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COAL LIQUEFACTION PROCESS RESEARCH
QUARTERLY REPORT
FOR OCTOBER - DECEMBER 1979

MASTER

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INTRODUCTION AND SUMMARY

This quarterly report, for the period September through December 1979, summarizes the activities of Sandia's continuing program in coal liquefaction process research. The overall objectives are to:

(1) provide a fundamental understanding of the chemistry of coal liquefaction; (2) determine the role of catalysts in coal liquefaction; and (3) determine the mechanism(s) of catalyst deactivation. The program is composed of three major projects:

- Short-Contact-Time Coal Liquefaction
- Mineral Effects
- Catalyst Studies

These projects are interdependent and overlap significantly. We present our results in such a manner that the interrelationships will be clearly seen. The tasks associated with each project are outlined prior to a discussion of specific accomplishments:

Short-Contact-Time Coal Liquefaction: The objectives are to understand the chemical reactions and heat and mass transfer phenomena that occur during the dissolution of coal, and the subsequent formation of the liquid products. Specific tasks include low temperature (250° to 400°C) kinetics; installation and evaluation of instrumentation on the bench-scale tubular reactor for the measurement of three-phase residence times; evaluation of the factors affecting solvent quality; and measurement of heats of reaction by means of high-pressure differential scanning calorimetry.

Mineral Effects: The objectives are to understand the catalytic effects of naturally occurring minerals, and to prepare, characterize, test and evaluate disposable catalysts for coal liquefaction. Emphasis will be placed on pyrite (FeS_2) and several other iron sulfides (Fe_{1-x}S). Specific tasks include the study of high-surface-area iron sulfides as disposable slurry catalysts; a study of the role of sulfur in coal liquefaction; characterization of liquefaction residues by Mössbauer spectroscopy; determination of the effects of pyrite morphology on the conversion of coal to liquid products; and the evaluation of techniques for dispersing high-surface-area disposable catalysts in coal/solvent slurries.

Catalyst Studies: The objectives are to determine the mechanisms--both chemical and physical--for coal liquefaction catalyst deactivation, and to develop a model for catalyst selectivity and deactivation. Specific tasks include the analysis of tagged H-coal catalysts; determination of loss of selectivity as a function of catalyst age; determination of the effects of contaminants and processing conditions on pore size distribution, site poisoning, loss of promoter action and loss of active phase; and characterization of various catalysts by surface area, pore volume, density, electron microscopy, optical microscopy, emission spectroscopy, atomic absorption and electron microprobe analysis.

Accomplishments during this reporting period include:

- Parametric runs with Illinois No. 6 coal (Burning Star Mine) and SRC-II heavy distillate were carried out to determine the mechanisms of the initial dissolution of coal. Temperatures of 275° to 375°C and residence times of 6.5 and 26 min were selected. Mass balances were 99+ % based on initial feed. In all cases, there was a net production of preasphaltenes and the viscosities of the liquid products were greater than 100 poise at 90°C. Negative yields of asphaltenes and pentane-soluble oils were observed.
- A bench-scale, tubular flow, non-recycle reactor was modified to investigate coal liquefaction at relatively low (300° - 400°C) temperatures. These modifications included installation of: (1) a bypass to the upstream hydrogen buffer vessel; (2) a high-pressure downstream liquid sampling system; (3) residence-time measuring equipment; and (4) computer-aided, real-time analysis of reactor operation parameters. Feedstocks for the experiments are Illinois No. 6 (Burning Star Mine) coal and SRC-II heavy distillate.
- In-stream techniques were developed to determine the residence time of the reactant phases (solid, liquid and gas) present in the tubular flow reactor. Emphasis

has been placed upon solid and liquid bulk phase velocity measurements utilizing particulate tracers. Phase-locked inductance coil detectors were placed at the entrance and exit of the reactor, and the passage of the magnetic material through the coil was recorded as a peak on a strip chart recorder. The bulk phase residence time is the time between peaks. Twenty experiments were conducted using the low pressure flow loop to determine operational parameters as well as to evaluate tracer materials. Particulate iron and magnetite (Fe_3O_4) were successfully used at low temperatures, to measure bulk residence time of the solid phase. In these experiments, Ferrofluids (50-150 Å colloidal suspension of Fe_3O_4 , as supplied by Ferrofluidics Corp.) were evaluated for the measurement of the bulk liquid phase residence time. Residence time measurements made at the assumed reactor conditions provided data (6-9 minutes/20 ft of reactor length) consistent with previous observations made during the operation of tubular flow reactor.

- Differential Scanning Calorimetry (DSC) was used to study the heats of reaction at typical liquefaction conditions. Initial experiments were performed to demonstrate the sensitivity of DSC at high pressure in the temperature range 300-450°C. Preliminary data have shown that increasing cell pressure does not seem to reduce the sensitivity of the DSC instrument due to the increase in the thermal conductivity of the gas.
- Work has begun on the synthesis and characterization of high-surface area iron sulfides. The first syntheses will be metathesis reactions using lithium sulfide and either ferrous or ferric chloride with tetrahydrofuran as solvent. Three iron sulfide samples were prepared by Al Stiller at West Virginia University. All these samples were prepared by the same technique. The starting materials were solutions

of 2M ferrous sulfate and 2M $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$. The solutions were cooled to 4°C and mixed together under a nitrogen atmosphere, yielding a black precipitate. One mole of elemental flowers of sulfur was then added and the mixture was maintained at 85°C for about three weeks. The first two samples were treated in hydrothermal bombs at 230°C and 180°C, respectively, for four days to alter the crystallinity.

- Samples of Robena pyrite (minus 5 μm particle size; 70% pyrite) were subjected to three shock-loading tests in an attempt to produce a large number of point defects. Experiments were carried out at 15 GPa (explosive loading), 20 GPa (impact loading), and 40 GPa (explosive loading). (All pressures are those produced in the copper capsules, not in the samples.) The 15 GPa sample was analyzed by x-ray diffraction and the bulk of the material was found to be a pyrite, but with substantially enhanced defect levels. About 3% of the shocked sample was magnetically separated and found to be mainly Fe_3C with some pyrrhotite.
- In order to gain information on the extent to which pyrite in coal is transformed into pyrrhotite, experiments were carried out with Illinois No. 6 coal (River King Mine) and SRC-II solvent at 325°, 405°, and 425°C. Mössbauer spectroscopy was used to determine the stoichiometry of pyrrhotite (Fe_{1-x}S) in the liquefaction (vacuum bottom) residues. After 5 minutes at 325°C, most of the pyrite was still present, but some pyrrhotite has already been formed. After 30 minutes at 405° and 425°C, the pyrite had been completely transformed into pyrrhotite. The differences in the spectra of these two samples were due to differences in the stoichiometry of the pyrrhotites in the liquefaction residues.

- Three and one-half pounds of radioactively-tagged (390 μCi ^{60}Co) American Cyanamid HDS 1442A CoMo catalyst was added to the H-coal PDU during the third day of a 28-day run (PDU Run No. 9). The objective of the experiment was to determine the rate of catalyst deactivation. This was accomplished by measuring the ^{60}Co in the daily catalyst withdrawals and by determining the activity of catalysts of known age. Preliminary analyses have shown that hydrocarbon residues increased with time, consistent with the increasing age of the catalysts. Also, the molybdenum concentration decreased with catalyst age, implying that there was a continuous buildup of inorganic species. Most of the hydrocarbon residue was incorporated into the catalyst rapidly--probably within one day.
- Selectivity changes are being measured on American Cyanamid 1442A CoMo catalyst that was aged for two weeks in the HRI bench-scale reactor. The objective of this work was to identify deactivation mechanisms by: (1) evaluating loss of activity of specific catalyst functions (e.g., hydrodesulfurization, hydrogenation and hydrocracking) by using model compounds; (2) determining the number of active sites by selective poisoning; and (3) measuring diffusion rates of aromatic solutes into aged catalyst. Hydrodesulfurization (HDS) activity was determined by reacting thiophene with both fresh and aged catalyst. The rate constants for fresh and aged catalyst pellets were 20.6 and 2.6, respectively, indicating a significant decrease in HDS activity as a result of catalyst aging. It was also found that lower activities of pellets, as compared with crushed catalyst, was partly due to a diffusional influence. Estimates of effectiveness factors for the thiophene reaction were made, and, in addition to lower intrinsic activity due to contaminant poisoning effects, there appeared to be an additional diffusional resistance at the pellet exterior which could account for the lower activity of catalyst pellets under processing conditions. Hydrogenation activity was considerably lower for the aged catalyst,

and this reduction was about of the same order of magnitude as that found for HDS activity. Again, a significantly lower activity for the aged pellets compared to the aged crushed catalyst (effectiveness factors for both are about unity) was in line with the HDS results, suggesting that exterior pellet restrictive diffusional effects also apply to the hydrogenation reaction. The fresh catalyst showed some adsorption of naphthalene after heating at 100°C, but the aged catalyst showed no adsorption. This could indicate that the acid sites have been completely neutralized by deposits on the aged catalyst. Regeneration of the aged catalyst at 450°C in air, restored some acidic sites, but only about one-third of that obtained on the fresh catalyst at this temperature.

- Experiments were carried out to evaluate the interaction between H_2S and fresh American Cyanamid 1442A CoMo catalyst extrudates. The reactions were monitored by a Cahn model R100 microbalance that was modified for experiments under flowing H_2S . The specimens were allowed to react at fourteen different temperatures, ranging from 25° to 450°C. At temperatures greater than 75°C, the increase in weight is greater than predicted on the basis of MoS_2 formation. Some of the excess weight appeared to be due to elemental sulfur, which was observed downstream from the catalyst pellets. Specific surface area measurements by BET were obtained on the extrudates used in each of the experiments. The measured values ranged from 131 to 211 m^2/gm . The specific surface area for the fresh catalyst was 242 m^2/gm . A plot of the final weight gain (%) divided by the specific surface area, as a function of reaction temperature, revealed a pronounced peak at approximately 175°C. This was most likely due to the competing effects of increasing rates of decomposition of H_2S and sulfur evaporation with increasing temperature.

A Milestone Chart is shown in Figure 1.

Figure 1. Milestone Schedule

SHORT-CONTACT-TIME COAL LIQUEFACTION

Mechanisms of the Initial Dissolution of Coal (M. G. Thomas)

Data previously obtained on liquefaction at and below 300°C indicate that solvent is a reactant in the initial dissolution of coal.¹ Our study of these low temperature regions has now been expanded to include parametric runs between 275 and 400°C. The test matrix is given in Table 1.

Even at moderately low liquefaction temperatures, 275-375°C, a large fraction of the coal has been solubilized. Also, this initial dissolution is relatively unaffected by hydrogen gas and catalyst (e.g., Co/Mo).² Because all direct coal liquefaction processes traverse these temperature regimes during heatup, it is apparent that the relative rates and mechanisms of the initial dissolution step(s) must be understood as an integral part of all short-contact-time coal liquefaction studies.

Illinois No. 6 coal (Burning Star Mine, -45 mesh) and SRC-II heavy distillate (Ft. Lewis pilot plant) have been chosen as the feedstocks for these experiments. Analyses of coal and solvent are given in Tables 2 and 3, respectively. To date, three of the experiments have been completed (Runs 2, 3, and 4). Preliminary analytical data from these are given in Table 4. The mass balances obtained for the runs were 99+ %, negative production of pentane-soluble oil was observed in Run 2, and negative production of asphaltene was observed in Runs 2 and 3. In all cases, there was a net production of preasphaltenes. The viscosities of the liquid products were greater than 100 poise at 90°C. The remaining runs and associated product analyses will be completed during the next quarter.

Table 1. Parametric Runs to Evaluate Initial Dissolution of Coal

<u>Run</u>	<u>Temperature (°C)</u>	<u>Time (min)</u>	<u>Pressure (psig)</u>
1	275	6.5	200
2	300	6.5	200
3	325	6.5	200
4	350	6.5	200
5	375	6.5	200
6	300	26	200
7	325	26	200
8	350	26	200
9	375	26	200

Table 2. Proximate and Ultimate Analysis of Illinois No. 6 Burning Star Coal[†]

<u>Proximate Analysis Wt. %</u>	<u>LO-1981 (FY 80)</u>	<u>LO-1429 (FY 79)</u>
Moisture:	2.28 ± 0.14 ^{††}	3.41
Ash:	10.53 ± 0.08	10.39
Volatile:	38.64 ± 0.37	36.70
Fixed Carbon:	48.56 ± 0.31	49.50
<u>Ultimate Analysis Wt. %</u>		
Moisture:	2.28 ± 0.14	3.41
Carbon:	68.50 ± 0.27	69.90
Hydrogen:	4.69 ± 0.05	4.59
Nitrogen:	1.38 ± 0.02	1.15
Chlorine:	0.13 ± 0.01	0.07
Sulfur:	2.98 ± 0.07	3.06
Ash:	10.53 ± 0.08	10.39
Oxygen (diff):	9.52 ± 0.29	9.43
	<u>100.01</u>	<u>100.00</u>
<u>Sulfur Forms Wt. %</u>		
Pyritic:	0.88 ± 0.02	1.11
Sulfate:	0.26 ± 0.00	0.09
Organic (diff):	1.85 ± 0.08	1.86
Total Sulfur:	2.98 ± 0.07	3.06

[†] Analysis performed by Commercial Testing & Engineering Co.

^{††} Error limits based upon a 95% confidence interval using a sample size of 6.

Table 3. Analysis of SRC-II Heavy Distillate

Ash (%)	0.05
Carbon (%)	89.8
Hydrogen (%)	7.6
Nitrogen (%)	1.4
Sulfur (%)	0.4
Oxygen (%)	1.8
Pentane Insols (%)	10.0
Distillate Yield (%)	86.5 (850°F)

Table 4. Preliminary Data from Parametric Runs

Run	Temp (°C)	Time (min)	P (psi)	THF ^a Conv	MAF ^b Coal In	Asph ^c In	Oil ^d In	IOM ^e Out	PreA ^f Out	Asph Out	Oil Out
2	300	6.5	200	4	2.4	.58	4.75	2.1	.5	.46	4.7
3	325	6.5	200	22	2.4	.58	4.75	1.7	.47	.48	5.2
4	350	6.5	200	31	2.4	.58	4.75	1.5	.65	.61	5.1

++

(a) Conv = conversion

(b) MAF = Moisture and Ash Free

(c) Asph = Asphaltene = benzene soluble/pentane insoluble

(d) Oil = pentane-soluble oil

(e) IOM = Insoluble Organic Matter

(f) PreA = preasphaltene, THF soluble/benzene insoluble

Bench-Scale Process Liquefaction Studies (T. C. Bickel and R. M. Curlee)

Mass transfer, heat transfer, and fluid dynamics phenomena share an equal role with reaction kinetics in the liquefaction of coal. The study of the overall liquefaction process requires the use of a reactor system in which the relative effect of each factor is observed. A bench-scale, tubular flow, non-recycle reactor³ is being used to study the effects of these parameters on the coal liquefaction process. Previous work has shown that coal-derived solvent and coal interact quickly to form a high-viscosity preasphaltene in the temperature range of 400-475°C.⁴ In conjunction with other kinetic studies, the tubular flow reactor has been modified to investigate low temperature (300-400°C) process liquefaction.¹ Work discussed in the previous section noted the formation of a highly viscous product in the temperature range 300-350°C. In order to facilitate the sampling of such a product, and to measure the reactant residence time in the three-phase flow reactor, the following modifications have been made:

A. Installation of a Bypass to the Upstream Hydrogen Buffer Vessel:

This modification was performed in order to reduce the time required for the unit pressure to equilibrate following product sampling.

B. Installation of a High-Pressure Downstream Liquid Sampling System:

It is believed that a high viscosity product would "hang up" in the liquid sampling vessel. As a result, a high pressure parallel sampling unit has been added to the system to insure that the sample obtained is representative of the actual reactor operating parameters.

C. Installation of Residence-Time Measuring Equipment:

Low pressure testing of the residence-time detection equipment has been completed (see below). The

installation of the detection equipment on the reactor is currently in progress. Following this, the equipment will be evaluated under reactor operating conditions.

D. Installation of Computer-Aided Real-Time Analysis of Reactor Operation Parameters:

A communications link is being installed between the Kaye data logger on the reactor system and a Modcomp MODACS III (Modular Data Acquisition System) series computer. The link is interfaced through a Tektronix 4014 graphics terminal. After installation and testing, the computer link will provide real-time analysis of reactor operating parameters.

Experimental design for the tubular flow reactor will not be completed until the parametric studies outlined in Table 1 have been carried out. The experiments on the tubular flow reactor will use, as feedstocks, SRC II heavy distillate and Illinois No. 6 Burning Star coal (see Tables 2 and 3). A new lot of SRC-II heavy distillate has recently been obtained from the Fort Lewis pilot plant. This is currently being analyzed, and will include elemental composition, total distillate yield, ASTM D-1160 distillation, simulated distillation using gas chromatography and thermal analysis (high pressure differential scanning calorimetry and atmospheric thermogravimetric analysis).

Residence Time Measurements - Instrumentation and Techniques

(R. M. Curlee and T. C. Bickel)

In-stream techniques are being developed to determine the residence time of the reactant phases (solid, liquid and gas) in the tubular flow reactor. Emphasis, thus far, has been placed upon instrumentation and hardware for making solid-liquid bulk phase velocity measurements using particulate tracers. Feasibility and development of prototype electronic and detection hardware have been successfully demonstrated using a low-pressure loop to simulate the flow conditions assumed to exist in the reactor.

Phase-locked inductance coil detectors are placed at the entrance and exit of the reactor (see Figure 2). The passage of magnetic or electrically conductive material through the coils affects the resonant frequency of that tank circuit, and is displayed as a phase connective voltage on a strip-chart recorder. The bulk phase residence time is the time between peaks.

Twenty low-pressure experiments were conducted using lubricating oil and air at conditions shown in Table 5. These experiments were performed to determine operational parameters and to evaluate tracer materials. Particulate iron and magnetite (Fe_3O_4) were successfully used to measure the bulk residence time of a solid phase under these conditions.

MAGNETIC TRACER-RESIDENCE TIME APPARATUS

Figure 2. Magnetic Tracer Residence-Time Apparatus

Table 5. Low-Pressure Flow Apparatus Tracer Experiments.

Liquid Volumetric Flowrate (cm ³ /sec)	Gas Volumetric Flowrate (cm ³ /sec)	Temperature (°C)	Injected Tracer Volume (25 vol.% ₃ mag. part.) (cm ³)
~ 0.14	0.28	25	~ 0.01
~ 0.28	0.56	25	~ 0.01

Residence time measurements made at the assumed reactor conditions gave data (6-9 minutes/20 ft of reactor, as seen in Figure 3) consistent with previous observations made during the operation of the tubular flow reactor. Ferrofluids (50-150 Å colloidal suspension of Fe₃O₄, as supplied by Ferrofluidics Corp.) are being evaluated as a tracer for measurement of the bulk liquid phase residence time.

Design, fabrication and testing of high pressure versions of the detector and injection system has been completed and detector prototypes have been installed in the tubular flow reactor. Initial experiments to evaluate the previously described techniques at high pressure will be conducted at the conditions shown in Table 6.

Table 6. Residence-Time Experiment Test Conditions

Pressure (H ₂):	2000 psig
Temperature:	425°C
Slurry Flow Rate:	0.5 lb/hr (33 w/o Illinois No. 6 Burning Star coal in SRC-II distillate)
H ₂ Flow Rate:	20 MSCF/ton of coal
Reactor Dimensions:	0.203 inch diameter x 20 ft long

Figure 3. Typical Strip-Chart Data for Bulk Phase Residence-Time Measurements

Differential Scanning Calorimetry (T. C. Bickel and T. M. Massis)

Differential Scanning Calorimetry (DSC) is being used to study the heats of reaction at typical liquefaction conditions. Experiments have been carried out to demonstrate the sensitivity of DSC, at high pressure, in the temperature range 300-450°C. Phase change measurements of zinc and KClO_4 under helium[†] were made at various pressures. Shown in Table 7 are the data from sensitivity^{††} experiments. While there is a change in the responses of the standards when helium is substituted for air, the effect of pressure on instrument response is minimal. In addition to the gradual increase in thermal conductivity due to increasing pressure, it has been demonstrated that a large anomaly in thermal conductivity exists near the critical point. The range of liquefaction temperatures and pressures (300-450°C and 2000 psi), however, are well beyond the critical point, as shown in Table 8, and this effect should not be important in thermal analysis experiments.

Table 7. DSC Sensitivity as a Function of Pressure

	<u>Air</u> <u>0 psig</u>	<u>Helium</u> <u>10 psig</u>	<u>Helium</u> <u>200 psig</u>	<u>Helium</u> <u>500 psig</u>	<u>Helium</u> <u>900 psig</u>
Zinc	5.455×10^5	3.433×10^5	3.413×10^5	3.439×10^5	3.513×10^5
KClO_4	4.621×10^5	2.873×10^5	2.834×10^5	2.933×10^5	3.028×10^5

Work is in progress to obtain the volatility of the solvent as a function of pressure, and to determine the effect of this on the DSC measurements.

[†] The Dupont 990 DSC instrument is hydrogen-incompatible and must be modified.

^{††} The sensitivity of the DSC was measured as the integral of the instrument heat flow response.

Table 8. Reduced Temperature and Pressure of Helium and Hydrogen at 400°C and 2000 psia

	T_c °K	P_c (atm)	T_R	P_R
Helium	5.3	2.26	126.9	25.7
Hydrogen	33.3	12.8	20.21	10.03

MINERAL EFFECTS IN COAL LIQUEFACTION

Preparation of High-Surface-Area Iron Sulfides (F. V. Stohl)

The objective of this work is to prepare, characterize, and test high-surface-area iron sulfides as disposable catalysts for coal liquefaction. A low-temperature solution method for the formation of group 4B, 5B, and 6B transition metal dichalcogenides has been reported by Chianelli and Dines.⁶ Synthesis methods reported prior to their work required high temperatures (> 400°C) to give reasonable reaction rates and yielded highly crystalline, non-stoichiometric, multiphase products with low surface areas. The techniques presented by Chianelli and Dines, however, yield products which are poorly crystalline, amorphous powders, gels, glasses or homogeneous dispersions. These products are extremely fine-grained (submicron range) and have very high surface areas. The starting materials are commercially obtained transition metal halides, such as $TiCl_4$, and commercially obtained lithium sulfide or ammonium or amine hydrosulfides. Poorly crystalline lithium sulfide reacts violently with the transition metal halides, whereas well crystalline lithium sulfide requires heat to react.

Chianelli et al. described the structure of a poorly crystalline molybdenum disulfide which was prepared by these techniques.⁷ The structure, as analyzed by the use of high-resolution electron microscopy, consists of highly folded and disordered molybdenum disulfide layers which are about 20-30 Å thick in the stack direction and extend several thousand angstroms perpendicular to the stack direction. BET surface area measurements of this sample gave about 50 m²/g.

Passaretti et al. used similar techniques to prepare ruthenium disulfide with the pyrite structure.⁸ The product formed by the reaction of anhydrous ruthenium trichloride with ammonium hydrogen sulfide in 2-methoxyethyl ether was pyrophoric. Treatment of this product with hydrogen sulfide at 250°C enabled it to be exposed to air. Subsequent annealing experiments caused the crystallization of a phase with the pyrite structure.

Methods similar to those cited above are being used at Sandia for the preparation of iron sulfides with varying particle sizes and surface areas. The preparations will be carried out in a glovebox under an argon atmosphere. An extra gas line has also been inserted into the entry port of the glovebox so that the port can be filled with clean argon or air before it is opened into the room.

The first preparations will be made with lithium sulfide and either ferrous or ferric chloride, with tetrahydrofuran as solvent. The Cerac FeCl_2 sample gave a good x-ray pattern for FeCl_2 with one extra weak line which could not be identified. The Cerac Li_2S gave a very strong pattern for Li_2S indicating that the material was highly crystalline. There were approximately 12 very weak extra lines, many of which correspond to LiOH . Any lithium chloride formed during the reaction will be removed by repeated washings with tetrahydrofuran. A mass balance record will be kept during the experiments to determine the completeness of the reaction and whether or not any tetrahydrofuran was incorporated into the structure. The products will be characterized by the following techniques:

- X-ray diffraction
- X-ray fluorescence
- Emission spectroscopy
- BET surface area analysis
- Particle size analysis
- Density

Three iron sulfide samples have been prepared by Al Stiller at West Virginia University. All three of these samples were prepared by the same technique. The starting materials were solutions of 2M ferrous sulfate and 2M $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$. The solutions were cooled to 4°C and mixed together under a nitrogen atmosphere, yielding a black precipitate. One mole of elemental flowers of sulfur was then added and the mixture was maintained at 85°C for about three weeks. The mixture was

filtered and the residue was washed to remove salts, unreacted iron sulfide, water and excess sulfur. The first two samples were treated in hydrothermal bombs at 230°C and 180°C, respectively, for four days to alter (i.e., increase) the crystallinity. The third sample was untreated. Stiller reports that these samples are pyrites, one of which was pyrophoric. We are currently characterizing them.

Introduction of Defects in Iron Sulfides (F. V. Stohl and R. A. Graham)

Montano and Granoff have recently observed a correlation between the stoichiometry of pyrrhotites (Fe_{1-x}S) in liquefaction residues and the yield of benzene-soluble liquid products.⁹ Differences in the iron contents of the pyrrhotites were attributed to differences in the number of iron vacancies. It is possible that increased catalytic activity, in general, may be related to increased defect (i.e., vacancy) content. For this reason, we need to understand the relationship(s) between defect content and catalyst behavior.

It is important to develop techniques for producing defects in materials that may be used as catalysts for coal liquefaction. This could result in improved catalytic activity. A recent study of the Soviet effort¹⁰ in shock-induced solid state chemistry has revealed a major effort in activation of catalysts with shock loading. The Soviets have demonstrated substantial improvements in catalytic activity due to shock-induced introduction of massive numbers of point defects. Accordingly, we have initiated exploratory work to investigate the feasibility of inducing defects in iron sulfides.

Samples of Robena pyrite¹¹ have been subjected to three shock-loading tests. This pyrite is a coal-derived concentrate which contains about 70% pyrite, 30% other coal minerals and a small amount of organic matter. This material, which was pulverized to $\sim 5 \mu\text{m}$, has an average particle size of $1.8 \mu\text{m}$, a surface area of $4.7 \text{ m}^2/\text{g}$, and a helium density of 4.07 g/cm^3 .

The copper recovery capsules designed to preserve the samples from the shock loading tests were ruptured by the shock in each of the three experiments at 15 GPa (explosive loading), 20 GPa (impact loading), and 40 GPa (explosive loading). (All pressures are those produced in the copper capsules, not in the samples.) About one-third of the material was recovered from the 15 GPa experiment but all other samples were lost. It appears that shock-induced gas formation within the sample cavity caused the rupture of the capsules.

The 15 GPa sample was analyzed by B. Morosin (Org. 5154) using X-ray diffraction techniques. About 3% of the shocked sample was found to be a magnetically active Fe_2C with the carbon probably being derived from the organic material or the calcite in the Robena pyrite. The bulk of the material was found to be pyrite with enhanced defect levels.

Mössbauer Studies of Coal Liquefaction Residues (B. Granoff and P. A. Montano*)

We have recently shown that the stoichiometry of iron sulfides in coal liquefaction residues can be obtained by Mössbauer spectroscopy.⁹ The overall objective of this work is to determine if pyrrhotite (Fe_{1-x}S) is an active catalyst for the conversion of coal to distillate liquid fuels, and to understand the mechanism(s) by which pyrite (FeS_2) is transformed into pyrrhotite. This work is in support of our studies on the development of high-surface-area iron sulfides for use as disposable catalysts.

The coals used were Illinois No. 6 (River King) and West Virginia (Blacksville No. 2, Pittsburgh seam). The solvent was SRC-II heavy distillate. The coals were liquefied in a one-liter stirred autoclave at a solvent-to-coal ratio of 2:1. All runs were made at 1800 ± 10 psig ($12.4 \text{ MPa} \pm 69 \text{ KPa}$). Details concerning coal and solvent analyses as well as experimental procedures have been described elsewhere.¹² The liquefaction residues were obtained by extracting the liquid product vacuum bottoms (850°F^+) with tetrahydrofuran (THF). The THF-insolubles were pulverized to minus 200 mesh prior to analysis, and the powdered samples were hermetically sealed in lucite containers. The Mössbauer spectrometer was a conventional constant acceleration instrument. The source consisted of 50 mCi of ^{57}Co in a Pd matrix. Most spectra were obtained at room temperature, and were analyzed using a non-linear least squares fit, assuming Lorentzian line shapes. The zero velocity is given with respect to alpha-iron.

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A Mössbauer spectrum of the West Virginia coal is shown in Figure 4. In this coal, the only iron-containing species is pyrite, and the resulting spectrum is typical of this mineral.^{13,14} The spectrum of a residue obtained by heating pyrite (pulverized to minus 5 μ m) and SRC-II heavy distillate to 425°C for 30 minutes--in the absence of coal--is shown in Figure 5. This six-line spectrum is typical of a disordered, hexagonal pyrrhotite.^{14,15} The data suggest that, under these experimental conditions, the pyrite was completely transformed into pyrrhotite.

In order to gain information on the extent to which pyrite in coal is transformed into pyrrhotite, a few experiments were carried out with Illinois No. 6 coal and SRC-II solvent at 325°, 405°, and 425°C. The residence time at 325°C was 5 minutes; the residence times at 405° and 425°C were 30 min. The Mössbauer spectra of the THF-insolubles are shown in Figure 6. After 5 minutes at 325°C, most of the pyrite was still present, but some pyrrhotite has already been formed. After 30 minutes at 405° and 425°C, the pyrite has been completely transformed into pyrrhotite. The differences in the spectra of these two samples are due to differences in the stoichiometry of the pyrrhotites in the liquefaction residues.

The Mössbauer spectra of residues from runs (425°C, 30 min) with the West Virginia coal, and of the parent coal itself, are shown in Figure 7. In one experiment, American Cyanamid HDS 1442A catalyst (5% by weight of coal; crushed to minus 200 mesh) was added to the feed slurry. The spectra of the resulting residue (Figure 7c) was markedly different from the one where no catalyst had been added. These differences are due to changes in the stoichiometry of the pyrrhotites. The pyrrhotite produced in the catalyzed run is similar to the pyrrhotite that was obtained in the blank run (Figure 5). It is not clear at this time how the Co/Mo catalyst can affect the transformation of pyrite to pyrrhotite, but it is hoped that future experiments will provide additional insights into these mechanisms.

Figure 4. Mössbauer spectrum of West Virginia (Blacksville No. 2) coal

Figure 5. Mössbauer spectrum of pyrrhotite obtained from blank run (425°C, 30 min, 1800 psig) with pyrite and SRC-II heavy distillate.

Figure 6. Mössbauer Spectra of Residues from Illinois No. 6 coal (River King)

Figure 7. Mössbauer Spectra of West Virginia coal (Blacksville No. 2): (a) Original coal; (b) Residue without added catalyst; (c) Residue with CoMo catalyst added.

CATALYST STUDIES IN COAL LIQUEFACTION

The Analysis of Catalyst from H-Coal PDU Run No. 9 (M. G. Thomas and T. C. Bickel)

The H-Coal process for the direct liquefaction of coal utilizes an ebullated bed, with daily addition and withdrawal of catalyst.¹⁶ In order to obtain information on catalyst aging and deactivation within the bed, we added a radioactively-tagged charge of fresh catalyst during PDU Run No. 9. The primary objective of the experiment was to determine the rate of catalyst deactivation. Data from the experiment are also being used to obtain information about catalyst mixing, fluid flow and catalyst losses due to attrition.

Four pounds of American Cyanamid HDS 1442A CoMo catalyst (~ 15 wt% Mo, 3 wt% Co on γ alumina) was irradiated by a thermal neutron flux of 2×10^{12} N/cm² sec for ~ 5 minutes by Union Carbide Corporation, White Plains, New York. The specified activity of 3.5 lbs was 390 μ Ci ⁶⁰Co. Although several short-life-time species were produced, only the activity of the ⁶⁰Co was significant after a two-week cool-down period. The remaining 0.5 lb of irradiated tagged catalyst was reserved for analytical comparisons.

The experiment was performed in the H-Coal PDU by Hydrocarbon Research, Inc., at Lawrenceville, NJ. The PDU run included a two-day start-up period in which the reactor feed stream was a coal-derived solvent without coal. The ebullated bed was operated for an additional two days with coal (Kentucky Fies Mine) in order to reach steady state. The 3.5 lbs of ⁶⁰Co tagged catalyst was added during the third day of a 28-day run. The catalyst was added in the normal manner at the top of the reactor and removed from the bottom. The initial charge of catalyst in the PDU was 100 lbs, with ~ 3.5 lbs of catalyst added and withdrawn daily.

The daily reactor withdrawals and the final catalyst bed dump were shipped, in total, to Sandia National Laboratories for counting and further analysis. The ⁶⁰Co in the daily withdrawals is given in Table 9. Approximately 57% of the tagged charge was removed in the withdrawals before the termination of the PDU run. Counting was accomplished using a germanium-lithium drifted solid state crystal. A step-wedge function was used for calibration.

Table 9. Amount of ^{60}Co Tagged Catalyst in Daily Withdrawals and Final Reactor Dump

Operation Time (day)	Sample Activity (μCi)	Sample Weight (gr)
0*	0.0	-
1	3.3	5012
2	14.5	4565
3	†	†
4	11.0	2610
5	15.3	3435
6	16.6	3377
7	16.7	3391
8	16.9	3434
9	15.0	3377
10	†	†
11	13.7	3402
12	†	†
13	13.7	3412
14	13.4	3458
15	9.3	2024
16	10.9	3432
17	9.9	3425
18	6.7	1956
19	7.5	3552
20	7.7	3658
21	7.1	3468
22	6.3	3401
23	5.7	3601
24	4.7	3513
Final Dump	156.5	

* Tagged catalyst injection.

† Sample not collected.

Analyses of catalyst included toluene Soxhlet extraction (for clean-up) and determination of total organics by ashing and metals by atomic absorption analysis. Previous attempts to obtain correlations between catalyst aging and buildup of organics and/or inorganics, for samples taken from H-coal PDU runs, have not been successful.¹⁷ Reasons for this are not known, but analyses of catalysts from PDU Run No. 9 have disclosed two interesting correlations. First, as shown in Figure 8, hydrocarbon residues increase with time, consistent with the increasing catalyst age of the withdrawn samples. Second, as shown in Figure 9, the molybdenum concentration appears to decrease with age, and this suggests that there is a continuous buildup of inorganic species. Most of the carbonaceous deposits are added rapidly--probably within one day. The inorganics, however, appear to increase more slowly.

The external age distribution of the catalyst and the average residence time of the samples taken from the PDU can be obtained from the measured quantity of ^{60}Co in the withdrawals. At present, the average catalyst residence time and the length of time required to

Figure 8. Weight Loss Upon Ignition as a Function of Catalyst Age

Figure 9. Weight Percent Molybdenum on Catalyst as a Function of Catalyst Age

reach steady state, due to mixing, are being assessed. Concurrently, physical and chemical characterization of the catalysts is continuing.

Selectivity Changes of Aged H-Coal Catalysts (M. G. Thomas and F. E. Massoth*)

Previous work on H-Coal catalysts has shown that the hydrocarbon residues and metals contamination contribute to the overall aging process.¹⁸ Current studies on tagged catalysts corroborate these earlier findings. However, it has not been shown previously how catalyst contamination leads to deactivation, and, furthermore, what relative contributions coke and metals make to deactivation.

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We have studied American Cyanamid 1442A CoMo catalyst that was aged for two weeks in the catalyst testing program (bench-scale) at Hydrocarbon Research Inc. (HRI), Trenton, New Jersey. Though these catalysts had been used only a relatively short time, their activity, based upon changes in product quality throughout the run, had dropped significantly.¹⁸ The objective of this work was to identify deactivation mechanisms. This was accomplished by: (1) evaluating loss of activity of specific catalyst functions (e.g., hydrodesulfurization, hydrogenation and hydrocracking) by using model compounds; (2) determining the number of active sites by selective poisoning; and (3) measuring diffusion rates of aromatic solutes into aged catalyst.

Experimental

Catalysts studied were a fresh American Cyanamid 1442A CoMo catalyst (designated as LO 1176) and the same catalyst which had been used in H-Coal processing (designated as LO 1154). Tests were made on as-received pellets and on pellets crushed and sieved to 25 to 40 mesh. Physical properties of the catalysts are given in Table 10.

Table 10. Properties of American Cyanamid 1442A CoMo Catalysts

	Fresh (L1176)	Aged (L1154)
Mo, %	15.6	11.7
Co, %	2.8	2.0
Ti, %	-	3.3
Fe, %	-	1.0
B, %	-	0.8
Mg, %	-	0.5
Ca, %	-	1.0
SA, m ² /g	308	160
Solid density, g/cm ³	3.8	2.8
Pore volume, cm ³ /g	0.80	0.38
Pellet diameter, cm	0.08	0.08
Crushed diameter, cm	0.028	0.028

A fixed-bed, microcatalytic reactor was used and is shown in Figure 10. Catalyst charges of 1/2 to 1 gram are mixed with about 3 cm³ of glass beads to assure good contact of the catalyst particles with the reaction stream. Gas flow rates are monitored by means of calibrated mass flow meters. Thiophene and 1-hexene are introduced separately by bubblers, the upstream bubbler being held at 0°C by means of an ice bath. Catalysts are presulfided in situ in the reactor at 400°C for 2 hours with a 10% H₂S/H₂ mixture. After sulfiding, temperature is lowered to 350°C in a stream of He. Next, a thiophene/H₂ stream is passed over the catalyst at a standard flow rate overnight. The next day, the conversion is determined by analyzing the reactor exit stream with a gas chromatograph using a flame ionization detector. Several different flow rates are then run to evaluate the reaction kinetics. One to two hours are required between different flows to obtain a steady state. The last flow run is a repeat of the standard flow to check for catalyst deactivation. Following this, the thiophene bubblers are replaced by ones containing 1-hexene and a conversion is determined under a standard flow condition for H₂ with added H₂S/H₂.

Adsorption of naphthalene is determined by placing the catalyst in a solution of naphthalene in cyclohexane at room temperature and shaking for several days. Naphthalene left in solution is analyzed by UV spectrometry, from which the amount adsorbed can be calculated. Naphthalene adsorbs on catalyst acid sites whereas cyclohexane does not adsorb.

Figure 10. Catalytic Microreactor System

Thiophene HDS Reactivity

The reaction of thiophene over Mo-containing catalysts gives predominantly butenes, butane, and H_2S . The current results agreed with this; however, small amounts (less than 5%) of lighter products were also observed, probably C_2 and C_3 's from cracking. The kinetics of the reaction were analyzed in terms of H_2S inhibition.¹⁹ The following rate form, derived from Langmuir-Hinshelwood kinetics, seemed to apply:

$$r_T = \frac{k'_T K_T p_T}{1 + K_S p_S} \quad (1)$$

where r_T is the rate of disappearance of thiophene, k'_T is a global rate constant, K_T and K_S are adsorption constants for thiophene and H_2S , and p_T and p_S are partial pressures of thiophene and H_2S , respectively. In terms of conversion of thiophene, x_T , equation (1) becomes, for a fixed bed reactor,

$$-\frac{\ln(1-x_T)}{x_T} = \frac{k'_T K_T}{1 + K_S p_T^O} \frac{1}{x S_V} + \frac{K_S p_T^O}{1 + K_S p_T^O} \quad (2)$$

where p_T^O is the inlet thiophene partial pressure and S_V is the space velocity given by

$$\frac{1}{S_V} = \frac{W_C}{F} \quad (3)$$

W_C being catalyst weight and F total flow rate. Previous results with similar catalysts had shown that $K_S p_T^O \gg 1$.²⁰ Therefore, equation (2) simplifies to

$$Y = k_T X + 1 \quad (4)$$

where

$$Y = -\frac{\ln(1-x_T)}{x_T}$$

$$X = 1/X_T S_V$$

$$k_T = k'_T K_T / K_S p_T^O$$

It is to be noted that k_T is a composite of a rate constant and equilibrium constants.

The results of the thiophene runs on fresh and aged catalysts are given in Figure 11. Data correlation agreed well with equation (4) as shown in Figure 12. The slopes of these plots give values of k_T , which can be considered relative activity parameters for HDS. Table 11 gives the values obtained on a catalyst-charge weight basis and on a corrected fresh catalyst basis. In the latter case, the aged catalyst was corrected for the presence of sulfur and deposits based on data available at Sandia.¹⁸ Based on Al_2O_3 content of the fresh catalyst, the correction was calculated to be 1.36, whereas a value of 1.33 was calculated on the basis of Mo content.

Figure 11. Thiophene Conversion for Various Catalysts

Figure 12. Thiophene Kinetics on Fresh and Aged Catalysts

TABLE 11. Catalyst Activity Comparisons

Catalyst	As Rec'd Basis		Fresh Basis ¹	
	k_T^2	k_H^3	k_T^2	k_H^3
Fresh, crushed	28.4	--	28.4	--
Fresh, pellets	20.4	62.2	20.6	62.2
Aged, crushed	4.4	11.7	6.0	15.9
Aged, pellets	1.9	8.6	2.6	11.7

¹ Corrected for sulfiding and deposits by a factor of 1.36.

² From Eq. (4).

³ From Eq. (5).

Reference to Figure 11 shows that the fresh pellets were slightly less reactive than the crushed catalyst. Aged catalysts were significantly lower in activity and also showed a particle size effect. The aged catalysts were not completely deactivated for thiophene HDS nor for hexene hydrogenation (Table 11 and following section); that is, a residual activity was still observed. We cannot be sure from the value of k_T derived from the kinetic analysis of Eq. (4) that the decrease in HDS activity is due to less active sites (lower k_T'), a lower K_T or a higher K_S . However, it is reasonable to expect that the predominant cause is due to poisoning of active sites by contaminants present on the aged catalyst, i.e., coke and/or metals.

The lower activities of the pellets, as compared with the crushed catalyst, is partly due to a diffusional influence. Estimates of effectiveness factors for the thiophene reaction were made following Satterfield²¹ and values are given in Table 12. For the fresh crushed catalyst, the effectiveness factor, η , is close to unity, whereas for the pellets, a slightly lower value is indicated. The estimated pellet-to-crushed ratio agrees well with the corresponding ratio obtained directly from conversion data. In the latter case, the rates of reaction are assumed proportional to conversion, even though this is not strictly true. Within the accuracy of these calculations, then, the slightly lower activity of the pellets can be accounted for

Table 12. Effectiveness Factors for Thiophene Reaction

	Est.	<u>Pellet/Crushed Ratio</u>	
	<u>η</u>	<u>Est.</u>	<u>Obs.¹</u>
Fresh, crushed	0.98	0.88	0.86
Fresh, pellets	0.86		
Aged, crushed	0.99	0.94	0.67
Aged, pellets			

¹ From ratio of conversions at constant $1/S_v$.

on the basis of an intraparticle diffusion effect due to the larger particle size.

For the aged catalysts, the estimates for η predict no diffusional restrictions for the crushed catalyst, and only a small effect for the pellets; that is, the lower activity should be an intrinsic property unaffected by diffusional phenomena. The observed ratio, based on conversions, is significantly lower than the predicted ratio (Table 12). This interesting finding indicates that the activity response of the catalyst pellets is affected by an additional factor not accounted for by particle size alone. It is most likely due to the high concentration of metal deposits found in this catalyst near the pellet exterior. This results in a severe, localized, restrictive diffusion at the outer portion of the pellets, which is not present when the pellets are crushed. Thus, in addition to lower intrinsic activity due to contaminant poisoning effects, there appears to be an additional diffusional resistance at the pellet exterior which accounts for the lower activity of catalyst pellets under processing conditions.

Hexene Hydrogenation

Reaction of 1-hexene over the catalysts was conducted at only one reaction condition and, therefore, kinetics data could not be obtained. This reaction was carried out after the thiophene runs and so was done on a stable catalyst which had reached steady state. Some H_2S was added with the hexene/ H_2 feed to maintain the catalyst in the sulfided state. These tests are designed to compare hydrogenation activities of the various catalysts, since this catalytic function is believed

to take place on different active sites than those for the HDS reaction.²²

In order to compare hydrogenation activities on the same basis, since runs were conducted at slightly different flow rates for the various catalysts, we used a pseudo-first order rate expression for the hydrogenation. In a fixed bed reactor, this is given by²³

$$-\ln(1-x_H) = \frac{k_H}{S_V} \quad (5)$$

where x_H is the conversion of hexene to hexane and k_H is the pseudo-first order rate constant. The value of k_H is then calculated from the conversion at a given value of S_V .

Values of k_H for the various catalysts are given in Table 11. These values are directly related to catalyst activity for hydrogenation. Hydrogenation is considerably lower for the aged catalyst, and this reduction is about of the same order of magnitude as that found for HDS activity. Again, a significantly lower activity for the aged pellets compared to the aged crushed catalyst (effectiveness factors for both are about unity) is in line with the HDS results, suggesting that exterior pellet restrictive diffusional effects also apply to the hydrogenation reaction.

Adsorptivities

The data for adsorption of naphthalene on the various catalysts are given in Table 13. This was carried out on finely-divided catalysts to speed up attainment of equilibrium. Adsorption values depend strongly on the amount of adsorbed water on the catalyst, which, in turn, depends on the heat treatment given the catalyst. Thus, catalysts must be compared under the same calcining conditions. Adsorption of naphthalene is believed to take place on catalyst acid sites.²⁰

The fresh catalyst showed some adsorption of naphthalene after heating at 100°C, but the aged catalyst showed no adsorption. This likely indicates that the acid sites have been completely neutralized by deposits on the aged catalyst. Regeneration of the aged catalyst at 450°C in air restored some acidic sites, but only about one-third of that obtained on the fresh catalyst at this temperature. During

Table 13. Catalyst Adsorptivities

<u>Catalyst</u> ¹	<u>Calcining</u> <u>Temp, °C</u>	<u>Adsorption</u> ² , mg/g	
		<u>As Rec'd</u>	<u>Fresh Basis</u> ³
Fresh	100	0.32	0.32
Fresh	450	0.76	0.76
Aged	100	0	0
Aged, regen.	450	0.19	0.26

¹ On finely crushed catalyst.

² Naphthalene (in cyclohexane) at room temperature.

³ Corrected for sulfiding and deposits by a factor of 1.36.

regeneration (air oxidation), coke and sulfur are removed but not metal deposits. Therefore, it appears that both coke and metal deposits contribute to loss in acidity of the aged catalyst. Since acidity is usually associated with catalyst cracking activity, the aged catalyst has probably lost its hydrocracking ability.

During the next quarter, samples from an H-Coal PDU run, with known residence times, will be studied for aging characteristics. Subsequently, the activity of these catalysts for the various reactions will be assessed. The results should provide rates of deactivation for the various functions of the catalyst.

Reaction of H₂S with Catalytic Substrates (M. G. Thomas and F. G. Yost)

This study was initiated to determine the mobility of MoS₂ in CoMo catalysts used for coal liquefaction. We attempted to collect basic information on the sulfidation kinetics of Co/Mo catalyst and, if possible, to artificially induce growth of MoS₂ crystallites, as had been observed in used H-Coal catalyst.¹⁸

A series of experiments was carried out to evaluate the interaction between H₂S and fresh American Cyanamid 1442A CoMo catalyst extrudates (see Table 10 for catalyst properties). Four or five pellets, weighing 40-43 milligrams, were used in each experiment. The reaction was monitored by a Cahn model R100 microbalance that was modified for experiments under flowing H₂S. The specimens

were allowed to react at fourteen different temperatures, ranging from 25° to 450°C. Before initiating the flow of H_2S and while heating, the balance and specimen were purged with argon. There was a decrease in weight during this period which was believed to be due to loss of water. All specimens were heated to their respective reaction temperatures; consequently, specimens whose reaction temperature was less than 100°C may have contained some residual moisture. When the initial weight loss ceased and when the specimens reached the desired reaction temperature, H_2S was allowed to flow with argon in a 50:50 mixture at a rate of 20 cm³/min. The sensitivity of the weight measurements was ± 10 micrograms.

Representative percentage weight-gain-versus-reaction-time curves are shown in Figure 13. At temperatures greater than 75°C, the increase in weight is greater than predicted on the basis of MoS_2 formation. The Mo content of these catalysts is 9.3% and the sulfur would thus correspond to ~ 3.75 weight percent (for MoS_2). This amount is identified in Figure 13. Since the Mo is originally coordinated to oxygen, this 3.75 weight gain is a maximum value. Some of the excess weight appears to be due to elemental sulfur which was observed downstream from the catalyst extrudates.

Specific surface area measurements by BET were obtained on the extrudates used in each of the experiments. The data are presented in Table 14. The measured values ranged from 131 to 211 m²/gm. The specific surface area for the fresh catalyst was 242 m²/gm. Shown in Figure 14 is the final weight gain (%) divided by the specific surface area as a function of reaction temperature. The curve shows a pronounced peak at approximately 175°C which is most likely due to the competing effects of increasing rates of decomposition of H_2S and sulfur evaporation with increasing reaction temperature.

Table 14. Weight Gain and Surface Area of
CoMo Catalyst Exposed to H₂S

Reaction Temperature (°C)	Final Weight Gain (%)	Specific Surface Area m ² /gm
350	4.81	188.59
425	4.39	198.09
250	7.84	184.11
125	9.20	152.96
111	10.79	172.89
50	3.24	211.85
100	5.98	134.66
150	13.00	182.58
75	3.95	131.02
175	13.42	175.64
300	6.28	184.70
200	9.16	159.91
450	4.03	209.64
23	1.12*	208.78
150	10.41	155.41

* Extrapolated

During the next quarter, methods for determining the vapor pressure of MoS₂ will be evaluated. In addition, a set of static experiments with H₂S over CoMo catalyst has been initiated in an attempt to grow MoS₂ crystals. The application of these techniques to studies of other available metal sulfides is under review.

Figure 13. Weight gain as a function of reaction time for CoMo catalyst exposed to H₂S. Dashed line shows theoretical value for stoichiometric MoS₂

Figure 14. Total weight gain per unit surface area for CoMo catalyst exposed to H_2S

FUTURE WORK

The following activities are planned for the next quarter:

1. Installation, testing and preliminary evaluation of detectors for determining solid-phase residence time in the tubular flow reactor.
2. Continuation of parametric tubing bomb experiments to study the initial dissolution of coal.
3. Installation of a communications link between the reactor and a Modcomp classic computer to determine if the Kaye data logger is adaptable to computer data acquisition.
4. Development of a distillation technique to split liquid product from the reactor into several boiling range fractions for solvent quality tests.
5. Determine the extent of solvent volatilization in coal/solvent slurries by means of DSC experiments.
6. Continuation of initial efforts to prepare, characterize and test several high-surface-area iron sulfides as disposable catalysts for coal liquefaction.
7. Preparation of acid-demineralized Robena pyrite for use in shock-loading experiments.
8. Evaluation of inexpensive, low-surface-area, supported catalysts (CoMo and NiMo on alumina) for coal liquefaction.
9. Determination of the mean residence time of catalyst samples taken from H-Coal PDU run No. 9.
10. Continuation of the physical and chemical characterization of catalyst from H-Coal PDU run No. 9.
11. Determination of the aging characteristics and changes in selectivity of catalysts with known residence times from the H-Coal PDU.
12. Determination of the vapor pressure of MoS_2 , and attempt to grow MoS_2 crystals by reacting H_2S with CoMo catalyst.

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