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MECHANISMS AND KINETICS OF COAL HYDROGENATION

Quarterly Progress Report, July—September 1980

By
J. H. Gary
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Chemical and Petroleum-Refining Engineering Department
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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 modifications to the CSM continuous processing unit were completed to permit operation at short residence times, approximately 6.5 minutes. Reproducibility experiments have been completed, and during the next reporting period, collection of baseline data at short residence times will be started.

Experimental data collection in the area of coal reactivity has continued during the past quarter. Approximately one-half of the suite of bituminous coals chosen for study has been run, and kinetic modeling has been initiated. Analysis of the data from runs made to date indicates that coal conversion may be adequately modeled by a pseudo-second-order rate expression, and that the model is sufficient to differentiate between coal reactivities.

Baseline runs have been completed on the disposable catalyst study and a limited number of mineral matter additive runs using pyrite, pyrrhotite, moly ore, and MoS_2 have been made. The initial screening program will be completed during the next quarter.

Equipment modifications have been completed on the preasphaltene/asphaltene kinetics system and feed material preparation has been started. During the next quarter, feed material preparation will be completed and shakedown runs on the system will be made.

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, catalized 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 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. 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 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 1 (cont.)

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.

The work completed to date has included all the modifications, both to the equipment and to existing operating procedures necessary to attain shorter residence times and the tests required to probe the limits of the equipment itself. The experimental work is to be done with a minimum of preheat to the STR. Heating tests using creosote oil at 1900-2000 psig helium partial pressure were conducted to determine the amount of preheat necessary for the short residence times desired. The tests indicated that a preheat temperature of 340C was necessary to reach a reaction temperature of 430C at a residence time of 6.5 minutes, which are the highest temperature and the shortest residence time to be used during the experimental portion of this study. As Figure 2 indicates, the time the slurry is at 340C is small compared to the reaction time, thus preheat should have a negligible effect on overall conversion. When a residence time of 20 minutes is used no preheat is required. These data have essentially completed Phase 1 of the experimental plan. Work on Phase 2 commenced with the running of reproducibility tests. The fixed parameters were as follows:

Coal - Kentucky #9 from Pittsburg & Midway Coal Mining Co., Fort Lewis,
Washington Pilot Plant

Figure 2
Continuous STR Heating Curve

Solvent - Process Solvent sample #1295B from Pittsburgh & Midway
Coal Mining Co., Fort Lewis, Washington Pilot Plant
Solvent-to-Coal Ratio - 4:1 by weight

Pressure - 1900-2000 psig hydrogen

Gas Introduction Point - stirred tank reactor

Gas Treatment Rate - 15,000 scf/ton of coal

The reproducibility runs have been made using the following procedure.

The reactor is brought up to temperature and pressure simultaneously. When the desired operating conditions are attained, the unit is allowed to stabilize until a steady-state condition exists within the reactor. A period of 5 residence times has been found to be sufficient to reach steady state. At the end of the 5th residence time, the High Pressure Separator is emptied. Every $3/4$ of a residence time thereafter the High Pressure Separator is drained and a sample is transferred immediately into a centrifuge tube. This is repeated until 4 samples of about 10 grams each are obtained. The samples are subjected to solvent extraction to determine oils, preasphaltenes, asphaltenes, unreacted coal, and ash (see Figure 9). The conversions are calculated using maf ash as a tie element, with the exception of the oils and gas which are calculated by difference. Results of the reproducibility runs are shown in Table 1. The percent conversion figures show excellent reproducibility, and since they are calculated on a mass basis, can be considered valid.

Evaluation of the validity of preasphaltene and asphaltene values obtained is not complete at this time. The amounts of these fractions obtained indicates a possible sampling problem in obtaining representative samples for analysis.

During the next reporting period, work will be devoted to determining the best procedure to use to insure that representative samples are obtained

for analysis and the second phase of the study, (measurement of baseline hydrogenation yields) will be continued.

TABLE 1

RESULTS OF REPRODUCIBILITY TESTS FOR CONTINUOUS UNIT

RUN	TEMPERATURE C	RESIDENCE TIME (min)	CONVERSION (wt %)
CR7	350	20.5	33.97 $\pm$ 2.11
CR9	350	20.2	31.60 $\pm$ 1.07
CR8	430	6.5	68.78 $\pm$ 1.02
CR10	430	6.5	65.34 $\pm$ 1.49

RUN	PREASPHALTENES (wt %)	ASPHALTENES (wt %)	UNREACTED COAL (wt %)	GAS & OIL (wt %)
CR9	30.45 $\pm$ 1.12	43.88 $\pm$.896	68.41 $\pm$ 1.07	-42.73 $\pm$ 2.71
CR10	46.77 $\pm$ 2.49	73.29 $\pm$ 4.59	34.698 $\pm$ 1.45	-54.76 $\pm$ 6.34

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.

At last reporting, four coals from the suite selected from the Penn State coal bank had been run and the data were reported. Additionally, reproducibility data were reported for runs on a Kentucky, Fies Mine #9 coal.

During the current reporting period, the method of calculating the yields of coal products was modified, two more PSOC coals and the Colorado Energy Mine #1 coal used for the disposable catalyst studies were run, and initial attempts were made at data modeling using pseudo-second order rate expressions for the total conversion of coal to products data set (THF insolubles).

Modified Basis of Calculation

In previous studies, product quality was determined by selective solvent fractionation (SSF), using coal derived ash as a non-reactive tie element to calculate the amounts of unreacted coal, preasphaltenes, asphaltenes, and oils in product samples. The weight of ash in the sample was used in conjunction

Figure 3One Liter Batch Autoclave Reactor

with the parent coal ash content to determine the amount of total coal derived materials that should be present in the sample. The sample weights of preasphaltenes and asphaltenes obtained in the SSF procedure were divided by the amount of MAF coal derived material theoretically present to determine product yields. Unfortunately, the ash-tie-element method gave a significant number of negative conversions since this calculational method is very sensitive to small variations in ash content of samples taken during the run, especially in cases where the ash content of parent coal is low. Therefore, a different method of calculating yields was developed which is less sensitive to sample inhomogeneities.

The new method is based upon the ratio of the weight of coal fed to the reactor to the weight of total material (coal plus solvent) fed to the reactor. This ratio was assumed to remain constant during experimental runs, and that samples taken during the course of the runs contained this same ratio of coal derived materials to solvent. Using these assumptions the amount of coal derived materials in product samples was directly calculated from sample weight. Sample calculations for the ash-tie-element method and the constant weight ratio method (CWR) are presented in Appendix A. When using the CWR method, the percent ash in the coal derived products was calculated and compared to the parent coal ash value to determine whether or not representative samples were obtained during the experiment.

Tables II and III present data given in our last progress report, 79ET14881-2, with yields recalculated using the CWR method of calculation. The reported values are significantly different from the earlier results. Conversion values calculated by the CWR method do not show negative yields,

TABLE II

Reactivity Kinetic Data Calculated by CWR method

Run Number		16	17	18	19	21	22	23	24
Sample Time (minutes)									
	5	35.7	30.8	52.8	49.0	45.9	41.3	30.5	31.3
Conversion	10	51.6	47.5	66.2	63.4	56.5	54.1	42.0	46.4
	30	72.1	68.6	77.5	77.6	72.4	70.9	70.5	71.4
	60	86.1	85.5	84.5	85.5	84.5	82.9	80.4	81.6
Unreacted Coal	5	64.3	69.2	47.2	51.0	54.1	58.7	69.5	68.7
	10	48.4	52.5	33.8	36.6	43.5	45.9	58.0	53.6
	30	27.3	31.4	22.5	22.4	27.6	29.1	29.5	28.6
	60	13.4	14.5	15.5	14.5	15.5	17.1	19.6	18.4
% Pre- Asphaltenes	5	16.9	13.5	22.2	17.9	9.0	7.1	11.0	7.7
	10	21.9	19.4	25.4	22.0	12.0	11.7	15.8	14.4
	30	26.0	24.7	25.5	23.3	16.6	15.5	27.8	23.7
	60	26.4	25.5	23.8	19.3	18.8	20.3	26.7	22.5
% Asphaltenes	5	16.5	14.9	20.0	20.1	12.5	14.4	11.6	10.17
	10	20.1	20.2	22.1	25.0	15.6	17.17	15.7	15.0
	30	27.5	26.7	28.2	31.5	19.9	23.1	24.1	24.1
	60	32.0	32.5	31.4	36.7	23.8	24.1	29.9	29.7
Oil & Gas	5	2.4	2.3	10.5	11.0	24.3	19.8	7.9	12.9
	10	9.6	7.9	18.6	16.4	28.9	24.7	10.5	17.0
	30	18.5	17.2	23.8	22.8	35.8	32.3	18.6	23.6
	60	28.2	27.5	29.2	29.6	41.8	38.5	23.8	29.4
% Ash (Calculated)	5	1.63	2.06	1.93	2.10	5.95	5.61	4.18	4.53
	10	2.14	2.16	2.13	2.28	5.64	5.80	4.49	4.15
	30	1.79	2.00	1.88	1.52	5.69	6.19	4.57	4.82
	60	0.90	0.71	1.57	0.63	5.42	5.33	4.92	4.65
%Coal		9.60	9.55	5.58	5.28	8.35	9.62	9.61	9.60
% Ash In Coal		2.81	2.94	4.57		6.89	6.55	5.53	3.51
Coal (PSOC)		444		437		071		107	

TABLE III

Reproducibility Kinetic Data Calculated by CWR Method

		RUN7	RUN8	RUN9	RUN10	RUN11	RUN15	x + S
wt% Conversion (MAF)	5	51.11	43.45	44.67	47.31	43.43	45.69	45.9 + 2.9
	10	65.01	56.50	59.48	65.66	63.89	61.79	62.1 + 3.5
	30	83.57	79.95	79.39	86.78	79.29	77.10	81.0 + 3.5
	60	88.43	85.47	87.34	89.25	88.20	86.41	87.5 + 1.4
wt% UC (MAF)	5	48.9	56.6	55.3	52.7	56.6	54.3	54.1 + 2.9
	10	35.0	43.5	40.5	34.3	36.1	38.2	38.0 + 3.5
	30	16.4	20.1	20.6	13.2	20.7	22.9	19.0 + 3.5
	60	11.6	14.5	12.7	10.8	11.8	13.6	12.5 + 1.4
wt% Preasph (MAF)	5	20.1	21.8	15.6	18.2	16.0	21.2	18.8 + 2.6
	10	25.6	24.3	20.3	22.6	22.1	24.3	23.2 + 1.9
	30	27.7	28.9	26.2	25.6	26.9	25.3	26.8 + 1.4
	60	25.1	24.7	21.3	26.8	22.8	24.4	24.2 + 1.9
wt% Asph (MAF)	5	16.4	14.6	20.3	19.2	18.0	19.7	18.0 + 2.2
	10	19.7	22.9	25.1	23.5	21.9	25.2	23.1 + 2.1
	30	26.3	30.9	30.5	33.1	27.0	33.4	30.2 + 3.0
	60	26.1	34.8	34.6	32.3	29.9	37.1	32.5 + 4.0
wt% Oil & Gases (MAF)	5	14.6	7.1	8.9	9.8	9.4	4.8	9.1 + 3.3
	10	19.7	9.3	14.0	19.5	19.9	12.3	15.8 + 4.5
	30	29.6	20.1	22.7	28.1	25.4	18.4	24.1 + 4.4
	60	37.2	25.9	31.4	30.2	35.5	24.9	30.9 + 5.0
wt% Ash (calculated)	5	9.67	9.57	10.03	9.38	10.23	12.37	10.21 + 1.10
	10	9.44	9.67	10.43	8.51	9.02	9.68	9.46 + 0.65
	30	9.92	9.48	8.30	12.94	9.20	9.10	9.82 + 1.62
	60	10.61	9.47	9.59	8.76	10.08	8.81	9.55 + 0.72
								Overall: Ash =
								9.76 + 1.06

and no large negative oil and gas yields, particularly for coal PSOC 437 seen previously, were observed.

Possible sources of variation in ash level are deviations from ideal stirred tank reactor behavior in the reactor and hold-up of solids in the sampling line, both of which directly affect ash content. Since the majority of the coals in the suite selected for analysis are low in reported mineral matter content, approximately 5 wt%, and the ash-tie-element method of calculation is very sensitive to variations in ash content, the CWR method will be used in the future.

Experimental Results

Two more PSU coal bank coals were run during the past quarter. PSOC 370, a Kentucky, Hazard #7, HVAB coal and PSOC 151, a New Mexico, Lower Split of Blue, HVCB were run in duplicate. The data from these runs are reported in Table IV.

In order to help determine which of the two methods of calculation was more accurate, the coal being used in the disposable catalyst investigation, Task II-C, was also run. In Task II-C, a large number of reproducibility experiments for a Colorado Energy Mine #1, HVCB coal, were made in which quantitative selective solvent fractionation of all the reaction products was performed. Both methods of calculation gave similar results when using all of the products in the SSF procedure.

Three experimental runs were made using this coal, two at the conditions used in this study (400°C, 2000 psig H₂, and 10 wt% coal in tetralin) and one at conditions used in Task II-C (380°C, 2000 psig H₂, and 10 wt% coal in tetralin). The results of the 400°C experiments are shown in Table IV.

Table V gives the data from the disposable catalyst experiments in comparison to 10 and 60 minute samples from the 380°C run made in this study,

TABLE IV

Additional Reactivity Kinetic Data, CWR Method of Calculation

Run Number		25	26	27	28	29	30
Sample Time (minutes)							
	5	26.3	30.2	47.6	46.8	36.4	39.5
%	10	43.1	43.4	60.0	58.4	50.2	53.6
Conversion	30	66.2	64.5	73.6	70.5	67.8	71.1
	60	76.6	73.7	81.5	78.6	77.6	80.8
	5	73.7	69.8	52.4	53.2	63.6	60.5
%	10	56.9	56.5	40.0	41.6	49.8	46.4
Unreacted	30	33.8	35.5	26.4	29.5	32.2	28.9
Coal	60	23.4	26.3	18.5	21.4	22.4	19.2
	5	15.4	13.1	16.0	17.6	16.4	16.2
% Pre-	10	21.9	21.2	19.1	21.0	21.4	20.9
Asphaltenes	30	28.3	26.1	19.4	20.2	23.8	23.8
	60	25.7	25.9	17.2	18.0	23.2	23.6
	5	10.6	14.4	17.2	15.6	14.8	13.7
%	10	16.8	19.5	21.3	19.2	19.7	17.6
Asphaltenes	30	25.4	27.3	25.9	25.3	26.6	23.4
	60	31.2	32.4	29.7	30.3	31.8	27.9
	5	0.3	2.7	14.4	13.6	5.3	9.7
% Oil	10	4.3	2.7	19.6	17.5	9.2	15.0
	30	12.5	10.8	28.3	25.1	17.5	24.0
	60	19.6	15.4	34.6	30.2	22.7	29.5
	5	16.52	16.90	5.1	4.2	4.85	5.05
% Ash	10	16.90	17.54	4.0	4.8	5.35	4.95
(Calculated)	30	18.03	18.17	4.3	4.7	4.95	4.69
	60	18.15	18.52	3.6	5.2	4.88	4.44
% Ash in Coal		19.29	18.76	5.43	5.80	5.45	5.63
% Coal		9.65	9.63	9.58	9.66	9.56	9.56
Coal		PSOC 370		PSOC 151		Colorado Energy	

TABLE V

Comparison of 380°C Colorado Energy Mine Coal
Data to Disposable Catalyst Study Batch Data

	Calculated by Ash- Tie-Element Method		Calculated by CWR Method	
	Disposable		Disposable	
	Run 31	Cat. Baseline	Run 31	Cat. Baseline
% Conversion				
10 min	26.6	32.5	38.5	33.4
60 min	58.1	58.0	62.9	60.6
% Unreacted Coal				
10 min	73.5	67.5	61.5	66.6
60 min	41.9	42.0	37.1	39.4
& Preasphaltenes				
10 min	15.8	9.1	13.2	9.0
60 min	23.4	24.9	20.6	23.3
% Asphaltenes				
10 min	18.1	16.5	15.2	16.4
60 min	28.6	18.2	25.3	17.0
Oil + Gas				
10 min	-7.3	6.9	10.1	8.2
60 min	6.1	14.8	17.1	20.4

run 31. The ten-minute results show better agreement when calculated by the CWR method, while the 60-minute results are generally closer when calculated by the ash-tie-element method. Overall, it appears that the CWR method gives better agreement with the average baseline values being used in the disposable catalyst study. If mineral matter segregation does not take place, both the CWR and ash-tie-element approaches give identical results.

Modeling

Kinetic modeling of the experimental data is in its initial stages, and only simple kinetic models have been tested to date. Conversion data have been successfully modeled by pseudo-second-order kinetics. The rate of disappearance of unreacted coal was expressed by

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

where

x = coal conversion to THF solubles

k = pseudo-second-order rate constant

a = equilibrium fractional conversion

t = time in minutes

This rate expression was integrated and rearranged to give the following expression:

$$\frac{1}{x} = K\left(\frac{1}{t}\right) + \frac{1}{a}$$

where, $K = \frac{1}{ka^2}$

K and $1/a$ were determined using a linear least squares fit for $1/x$ as a function of $1/t$. Table VI shows K , $1/a$, r^2 , and 95% confidence limits on K for the coals run to date. The least squares fit modeling used 8 data points (2 experiments, 4 samples per experiment) for all the coals except the coal

TABLE VI

Linear Regression Coefficients for Psuedo-2nd-Order Fit of Conversion⁻¹ vs Time⁻¹

Coal	PSOC#	1/a	K+95% C.L.	k	r ²
Kent. Fies Mine #9	---	0.01048	0.0568 $\pm$.0057	0.143	0.965
Colo. Colorado E	444	0.01041	0.0991 $\pm$ 0.173	0.109	0.970
Utah Utah B	437	0.01126	0.0421 $\pm$.0060	0.301	0.980
Wash. Rogers	071	0.01165	0.0583 $\pm$.0114	0.233	0.963
Ind. Brazil Block	107	0.01074	0.1101 $\pm$.0112	0.105	0.990
Kent. Hazard #7	370	0.01121	0.1213 $\pm$.0172	0.104	0.980
N.M. Lower Split, Blue	151	0.01208	0.0451 $\pm$.0048	0.316	0.989
Colo. Colo. Energy	---	0.01171	0.0739 $\pm$.0096	0.185	0.983

used in the reproducibility tests, for which there were 24 data points (6 experiments, 4 samples per experiment). Figure 4 shows the least squares model in comparison to experimental data plotted on a conversion as a function of time graph. As can be seen, second-order kinetics provide an adequate description of the experimental data.

Using the pseudo-second-order model, the New Mexico coal, PSOC 151, has the largest rate constant, $3.16 \times 10^{-3} \text{ min}^{-1}$, and would be considered the most reactive coal tested. The Kentucky coal, PSOC 370, and the Indiana coal, PSOC 107, would be considered the least reactive coals using this model. The ratio of the highest rate constant to the lowest rate constant is approximately 3 to 1. Additional work is being done to determine standard deviations on the calculated rate constants. It is interesting to note that different conclusions regarding reactivity would have been reached using an equilibrium definition for reactivity rather than the kinetic definition employed.

While the pseudo-second-order modeling permits evaluation of the suite of coals by a kinetically defined reactivity, it does not provide information about the selectivity of the conversion reactions to form preasphaltenes, asphaltenes, and oils. Additional modeling work is underway to expand the kinetically defined reactivity analysis to include the relative amounts of products formed.

Future Work

One additional coal, PSOC 001, has been added to the original suite of coals selected for investigation. This coal, a Kentucky upper Elkhorn #3 HVAB coal, was added because of its low vitrinite, 54.8%, and similar inertinite/liptinite amounts, 21.7% and 23.5%, respectively. During the next reporting period, the eight remaining coals will be tested. Work will continue on development of kinetically defined reactivity models.

FIGURE 4: CONVERSION VERSUS TIME FOR PSOC 151

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 5 and 6.

Modification of the unit has progressed to the point that all lines connecting the various systems have been completed, as well as installation of the motor, tachometer, and motor-drive control system. In addition, the installation and testing of a diaphragm seal on the compressor pressure controller has been completed.

Figure 5

Flow Micro-reactor System

Figure 6
KEY TO SYMBOLS

B	Buret		Pump
D	Demister	MV	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)		

With completion of the assembly of the unit, pressure testing of the unit was initiated. Pressure testing was done with helium gas at 500, 1,000, 1,500, and 2,000 psig. Connections and seals were tightened to eliminate any observed leaks.

Following pressure testing, flow testing of liquids at a pressure of 1500 psig was begun. Initial results of flow testing were erratic and not reproducible. The pump was then taken apart for cleaning and adjustment of internal valves. Once maintenance was completed, results of flow testing were reliable. The curve of pump setting versus flow rate is shown in Figure 7.

The choice of parameters to be used for this study has been made. The solvent will be tetralin (98% pure) with a solvent/feed ratio of 9/1 on a weight basis (10% feed by weight). The conditions to be varied during actual runs of the asphaltene portion of the study include:

Residence Time (most probably 15 min, 30 min, 1 hour)

Temperature (350°C, 400°C, 450°C)

Pressure (1500 psig, P_2 - to be determined later)

The feedstock of pure asphaltenes or preasphaltenes is now being obtained by extraction of solvent refined coal obtained from the Wilsonville SRC-I Pilot Plant. An analysis of solvent refined coal on hand shows an asphaltene content of approximately 45% by weight. An extraction procedure using benzene has been established with the capability of processing 180 g of solvent refined coal each day. The amount of asphaltenes successfully extracted and recovered has been averaging approximately 75% of the available asphaltenes (34% of the total solvent refined coal).

During the next quarter, the extraction and recovery of sufficient quantities of asphaltenes for the asphaltene portion of this study will be completed. In addition, final shakedown testing in the form of heat testing

Figure 7Pump Calibration Curve for Lapp Pump

will be completed on the unit. Finally, the running of a model compound to test the reaction system will be accomplished.

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 8. 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.

A reproducible experimental procedure has been developed for testing the coal and the catalysts. The following is a description of the procedure used for the baseline runs (i.e., the coal with no catalyst):

1. The empty, clean reactor and sample vessel are tared.
2. 140 gm of tetralin are charged to the reactor and the reactor is then reweighed.
3. The reactor and sample vessel are connected to the system and pressure tested for leaks using helium.

Figure 8
300cc Batch Autoclave Reactor

4. A slurry of approximately 22 grams of coal and 44 grams of tetralin is prepared, well mixed, and then charged to the sample vessel. The slurry which sticks to the mixing and loading apparatus is weighed and washed off with acetone. The slurry/acetone mixture is centrifuged and decanted. This procedure is repeated twice before the coal is dried and weighed to determine the unloaded coal.

5. The reactor is purged with hydrogen three times before pressurizing it to 400 psig (with hydrogen).

6. While the tetralin in the reactor is heating, a vacuum is drawn on the sample vessel to remove air. This is done by connecting a vacuum pump line to the quick connect off of V4 and opening V4 and V3 (see Figure 8). After the vacuum is drawn, the sample vessel is pressurized to the injection pressure with hydrogen.

7. When the tetralin reaches a temperature of 410°C, the coal slurry is injected into the reactor by opening V8. Timing begins the instant the injection pressure is realized in the reactor.

8. The reactor is kept at 380°C ($\pm$ 5°C) for the duration of the run (10 or 60 min) and the maximum pressure reached is recorded.

9. When the reaction time is reached, the heater is lowered and the reactor is cooled with a high speed fan.

10. After the reactor has cooled to ambient temperature, a gas sample is drawn into an evacuated sample bottle through V7. The remaining gases are vented through V6 and V5.

11. The sample vessel is removed, weighed, and the uncharged slurry washed out with acetone. The wash procedure described in step 4 is used to determine the uncharged coal.

12. The reactor is removed from the system and weighed.

13. The liquid products are poured into a tared blender which is then weighed.

14. The liquid products are divided into eight representative samples by first stirring the mixture with a high speed blender and then drawing the samples off using a pipet.

15. The reactor, blender, and pipet are washed with acetone according to the procedure in step 4.

16. After determining the sample weights, a series of washes are done, as outlined in Figure 9.

17. The remaining material after the washes, along with the unloaded and uncharged coal, the reactor wash-out material, and three samples of the parent coal, are placed in a muffle furnace. The temperature is increased slowly to 750°C, where it is maintained for at least two hours. From this the percentage ash from each sample is determined and an overall ash balance is done.

18. The gas sample is analyzed using a gas chromatograph. The oils, preasphaltenes, and asphaltenes are analyzed for elemental C, H, and N on a Carlo Erba Elemental Analyzer, and for total sulfur on a Leco Total Sulfur Analyzer.

Two methods of calculating the overall conversion and yields of the products (i.e., % preasphaltenes, % asphaltenes, % oils) were developed and are described in detail in the "Coal Reactivity Study, Task II-A" section of this report. In this study (Task II-C), both methods of calculation should yield comparable results since representative samples are more easily obtained. When this was not the case, the product samples were considered non-representative and the data were disregarded. Results from the baseline runs and the catalysts tested to date using both methods of calculation are

Figure 9

Selective Solvent Fractionation Analysis

* washes consist of 5 minutes of sonication,
5-10 minutes of centrifugation (1400-2100 G),
decantation, then drying after last wash;

PENTANE WASHES: three 150-ml. washes

BENZENE WASHES: one 200-ml. wash
two 150-ml. washes

THF WASHES: one 100-ml. wash
one 200-ml. wash
two 150-ml. wash

given in Table VII. These data must be regarded as preliminary, and thus discussion of the significance of the added minerals will be deferred until the experimental portion of the program has been completed. These results do, however, indicate the presence of catalytic activity for pyrite, pyrrhotite, and (surprisingly) no activity for MoS_2 and moly ore.

The moly ore is a high grade ore obtained from the AMAX Henderson Mine. The pyrite was extracted from a coal sample supplied by the Pittsburgh and Midway Coal Mining Company Colonial Mine in Madisonville, Kentucky. The MoS_2 was purchased from a chemical supplier.

The pyrrhotite was prepared by hydrogenating 48 grams of the coal-derived pyrite in the reactor for one hour in the presence of 140 grams of tetralin and 966 psig (cold pressure) of hydrogen. The product was subjected to both Mossbauer Analysis and X-ray diffraction to determine how much of the pyrite was converted. The results from the Mossbauer analysis are shown in Figures 10 and Table VIII. The top graph in Figure 10 is the pyrite before hydrogenation, and the bottom graph is the product after hydrogenation. Table VIII shows that 51% of the pyrite was converted to $\text{Fe}_{0.9}\text{S}$. X-ray diffraction, being able to give only semi-quantitative analysis ($\pm 10\%$), determined 50% of the pyrite to have been converted to $\text{Fe}_{0.9}\text{S}$.

Slight modifications in the experimental procedure were necessary when using the catalysts. The moly ore, pyrrhotite, and MoS_2 were added to the reactor with the initial charge of tetralin. This enabled accurate determination of the weight of catalyst to the weight of coal in the reactor, which is a critical factor in determining the overall conversion and product yields.

The pyrite, however, could not be added directly to the tetralin because it would partially react during heat up. Therefore, it was added to the coal

TABLE VII

Results of Disposable Catalyst Study

Run	Conditions		% Conversion	% Unreacted Coal	% Preasphaltenes	% Asphaltenes	% Oils
C2	60 min Base	(1)*	58.8211	41.1789	24.5136	19.2117	15.0959
		(2)*	61.7098	38.2902	22.7201	17.7059	21.2837
C9	60 min Base	(1)	58.1044	41.8956	20.9167	21.5154	15.6723
		(2)	60.4857	39.5143	19.5368	20.2125	20.7364
C16	60 min Base	(1)	56.2896	43.7104	27.0589	13.8779	15.3529
		(2)	58.5160	41.4840	25.6240	13.1239	19.7681
C25	60 min Base	(1)	58.6651	41.3348	27.1368	18.2916	13.2368
		(2)	61.7089	38.2911	25.1391	16.9390	19.6308
C18	60 min Moly ore	(1)	58.9120	41.0880	34.0433	16.0204	8.8481
		(2)	61.6698	38.3302	30.9815	14.5521	16.1362
C23	60 min FeS ₂ (Madisonville)	(1)	70.0209	29.9791	36.1066	19.5690	14.3620
		(2)	70.1925	29.8646	37.1019	20.2260	12.8075
C24	50 min FeS	(1)	65.0580	34.9421	37.2040	18.2219	9.6320
		(2)	69.2011	30.7990	34.4836	16.9066	17.8109
C5	10 min Base	(1)	34.6147	65.3853	7.8831	22.2380	4.4936
		(2)	33.4229	66.5771	8.0190	22.5667	3.1690
C12	10 min Base	(1)	30.3180	69.6820	10.3323	10.7391	9.2466
		(2)	33.3582	66.6418	9.9294	10.2603	13.1684
C26	10 min Ease	(1)					
		(2)					
C22	10 min Moly ore	(1)	22.0740	77.9260	13.7185	10.2748	-3.3479
		(2)	29.6750	70.3250	12.1460	9.2717	8.1573

*(1): Ash is used as the element

*(2): Coal fraction is used as the tie element

Figure 10

Mossbauer Analysis Results for Pyrite-Pyrrhotite

TABLE VIII

Mossbauer Analysis of Hydrogenated Pyrite Sample

Pyrite prior to Hydrogenation:

98% FeS_2 2% Fe^{2+}

Sample after Hydrogenation:

39% FeS_2 59% Fe_{1-x}S x was shown to be 0.102% Fe^{2+}

On a Weight Basis:

49.04% FeS_2 50.96% $\text{Fe}_{0.9}\text{S}$

slurry. Knowing the exact amounts of pyrite and coal going into the slurry and using the fact that approximately 5% of the parent coal is soluble in tetrahydrofuran (THF), the unloaded and uncharged coal/catalyst samples were washed three times with 100 ml of THF; the weight loss and, therefore, the amounts of coal and catalyst charged to the reactor were determined.

Assumptions have been made concerning the form of the catalyst in the products. The moly ore is assumed to have not reacted, whereas the pyrite is assumed to have completely reacted to form Fe_7S_8 . A product sample from the pyrrhotite run has been submitted for Mossbauer analysis and X-ray diffraction to determine how the catalyst has changed during the run. Mossbauer analysis results have not been received at the time of this report, but the X-ray diffraction shows the hydrogenated pyrite sample to have been completely converted to Fe_7S_8 .

When using the MoS_2 as a catalyst, the product samples cannot be ashed by the described procedure because the MoS_2 sublimes at 450°C . It was, therefore, necessary to locate an apparatus to ash the samples at low temperatures. USGS has such an apparatus available, and work on ashing the product samples has just begun.

In the coming quarter, initial testing of the catalysts will be completed.

APPENDIX A

Summary of Data Reduction Techniques for Task II-A
Using 30 min Data, Run #29

ASH AS TIE-ELEMENT APPROACH

ASSUMPTIONS:

1. Assume representative samples
2. Ash remains constant during run (ie, no mineral RXNS)
3. No ash carried over w/SSA solubles

wt ash in sample = wt ash of parent coal represented by sample

$$\frac{\% \text{ Ash in Ti}}{100} \times \text{wt Ti} = \frac{\% \text{ Ash in Coal}}{100}$$

x wt coal represented in sample

Wt of Coal Represented in Sample =

$$\begin{aligned} & \frac{\% \text{ Ash in Ti}}{\% \text{ Ash in Coal}} \times \text{wt Ti} \\ &= \frac{13.93}{5.45} \times 0.0989 = 0.253 \text{ g coal} \end{aligned}$$

on MAF BASIS:

$$\begin{aligned} \text{wt coal (MAF)} &= (\text{wt coal}) \left(1 - \frac{\% \text{ Ash in Coal}}{100}\right) \\ &= 0.253 \left(1 - \frac{5.45}{100}\right) \\ &= 0.239 \text{ g MAF coal} \end{aligned}$$

$$\begin{aligned} \% \text{ UC} &= \frac{\left(1 - \frac{\% \text{ Ash Ti}}{100}\right)(\text{wt Ti})}{\text{wt MAF coal}} \times 100 \\ &= \frac{(1 - 0.1393)(0.0989)}{0.239} \times 100 \\ &= 35.6\% \end{aligned}$$

$$\begin{aligned} \% \text{ PREASH} &= \frac{(\text{wt Bi}) - (\text{wt Ti})}{\text{wt MAF coal}} \times 100 \\ &= \frac{(0.1617) - (0.0989)}{0.239} \times 100 \\ &= 26.3\% \end{aligned}$$

% COAL IN REACTOR APPROACH

ASSUMPTIONS:

1. Assume representative sample
2. % "coal + coal products" in reactor is constant

% coal in reactor = % coal represented by sample

$$\frac{\% \text{ Coal in Reactor}}{100} \times \text{wt sample} =$$

wt of coal represented by sample

$$\frac{9.56}{100} \times 2.91 = 0.278 \text{ g}$$

$$\begin{aligned} \% \text{ OILS} &= \frac{\text{wt coal} - \text{wt Pi}}{\text{wt coal}} \times 100 \\ &= \frac{0.278 - 0.232}{0.278} \times 100 \\ &= 16.5\% \end{aligned}$$

$$\begin{aligned} \% \text{ ASPH} &= \frac{(\text{wt Pi}) - (\text{wt Bi})}{\text{wt coal}} \\ &\times 100 = 25.3\% \end{aligned}$$

$$\begin{aligned} \% \text{ PREASH} &= \frac{(\text{wt Bi}) - (\text{wt Ti})}{\text{wt coal}} \\ &\times 100 = 22.6\% \end{aligned}$$

$$\begin{aligned} \% \text{ ASH} &= \frac{(\% \text{ Ash, Ti})(\text{wt Ti})}{\text{wt coal}} \\ &= \frac{(13.93)(0.0989)}{0.278} = 5.0\% \end{aligned}$$

$$\begin{aligned} \% \text{ UC} &= 100 - (\% \text{ Ash} + \% \text{ PREA} + \\ &\quad \% \text{ ASPH} + \% \text{ OIL}) \\ &= 100 - (5.0 + 22.6 + \\ &\quad 25.3 + 16.5) = 30.7\% \end{aligned}$$

APPENDIX A (CON'T.)

$$\begin{aligned}\% \text{ ASPH} &= \frac{(\text{wt Pi}) - (\text{wt Bi})}{\text{wt MAF coal}} \times 100 \\ &= \frac{(0.2320) - (0.1617)}{0.239} \times 100 = 29.4\%\end{aligned}$$

$$\begin{aligned}\% \text{ OIL} + \text{GAS} &= 100 - (\text{UC} + \% \text{ PREA} + \% \text{ ASPH}) \\ &= 100 - (35.6 + 26.3 + 29.4) \\ &= 8.7\%\end{aligned}$$

On MAF BASIS:

$$\frac{100}{\% \text{ UC} + \% \text{ PREA} + \% \text{ ASPH} + \% \text{ OIL}}$$

x fract. = fract

eg:

$$\% \text{ ASPH (MAF)} =$$

$$\begin{aligned}&\frac{100}{30.7 + 22.6 + 25.3 + 16.5} \times 25 \\ &= 1.05 \times 25.3 = 26.6\%\end{aligned}$$