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MECHANISMS AND KINETICS OF COAL HYDROGENATION

January-June 1980

By
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July 1980

Work Performed Under Contract No. AC01-79ET14881

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Budget Summary
DE-AC22-79ET14481

Task I Milestone Chart

Task II Milestone Chart

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, CO-STEAM, and syngas processing conditions with and without added catalysts.
2. Investigation of the influence of coal rank and maceral distribution on the rate of hydrogenation of coal to preasphaltenes, asphaltenes, and oil in batch reactors.
3. Evaluation of the effect of operating conditions (temperature, pressure, and added catalysts) on the rate of hydrogenation of coal-derived preasphaltenes and asphaltenes in a continuous flow reactor.
4. Determination of the effect of selected disposable catalysts on the rate of batch hydrogenation of unreactive 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.

Summary of Technical Progress

Task I

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.

Work during the past 6 months has focused on completing modifications to the unit itself, as the bench-scale system was originally designed to be operated at residence times just under 30 minutes. The new residence times are to be, at the least, just less than 6 minutes. The experimental portion will be a comparative study of the effect of different processing conditions on the rate of coal liquefaction. These conditions will include thermal hydrogenation (no added catalysts) using hydrogen, CO-Steam, and syn-gas, and catalytic hydrogenation employing both hydrogen and CO-Steam reaction gas atmospheres. The current experimental plan will consist 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.
2. Measurement of thermal hydrogenation rate data. This will be baseline data for the remainder of the project. A fixed gas rate, fixed solvent to coal ratio and a fixed pressure will be used for this study.
3. Measurement of thermal CO-Steam rate data for comparison. The above conditions will remain fixed.
4. Measurement of catalytic CO-Steam data following the work of Chou, Stenberg, Appel and others.

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

During the past six months, work on the continuous unit has been confined to modifications and system tune-up. The tune-ups have included reworking the instrument air supply to provide clean well-regulated air for the controllers and air operated valves, a general clean up, inside as well as out, rerouting of various lines, and calibration of gauges. Major modifications have been necessary to provide for low residence times. The foremost was the installation of a Milroyal model "A" plunger pump with a capacity of 5 liters per hour. Some operational modifications were also necessary to handle the increased through-put, and testing of the system at all levels of pumping has just been completed. The pumping tests were run with a creosote oil and -200 mesh coal slurry under helium pressure from 1900-2000 psi, at ambient temperature. The slurry was a 4:1 solvent to coal ratio, which gave a coal throughput of 1.345 kg/hour at maximum flow. Maximum flow was 5.2 liters of slurry per hour which represented a residence time in the CSTR of 5.8 minutes. A linear relationship was developed between the pump % capacity and flow rate, or residence time (see Figure 1). Figure 1 indicates that a residence time of longer than 30 minutes with this pump will not be practical.

The work remaining to be completed in phase 1 is a test of the ability of the preheaters to heat the slurry at these high flow rates. This work has just been started and at this time no conclusions can be drawn. After these tests are completed the experimental portions of the research plan will be initiated.

Figure 1Slurry Pump Calibration

Milton Roy Slurry Pump
Milroyal Model A
Rated Capacity = 1.1 gph

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.

Early testing indicated that the system design, as last reported, was inadequate for the work at hand. The Ruska pump set up, which was to be used to feed the coal slurry to the slurry injection vessel, C1, did not work as planned as a great deal of slurry was held up in the pump and the lines which lead to C1. Since some of the coals to be studied were available only in small quantities this sample holdup required that far more slurry be prepared than actually reached the reaction vessel. In order to assure efficient coal utilization the Ruska pump and valve V3 (see p.7, Oct-Dec '79) have been removed. The modified system is shown in Figure 2. The procedure for injection has been modified appropriately, and slurry is now injected directly into vessel C1 through a 30 ml. syringe equipped with a 4" 17 gauge needle. The slurry is forced through the needle with pressure from a rubber bulb/stopper system. Once the slurry is in C1 the line between C1 and V2 is reinstalled and heatup is started. Following heatup, coal is injected into the reactor by pressurizing vessel C1, and opening valve V5.

Reproducibility Tests. A large amount of a Kentucky #9 coal was available for initial reproducibility tests on the system. This coal was not as completely characterized as the Penn State Coal Bank samples, but

Figure 2One Liter Batch Autoclave Reactor

substantial experimentation has been done on the coal in this laboratory and others in previous studies. Fifteen runs were made with this coal before experimentation started with the coal samples of more direct interest to the study. The objectives of these runs were:

1. Determine the reproducibility of data,
2. Establish a satisfactory operational technique for the system,
3. Determine proper temperatures and pressures prior to coal injection to assure the most rapid acquisition of stable reaction conditions (2000 PSIG H_2 , $400^{\circ}C$),
4. Determine coal/tetralin quantities in the slurry and reactor which gave 10% coal in the reactor after injection,
5. Test to what extent the product distribution was affected by the withdrawal of samples during the course of the run.

Many of the initial runs were plagued by small problems which were the results of operator inexperience and system peculiarities. After six runs, the more substantial problems had been ironed out. The last six runs in which there were no system or analytical problems which would obviously compromise results were used to establish the reproducibility of the system. These data are tabulated in Table 1. The solvent separation analysis method used in determining the asphaltenes, etc. is outlined in Figure 3. The data from Table 1 are shown in Figure 4 with error bars representing 90% confidence limits for all of the data obtained for the reproducibility tests. Also shown in Table 1 is a column representing the mean value for each sample, with a calculated standard deviation. This column was calculated with the high and low outliers rejected from the data set before the mean and standard deviation were computed. High and low outliers were identified from the data set, and a check was then run on the samples to indicate whether or not these data points

Table 1.

RESULTS OF REPRODUCIBILITY TESTS

	<u>TIME</u>	<u>RUN 7</u>	<u>RUN 8</u>	<u>RUN 9</u>	<u>RUN 10</u>	<u>RUN 11</u>	<u>RUN 15</u>	<u>$\bar{x} \pm S$</u>	<u>90 and 95% Limits</u>
% Conversion	5	44.35	36.24	39.55	37.85	38.64	55.83	40.10 $\pm$ 2.92	95:39.3 $\pm$ 3.1, 90:38.1 $\pm$ 1.4
	10	59.04	51.53	57.65	54.92	54.99	59.09	56.65 $\pm$ 2.04	56.2 $\pm$ 2.9
	30	81.82	77.17	72.26	89.10	74.71	73.73	76.86 $\pm$ 3.61	78.1 $\pm$ 6.3
	60	88.12	83.44	85.45	86.33	86.99	83.86	85.66 $\pm$ 1.35	85.7 $\pm$ 1.8
% UNREACTED COAL	5	55.6	63.8	60.4	62.2	61.3	44.2	59.99 $\pm$ 2.9	95:60.7 $\pm$ 3.1, 90:61.9 $\pm$ 1.5
	10	40.9	48.5	42.4	45.1	45.0	40.9	43.4 $\pm$ 2.1	43.8 $\pm$ 3.0
	30	18.1	22.8	27.7	10.8	25.3	26.3	23.1 $\pm$ 3.7	21.8 $\pm$ 6.4
	60	11.8	16.5	14.6	13.7	13.0	16.1	14.4 $\pm$ 1.3	14.3 $\pm$ 1.8
% PREASPHALTENES	5	22.9	24.6	17.0	21.5	17.4	17.2	19.8 $\pm$ 2.9	20.1 $\pm$ 3.3
	10	30.0	27.1	21.3	29.7	27.6	26.0	27.6 $\pm$ 1.6	95:27.0 $\pm$ 3.2, 90:28.1 $\pm$ 1.7
	30	30.6	33.0	35.2	21.0	32.8	29.0	31.4 $\pm$ 1.9	32.1 $\pm$ 2.4
	60	25.8	28.2	24.5	34.1	25.1	29.0	27.0 $\pm$ 1.9	95:27.8 $\pm$ 3.6, 90:26.5 $\pm$ 2.0
% ASPHALTENES	5	18.8	16.4	22.1	22.7	19.5	16.1	19.2 $\pm$ 2.3	19.3 $\pm$ 2.8
	10	23.2	25.6	26.3	30.8	27.3	27.0	26.6 $\pm$ 0.8	26.7 $\pm$ 2.5
	30	29.1	35.1	41.0	27.2	32.9	38.3	33.9 $\pm$ 3.9	33.9 $\pm$ 5.3
	60	26.8	39.7	39.8	41.0	32.9	44.1	38.4 $\pm$ 3.7	37.4 $\pm$ 6.3
% OIL + GASES	5	2.7	-4.8	0.5	-6.4	1.8	22.6	0.1 $\pm$ 3.4	-1.2 $\pm$ 4.1
	10	5.9	-1.2	10.0	-5.6	0.1	6.1	2.7 $\pm$ 3.8	2.6 $\pm$ 5.8
	30	22.2	9.1	-3.9	40.9	9.0	6.4	11.7 $\pm$ 7.1	14.0 $\pm$ 15.6
	60	35.6	15.6	21.1	11.1	28.9	10.7	19.2 $\pm$ 7.7	20.5 $\pm$ 10.1
% ASH IN COAL		10.87	10.66	10.86	10.88	11.00	10.30		

Figure 3

Solvent Separation Analysis

- * washes consist of 5 minutes of sonication, 5-10 minutes of centrifugation (1400-2100 G), decantation, then drying after last wash; 1st wash @ 150 ml solvent, 2nd & 3rd (& 4th in benzene washes) @ 100 ml solvent

Figure 4
Summary of Reproducibility Test Data

were due to non-representative samples from the reactor. For a constant density system, if samples from the reactor were representative, the percent ash in each sample withdrawn from the reactor should be a constant. Those data points rejected generally did not obey this simple principle in comparison to other samples from the same data set. This may provide an experimental basis for rejection of future data points on the basis of non-representative reactor sampling.

A substantial amount of variation was present in the data particularly in the 30 minute points as shown in Table 1. Several factors could contribute to these variations. Fifty grams of coal were drawn at a time for these experiments from a large batch of coal. Although great care was taken to thoroughly riffle the batch, variations within the sample in terms of surface oxidation and other such factors cannot be ruled out. Another potential source of error in these runs was the use of recovered solvents in the solvent separation analysis. Impurities in the solvents due to cross contamination in the rotavaps or poor distillation techniques in previous runs could have caused some loss of solvent integrity. This potential source of error was eliminated in later runs by using fresh solvents whenever possible. Another point of concern is the high precision with which the sample washes have been weighed. Since the sample size from the system has been minimized (3. grams at each time) in order to avoid substantial alteration of the reactant mixture during operation, the centrifuge tubes in which the SSA washes are carried out are weighed to four places after each set of solvent washes. For such precision to be meaningful, extreme care is required during sample washing and decantation as even a spurious fingerprint on the bottle will affect the weight at a 0.1 milligram level.

In order to determine whether the taking of samples during the course of the run caused variation in the conversion and product distribution, a run was made in which no samples were taken until sixty minutes had elapsed. By comparing this sample with the sixty minute samples obtained when 5, 10, and 30 minute samples were also taken during the run it could be ascertained whether there was substantial variation due to the depletion of reactant material during a run. The data are presented in Table 2.

Slightly higher conversions were noted and correspondingly higher product percentages were observed but the variations were not deemed unwarrantedly high especially in light of the interrun variabilities noted in the previous discussion.

The temperature-pressure profiles for a typical run are shown in Figure 5. In order to obtain the 400°C, 2000 PSIG H₂ operating conditions in as rapid a manner as possible after injection, the system is preheated to 425°C. This is accomplished by initially pressurizing to 400 PSIG H₂ and setting the heater controller to 430°C. When the temperature reads 425°C with the temperature still on the upswing the slurry in C1 is injected with 2000 PSIG H₂ on C1 by opening V5. This amounts to a 1000 PSI overpressure which quickly injects the slurry. The pressure in the reactor rises to 2000 PSIG and the temperature drops to 380°C. Within five minutes the temperature has stabilized at 400°C, with an accompanying pressure rise to 2200 PSIG. The pressure is back down to 2000 PSIG after 10 minutes due to pressure losses accompanying the first two sample drawoffs at 5 and 10 minutes.

Because the temperature-pressure profiles are not steady state at the 1 minute point in the run the proposed 1 minute sample was discontinued. Initial runs in the reproducibility tests showed values in this point which varied wildly (6.18 to 21.79% conversion) and sampling at this time was not deemed useful.

TABLE 2:

DATA FOR RUN #4, REPRODUCIBILITY TESTS
SAMPLES TAKEN ONLY AT 60 MINUTES

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Average Of Runs With Four Samples</u>
% Conversion	89.65	89.94	85.7
% Unreacted Coal	8.3	8.1	14.3
% Preasphaltenes	35.2	33.0	26.5
% Asphaltenes	31.3	27.8	37.4
% Oil & Gas	25.2	31.1	20.5

Figure 5

Temperature - Pressure Profile for a Typical Run

In order to obtain approximately 10% coal in the reactor on a weight basis, 50 grams of coal in 500 grams of reaction mixture was required. The reproducibility tests showed that by beginning with 50-52 grams of coal 9.6-9.8% coal in the reactor could be obtained. Of the 50 gram charge on the average 0.8 grams was "uncharged" and 1.29 grams was "uninjected".

Once the reproducibility tests were completed, the characterized coals from the Penn State coal bank were prepared for experimentation. Coals chosen for this study are shown in Table 3.

In order to avoid injection problems and analytical complications due to mass transfer limitations the coals were ground to -200 mesh for the work at hand. In order to avoid surface oxidation effects the samples were ground just before usage and were wet ground in a ball mill. Samples were dried under vacuum at 55°-80°C until thoroughly dry and then screened. The coal which did not pass through the screen was then reground, dried and screened again.

The first of the Penn State fully characterized samples selected for testing was PSOC 444, a Colorado high volatile B bituminous coal. This particular coal was chosen because of its extraordinarily high vitrinite content (94.4%).

PSOC 437, a Utah high volatile A coal was run next because of its similarity in maceral distribution to the Colorado coal. Then PSOC 071 and PSOC 107, a Washington HVC coal and an Indiana HVB, respectively, were chosen for their intermediate and low vitrinite contents. The results of these eight runs are tabulated in Table 4.

Two unanticipated problems should be mentioned at this point. First, the two runs on the Utah coal (PSOC 437) and an attempted third all yielded very poor coal injection characteristics. In the reproducibility runs tendency for

TABLE 3

Coals Selected for Experimental Work

FSOC#	rank	COAL		state	ULT. AN. (dmmf(PARR))				% min. matter	%S (daf)		MACERAL COMP. (dmmf vol%)		
		seam			C	H	N	O *		tot.	pyr.	vit.	iner.	lipt.
056	HVCB	Arizona #2		Ariz.	77.37	5.90	1.34	15.39	6.92	0.45	0.01	83.9	12.8	3.3
071	HVCB	Rogers		Wash.	78.00	5.88	1.68	14.44	7.41	0.58	0.07	86.5	7.7	5.8
107	HVBV	Brazil Block-Top Vein		Ind.	81.97	5.07	1.37	11.59	6.42	0.53	0.11	62.4	14.6	23.0
130	MV	Pocahontas #3		W.V.	91.37	4.33	1.13	3.17	7.19	0.56	0.04	76.5	23.2	0.3
151	HVCB	Lower Split of Blue		N.M.	78.37	5.87	1.24	14.51	5.80	0.47	0.05	78.6	10.8	10.6
236	MV	Colorado Basin B		Colo.	90.35	5.29	1.68	2.68	8.93	0.53	0.03	92.2	7.8	0.0
370	HVAB	Hazard #7		Kent.	83.97	5.77	1.64	8.62	21.17	0.67	0.04	71.7	18.6	9.6
437	HVAB	Utah E		Utah	80.26	6.20	1.47	12.07	5.63	0.51	0.11	92.1	6.0	1.9
444	HVBV	Colorado E		Colo.	78.87	6.47	1.57	13.09	2.46	0.46	0.06	94.4	3.9	1.7
456	HVAB	Blind Canyon		Utah	79.49	6.43	1.58	12.50	4.91	0.37	0.06	88.7	10.2	1.1
577	HVBV	unnamed		Texas	79.97	5.68	1.32	13.04	25.51	1.17	0.17	~87.2*	11.7	1.1
647	LV	Philpott		Ark.	91.70	4.60	1.87	1.84	6.24	0.76	0.07	89.3	10.7	0.0
737	HVAB	Upper Kittanning		W.V.	86.80	5.31	1.26	6.63	7.90	0.71	0.03	53.3	39.4	7.3

* oxygen by difference

* non-standard maceral designations used

TABLE 4

RAW REACTIVITY KINETIC DATA

RUN NUMBER:		16	17	18	19	21	22	23	24
SAMPLE TIME (minutes)									
CONVERSION	5	-12.28	0.32	-14.93	-14.13	36.72	30.81	6.86	15.47
	10	36.19	27.85	25.59	25.04	46.19	47.78	27.74	27.88
	30	55.82	53.37	43.97	30.40	66.15	69.07	63.90	67.11
	60	57.04	38.16	53.31	-10.14	79.94	78.72	77.86	77.99
UNREACTED COAL	5	112.3	99.7	114.9	114.0	63.3	69.2	93.2	84.4
	10	63.9	72.1	74.4	74.9	53.8	52.2	72.3	72.1
	30	44.2	46.6	56.1	69.6	33.8	30.9	36.1	32.9
	60	42.9	61.8	46.7	110.1	20.1	21.3	22.1	22.0
% PRE- ASPHALTENES	5	29.6	19.5	54.0	39.9	10.6	8.3	14.7	9.5
	10	29.0	26.6	55.9	45.0	14.8	13.3	19.7	19.4
	30	41.2	36.7	63.6	72.3	20.4	16.4	34.0	27.2
	60	84.6	108.5	71.7	146.3	24.2	25.3	30.3	27.0
ASPHALTENES	5	28.8	21.4	48.6	44.9	14.7	17.0	15.5	13.1
	10	26.5	27.8	48.7	51.2	19.3	20.1	19.6	20.1
	30	43.5	39.7	70.5	97.8	24.4	24.6	29.4	27.8
	60	102.2	138.1	94.5	278.6	30.7	30.0	33.9	35.5
% OIL & GAS	5	-70.7	-40.6	-117.5	-98.9	11.5	5.5	-23.4	-7.0
	10	-19.3	-26.5	-79.0	-71.2	12.1	14.3	-11.6	-11.7
	30	-28.9	-23.0	-90.1	-139.7	21.4	28.1	0.5	12.1
	60	-129.7	-208.4	-112.9	-435.0	25.0	23.5	13.8	15.5
% COAL		9.6	9.6	5.6	5.3	8.3	9.6	9.6	9.6
% RECOVERY		X	97.2	100 ⁺	100 ⁺	96.9	99.8	98.8	97.8
% ASH IN COAL		2.81	2.94	4.57		6.89	6.55	5.53	5.51
COAL (PSOC):		444		437		071		107	

the coal to plug the syringe when charging the C1 vessel had been noted, but back flushing of the needle usually remedied this situation. No such problems appeared with the Utah coal, but for some as yet unexplained reason only about half the coal in C1 passed into the reactor upon injection. This could be caused by swelling of the coal due to absorption of tetralin or some tendency of the coal to agglutinate in this solvent and form a nearly solid mass. There is evidence for the latter possibility in the results of the postrun mass balance on the vessel C1. Although, the coal-tetralin slurry mixture charged to C1 was 1:2 by weight the coal/tetralin mixture which was uninjected was 1.8:1, thus mostly coal was left behind after injection. For the two runs on the Utah coal only 5.6% and 5.3% coal reached the reactor, a considerable departure from the 9.5%-10.0% value desired.

The second problem encountered was with the Washington coal (PSOC 071). In this case great difficulty with charging the coal to C1 through the syringe was the adversity. Although this trouble had been seen previously, as mentioned above, the problem was much more profound in this case. In the first run only 8.35% coal eventually reached the reactor. The problem was encountered again in the initial attempt at a second run, but was overcome by passing the slurry through a blender before charging it to C1. This solution proved quite adequate and resulted in 9.62% coal in the reactor.

Preliminary raw results on the 4 fully characterized samples run to date are presented in Table 4. These data are preliminary, and conclusions regarding the relationship between reactivity and coal properties may not as yet be determined. Work in the following quarter will focus on data reduction and correlation, and continued experimentation on coals listed in Table 3.

B. Hydrogenation of Preasphaltenes and Asphaltenes Study

The liquefaction of coal produces preasphaltenes and asphaltenes which are deficient in hydrogen compared to oils. This project will study the rate of formation of oils from coal derived preasphaltenes and asphaltenes by the addition of hydrogen at high temperature and pressure. The intent of the study is to determine the reaction sequence and analyze the kinetics of the following reactions:

1. The formation of asphaltenes by hydrogen addition to preasphaltenes.
2. The reverse reaction of asphaltenes to preasphaltenes.
3. The formation of oils from asphaltenes, and the reverse reaction.
4. The direct conversion of preasphaltenes to oils, and the reverse reaction.

The overall reaction scheme to be studied is shown below.

The equipment to be used in this study consists of a modification to a presently existing unit to allow operation with a continuous stirred tank reactor. The overall unit is composed of the following systems:

1. Gas flow control system The gas flow control system consists of hydrogen being compressed by a compressor then passing through a surge tank, forward pressure regulator, metering valve, flow controller and back pressure regulator on its course to the reactor.
2. Liquid feed system The asphaltenes and preasphaltenes will be mixed with solvent, placed in burets, and fed by gravity to a positive displacement pump. From there, the liquids will be pumped to the reactor continuously.

3. Reactor system The reactor system is comprised of the reactor (a 300cc stirred Autoclave reactor), the reactor impeller drive, motor, and a variable speed controller. In addition, a tachometer will be mounted so that a record can be kept of the rotation speed of the stirrer impeller.

4. Temperature control system The temperature control system is made up of a thermocouple mounted in a thermowell of the reactor, a temperature controller, temperature recorder and a heater for the reactor. The heater will be mounted on a pulley system designed to allow for quick cooling of the reactor.

5. Liquid-gas separation system The gas and liquid mixture from the reactor pass through a high pressure separator controlled by a liquid level controller. The gases proceed to a demister followed by passage through a pressure reduction system. The liquids proceed to a series of low pressure separators; the remaining liquids pass out as liquid product while the remaining gases are demisted and rejoined with gases from the high pressure separator.

6. Pressure reduction system The gases are reduced to atmospheric pressure by means of a pneumatic control valve and a pressure controller. From here, the gases pass to the clean-up and sampling system.

7. Gas sampling and clean-up system The exit gas is scrubbed by passing through concentrated sodium hydroxide solution to remove any hydrogen sulfide gas. The gas can then be sampled, measured and vented.

A flow diagram of the entire unit is shown in Figure 6.

Work on modification of the unit began on June 23, 1980. To date, all the work that has been done is on the revision of the unit as needed to

Figure 6

Flow Micro-reactor System

KEY TO SYMBOLS

22

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)		

incorporate the facets discussed in the equipment section. This has entailed removing the existing reactor and supporting structure as well as the dismantling of the liquid-gas separation system. At that point, the reactor support was rebuilt to accommodate the continuous stirred tank reactor and furnace. Work is now progressing on reassembly of the reactor and liquid-gas separation system, as well as installation of the drive motor and drive controller. Tubing and control lines are being installed to connect the reactor and various vessels in the liquid-gas separation system. During the next quarter, system modifications will be completed and shakedown testing will be initiated.

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 coal. Responses to be measured will be the rates of formation of preasphaltenes, asphaltenes and oil. During the past six months, effort has been directed towards selection of the coal and catalysts to be tested, construction of the experimental apparatus, and initial testing of the equipment.

The coal to be tested was selected from the Penn State Coal Sample bank using the following criteria:

1. high volatile bituminous coal
2. low reactivity (as measured by Given et al.)
3. low sulfur content
4. western United States geographical location - preferably a coal from Colorado.

Two coals were selected and samples from each mine requested. Upon receipt, the samples were sent to the Colorado School of Mines Research Institute (CSMRI) for proximate, ultimate, and ash analyses. The results from these analyses were used for the final selection and are shown in Tables 5 and 6. Because coal mineral matter is one of the catalysts to be tested, the Energy Mine coal was chosen due to its low ash content compared to the Somerset sample.

The coal was prepared for testing by wet grinding the sample in a 30-gallon batch ball mill with a seasoned load for one and one-half hours. The wet coal was filtered using a Buchner funnel and then set out in the air to dry. It was then screened to -200 mesh on a Sweeco and stored under a nitrogen atmosphere.

The disposable catalysts chosen to be tested are:

1. MoS
2. SnO
3. Fe_2O_3
4. chemical grade iron sulfide (FeS)
5. coal-derived pyrrhotite (FeS)
6. molybdenum ore
7. molybdenum tailings
8. coal mineral matter (LTA)

The molybdenum ore and tailings were obtained from AMAX's Henderson Mine in Berthoud, Colorado. The ore was analyzed by CSMRI using emission spectroscopy and was found to contain 0.2% molybdenum, making it a high grade ore. The tailings were extracted with boiling water in a soxhlet apparatus for 24 hours to remove any cyanides and HCl, and then sent to CSMRI for a total chloride analysis. The results from this analysis are still pending.

TABLE 5:

ULTIMATE & PROXIMATE ANALYSIS
OF SELECTED COALS

	<u>Wadge Seam</u> <u>Energy, Colo.</u>	<u>Seam B2</u> <u>Somerset, Colo.</u>
Moisture %	5.82	1.46
Ash % (Dry)	5.99	12.5
Volatile % (Dry)	39.2	36.5
Fixed C (Dry)	54.8	51.0
BTU/lb (Dry)	12,901	12,742
Total S (Dry)	0.56	0.59
Carbon % (Dry)	73.3	71.1
Hydrogen % (Dry)	4.98	5.59
Nitrogen % (Dry)	1.76	1.54
Oxygen % (Dry)	13.4	8.68
Sulfate S %	<0.05	<0.05
Pyritic S %	0.05	0.05
Organic S % (max.)	0.51	0.54

TABLE 6

ASH ANALYSIS OF SELECTED COALS

	<u>Wadge Seam</u> <u>Energy, Colo.</u>	<u>Seam B2</u> <u>Somerset, Colo.</u>
SiO ₂	47.1	58.6
Al ₂ O ₃	32.6	23.5
Fe ₂ O ₃	3.30	4.36
TiO ₂	1.05	0.72
P ₂ O ₅	1.74	1.07
CaO	6.48	3.93
MgO	1.48	2.24
Na ₂ O	0.14	1.60
K ₂ O	0.47	1.42
SO ₃	4.64	1.32

A high pyrite content coal was requested from the Pittsburgh and Midway Coal Mining Company and a sample was received from their Colonial Mine in Madisonville, Kentucky. The coal was ground using a jaw mill and shatter box and the pyrite separated out using a shaker table. X-ray diffraction verified that the separated portion was in fact pyrite. The pyrite will be reduced to pyrrhotite by high temperature hydrogenation using a hydrogen-donor solvent. The coal mineral matter will be derived from the parent coal by low temperature ashing. All other catalysts have been purchased from chemical suppliers.

Construction of the experimental apparatus has been completed. The system is shown in Figure 7. The reactor is a 300cc 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 small sample vessel using high pressure hydrogen.

Initial testing of the equipment included heating tests, slurry injection tests, and a sample run. The points to be verified were:

1. proper functioning of the heater, controller, temperature recorder and injection system, and
2. establishment of operating conditions.

For the heating test, the reactor was charged with 139.52 grams of tetralin. The system was then reconnected, pressure tested for leaks, and then pressurized with hydrogen to 373 psig. The temperature setting on the controller was increased to 390°C in varying increments and the controller temperature, recorder temperature, and the reactor pressure noted. The recorder and controller temperatures were found to differ by 10°C, otherwise the system functioned properly.

Figure 7
300cc Batch Autoclave Reactor

A slurry of tetralin and coal in a 2:1 weight ratio was prepared for the injection test and charged to the sample vessel. The reactor was pressurized to 400 psig and the sample vessel to 2000 psig. When V8 (see Figure 7) was opened, the slurry was injected into the reactor. From mass balance calculations, it was found that 96.42% of the slurry was injected into the reactor.

To begin the sample run, 140.76 grams of tetralin were put into the reactor. The system was then reconnected, pressure tested with helium for any leaks, and then pressurized to 400 psig with hydrogen. A slurry containing 20.05 grams of coal and 40.05 grams of tetralin was prepared and 58.05 grams of the slurry were charged to the sample vessel. The tetralin in the reactor was heated to 400°C and the slurry was then injected using 2000 psig of hydrogen. Upon injection the temperature dropped to 345°C and the pressure rose swiftly to over 2200 psig. Temperature recovery to 380°C was realized in 2-3 minutes, however as the reaction mixture was heated the pressure rose to over 2400 psig and the run was terminated.

From these preliminary tests, proper functioning of the system was verified and the following operating conditions established:

1. a 2:1 weight ratio of tetralin:coal will be used to prepare the slurry
2. the catalyst will be added to the slurry in a weight ratio of 1:10 catalyst:coal
3. the solvent will be preheated to 410°C prior to injecting the slurry
4. the actual reaction temperature will 380°C
5. the slurry will injected using 1600-1650 psig H₂.

Two base runs have been made since the completion of the preliminary testing. The reaction time on both was 60 minutes and no catalyst was used. The results are shown in Table 7. Two additional base runs using no catalyst

TABLE 7

RESULTS FROM 60-MINUTE BASE RUNS

<u>RUN</u>	<u>% UNREACTED COAL</u>	<u>% PRE- ASPHALTENES</u>	<u>% ASPHALTENES</u>	<u>% OIL & GAS</u>	<u>% ASH</u>	<u>% CONVERSION</u>
C2 B	37.86	23.34	19.65	19.15	11.93	62.15
C	37.50	23.04	18.44	21.02	12.03	62.48
D	37.40	20.74	14.52	27.34	12.06	62.59
AVG.	37.59 ± 0.24	22.37 ± 1.42	17.54 ± 2.68	22.50 ± 4.29	12.01 $\pm .07$	62.41 $\pm .23$
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C4 A	35.80	24.34	22.13	17.73	12.53	64.20
C	37.12	23.83	22.75	16.30	12.14	62.87
D	36.00	22.23	18.90	22.87	12.47	64.00
AVG.	36.31 ± 0.71	23.47 ± 1.10	21.26 ± 2.07	18.97 ± 3.46	12.38 $\pm .21$	63.69 $\pm .72$
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and a 10 minute reaction time will be made. These initial runs will give a basis for identification of any catalytic effects shown in the later runs. Testing of the catalysts in this screening program should be completed in the coming quarter.