a Utah, Blind Canyon, hvAb coal were run twice each. Additionally

Figure 3

One Liter Batch Autoclave Reactor

PSOC 647, a low volatile bituminous coal from the Philpott seam in Arkansas has been run once. The data from these 11 runs are given in Table 1. These data were calculated by the constant weight ratio of coal (CWR) method described in the last progress report 79ET14881-3.

In order to check the rate constants previously determined, PSOC 444, a Colorado E, hvCb coal was run another time. The results of this run (Run #42) are given in Table 2 along with the results of the previous two runs on this coal. These data were calculated by the CWR method, and are discussed below.

Of the data reported in Table 1, three of the coals yielded data which are obviously in error. PSOC 130, PSOC 236, and PSOC 647 all yielded results which are widely scattered and which gave very poor correlations for the pseudo-second order coal reactivity fits as described in the last progress report. Examination of the properties of these three coals reveals the obvious similarities; all three coals are of lower volatility than other coals in the suite which were run successfully and all three coals have very high mean-max vitrinite reflectances relative to the other coals. Properties data are reported in Table 3 for all twelve of the coals which have been run to date.

A physical manifestation of this problem was visible for the runs in question in each case. Upon disassembly of the reactor system in each of the questionable runs conglomeration of solids was observed on all of the internal portions of the reactor which had been in intimate contact with the reaction mixture. This solid was present in flakes over the stirrer assembly, reactor baffle, and over the walls on the inside of the reactor vessel itself. This solid was very difficult to remove and had to be chipped from the walls of the vessel. Since most of the solid coal seems to have

TABLE 1

Reactivity Kinetic Data for Six PSOC Coals

Run Number: 32		33	34	35	36	37	38	39	40	41	43
Sample Time (min.)											
% Conversion	5	73.7	86.1	46.4	48.6	27.9	25.0	86.0	18.9	54.4	54.6
	10	61.3	45.5	59.4	59.5	42.2	39.1	82.6	86.6	66.3	64.9
	30	89.0	50.9	73.3	71.7	62.1	57.0	83.0	89.8	80.9	77.8
	60	91.1	92.1	85.6	80.0	73.8	71.0	87.4	89.8	90.1	86.8
% Unreacted Coal	5	26.3	13.9	53.6	51.4	72.1	75.0	14.0	81.1	45.6	45.4
	10	38.7	54.5	40.6	40.5	57.8	60.9	17.4	13.4	33.7	35.1
	30	11.0	49.1	26.7	28.3	37.9	43.0	17.0	10.2	19.1	22.2
	60	8.9	7.9	14.4	20.0	26.2	29.0	12.6	10.2	9.9	13.2
% Pre-Asphaltenes	5	8.5	7.6	16.6	18.3	14.6	11.9	10.3	9.6	23.4	25.2
	10	9.8	9.2	19.9	21.1	20.1	16.8	11.0	9.6	27.5	28.6
	30	11.6	13.6	19.8	20.4	27.3	20.8	15.4	13.3	26.2	26.1
	60	11.1	12.8	18.6	18.8	25.4	23.0	20.2	17.2	22.5	19.8
% Asphaltenes	5	9.5	12.3	12.6	13.1	13.4	14.8	10.9	11.8	16.5	17.8
	10	10.6	13.4	17.2	16.8	18.5	19.2	12.1	13.2	19.1	20.6
	30	15.3	17.1	23.0	22.4	25.2	27.2	16.8	16.9	26.2	26.9
	60	19.2	21.1	28.3	25.6	33.4	33.6	17.7	21.0	30.8	33.2
% Oil	5	55.7	66.3	17.4	17.1	-0.1	-1.7	64.8	-2.7	14.3	11.5
	10	40.8	22.9	22.2	21.6	3.7	3.1	59.4	63.8	19.7	15.8
	30	62.0	20.3	30.5	28.9	9.5	9.1	50.8	59.6	28.5	24.8
	60	60.8	58.0	38.7	35.5	15.1	14.4	49.5	51.6	36.8	33.8
% Ash (Calculated)	5	2.7	1.0	5.0	4.9	4.0	4.1	1.7	8.8	2.7	2.9
	10	3.4	5.2	5.1	4.9	3.4	3.8	1.9	1.7	3.1	3.0
	30	0.7	5.2	5.7	5.1	3.4	3.6	2.3	1.2	2.7	3.2
	60	0.5	0.4	8.5	5.2	3.3	4.1	1.4	1.2	2.5	3.0
% Ash in Coal		8.07	6.43			3.64		8.98		4.38	5.94
% Coal		9.80	9.76	9.76	9.73	9.69	9.71	9.74	9.45	9.57	9.72
Coal		PSOC 130		PSOC 056		PSOC 001		PSOC 236		PSOC 456	PSOC 647

TABLE 2

Reactivity Kinetic Data for PSOC 444

	Run #	42	16	17
	Time (Min)			
% Conversion	5	40.1	35.7	30.8
	10	57.3	51.6	47.5
	30	77.4	72.1	68.6
	60	89.4	86.6	85.5
% Unreacted Coal	5	59.9	64.3	69.2
	10	42.7	48.4	52.5
	30	22.6	27.9	31.4
	60	10.6	13.4	14.5
% Preasphaltenes	5	18.6	16.9	13.5
	10	25.9	22.0	19.4
	30	30.7	26.0	24.7
	60	30.3	26.4	25.5
% Asphaltenes	5	15.6	16.5	14.9
	10	21.3	20.1	20.2
	30	29.0	27.5	26.7
	60	34.4	32.0	32.5
% Oil + Gas	5	5.9	2.4	2.3
	10	10.2	9.6	7.9
	30	17.7	18.5	17.2
	60	24.6	28.2	27.5
% Ash (Calculated)	5	2.5	1.63	2.06
	10	2.6	2.14	2.16
	30	2.3	1.79	2.00
	60	1.7	0.90	0.71
% Ash in Coal:		3.36%	2.81	2.94

$$k = 0.001402$$

$$a = 98.33$$

$$r^2 = 0.9988$$

$$k = 0.00109$$

$$a = 96.1$$

$$r^2 = 0.998$$

Table 3Reflectances, Volatilities, and Coal Reactivities

<u>Coal</u>	<u>R_o</u>	<u>Volatility</u>	<u>k</u>
PSOC 444	0.69	41.4	0.140
437	0.56	48.3	0.301
071	0.60	45.6	0.233
107	0.78	37.2	0.105
370	0.81	38.7	0.184
151	0.40	45.4	0.316
130	1.42	22.4	N/A
056	0.57	47.3	0.298
001	0.85	37.9	0.122
236	1.44	24.2	N/A
456	0.52	50.5	0.330
647	1.82	17.1	N/A
Fies Mine #9	0.69	N/A	0.193
Colo. Energy Coal	N/A	N/A	0.185

Key:

R_o = mean-max vitrinite reflectance

Volatility = % volatile on dmmf (PARR) basis

k = pseudo second order rate constant (mass fraction-min)⁻¹

N/A = not available

been caked onto the reactor system, very little solid material could have been drawn through the sampling lines. Since both the ash as tie element and CWR methods of data reduction depend on representative amounts of solids in the samples neither method yielded reasonable results. Furthermore, since good coal dispersion during reaction is doubtful based on these observations, it is not probable that a set of kinetic constants for these runs would be meaningful even if they could be obtained. These problems narrow the scope of the study somewhat, since reproducible data can apparently be obtained only for the higher volatile coals at these reaction conditions. It is possible that this agglomeration effect might be minimized by running at a lower temperature (Guin, et al., Ind. Eng. Chem. Process Des. Dev., 15, 490 (1976)), but as a substantial data base has already been obtained at 400°C and several of the coals run to date are in very short supply no plans currently exist to pursue this proposition.

Table 4 gives the pseudo-second order reaction rate constants for the three coals for which data were successfully obtained. The constants were calculated for two replicate runs at each of four times (5,10,30, and 60 minutes) for the reaction of coal to THF soluble products on a dmmf basis. The model, as discussed in the last report is:

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

where x = fractional coal conversion to THF solubles

k = pseudo-second-order rate constant (mass fraction-minutes)⁻¹

a = equilibrium fractional conversion

t = time (minutes)

Table 4

Pseudo-Second Order Rate Constants for Three Coals

Coal:	PSOC 056	PSOC 001	PSOC 456
Run #'s:	34, 35	36, 37	40, 41
K:	0.04702	0.1228	0.03733
1/a:	0.01183	0.01226	0.01112
* r ² :	0.9793	0.961	0.980
** k:	0.298	0.122	0.331
*** a:	84.5	81.6	89.9

Fit of 8 points (2 runs, 4 times) for production of THF-soluble coal products by the model:

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

with solution:

$$x^{-1} = Kt^{-1} + a^{-1}$$

where:

$$k = \frac{1}{ka^2}$$

* - correlation coefficient

** - pseudo second-order rate constant, (mass fraction - min)⁻¹

*** - pseudo equilibrium conversion

The constants are evaluated by a least squares fit of the integrated form of the model:

$$\frac{1}{x} = \frac{1}{ka^2} \left(\frac{1}{t}\right) + \frac{1}{a}$$

Computer Modeling

Initial work has been done on computer analysis of potential reaction networks for the conversion data obtained thusfar. A versatile Share Program Library Agency routine for "Nonlinear Parameter Estimation and Programming" is being used for this purpose.*

The form of the program used in these initial studies is a Gauss-Newton, weighted least squares program with great versatility in terms of setting upper and lower boundaries on unknown parameters and concentration variables.

Several models were tested for the Fies Mine coal and Colorado Energy coal data. As selection of the simplest feasible model is still pending only one, fairly complex, model is shown here.

The Fies Mine coal, for which six runs were made as reproducibility tests, was modeled very successfully by the complex reaction network:

where: C = Unreacted coal
 P = Preasphaltenes
 A = Asphaltenes
 phi = Oil + gas

* Y. Bard, Program No. 360D-13.6.003, Triangle Universities Computation Center, Research Triangle Park, N.C. (1967)

The rate constants, k_i , are first-order irreversible rate constants, except for those involving the unreacted coal fraction. These constants (k_1 , k_2 , and k_6) are pseudo-second order. The modeling equations are:

$$\begin{aligned} dC/dt &= -(k_1+k_2+k_6)(C-\alpha)^2 \\ dP/dt &= k_1(C-\alpha)^2 - (k_3+k_4)P \\ dA/dt &= k_2(C-\alpha)^2 + k_4P - k_5A \\ d\phi/dt &= k_6(C-\alpha)^2 + k_3P + k_5A \end{aligned}$$

Here, α is considered to be a seventh unknown parameter and represents, effectively, the fraction of unreactive organics present in the parent coal.

These constants were obtained for several of the coals and are reported in Table 5. Consideration of the model indicates that the sum of the three rate constants k_1 , k_2 , and k_6 should correlate very well with the pseudo-second-order rate constants previously reported. In Table 6 the sum $k_1+k_2+k_6$ for each of the eight coals is reported along with the k values from the second-order conversion correlations. Additionally, the value of $1-\alpha$ should correlate well with the parameter "a" from the second-order modeling work. As shown in Table 6, acceptable agreement is observed between these two constants. As may be seen, almost identical reactivity rankings are obtained when using either the lumped first-order rate constants ($k_1+k_2+k_6$) or the pseudo-second-order rate constant. This result lends considerable support to the techniques being used for reactivity determinations for this study.

By substituting the constants into a Runge-Kutta numerical integration program which has been modified by the addition of a plotting routine the

Table 5

Rate Constants for Seven-Parameter Model for Eight Coals

COAL	k_1	k_2	k_3	k_4	k_5	k_6	α
Colo. Energy Mine	0.0792	0.0674	0.0055	0.00141	0.0	0.0442	0.1476
PSOC 151	0.1094	0.1019	0.0073	0.00275	0.0	0.0916	0.1656
PSOC 370	0.0565	0.0454	0.0087	0.00026	0.0	0.0078	0.1203
PSOC 444	0.0467	0.0441	0.0088	0.0	0.00265	0.0141	0.0263
PSOC 437	0.1166	0.1096	0.0072	0.00171	0.0	0.0687	0.1085
PSOC 071	0.0436	0.0590	0.00	0.00002	0.00060	0.0937	0.1110
PSOC 107	0.0345	0.0324	0.0011	0.00188	0.0	0.0294	0.0439
Fies Mine #9	0.0791	0.0750	0.0075	0.0	0.00044	0.0440	0.0484

$k_1, k_2, k_6 = (\text{mass fraction} - \text{min})^{-1}$

$k_3, k_4, k_5 = \text{min}^{-1}$

Table 6

Comparison of the Seven-Parameter Model with the Coal-Conversion Model

COAL	Seven-Parameter Model		Coal Conversion Model	
	$*k_1+k_2+k_6$	$**100(1-\alpha)$	$*k$	$**a$
Colo. Energy Mine	0.1908	85.2	0.185	85.4
PSOC 151	0.3029	83.4	0.316	82.8
PSOC 370	0.1097	88.0	0.104	89.2
PSOC 444	0.1049	97.4	0.109	96.1
PSOC 437	0.2949	89.1	0.301	88.8
PSOC 071	0.1963	88.9	0.233	85.8
PSOC 107	0.0963	95.6	0.105	93.1
Fies Mine #9	0.1981	95.2	0.193	95.4

* Units = (min-mass fraction)⁻¹

** Percentage conversion to THF solubles

calculated curves for the mass fractions versus time have been plotted. The experimental data have also been plotted on the same set of coordinates. One such plot, for the six runs of the Fies Mine coal and the seven-parameter model given above is shown in Figure 4.

Correlations Between Coal Properties and Reactivities

Initial attempts were made to establish correlations between the pseudo-second order coal reactivities and coal properties. Many correlations between coal properties and conversion at a fixed time have been reported in the literature in recent years. Several of these established correlations were examined for this data base and in many cases similar correlations were found for our kinetically-defined reactivities. Particularly good correlations were found when the pseudo-second order rate constants were plotted against the mean-max reflectances of the coals (Figure 5), and atomic H/C ratios (Figure 6). The correlating equations and r^2 (goodness of fit values) determined from linear least-squares fits are shown on the figures.

Examination of these figures particularly the H/C ratio plot reveals the reason for the extra run of PSOC 444 reported in Table 2. In all correlations PSOC 444 is a substantial "outlier". Since PSOC 444 was the first sample bank coal run in these experiments it was postulated that inconsistencies in early operator techniques might have caused erroneous data. The rerun of this coal did, indeed, yield a substantial change in the value of k , but not a sufficient enough difference to account for its large deviation from the correlation curves. It is possible that the PSOC 444 data point is real, that the k values do decrease substantially

Figure 4

FIES MNE, RUNS 07-15

Figure 5

VARIATION IN RATE CONSTANT WITH REFLECTANCE

Figure 6

VARIATION IN RATE CONSTANT WITH H/C RATIO

at higher atomic H/C ratio values. Other researchers have reported similar trends when comparing short residence time yields with carbon content (Whitehurst, D. D., ACS Symp. Ser. 139, p 143, 1980). Additional data in this same range of H/C ratios would be needed to properly evaluate the validity of the data point.

Initial attempts at correlating the pseudo-second order rate constants as a function of the classically defined reactive maceral fraction, that is, as a function of vitrinites plus liptinites were unsuccessful. A more detailed examination of the maceral analyses of the suite of coals has led to the correlation shown in Figure 7. In this correlation the reactive maceral fraction was developed in the following manner:

- 1) The basis for the correlation was the complete maceral analysis given by the Pennsylvania State University data bank. Unfortunately, not all of the reported analyses included weight percent values. Therefore, DMMF volume percent values have been used.

- 2) The reactive maceral fractions were calculated on an unreactive maceral free basis. This assumption was justified by noting that the rate constant was calculated by incorporating an equilibrium conversion value into the kinetic model. Therefore, the exclusion of unreactive macerals should approximate the basis used in the kinetic model.

- 3) The reactive maceral fraction included the lower reflectance vitrinites (V6 and lower) and the liptinites, excluding sporinite. The vitrinites were divided after noting that k was a negative function of vitrinite reflectance, as shown in Figure 5. Sporinite was excluded from

Figure 7

VARIATION IN RATE CONSTANT WITH REACTIVE MACERALS

the reactive maceral fraction based upon reports by Given, et al., that sporinite is less reactive than vitrinite (Whitehurst, ACS Symp. Ser. 139, p 23, 1980).

4) A medium reactive fraction including higher reflectance vitrinites (V7 and higher), pseudovitrinite, and sporinite was excluded from the reactive macerals, as were all inertinite macerals.

5) Numerically the reactive maceral fraction can be presented as

$$\text{Reactive maceral fraction (DMMF)} = \frac{\text{Reactive macerals}}{100 - (\text{inertinites} + \text{medium reactive mac.})}$$

Future Work

During the next two reporting periods the final two coals in the suite, PSOC 577, and unnamed Texas hvBb coal and PSOC 737, a West Virginia Upper Kittanning, hvAb coal will be run. A third temperature (360°C) will be run on the Colorado Energy coal, so that activation energy and Arrhenius constant data may be calculated. Computer modeling will be refined to determine a suitable reaction network for the coals in the suite. Further development of correlations between coal properties and kinetically defined reactivities will be explored.

B. Hydrogenation of Preasphaltenes and Asphaltenes Study

The purpose 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:

The method of investigation used in this study consists of separation from solvent-refined coal of either preasphaltenes or asphaltenes by solvent extraction, concentration of the solution by rotary evaporation of the majority of solvent, and precipitation of the fraction using an appropriate solvent. The feedstock, either asphaltene or preasphaltene, will then be dissolved in a donor solvent and reacted in a continuous stirred tank micro-reactor at high temperatures (350-450°C) and hydrogen pressures of approximately 1500 psig.

The equipment to be used in this study is a continuous stirred tank reactor with the following subsystems:

- 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 in Figures 8 and 9.

Construction of the unit is essentially complete. The unit is currently being run through shakedown testing. Pressure testing has been completed on all the subsystems to assure that no leaks are present. Flow testing of the liquid feed system to correlate volumetric flow with pump setting has also been completed. Work is progressing on the testing of the pressure reduction system and flow testing of the gas flow system. Gas

Figure 8

Flow Micro-reactor System

Figure 9

Key to Symbols for Flow Micro-reactor Systems

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

flow into the unit is controlled by a metering valve located in the gas flow system. Volumetric flow rate is determined using a wet-test meter and correcting to standard conditions. A correlation between the setting on the metering valve and the volumetric flow rate is under development.

Testing of the temperature control system is yet to be completed.

The parameters to be investigated in this study are:

- 1) The effect of temperature on conversion (350°C , 400°C , 450°C).
- 2) The effect of pressure on conversion (1500 psig, P_2 - to be determined later).
- 3) The effect of residence time on conversion (most probably 15 min, 30 min, and 1 hour).

The study will begin with investigation of the reactivity of asphaltenes. The solvent used will be tetralin (98% pure) with a solvent/feed ratio of 9/1 on a weight basis (10% feed by weight). Completion of the separation of feedstock asphaltenes was accomplished this quarter. The apparatus and feed for this process consisted of a Soxhlet extraction apparatus and solvent refined coal from the Wilsonville SRCI pilot plant as a source of asphaltenes. An analysis of the solvent refined coal showed a 45% asphaltene content by weight. The solvent refined coal was extracted with benzene, at a process rate of 180g of the SRC each day. The solution was then concentrated using a rotary evaporator to produce a thick liquor. Pentane was then added to precipitate the asphaltenes, with additional washes with pentane to remove any benzene or oils from the concentrate.

Future Work

During the next quarter, completion of the unit testing will be

accomplished. In addition, the liquid recovery system will be modified as an added safety precaution. The external sampling system will be encased in Lexan with remote control for the removal of liquid products during operation. Finally, testing of a model compound in the unit 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 are the rates of formation of preasphaltenes, asphaltenes, and oil and the rate of disappearance of unreacted coal. During the past reporting period initial testing of selected catalysts has been completed and modifications in the methods of calculating the product yields were made.

The experimental apparatus used in this study is shown in Figure 10. The reactor used is a 300 cc batch, stirred tank reactor manufactured by Autoclave Engineers. The system is designed to allow a small amount of concentrated coal slurry to be rapidly injected into the reactor from an external sample vessel using high pressure hydrogen.

Modifications in Calculations

In this study, product quality is determined using selective solvent fractionation (SSF). In the last progress report, two methods of calculating the amounts of unreacted coal, preasphaltenes, asphaltenes, and oils in the product samples were given. The first method used coal-derived ash as a non-reactive tie element. The assumptions made using this method include:

- 1) Representative samples

Figure 10
300cc Batch Autoclave Reactor

- 2) Ash remains constant (i.e. no mineral reactions)
- 3) No ash is carried over with the SSF solubles.

The second method assumes a constant ratio between the weight of coal fed to the reactor and the total weight of material fed to the reactor (coal plus solvent). With this assumption, and by assuming representative samples, the amount of coal-derived materials in the product samples can be calculated directly from the sample weights.

The ash-tie-element method is very sensitive to small variations in ash content of the products. Therefore, the constant-weight ratio method (CWR), being less sensitive to these variations, was used to calculate product yields. These yields were compared to the ash-tie-element values to determine if the product samples were, in fact, representative.

Additional modifications were made to the data reduction method to account for solids segregation in those experimental runs in which there was a mineral additive. When the products were removed from the reactor, solid material would settle out and stick to the walls. This material was washed out of the reactor and included in the reactor wash sample. Upon ashing the reactor wash sample, a disproportionately high percentage of ash was found, indicating inhomogeneities in the product samples. Therefore, a correction factor to account for ash segregation between the product samples and the reactor wash was deemed necessary in both calculation methods for the runs with a mineral additive.

Sample calculations for both methods are presented in Appendix A.

Catalysts Tested

Results have been obtained using the following five disposable catalysts:

1) Moly Ore

A high grade ore obtained from AMAX Henderson Mine and ground to -200 mesh.

2) Coal-Derived Pyrite

Extracted from a high pyrite-content coal obtained from the Pittsburgh and Midway Coal Mining Company's Colonial Mine in Madisonville, Kentucky. After extraction, pyrite was ground to -200 mesh and analyzed for purity by Mössbauer spectroscopy.

3) Mixture of Coal-Derived Pyrite and Pyrrhotite

A few grams of the -200 mesh pyrite was hydrogenated using tetralin as a hydrogen-donor solvent and 2000 psig of hydrogen at 380°C for one hour. The product was analyzed by Mössbauer spectroscopy and found to contain 49% (wt %) pyrite (FeS_2) and 51% pyrrhotite ($\text{Fe}_{0.9}\text{S}$).

4) Pyrrhotite

A few grams of the -200 mesh pyrite was hydrogenated three times using the same procedure as in the pyrite-pyrrhotite mixture. Mössbauer spectroscopy showed the final product to be 100% $\text{Fe}_{0.93}\text{S}$.

5) Tech-Grade FeS

Purchased from a chemical supplier. After grinding to -200 mesh, a sample was analyzed by Mössbauer spectroscopy.

To test the mineral additives, the moly ore, 100% pyrrhotite and Tech-grade FeS were added to the reactor with the initial charge of tetralin.

This enabled accurate determination of the weight of the potential catalyst to the weight of coal in the reactor, which is a critical factor in determining the overall conversion and product yields. The pyrite and the pyrite-pyrrhotite mixture, however, could not be added directly to the tetralin for fear of reaction during heat-up. Therefore, these were added directly to the coal slurry. Knowing the exact amounts of additive and coal in the slurry and knowing that approximately 5% of the parent coal was soluble in tetrahydrofuran (THF), the uncharged coal/catalyst samples were washed three times with 100 ml of THF. The weight loss and, therefore, the amounts of coal and catalyst actually charged to the reactor were determined.

Results from the disposable catalyst study are shown in Table 7. The results from the baseline runs are included along with the results from the mineral additive runs.

Future Work

Statistical analyses of the data will begin in the upcoming reporting period. These will include a two-way analysis of variance (ANOVA) with unequal replication and Dunnett's method for comparison against a control. The effect of catalyst addition and time on various factors will be determined. Such factors include overall conversion, preasphaltene, asphaltene and oil yields, and H/C ratios and sulfur content of the various fractions.

The elemental analyses of the product fractions is being completed presently. In the coming quarter, the initial testing and statistical analysis will be completed.

Table 7

Results of Disposable Catalyst Study

Run No.	Time	Catalyst	% Conversion	% Preasphaltenes	% Asphaltenes	% Oil & Gas
C2	60	None	61.71	22.72	17.71	21.28
C9	60	None	60.49	19.54	20.21	20.74
C16	60	None	58.52	25.62	13.12	19.77
C25	60	None	61.71	25.14	16.94	19.63
C30	60	None	59.02	25.31	13.84	19.86
C34	60	None	61.78	32.23	13.09	16.46
C18	60	Moly Ore	61.67	30.98	14.55	16.14
C23	60	FeS ₂	70.60	37.07	19.94	13.60
C24	60	FeS ₂ /Fe _{.9} S	70.54	34.15	17.80	18.59
C28	60	FeS ₂ /Fe _{.9} S	68.71	30.90	18.39	19.40
C32	60	FeS (TECH)	61.76	30.79	11.41	19.54
C36	60	Fe _{.93} S	61.56	30.14	13.05	18.37
C5	10	None	33.42	8.02	22.57	3.17
C12	10	None	33.36	9.93	10.26	13.17
C26	10	None	28.69	12.71	7.07	8.91
C22	10	Moly Ore	29.67	12.25	9.27	8.16
C29	10	FeS ₂	39.39	20.54	8.46	10.38
C27	10	FeS ₂ /Fe _{.9} S	35.98	16.57	10.92	8.50
C31	10	FeS (TECH)	30.83	16.95	4.06	9.82
C35	10	Fe _{.93} S	31.07	12.40	7.83	10.84

APPENDIX A

Summary of Data Reduction Methods for Experimental Runs

Incorporating Mineral Additives in Task II-C

ASH AS TIE-ELEMENT METHOD

$$\frac{\text{wt. ash from catalyst}}{\text{wt. ash from coal}} = \left(\frac{\text{initial cat. wt.}}{\text{initial coal wt.}} \right) \times \left(\frac{\text{wt cat. after ashing}}{\text{initial cat wt.}} \right) \times \left(\frac{100}{\% \text{ ash in parent coal}} \right)$$

$$\begin{array}{l} \text{grams ash from} \\ \text{coal in samples} \\ (= \text{ash}_c) \end{array} = \begin{array}{l} \text{total weight} \\ \text{of ash from} \\ \text{sample} \end{array} \times \left(\frac{1}{1 + \frac{\text{wt. ash from cat.}}{\text{wt. ash from coal}}} \right)$$

$$\begin{array}{l} \text{THF organic insolubles} \\ (= \text{Tiorg}) \end{array} = \begin{array}{l} \text{THF insolubles} \\ \text{in sample} \end{array} - \begin{array}{l} \text{total weight of} \\ \text{ash from sample} \end{array}$$

$$\frac{\text{wt. ash}}{\text{wt. MAF coal}} = \frac{\% \text{ ash in parent coal}}{1 - \frac{\% \text{ ash in parent coal}}{100}}$$

TO CALCULATE ASH SEGREGATION CORRECTION FACTOR:

$$O = \begin{array}{l} \% \text{ of TOTAL, THFi} \\ \text{organics in samples} \end{array} = \frac{\Sigma (\text{sample wt} - \text{wt ash in sample})}{\begin{array}{l} \text{Total wt of} \\ \text{samples + wt} \\ \text{of reactor} \end{array}} \frac{\begin{array}{l} \text{Total wt of} \\ \text{ash in samples} \\ \text{+ ash in r.w.} \\ \text{wash} \end{array}}$$

$$A = \begin{array}{l} \% \text{ of TOTAL, ASH} \\ \text{in samples} \end{array} = \frac{\Sigma \text{ ash in samples}}{\begin{array}{l} \text{Total wt of ash} \\ \text{+ wt of ash in r.w.} \end{array}}$$

$$f' = O/A = \text{correction factor}$$

$$\% \text{ U. C.} = \left(\frac{\text{Tiorg}}{(\text{ash}_c) \times f'} \right) \times \left(\frac{\text{wt ash}}{\text{wt MAF coal}} \right) \times 100$$

$$\% \text{ PREASP} = \frac{(\text{wt Bi}) - (\text{wt Ti})}{(\text{ash}_c) \times f'} \times \left(\frac{\text{wt ash}}{\text{wt MAF coal}} \right) \times 100$$

$$\% \text{ ASP} = \frac{(\text{wt Pi}) - (\text{wt Bi})}{(\text{ash}_c) \times f'} \times \left(\frac{\text{wt ash}}{\text{wt MAF coal}} \right) \times 100$$

$$\% \text{ OIL \& GAS} = 100 - (\% \text{ U. C.} + \% \text{ PREASP} + \% \text{ ASP})$$

CONSTANT-WEIGHT RATIO METHOD

$$C^* = \frac{\% \text{ coal in Reactor}}{100} \times \text{wt sample} = \text{wt of coal represented by sample}$$

$$CAT^* = \frac{\% \text{ catalyst in Reactor}}{100} \times \text{wt sample} = \text{wt of catalyst represented by sample}$$

TO CALCULATE ASH SEGREGATION CORRECTION FACTOR:

$$M = \frac{(\text{total wt of samples before washes})}{(\text{total wt of material charged to reactor})}$$

$$B = \frac{(\text{Total wt of ash from samples})}{\text{total wt of ash from samples} + \text{wt of ash from reactor wash}}$$

$$f_M = B/M$$

$$\% \text{ OIL} = \frac{C^* - (\text{wt Pi}) + (CAT^* \times f_M)}{C^*} \times 100$$

$$\% \text{ ASP} = \frac{\text{wt Pi} - \text{wt Bi}}{C^*} \times 100$$

$$\% \text{ PREASP} = \frac{\text{wt Bi} - \text{wt Ti}}{C^*} \times 100$$

$$\% \text{ ASH} = \% \text{ ASH in parent coal}$$

$$\% \text{ UC} = 100 - (\% \text{ Oil} + \% \text{ PREASP} + \% \text{ ASP} + \% \text{ ASH})$$

FOR MAF BASIS:

$$\text{FRACTION} \times \frac{100}{100 - \% \text{ ASH IN COAL}}$$