280
7/10/81
M.E.

(2)

DR-2824

DOE/ET/14806-T3

MASTER

THE ROLE OF NON-FERROUS COAL MINERALS AND BY-PRODUCT
METALLIC WASTES IN COAL LIQUEFACTION

Technical Progress Report for the Period December 1, 1979–February 29, 1980

By
D. Garg
E. N. Givens
J. H. Clinton
A. R. Tarrer
J. A. Guin
C. W. Curtis
S. M. Huang

D134-217
DT15-25

March 1980

Work Performed Under Contract No. AC22-79ET14806

Air Products and Chemicals, Inc.
Allentown, Pennsylvania

and

Auburn University
Auburn, Alabama

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE.

It has been reproduced from the best
available copy to permit the broadest
possible availability.

U. S. DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A06
Microfiche A01

DOE/ET/14806--T3

DE81 022044

**The Role of Non-Ferrous Coal Minerals
And By-Product Metallic Wastes in Coal Liquefaction**

Technical Progress Report

For Period December 1, 1979 - February 29, 1980

Air Products and Chemicals, Inc.

**D. Garg
E. N. Givens**

Auburn University

**J. H. Clinton
A. R. Tarrer
J. A. Guin
C. W. Curtis
S. M. Huang**

March 1980

Prepared for

The U.S. Department of Energy

Under Contract No. DE-AC02-79ET14806

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

Table of Contents

	<u>Page</u>
ABSTRACT	iv
OBJECTIVE	v
TECHNICAL PROGRESS	
Task 1.0 Feedstock Acquisition, Preparation and Characterization	1
1.1 Coal Feedstocks	1
1.2 Minerals, Metallic Wastes and Metal Containing By-Product Samples	3
1.3 Process Solvent	9
Task 2.0 Thermal Behavior of the Minerals and Metallic Wastes	9
Task 3.0 Standardization Runs and Base Case Determination	83
Task 4.0 Effect of Coal Minerals on Coal Liquefaction	83
4.1 Autoclave Screening Studies at Auburn	96
REFERENCES	100
APPENDIX A	101
APPENDIX B	104
APPENDIX C	105

ABSTRACT

This report describes work done in the second quarter of a study of the role of coal minerals and by-product metallic wastes in coal liquefaction. Samples of Elkhorn #3 coal (Letcher County, Kentucky), Robena pyrite and several minerals and metallic by-product waste were acquired. Distillation of SRC-II Fuel Oil Blend was performed to obtain additional amounts of 550°F+ fraction to be used for coal liquefaction runs. The thermal behavior of various minerals and metallic by-product wastes was evaluated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) in the presence of hydrogen, nitrogen and air. Magnetite was found to lose only 10% of the weight loss necessary for complete stoichiometric reduction at 450°C and 1000 psig hydrogen pressure. The chemical forms of zinc present in the zinc flue dust (high and low zinc contents) samples were identified as ZnFe_2O_4 and ZnO . On hydrogen reduction the amount of ZnFe_2O_4 present in the samples diminished while elemental iron and the FeO isomorph appeared in the product. The quantity of ZnO was not greatly affected by the hydrogen treatment. Zircon, quartz, calcite, kaolinite and feldspar were unaffected by hydrogen treatment at 450°C and 1000 psig pressure. The pyrolysis of pyrite was found to be independent of particle sizes. The pyrite sample (-325 mesh) was reduced in the PTGR at different reaction temperatures and 1000 psig hydrogen pressure. The hydrogen-reduced sample at 450°C was analyzed by x-ray diffraction and Mossbauer and found to be FeS, troilite; whereas the sample reduced at 600°C was found to have elemental iron in addition to troilite. The extent and rate of pyrite reduction were found to increase with reaction temperature. Various coal preparation plant waste materials were found to lose from 16 to 32% of their initial weight in the presence of nitrogen and hydrogen gases.

The coal process development unit (CPDU) was operated for 220 hours to obtain baseline data and provide information on the catalytic activity of Robena pyrite in solvent hydrogenation and coal liquefaction. During this reporting period, we established that the base line reaction conditions to evaluate the activity of the various minerals, metallic wastes and by-products will be a tubing-bomb reactor of 46.3 ml volume at a reaction temperature of 450°C

for reaction times of 60 minutes. The reduced pyrite, Robena pyrite and Siniola Mexico pyrite were found to give similar product distribution and coal conversion. The oil production in the cases of reduced pyrite and pyrite was 4 times higher than that of no-catalyst run. Iron oxide (Fe_2O_3) was shown to give slightly higher coal conversion and oil production than pyrites and reduced pyrite. Presulfided Co-Mo-Al was found to give the highest coal conversion and oil production. The increase in oil production in the case of Co-Mo-Al was due to the conversion of both asphaltenes and preasphaltenes.

OBJECTIVE

The objective of this research program is to investigate options for the development of low-cost disposable catalysts for use in enhancing the performance and economics of coal liquefaction. Various minerals, metal containing by-products and waste materials will be studied to determine whether coal conversion and product quality are affected by their addition as catalysts. The research program is divided into six major tasks with several subtasks within each area. An outline of the program is given below.

1. Select and acquire minerals and metal-containing waste materials.
2. Examine these materials both chemically and physically for uniformity, composition, foreign matter, moisture and cleanliness.
3. Select methods and prepare samples based on physical and chemical results and prior experience in evaluating catalytic materials.
4. Evaluate additives in preliminary autoclave screening tests, both alone and in the presence of iron sulfide.
5. Prepare additional samples for the screening tests in the continuously stirred tank reactor (CSTR) when warranted.
6. Evaluate promising materials under realistic reaction conditions where operating parameters approximate commercial design conditions.

TECHNICAL PROGRESS

Task 1.0 Feedstock Acquisition, Preparation and Characterization

Task 1.1 Coal Feedstocks

Progress - The choice of Elkhorn #3 coal was based in large part on the results of Granoff and Thomas (1) who found that conversion levels were quite low for this low pyrite content coal. The Penn State Coal Data Base (PSDB) contains numerous examples of Elkhorn coals which, as shown below, have low ash and mineral contents with low levels of pyrite.

<u>Sample I.D.</u>	<u>% Ash</u>	<u>% Pyrite Sulfur</u>
PSOC-001	3.96	0.10
PSOC-002	3.90	0.02
PSOC-003	4.65	0.01
PSOC-004	2.07	0.18
PSOC-005	4.78	0.77
PSOC-006	4.50	0.02

Therefore, in order to build a reaction network around a low pyrite content coal that also gives low conversion, we selected Elkhorn #3 coal as a logical approach to elucidating mineral effects on liquefaction.

The University of Kentucky Institute of Mining and Minerals Research (IMMR) graciously supplied us with information regarding the Elkhorn coals and offered to obtain both low ash and high ash samples. A sample of Elkhorn #3 coal was obtained (run of mine) from Floyd County and sent to Empire Coke Company for grinding and drying. The ground coal was found to contain 14.6% ash with a complete chemical analysis as shown in Table 1. This sample of coal has been extensively evaluated both here and at Auburn University.

Table 1
Analysis of Elkhorn #3 Coal Obtained from
Floyd County, Kentucky

Proximate Analysis

	<u>Weight %</u>
Moisture	1.81 $\pm$ 0.03
Volatile	37.56 $\pm$ 0.10
Fixed Carbon	46.03
Dry Ash	14.60 $\pm$ 0.02

Ultimate Analysis

C	69.40
H	4.88
N	1.00
S	1.94
O (by difference)	8.18

Distribution of Sulfur

Total Sulfur	1.94
Sulfate Sulfur	0.04
Pyrite Sulfur	1.19
Organic Sulfur	0.75

Another sample of Elkhorn #3 coal was obtained from Letcher County based on the Penn State Data Base (PSDB) number PSOC-001. This sample, again run of mine, was selected from a mine close to the location where the original sample (PSOC-001) was taken and represented a close approximation of that location. This sample, after being crushed and sieved to -200 U.S. Mesh, was submitted for ultimate and proximate analyses. The results will be reported when they become available. This coal was found to contain 34.34% ash as opposed to 3-4% ash reported for PSOC-001. The reason for the unexpectedly high ash content in the coal was that the ceiling of the mine was being scraped the day the sample was collected.

IMMR is assisting us in obtaining another low ash Elkhorn #3 coal sample. After extensive exploration, the decision was made to obtain a sample of Elkhorn #3 coal from Floyd County that had been processed in a coal preparation plant. This washed sample and the original run of mine sample will give us a good comparison of the activity of low ash and high ash coal samples.

Task 1.2 Minerals, Metallic Wastes and Metal Containing By-Product Samples

Objective - The objective of this subtask is to acquire, prepare, and characterize various minerals, metallic wastes and metal containing by-products. Several techniques such as grinding, washing, drying, sizing, etc. will be used for preparing the samples for autoclave screening tests.

Progress - Additional samples of various minerals and metallic wastes were received for preparation and characterization. The list of the samples along with their suppliers is given in Table 2. Two additional five gallon drums of pyrite were received from U.S. Steel's Robena Mine. This sample was dried at 110°C in nitrogen.

The chemical analyses of several of these materials provided by their suppliers are tabulated and presented in the Tables 3, 4, 5, 6, 7, and 8.

Table 2
Suppliers of Various Minerals and Metal Containing
By-Product Samples

Mexican Pyrite [FeS ₂]	Auburn University Geology Department Auburn, Alabama
Bornite Copper Ore [Cu ₅ FeS ₄]	Anaconda Birmingham, Alabama
Calcite [CaCO ₃]	Auburn University Chemical Engineering Department
Illite [KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂]	Department of Geology University of Missouri Columbia, MO 65211
Quartz [SiO ₂]	Sawyer Research Products 35400 Lakeland Boulevard East Lake, Ohio
Pea Ridge Magnetite Concentrates [Fe ₃ O ₄]	Bethlehem Steel Corporation Bethlehem, Pennsylvania
Blast Furnace Slag	Bethlehem Steel Corporation Bethlehem, Pennsylvania
Anhydrous Ferric Chloride [FeCl ₃]	Pennwalt Corporation Philadelphia, Pennsylvania
Molybdenite	Wards Natural Science Establishment Rochester, New York
South Dakota Pyrite [FeS ₂]	Wards Natural Science Establishment Rochester, New York
Molybdic Oxide [MoO ₂]	Climax Molybdenum Company Greenwich, Connecticut
Flue Dust	Air Products and Chemicals, Inc. Greenville, Pennsylvania
Super Alloy Grindings (Howmet)	Air Products and Chemicals, Inc. Greenville, Pennsylvania
Alnico Grindings (Hitachi)	Air Products and Chemicals, Inc. Greenville, Pennsylvania

Table 2
(continued)

X-Type Molecular Sieve	W. R. Grace and Company Upper Darby, Pennsylvania
Mordenite	W. R. Grace and Company Upper Darby, Pennsylvania
Chabozite	W. R. Grace and Company Upper Darby, Pennsylvania
Speculite [Fe₂O₃]	Chemalloy Company, Inc. Bryn Mawr, Pennsylvania
Red Oxide [Fe₂O₃]	Ferro Ottawa Chemical Division Toledo, Ohio
Red Mud	U.S. Department of Interior Bureau of Mines Tuscaloosa Research Center University, Alabama
Zinc Sulfide [ZnS]	Metals and Minerals Research Zerba Research Center Bethlehem, Pennsylvania

Table 3.

Typical Chemical Analyses of Speculite(Red Iron Oxide) Sample

	<u>Weight %</u>
Fe	65.1
Fe ₂ O ₃	94.1
SiO ₂	5.0
Al ₂ O ₃	0.75
Mn	0.03
P	0.025
S	0.03

Table 4

Chemical Analyses of Pea Ridge Magnetite Concentrate

	<u>Weight %</u>
Fe	69.7
SiO ₂	2.24
Al ₂ O ₃	0.3
CaO	0.36
MgO	0.29
S	0.015
P	0.084

Table 5

Chemical Analyses of Molybdic Oxide

	<u>Weight %</u>
Mo	58.7
S	0.10
Cu	0.02
Pb	0.07
P	0.01

Table 6
Chemical Analyses of Flue Dust,
Superalloy Grindings and Alnico Grindings

	Weight %		
	<u>Superalloy</u>	<u>Flue Dust</u>	<u>Alnico</u>
Ni	55.9	10.98	9.26
Cr	12.5	5.13	0.02
Mo	3.62	0.61	0.01
Co	9.27	7.66	15.71
W	3.10	--	--
Fe	0.53	20.32	42.13
C	--	3.00	1.05
Mn	--	0.52	0.13
S	--	0.50	0.08
SiO ₂	--	5.36	--
Cu	--	1.01	1.78
Pb	--	0.57	0.01
Sn	--	0.01	0.05
Al	--	2.46	4.92
Ti	--	0.30	0.45
V	--	0.05	0.01
Moisture	--	0.01	--
Mg	--	3.00	--
Acid Insolubles	9.13	9.09	23.39

Table 7
Chemical Analyses of Red Mud

	<u>Weight %</u>
Al_2O_3	15.0
Fe_2O_3	51.5
SiO_2	1.7
TiO_2	6.7
CaO	7.0
Na_2O	1.0
Loss of Ignition at 1000°C	9.3

Table 8
Chemical Analyses of Zinc Sulfide

	<u>Weight %</u>
Zn	62.6
S	31.2
Pb	0.54
Cu	0.21
Fe	1.0
CaO	0.28
MgO	0.14
SiO_2	2.45
Al_2O_3	0.03

Task 1.3 Process Solvent

Progress - Four different batches of SRC-II distillate (approximately 900 lbs each) were distilled to recover the 550°F+ fraction that was used in the standardization runs. Analysis of the 550°F+ fraction is reported in Table 9. The GC simulated distillation of the distilled solvent, which is presented in Table 10, showed that 11% of the material boiled below 550°F. The difference between vacuum distillation and the GC simulated distillation can be explained by the accuracy of simulated distillation as opposed to crude vacuum distillation; the simulated distillation column used here has 200 theoretical plates, whereas the vacuum distillation unit had only 15-20 plates. In order to cut distillation time and costs five additional drums of 550°F+ solvent were requested from the SRC-II pilot plant in lieu of distilling more full range fuel oil blend.

The elemental analysis of the process solvent and the distribution of hydrogen as determined by NMR are presented in Table 9. Of the hydrogen present in the sample, 42% was aromatic and 28% was benzylic. The transferable hydrogen is lumped into the benzylic hydrogen and is responsible for the transfer of hydrogen from the solvent to coal free radicals.

Task 2.0 Thermal Behavior of the Minerals and Metallic Wastes

Objective - The objective of this subtask is to evaluate the stability of minerals, metal by-products and metallic wastes under coal liquefaction conditions. The thermal stability will be evaluated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) in the presence of helium or nitrogen. The reactivity of the material with hydrogen will be evaluated in the TGA at atmospheric pressure and in the pressurized thermal gravimetric reactor (PTGR) at higher hydrogen pressures.

Table 9
Detailed Analysis of 550°F+ Fraction of
SRC-II Fuel Oil Blend

<u>Element</u>	<u>Weight %</u>
Carbon	88.79
Hydrogen	7.40
Oxygen	1.96
Nitrogen	1.20
Sulfur	<u>0.48</u>
	99.83
 Molecular Weight	 210
 Distribution of Hydrogen, %	
^H Aromatic	42.0
^H Benzylic	29.3
^H Other	28.7

Table 10
Simulated Distillation of 550°F+ Fraction of
SRC-II Fuel Oil Blend

<u>Weight % Off</u>	<u>Temperature °F</u>
I.B.P.	513
5%	536
10%	547
11%	550
20%	576
30%	597
40%	615
50%	638
60%	663
70%	690
80%	721
90%	773
95%	820
97%	850
99%	900
F.B.P.	921

Analyses

Several minerals and metallic waste samples were analyzed by TGA, DTA and in the PTGR in the presence of different gases. The results of these analyses are discussed below.

Magnetite - A magnetite sample reduced at 450°C under 1000 psig hydrogen pressure for 10 minutes in the PTGR (fast heating) lost approximately 2.7% weight. The mass distribution of products obtained from reduction of the magnetite in the PTGR is given in Table 11. This weight loss corresponds to only 10% of the weight loss necessary for complete stoichiometric reduction. Therefore, if magnetite is used as a disposable catalyst in coal liquefaction, only a small fraction of the total hydrogen required for coal liquefaction will be consumed in reducing the magnetite.

The DTA of magnetite in the presence of air showed a small exotherm from room temperature to 120°C (see Figure 1). This exotherm, the only thermal activity that was observed, was apparently due to oxidation of carbon and other impurities present in the sample.

Zinc Flue Dusts - Hydrogen reduction of zinc flue dusts (low and high zinc contents) was reported in the first quarterly progress report. The samples of zinc flue dusts before and after hydrogen reduction in the PTGR were analyzed by x-ray diffraction. The major difference between the two zinc samples was the concentration of zinc. The chemical forms of zinc present in the two samples were identified as ZnFe_2O_4 and ZnO . After hydrogen reduction the amount of ZnFe_2O_4 present in the sample diminished and elemental iron and the FeO isomorph appeared. The concentration of ZnO was not greatly affected by the treatment. Zinc metal was not observed either before or after reduction. Apparently the iron oxide reduces in preference to the zinc oxide.

Table 11
Reduction of Magnetite in PTGR

Temp., °C	450
H ₂ Pressure, psig	1000
Initial Weight, g	3.0
Final Weight, g	2.92
Weight Loss, g	0.08
Weight Loss, %	2.67
Gas Analyses, g water	0.0378
Liquid Analyses*	--

*Not enough sample was available for analysis.

FIGURE 1
DTA OF MAGNETITE IN THE PRESENCE OF AIR

The DTA's of zinc flue dust samples (low and high zinc contents) in the presence of helium and air are shown in Figures 2, 3, 4 and 5. The low zinc and high zinc flue dust samples gave minor endotherms at 133 and 72°C, respectively, in the presence of helium. These endotherms are probably due to vaporization of moisture present in the samples. Similarly, minor endotherms were observed in the presence of air at somewhat lower temperatures. Also, very minor exotherms at 360°C (low zinc sample) and at 109°C (high zinc sample) were apparently due to the oxidation of the sample. The high zinc sample, in addition to both an endotherm and exotherm at low temperatures, also gave an endotherm at 495°C which was possibly due to fusion of the sample.

Fly Ashes

Green River (Blend) Fly Ash - The sample was obtained from Green River power plant located at Moorman, Muhlenberg Co., Kentucky. It was taken when burning a "blend" of two W. Kentucky coals in the power plant. The DTA of the sample in the presence of helium showed no thermal activity (see Figure 6), whereas in the presence of air an exotherm occurred around 587°C (see Figure 7). The exotherm is due to the oxidation of some of the compounds present in the fly ash.

Green River (High) Fly Ash - The sample was also obtained from Green River power plant. It was taken when burning "high" sulfur W. Kentucky coal in the power plant. The DTA's of Green River (High) Fly Ash were found to be similar to that of the blend except for an exotherm at 630°C instead of 587°C. The DTA's are shown in Figures 8 and 9.

Brown Fly Ash - The fly ash sample was obtained from E. W. Brown power plant located at Burgin, Mercer Co., Kentucky. The sample was taken when burning E. Kentucky coal in the power plant. The DTA in the presence of helium showed no thermal activity (see Figure 10). The DTA in the presence of air showed an exotherm at 660°C due to oxidation of the material (see Figure 11).

FIGURE 2
DTA OF LOW ZINC FLUE DUST IN THE PRESENCE OF HELIUM

FIGURE 3
DTA OF HIGH ZINC FLUE DUST IN THE PRESENCE OF HELIUM

FIGURE 4
DTA OF LOW ZINC FLUE DUST IN THE PRESENCE OF AIR.

FIGURE 5
DTA OF HIGH ZINC FLUE DUST IN THE PRESENCE OF AIR

FIGURE 6

**DTA OF GREEN RIVER FLY ASH (BLEND)
IN THE PRESENCE OF HELIUM**

FIGURE 7

**DTA OF GREEN RIVER FLY ASH (BLEND)
IN THE PRESENCE OF AIR**

FIGURE 8
DTA OF GREEN RIVER FLY ASH (HIGH)
IN THE PRESENCE OF HELIUM

FIGURE 9
DTA OF GREEN RIVER FLY ASH (HIGH) IN THE PRESENCE OF AIR

FIGURE 10
DTA OF BROWN FLY ASH IN THE PRESENCE OF HELIUM

FIGURE 11
DTA OF BROWN FLY ASH IN THE PRESENCE OF AIR

Paradise Fly Ash - The fly ash sample was obtained from Paradise power plant located at Paradise, Muhlenberg Co., Kentucky. The sample was taken when burning E. Kentucky coal. The DTA of Paradise Fly Ash in the presence of helium showed one minor endotherm at around 110°C due to the loss of moisture from the sample, whereas in the presence of air a minor exotherm at 631°C was observed due to oxidation of the sample. The DTA's are shown in Figures 12 and 13.

The results from the reduction of the above fly ashes, carried out at high pressure (1000 psig hydrogen) in the PTGR, are summarized in Table 12. The weight loss was insignificant for all the samples with the maximum weight loss being only 4%. Water, the major product of the reduction, was trapped in the dry ice trap but wasn't analyzed due to the small sample size.

Bottom Ashes

Green River Bottom Ash - The bottom ash sample was obtained from Green River power plant located at Moorman, Muhlenberg Co., Kentucky. The TGA of the sample in the presence of hydrogen and nitrogen is shown in Figure 14. The sample started losing weight at around 100°C and continued to lose weight up to 700°C. The sample appeared to contain some volatiles since it lost approximately 11% weight by the time it reached 700°C in the presence of nitrogen. The weight loss was even greater in the presence of hydrogen because of reduction taking place in addition to pyrolysis.

The sample was analyzed by DTA in the presence of air to determine combustible material present in the sample. The sample gave a strong exotherm at around 400°C (see Figure 15), which verified the presence of volatile/combustible material in the sample.

FIGURE 12
DTA OF PARADISE FLY ASH IN THE PRESENCE OF HELIUM

FIGURE 13
DTA OF PARADISE FLY ASH IN THE PRESENCE OF AIR

Table 12

Reduction of Fly Ashes in the PTGR

Reaction Time = 10 Minutes, Temp. = 450°C

Pressure = 1000 psig H₂

Sample	Initial Weight, g	Final Weight, g	Weight Loss		Gas Analyses, g		Total Recovered Product, g	% Recovery of Lost Wt.
			g	%	N ₂	H ₂ O		
Brown Fly Ash	3.00	3.00	0.0	0.0	--	--	--	--
Paradise Fly Ash	3.00	2.88	0.12	4.0	0.0040	0.0400	0.044	37.0
Green River Fly Ash								
Blend	3.00	2.91	0.09	3.0	0.0030	0.0350	0.038	42.0
High	3.00	2.92	0.08	2.7	0.0036	0.0355	0.040	50.0

FIGURE 14
TGA OF GREEN RIVER BOTTOM ASH IN THE PRESENCE
OF HYDROGEN AND NITROGEN GASES

FIGURE 15
DTA OF GREEN RIVER BOTTOM ASH
IN THE PRESENCE OF AIR

Paradise Bottom Ash - The sample was obtained from Paradise power plant located at Paradise, Muhlenberg Co., Kentucky. The TGA of Paradise Bottom Ash showed no weight loss either in the presence of hydrogen or nitrogen, as shown in Figure 16. The DTA of the sample in the presence of air, Figure 17, showed a broad exotherm over much of the temperature range, due to the oxidation of various sample components.

Brown Bottom Ash - The bottom ash sample was obtained from E. W. Brown power plant located at Burgin, Mercer Co., Kentucky. The sample lost approximately 2 and 5% weight at 600°C in the presence of nitrogen and hydrogen, respectively. The sample started losing weight at around 450°C in the presence of nitrogen and at 200°C in the presence of hydrogen, as shown in Figure 18. The higher loss in weight in the presence of hydrogen as opposed to nitrogen is due to reduction of the sample in addition to pyrolysis. The DTA of the sample in air (see Figure 19), showed one broad exotherm in the range 100 to 300°C and one sharp exotherm at around 440°C. The sharp exotherm is due to oxidation of the organic material present in the sample. The origin of the broad exotherm is not explainable at the present moment.

The reduction of the bottom ashes is being carried out at higher hydrogen pressure in the PTGR and the results will be reported when they are completed.

Copperas (Ferrous Sulfate) - The DTA of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the presence of air is shown in Figure 20. A small endotherm followed by a very large endotherm were observed in the temperature range of 75 to 150°C. The endotherms were due to the loss of water of crystallization. A small exotherm just above 200°C may be due to the oxidation of ferrous iron. This sample will be dried to remove water of crystallization before using it as an additive in coal liquefaction.

FIGURE 16
TGA OF PARADISE BOTTOM ASH IN THE PRESENCE
OF HYDROGEN AND NITROGEN GASES

FIGURE 17
DTA OF PARADISE BOTTOM ASH IN THE PRESENCE OF AIR

FIGURE 18
TGA OF BROWN BOTTOM ASH IN THE PRESENCE OF
HYDROGEN AND NITROGEN GASES

FIGURE 19
DTA OF BROWN BOTTOM ASH IN THE PRESENCE OF AIR

FIGURE 20
DTA OF $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ IN THE PRESENCE OF AIR

Terra Alba F&P Gypsum - The TGA of Terra Alba F&P gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the presence of hydrogen and nitrogen is shown in Figure 21. A sharp 19% initial weight loss was observed between 100 and 200°C in the presence of both gases. The weight loss is due to loss of water of hydration. The combined water present in the gypsum was reported to be 19.8% (see first quarterly progress report). So, the observed weight loss of 19% corresponds very well to the amount of combined water present in the sample. The sample lost water of hydration at lower temperature in the presence of hydrogen than in the presence of nitrogen. This is probably due to the differences in the flow rates of the two gases used. The influence of gas flow rate on weight loss is presently being evaluated and results will be reported when they become available.

The DTA of two different gypsums (Terra Alba F&P and Terra Alba #105) gave a large endotherm between 100 and 150°C (see Figures 22 and 23). The endotherm is due to loss of water of hydration. The sample, after losing waters of hydration, was thermally stable in the presence of air up to 550°C. The waters of hydration of the gypsum will be removed before using it as an additive/catalyst in coal liquefaction.

Kaolinite (Burgess #10) - The sample was stable from room temperature to 300°C both in the presence of hydrogen and nitrogen. The sample lost approximately 13% weight at about 625°C in the presence of both gases, as shown in Figure 24. The loss in weight is due to loss of structural water from clay matrix. This point will be kept in mind when using this material in coal liquefaction run.

The kaolinite sample was reduced at high hydrogen pressure in the PTGR and the results are reported in the Table 13. Negligible weight loss was observed at 450°C and 1000 psig hydrogen pressure. This simply means that kaolinite is chemically and thermally stable at typical coal liquefaction reaction conditions.

FIGURE 21
TGA OF GYPSUM (TERRA ALBA F&P) IN THE PRESENCE
OF HYDROGEN AND NITROGEN GASES

FIGURE 22
DTA OF TERRA ALBA F&P GYPSUM
IN THE PRESENCE OF AIR

FIGURE 23
DTA OF TERRA ALBA #105 GYPSUM
IN THE PRESENCE OF AIR

FIGURE 24
TGA OF KAOLINITE (BURGESS #10) IN THE PRESENCE
OF HYDROGEN AND NITROGEN GASES

Table 13

Reduction of Minerals in the PTGR

Reaction Time = 10 Minutes, Temperature = 450°C

Pressure = 1000 psig, H₂

<u>Sample</u>	Initial Weight <u>g</u>	Final Weight <u>g</u>	<u>Weight Loss</u>	
			<u>g</u>	<u>%</u>
Zircon -325 Mesh	2.82	2.82	0.0	0.0
Zircon Concentrate	2.82	2.82	0.0	0.0
Quartz U.S.A.	2.82	2.82	0.0	0.0
Quartz Brazil	2.82	2.82	0.0	0.0
Calcite	2.82	2.82	0.0	0.0
Kaolinite Burgess #10	2.82	2.80	0.02	0.02
Feldspar NC 4	3.00	3.00	0.0	0.0

The DTA of kaolinite in air is shown in Figure 25. An endotherm observed around 400°C was very broad and continued beyond the temperature range used in the experiments. The endotherm is due to loss of lightly bound water in the clay matrix.

Apatite (Monocalcium, Dicalcium, and Tricalcium Phosphate) -

Endotherms were observed at around 270 to 290°C due to loss of water of hydration and condensation of hydroxyl groups into the oxide (see Figures 26, 27, and 28). The monocalcium phosphate showed this process most clearly, whereas the latter process dominated in the dicalcium phosphate. The tricalcium phosphate has no hydroxyl group to lose, hence no endotherms appeared in the DTA trace at the indicated temperature. There is some indication of loss of moisture around 200°C.

Zircon and Zircon Concentrates - The small endotherms between 100 and 200°C in air (see Figures 29 and 30) were due to the loss of absorbed water. Both zircon samples are thermally stable up to 500°C.

Both zircon samples were stable at 1000 psig H₂ pressure and 450°C temperature (see Table 13).

Quartz U.S.A. - DTA of quartz (Figure 31) showed no major features up to 500°C. The curve basically represents the shift in the base line. The apparent endotherm around 175°C could be due to impurities present in the sample.

The sample was subjected to hydrogen reduction conditions in the PTGR, but no reduction was observed at 1000 psig hydrogen pressure and at 450°C (see Table 13).

Calcite - The DTA of calcite gave no endothermic or exothermic activities, as shown in Figure 32. The curve represents the fluctuation in the baseline. Also, no reduction of the sample was observed in the PTGR at 1000 psig hydrogen pressure and 450°C, as shown in Table 13.

FIGURE 25
DTA OF KAOLINITE (BURGESS #10)
IN THE PRESENCE OF AIR

FIGURE 26
DTA OF APATITE (MONOCALCIUM PHOSPHATE)
IN THE PRESENCE OF AIR

FIGURE 27
DTA OF APATITE (DICALCIUM PHOSPHATE)
IN THE PRESENCE OF AIR

FIGURE 28
DTA OF APATITE (TRICALCIUM PHOSPHATE)
IN THE PRESENCE OF AIR

FIGURE 29
DTA OF ZIRCON IN THE PRESENCE OF AIR

FIGURE 30
DTA OF ZIRCON CONCENTRATES IN THE
PRESENCE OF AIR

FIGURE 31
DTA OF QUARTZ, USA IN THE PRESENCE OF AIR

FIGURE 32
DTA OF CALCITE IN THE PRESENCE OF AIR

Rutile - There were no major features in the DTA of rutile in the presence of air. The small endotherms between 150 to 225°C (see Figure 33) were due to loss of water adsorbed on the surface of the mineral.

Ilmenite - No sharp features were observed in the DTA of ilmenite in air. A broad endotherm around 400°C, as shown in Figure 34, was due to impurities present in the mineral.

Feldspar (NC4) - No major features in the DTA in air (see Figure 35) were observed. The material was also found to be insensitive to hydrogen reduction at high pressure in the PTGR (see Table 13).

Illite - Small exotherms were observed in the DTA of illite in the presence of air, as shown in Figure 36. The exotherms are due to oxidation of inorganic and iron constituents of the mineral.

Pyrite - The pyrolysis of several particle sizes (+40, 40 x 80, 140 x 200 and -200 mesh) of Robena pyrite was discussed in the first quarterly progress report. Different particle size pyrite samples, except for the -200 mesh size, were found to decrease in weight by 22-23 percent. The -200 mesh fraction behaved differently in that it lost only 18% weight at 600°C. Two reasons for the differences in weight loss were:

- (1) the larger size fractions contained on average 20% higher total sulfur than the -200 mesh fraction, so they had more available sulfur for thermal distillation;
- (2) mineral analysis as determined by x-ray diffraction analysis showed different mineral concentrations in these fractions.

Gamma-FeS₂ which was present as pyrite and marcasite was found in all the fractions. The -200 mesh fraction contained Fe₃O₄ (magnetite) in addition to gamma-FeS₂. Fe₃O₄ had earlier been shown to be thermally stable up to 600°C. So, the presence of Fe₃O₄ as an impurity in the sample would account for some reduction in weight loss of the -200 mesh sample.

FIGURE 33
DTA OF RUTILE IN THE PRESENCE OF AIR

FIGURE 34
DTA OF ILMENITE IN THE PRESENCE OF AIR

FIGURE 35
DTA OF FELDSPAR (NC4) IN THE PRESENCE OF AIR

FIGURE 36
DTA OF ILLITE IN THE PRESENCE OF AIR

The total sulfur content of the -325 mesh sample of Robena pyrite and its thermogram as shown in Figure 37 were found to be similar to that of other fractions except for the -200 mesh fraction. This supports pyrolysis of pyrite as being independent of particle size if total sulfur contents are the same.

Effect of Heating Rate - The pyrolysis of -325 mesh Robena pyrite was studied at three different heating rates. The initial decomposition was independent of heating rate. The initial loss in weight occurred at approximately 400°C for all heating rates. The overall final weight loss at 700°C was identical for all the heating rates studied here (see Figure 38).

The reduction of -200 and -325 mesh pyrite was performed in the PTGR at different temperatures and was compared as shown in Figure 39. The -325 mesh, which had a considerably higher total sulfur content than the -200 mesh (41.3% as opposed to 35.7%) material, lost more weight at all the temperatures than the -200 mesh fraction.

The reduced -200 mesh fractions, prepared at 450°C and 600°C, were analyzed by x-ray diffraction and Mössbauer to identify the iron-sulfur species and to determine the distribution of iron in the samples. By x-ray diffraction, the iron sulfide, identified as troilite, had approximately the same concentration in both samples. Both samples also had three other very weak unidentified peaks. The diffraction pattern also showed elemental iron in the 600°C sample but none in the 450°C sample.

The distribution of iron was determined by Mössbauer as shown in Table 14. The distribution between the two samples suggests that some of the pyrrhotite was reduced at the higher temperature. Although the effect of hydrogen sulfide partial pressure on the FeS reduction is well known (2), the amounts of H₂S in the reactor during these runs are unknown.

FIGURE 37
TGA OF -325 MESH ROBENA PYRITE IN THE PRESENCE
OF HELIUM GAS

FIGURE 38
EFFECT OF HEATING RATE ON PYROLYSIS OF -325 MESH PYRITE

FIGURE 39
HYDROGEN REDUCTION OF ROBENA PYRITE IN PTGR

Table 14
Distribution of Fe in the Hydrogen Reduced
Samples of Pyrite (-200 U.S. Mesh)

Reduction Pressure = 1000 psig H₂
Time = 10 Minutes

Temperature, °C	Fe Distribution, wt.%		
	Troilite	Fe ₃ O ₄	alpha-Fe
450	86	14	0
600	80	11	8

The hydrogen reduction kinetics of -325 mesh fraction of Robena pyrite studied in the PTGR are shown in Figure 40. It can be seen that as temperature increases more pyrite is reduced. Also, the reduction time decreases with increasing reaction temperature. At typical coal liquefaction reaction conditions of 450°C and 2000 psig, only 4 minutes are required to reduce the pyrite to pyrrhotite (the effect of pressure was shown to be negligible on pyrite reduction in the first quarterly progress report).

Robena Pyrite-Magnetite Mixture - The possibility of generating reduced pyrite by reacting a mixture of pyrite and magnetite simultaneously was examined in the PTGR. The individual and coupled reactions would be as follows.

Experimentally we reduced a 50-50 mixture by weight of pyrite and magnetite at 450°C and 1000 psig. Theoretically, if the reaction proceeded by Equations 1-3, a production distribution as developed in Appendix B would be expected (Table 15). From that distribution of materials the relative distribution of iron among the various iron species could be calculated as shown in Table 16.

The reaction product taken from the PTGR was analyzed by x-ray diffraction. FeS (troilite) and Fe₃O₄ were the major phases and elemental iron a minor phase present in the sample. The observed distribution of elemental iron in the sample, as determined by Mossbauer, is given in Table 16. The elemental iron distribution as calculated by Equation 3 does not match the Mossbauer result (Table 16). Thus, Equation 3 does not give a good representation of the behavior of magnetite and pyrite that we observed. Assuming no reaction occurred between magnetite and pyrite and both compounds reduced individually as pure compounds, we determined a calculated weight loss and compared with the observed weight loss (Table 17).

FIGURE 40
REDUCTION OF -325 MESH ROBENA PRYRITE
IN THE PTGR

Table 15
Reduction of Pyrite-Magnetite Mixture in the PTGR

Reaction Mixture:
 Pyrite = 1.5 g
 Magnetite = 1.5 g
 Reaction Temp. = 450°C
 Pressure = 1000 psig H₂

<u>Material</u>	<u>Theoretical* Distribution, Wt. %</u>
FeS	80.7
Fe ₃ O ₄	19.1
alpha-Fe	0.2

*From Appendix B

Table 16
Distribution of Elemental Iron as Determined by Mössbauer in the Reaction
Product of Pyrite Magnetite Reduction

	<u>Theoretical</u> <u>Distribution</u> <u>Weight %</u>	<u>Observed</u> <u>Distribution</u> <u>Weight %</u>
FeS	78.5	34.0
Fe ₃ O ₄	21.1	49.0
Fe	0.36	13.0
Other	--	4.0

Table 17
Reduction of Pyrite, Magnetite and a 50-50 Mixture

	<u>100% Pyrite</u>	<u>100% Magnetite</u>	<u>Pyrite - Magnetite 50-50</u>
U.S. Mesh Size	-200	-200	-200
Temp., °C	450	450	450
Initial Weight, g	3.00	3.00	3.00
Final Weight, g	2.48	2.92	2.73
Weight Loss, %	17.33	2.67	9.00
Calculated Weight Loss, *%	--	--	10.00

Distribution of Elemental Iron

	<u>Calculated Weight %</u>	<u>Observed Weight %</u>
FeS	38.8	34.0
Fe ₃ O ₄	58.6	49.0
alpha-Fe	2.5	13.0
Other	--	4.0

*Calculated on the basis of no reaction of pyritic sulfur with magnetite

The calculated and observed weight losses are very close. This calculation is based on the assumption that none of the H_2S produced from the pyrite reduction (Eqn. 1) reacts with the magnetite (Eqn. 2). Likewise, the calculated iron distribution for the 50-50 mixture and the Mössbauer distribution are also quite similar.

Therefore, on the basis of the above results there seems to be little interaction of magnetite with pyrite under these conditions. Likewise, these compounds appear to behave as individual compounds.

Coal Preparation Plant Waste Materials - The TGA of the various coal preparation plant waste materials listed in Table 18 studied in the presence of hydrogen and nitrogen are shown in Figures 41 to 48. These materials show very similar thermograms with weight losses varying between 16 and 32% of the initial weight. The weight loss is due to volatile organic matter (coal) present in the samples and the variation in weight loss is due to the different amounts of organic material present in the samples.

The DTA's of the above coal preparation plant waste materials in the presence of air are shown in Figures 49 to 54. All these samples show very similar thermograms, with two exothermic peaks, both quite broad and in the temperature range of 325 to 450°C. The exotherms are due to the oxidation of the carbonaceous material present in the samples. The DTA of the Colonial/P&M coal preparation plant waste material was repeated to check the reproducibility and is shown in Figure 54. Also, the sample after the DTA analysis was left in the instrument, cooled down to room temperature, and again analyzed in the presence of air for its thermal activities. On the second pass, the sample was essentially inert (Figure 54). So, once the carbonaceous material was oxidized, the oxidized product showed no more thermal activity in the presence of air.

Table 18

Coal Preparation Plant Waste Materials

Hendrix/Beth-Elkhorn

Gund/Island Creek

Spurlock/Island Creek

Gilbrator/Amax

Fies/Island Creek

Hamilton #1/Island Creek

Colonial/Pittsburg and Midway

FIGURE 41
TGA OF HENDRIX/BETH - ELKHORN COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF
HYDROGEN AND NITROGEN GASES
(SAMPLE NO. BEH-P-C)

FIGURE 42
TGA OF GUND/ISLAND CREEK
COAL PREPARATION PLANT WASTE MATERIAL
IN THE PRESENCE OF HYDROGEN GAS
(SAMPLE NO. ICG-P-C)

FIGURE 43
TGA OF GUND/ISLAND CREEK
COAL PREPARATION PLANT WASTE MATERIAL
IN THE PRESENCE OF HYDROGEN AND NITROGEN GASES
(SAMPLE NO. ICG-P-F)

FIGURE 44
TGA OF SPURLOCK/ISLAND CREEK
COAL PREPARATION PLANT WASTE MATERIAL
IN THE PRESENCE OF HYDROGEN AND NITROGEN GASES
(SAMPLE NO. ICS-P-C)

FIGURE 45
TGA OF GILBRATOR/AMAX COAL PREPARATION PLANT WASTE MATERIAL
IN THE PRESENCE OF NITROGEN AND HYDROGEN GASES
(SAMPLE NO. AG-P-M)

FIGURE 46
TGA OF FIES/ISLAND CREEK COAL
PREPARATION PLANT WASTE MATERIAL
IN THE PRESENCE OF HYDROGEN AND NITROGEN GASES
(SAMPLE NO. ICF-P-CM)

FIGURE 47
TGA OF HAMILTON #1/ISLAND CREEK COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF
HYDROGEN AND NITROGEN GASES
(SAMPLE NO. ICH1-P-CM)

FIGURE 48
TGA OF COLONIAL/P&M COAL PREPARATION PLANT WASTE MATERIAL
IN THE PRESENCE OF HYDROGEN AND NITROGEN GASES
(SAMPLE NO. PMC-P-C)

FIGURE 49
DTA OF HENDRIX/BETH ELKHORN
COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 50
DTA OF GUND/ISLAND CREEK COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 51
DTA OF SPURLOCK/ISLAND CREEK
COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 52
DTA OF GILBRATOR/AMAX COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 53
DTA OF FIES/ISLAND CREEK COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 54

DTA OF COLONIAL/P&M COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

Task 3.0 Standardization Runs and Base Case Determination

Progress - The coal process development unit (CPDU) was operated for 220 hours to obtain baseline data and provide information on the catalytic activity of Robena pyrite in solvent hydrogenation and coal liquefaction. During 220 hours of operation, 18 different samples were taken and submitted for detailed analyses. A detailed summary of the operating data of the runs is given in Appendix A. The analytical results of the standardization runs will be reported as they become available.

Task 4.0 Effect of Coal Minerals on Coal Liquefaction

Progress - Two small tubing-bomb reactors (17.5 and 46.3 ml volume) were designed and assembled at Auburn University for preliminary screening studies of the catalytic activity of the various minerals, metallic and by-product wastes. Reproducibility runs were carried out in the 17.5 ml reactor. Hydrogenation runs of process solvent (550°F+ fraction of SRC-II Fuel Oil Blend) were carried out three times and the reaction products were solvent separated. The reaction conditions and the solvent separation results are given in Table 19. Similarly, six different coal liquefaction runs were made and the results are summarized in Table 20. Maximum standard deviations of 14.0 and 6.5 percent were observed in the asphaltene fraction of the solvent hydrogenation and coal liquefaction runs, respectively. Maximum standard deviation of 6.5% in the case of coal liquefaction runs is well within the range of experimental error.

Base Case Determination - A number of coal liquefaction runs with and without catalyst were made to establish base line data. Reaction conditions were sought which would give a sizeable difference in oil production between a non-catalyzed and a strongly catalyzed coal liquefaction system. After these reaction conditions are found, they will be used in evaluating the catalytic activity of various coal minerals, metallic wastes and metal by-products.

Table 19
Reproducibility Test of Solvent Hydrogenation Runs

	Weight %	
	Mean	Standard Deviation
Oil	90.68	0.87
Asphaltene	8.66	1.21
Preasphaltene	0.46	0.31
Residue	0.19	0.06

Reaction Conditions:

Reactor - 17.5 ml tubing-bomb

Solvent - 550°F + fraction of SRC-II Fuel Oil Blend

Temperature - 410°C

Pressure - 1250 psig H₂ at 25°C

Reaction Time - 30 Minutes

Oil - Pentane soluble

Asphaltene - Pentane insoluble, toluene soluble

Preasphaltene - Toluene insoluble, methylene chloride/
10% methyl alcohol soluble

Residue - Methylene chloride/10% methyl alcohol insoluble

Table 20
Reproducibility Test of Coal Liquefaction Runs

	Weight %	
	Mean	Standard Deviation
Oil	62.92	0.62
Asphaltene	12.28	0.80
Preasphaltene	9.65	0.53
Residue	15.14	0.42

Reaction Conditions: Solvent - 6g
 Coal (Elkhorn #3, Floyd County) - 3g
 Reactor - 17.5 ml tubing-bomb
 Temperature - 410°C
 Pressure - 1250 psig H₂ at 25°C
 Reaction Time - 30 Minutes

Initially a 17.5 ml tubing-bomb reactor was employed. The reactor was charged with 3g coal, 6g solvent, and 1g additive (if any). The reactor was pressurized to 1250 psig hydrogen pressure at 25°C. The reaction mixture was then reacted at 410°C for 30 minutes and the reaction product was analyzed by solvent separation to determine the distribution of product. The results of the reactions in the absence of catalyst as well as in the presence of Mexico Pyrite and presulfided Co-Mo-Al catalyst are presented in Table 21. The production of oil was found to increase from 13.8% in the case of no-catalyst run to 16.9 and 22.8% in the Mexico pyrite and Co-Mo-Al runs. Although there is some improvement in oil production with the use of pyrite and Co-Mo-Al over the base coal run, the difference is not big enough to accomodate the experimental error and to clearly visualize the effect of added minerals. The search for appropriate reaction conditions was continued. Three important variables, e.g., size of the reactor (related to the amount of hydrogen available for reaction), reaction time, and temperature were explored.

In order to increase the oil production and also widen the difference between oil produced with no-catalyst and with Co-Mo-Al catalyst, the reaction temperature was increased to 450°C while maintaining other reaction conditions constant. The results are summarized in Table 22. Comparing the results at 410 and 450°C, it can be seen that the oil production decreased with increasing reaction temperature in the absence of catalyst; whereas the oil production remained practically the same in the case of Co-Mo-Al at both the temperatures. The asphaltene fraction increased and preasphaltene fraction decreased dramatically in both cases with increasing temperature.

The net effect of increase in temperature in the absence of catalyst was the hydrogenation of preasphaltene to asphaltene and the polymerization of low molecular weight oil compounds to larger molecular weight compounds classified as asphaltene; whereas in

Table 21
Preliminary Data for Base Case Determination

	Product Distribution Based on MAF Coal, %		
	No-Catalyst	Mexico Pyrite*	Co-Mo-Al
Oil	13.8	16.9	22.8
Asphaltene	17.0	24.7	23.0
Preasphaltene	33.1	29.4	31.9
Residue	36.1	29.0	22.3
Conversion	63.9	71.0	77.7

Reaction Conditions:

- Reactor - 17.5 ml tubing-bomb
- Solvent - 6g
- Coal (Elkhorn #3, Floyd County) - 3g
- Catalyst - 1g
- Temperature - 410°C
- Pressure - 1250 psig H₂ at 25°C
- Reaction Time - 30 Minutes

*Mexico pyrite was assumed to be completely reduced to FeS in calculating product distribution.

Table 22
Preliminary Data for Base Case Determination

	Product Distribution Based on MAF Coal, %	
	No-Catalyst	Co-Mo-Al
Oil	0.2	21.8
Asphaltene	39.3	41.2
Preasphaltene	22.2	14.5
Residue	38.3	22.5
Conversion	61.7	77.5

Reaction Conditions:

Reactor - 17.5 ml tubing-bomb

Solvent - 6g

Coal (Elkhorn #3, Floyd County) - 3g

Catalyst - 1g

Temperature - 450°C

Pressure - 1250 psig H₂ at 25°C

Reaction Time - 30 Minutes

the Co-Mo-Al case, the net effect was the conversion of preasphaltenes to asphaltene. The coal conversion was observed to be the same at both temperatures.

The increase in reaction temperature did not improve significantly the difference between oil production in the cases of no-catalyst and Co-Mo-Al catalyst. At this point, it was thought that the coal liquefaction reaction might be hydrogen starved in the small tubing-bomb (17.5 ml) reactor. So, a new larger tubing-bomb (46.3 ml) reactor was assembled and used with Co-Mo-Al using the same reaction conditions and amounts of solvent and coal. The yield of oil increased from 22% to 61% with the use of larger reactor (see Table 23). The amount of hydrogen consumed from the gas phase, as determined by G.C. analysis, was 0.05g in the small reactor and 0.14g in the large reactor. The total amount of hydrogen available in the smaller reactor was 0.065g. Consumption amounted to 77% of the total available hydrogen. The hydrogen consumption in the larger reactor was significantly higher than the total available hydrogen in the smaller reactor. It was interesting to note that the reaction in the smaller reactor did not consume all the available hydrogen since the results from the larger reactor showed that all of the available hydrogen could have been easily consumed. One more important point to observe was that the coal conversion had increased from 77% to 92% with the use of the larger reactor instead of smaller one. The increase in coal conversion could be due to better mixing in the larger bomb (large volume of reactor available for the same volume of reaction mixture) and improved gas/liquid mass transfer. The above observation indicated that the amount of available hydrogen was an important factor in limiting or encouraging the reaction and that a large bomb was necessary to provide sufficient hydrogen for reaction and also to increase the oil production.

Table 23
Effect of Reactor Size on Oil Production

	Product Distribution Based on MAF Coal, %	
	Small Reactor (17.5 ml)	Large Reactor (46.3 ml)
Oil	21.8	61.3
Asphaltene	41.2	19.2
Preasphaltene	14.5	11.8
Residue	22.5	7.7
Conversion	77.5	92.3

Reaction Conditions: Solvent - 6g
 Coal (Elkhorn #3, Floyd County) - 3g
 Catalyst -1g Co-Mo-Al
 Temperature - 450°C
 Pressure - 1250 psig H₂ at 25°C
 Reaction Time - 30 Minutes

In order to study the influence of increased amounts of available hydrogen, another coal liquefaction run in the absence of any catalyst was performed in the large bomb at the same reaction conditions. The results of runs in the presence of Co-Mo-Al and in its absence were compared and are presented in Table 24. The 55% difference in oil production (see Table 24) in the larger reactor was far greater than 21% difference in the smaller reactor (see Table 22) and large enough to accommodate the experimental error and to clearly visualize the effect of added minerals. The coal conversion in no-catalyst case was found to increase from 62% to 73% with the use of larger reactor instead of smaller reactor (see Tables 22 and 24). From the above observation it was finally decided to use the larger reactor for the future work.

The search for an optimum temperature for base line condition was continued in the large tubing-bomb reactor in the presence of Co-Mo-Al. The objective was to increase the coal conversion and oil production. Table 25 summarizes the results obtained at various reaction temperatures. The oil production was found to increase with reaction temperature up to 475°C and above 475°C it suddenly dropped (see Figure 55). This is because significant coking was observed in the reactor at 500°C. Reaction temperature of 475°C gave significantly higher oil production compared to 450°C, but it showed slightly lower coal conversion. The reaction temperature of 450°C was preferred over 475°C because of ease of CPDU operation at 450°C compared to 475°C. In order to offset the lower oil product at 450°C compared to 475°C, the reaction time was increased from 30 minutes to 60 minutes and Table 26 shows the effect of reaction time on oil production at 450°C. The oil production increased from 61% to 79% and the coal conversion remained practically the same. Thus, a tubing-bomb reactor of 46.3 ml volume, reaction temperature of 450°C and 60 minutes reaction time were chosen as the base line reaction conditions to evaluate the activity of the various minerals, metallic wastes and by-products.

Table 24
Effect of Catalyst on Oil Production

	Product Distribution Based on MAF Coal, %	
	No-Catalyst	Co-Mo-Al
Oil	6.0	61.3
Asphaltene	43.7	19.2
Preasphaltene	23.4	11.8
Residue	26.9	7.7
Conversion	73.1	92.3

Reaction Conditions:

Reactor - 46.3 ml tubing-bomb
 Solvent - 6g
 Coal (Elkhorn #3, Floyd County) - 3g
 Catalyst - 1g
 Temperature - 450°C
 Pressure - 1250 psig H₂ at 25°C
 Reaction Time - 30 Minutes

Table 25
Effect of Reaction Temperature on Coal Liquefaction
in the Presence of Co-Mo-Al

Temperature, °C	Product Distribution Based on MAF Coal, %			
	425	450	475	500
Oil	27.7	61.3	71.1	42.2
Asphaltene	34.6	19.2	15.9	31.1
Preasphaltene	27.3	11.8	2.4	2.2
Residue	10.4	7.7	10.6	24.5
Conversion	89.6	92.3	89.4	75.5

Reaction Conditions: Reactor - 46.3 ml tubing-bomb
 Pressure - 1250 psig H₂ at 25°C
 Reaction Time - 30 Minutes
 Coal (Elkhorn #3, Floyd County) - 3g
 Solvent - 6g
 Catalyst - 1g

FIGURE 55
EFFECT OF REACTION
TEMPERATURE ON OIL PRODUCTION
IN THE PRESENCE OF Co - Mo - Al CATALYST

REACTION CONDITIONS: SEE TABLE 22

Table 26
Effect of Reaction Time on Oil Production
in the Presence of Co-Mo-Al

Reaction Time Min.	Product Distribution Based on MAF Coal, %	
	30	60
Oil	61.3	78.8
Asphaltene	19.2	11.8
Preasphaltene	11.8	2.1
Residue	7.7	7.3
Conversion	92.3	92.7

Reaction Conditions: Reactor - 46.3 ml tubing-bomb
 Pressure - 1250 psig H₂ at 25°C
 Coal (Elkhorn #3, Floyd County) - 3g
 Solvent - 6g
 Catalyst - 1g

Task 4.1 Autoclave Screening Studies at Auburn

Task 4.1.2 Progress - Several coal liquefaction runs were performed in a tubing-bomb reactor (46.3 ml volume) at the reaction conditions discussed earlier in this report to evaluate the catalytic activity of the various minerals.

Mineral Effects - Table 27 summarizes the results of catalytic activity of some of the minerals studied so far. The reduced pyrite, Robena pyrite, and Siniola Mexico pyrite were found to give similar product distribution and coal conversion. The addition of pyrites and reduced pyrite gave 10% higher coal conversion over that of the non-catalyzed reaction. Also, the yield of oil increased by a factor of 4 with the use of reduced pyrite and pyrites over that of no-catalyst run. The increase in oil production was mainly due to decrease in preasphaltene yields and an increase in coal conversions. The catalytic activity of Fe_2O_3 is also presented in Table 27. Fe_2O_3 was shown to give slightly higher coal conversion and oil production than pyrites and reduced pyrite. Co-Mo-Al and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ gave significantly higher coal conversion and oil production over that of no-catalyst, reduced pyrite and pyrite runs. The increase in oil production in the case of Co-Mo-Al was due to the conversion of both asphaltenes and preasphaltenes, whereas it was mainly due to conversion of asphaltenes in the case of stannous chloride. From the available data it can be concluded that both Co-Mo-Al and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ act as strong catalysts for the production of oil and coal conversions. Pyrites and reduced pyrite enhanced the hydrogenation reaction and their catalytic activity is intermediate to that of no-catalyst and strong catalysts (Co-Mo-Al and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$). The catalytic activity of the Fe_2O_3 is slightly better than pyrites and reduced pyrite. More work is in progress and the results will be reported in the next quarterly progress report.

Table 27

Catalytic Activity of the Minerals and Co-Mo-Al in Coal Liquefaction

Product Distribution Based on MAF Coal, %

Catalyst	None	FeS	Robena Pyrite	Siniola Mexico Pyrite	Fe ₂ O ₃	Co-Mo-Al	SnCl ₂ ·2H ₂ O
Oil	7.8	35.5	29.1	33.1	41.0	78.8	73.0
Asphaltene	50.4	42.9	49.3	44.1	37.8	11.8	1.0
Preasphaltene	13.2	4.4	4.6	4.3	8.6	2.1	21.0
Residue	28.6	17.1	17.0	18.5	12.6	7.3	5.0
Conversion	71.4	82.9	83.0	81.5	87.4	92.7	95.0

Reaction Conditions:

- Solvent - 6g
- Coal (Elkhorn #3, Floyd County) - 3g
- Catalyst - 1g
- Reaction Temperature - 450°C
- Pressure - 1250 psig H₂ at 25°C
- Reaction Time - 60 Minutes
- Reactor - Tubing-bomb (46.3 ml volume)

Catalysts: FeS - See Appendix C for the preparation

Pyrites - Pyrites were assumed to be reduced to FeS in calculating product distribution

Co-Mo-Al - Manufactured by LaPorte Industries, Inc. (Comox 451)
3.7% CoO, 12.8% MoO₃, presulfided by reacting with creosote oil in the presence of hydrogen gas (sulfur content of the presulfided Co-Mo-Al was determined to be 2.76%).

SnCl₂·2H₂O - Water of hydration was assumed to be lost in calculating product distribution

Fe₂O₃ - It was assumed to be totally sulfided to FeS for product distribution calculation. More work is in progress to test the validity of this assumption.

Synergistic Effects of Minerals - The promoting and inhibiting effects of some of the minerals in the presence of Robena pyrite in the coal liquefaction reaction was studied. Promotion and inhibition was measured in terms of oil production and the hydrogen content of the oil fraction. The synergistic effect of some of the minerals is summarized in Table 28. The addition of bornite and calcite to the reaction mixture in addition to Robena pyrite was found to inhibit oil formation. Montmorillonite did not show any promoting or inhibiting activity. The addition of feldspar appeared to promote oil formation.

Table 28
Synergistic Effect of Minerals and Metallic Wastes

Product Distribution Based on MAF Coal, %				
Catalyst	Bornite + FeS_2	Calcite + FeS_2	Montmorillonite + FeS_2	FeS_2
Oil	23.3	25.7	28.1	29.1
Asphaltene	51.2	44.8	50.0	49.3
Preasphaltene	5.8	8.0	5.8	4.6
Residue	19.7	21.5	16.1	17.0
Conversion	80.3	78.5	83.9	83.0

Reaction Conditions:

Solvent - 6g

Coal (Elkhorn #3, Floyd County) - 3g

Robena pyrite - 1g

Other minerals - 1g

Temperature - 450°C

Reaction Time - 60 Minutes

Pressure - 1250 psig H_2 at 25°C

Reactor - 46.3 ml tubing-bomb

Catalysts: FeS_2 - FeS_2 is assumed to reduce to FeS

Calcite - Calcite is assumed to reduce to CaS

Others - no change

REFERENCES

1. Granoff, B. and M. Thomas, "Mineral Matter Effects in Coal Liquefaction -Autoclave Screening Study," ACS Division of Fuel Chemistry, paper presented at Chicago meeting, September, 1977.
2. Kor, G. J. W., "Desulfurization and Sulfidation of Coal and Coal Char Part II: Sulfidation of Coal Char and Synthetic Chars," ACS Division of Fuel Chemistry, paper presented at New Orleans meeting, March, 1977.

APPENDIX A

RUN CCL-25 SUMMARY OF OPERATING DATA

Feed Slurry Designation	Hours on Sample	Balance Period	Mode	Temperature, °F	Pressure, psig	Slurry Feed Rate g/hr.	H ₂ Feed Rate, SLPH	Main Rec. Product Rate g/hr.	Condensate Rate, g/hr.	Product Gas Rate SLPH	Product Rate, g/hr.
550-850°F Solvent	0- 12	0- 12	Line-Out	835-850	2000	988	244	873	4.0	274	—
	12- 13	12- 13	Sample	850	2000	1027	200	--	5.1	262	829
	13- 14	13- 14	Sample	850	2000	997	220	--	7.4	207	808
550-850°F Solvent + 10% Robena Pyrite	14- 26	14- 26	Line-Out	850	2000	1098	225	941	9.6	236	--
	26- 27	26- 27	Sample	850	2000	1092	227	954	14.3	239	1122
	27- 28	27- 28	Sample	850	2000	1060	223	--	12.1	247	994
550-850°F Solvent + 30% Elkhorn #3 Coal (Floyd County)	28- 37	28- 37	Line-Out	850	2000	1853	345	1664	--	371	--
	37- 38	37- 38	Sample	850	2000	1808	305	1771	25.0	394	1677
	38- 39	38- 39	Sample	850	2000	1830	354	1742	47.0	370	1676
	39- 49	39- 49	Line-Out	850-800	2000	1828	310	1606	--	353	--
	49- 50	49- 50	Sample	800	2000	1789	310	1769	21.3	344	1535
	50- 51	50- 51	Sample	800	2000	1794	305	1587	31.4	329	1645
	51- 61	51- 61	Line-Out	800	2500	1701	300	1447	24.0	322	--
	61- 62	61- 62	Sample	800	2510	1678	352	1248	20.6	378	1319
	62- 63	62- 63	Sample	800	2510	1713	352	1387	27.3	374	1736
	63- 73	63- 73	Line-Out	800	1500	1841	346	1639	22.0	371	--
	73- 74	73- 74	Sample	800	1500	1962	360	1488	22.2	393	1619
	74- 75	74- 75	Sample	800	1500	1851	350	1697	21.2	370	1654
550-850°F Solvent + 30% Elkhorn #3 Coal (Latcher County)	75- 85	75- 85	Line-Out	850	2000	1767	333	1624	18	365	--
	85- 86	85- 86	Sample	850	2000	1780	362	1604	19	394	1820
	86- 87	86- 87	Sample	850	2000	1741	362	1487	17	376	1597
	87- 97	87- 97	Line-Out	850-800	2000	1728	333	1657	18	378	--
	97- 98	97- 98	Sample	800	2000	1808	325	1520	15	402	1570
	98- 99	98- 99	Sample	800	2000	1830	330	1579	21	391	1636

APPENDIX A
(continued)

Feed Slurry Designation	Hours on Sample	Balance Period	Mode	Temperature, °F	Pressure, psig	Slurry Feed Rate g/hr.	H ₂ Feed Rate, SLPH	Main Rec. Product Rate g/hr.	Condensate Rate, g/hr.	Product Gas Rate SLPH	Product Rate, g/hr.
	99-109	99-109	Line-Out	800	2500	1662	333	1595	15	362	--
	109-110	109-110	Sample	800	2500	1598	--	1543	12	382	--
	110-111	110-111	Sample	800	2500	1658	352	1668	19	383	1957
	111-122	111-122	Line-Out	800	1500	1808	385	1621	13	420	--
	122-123	122-123	Sample	800	1500	1749	335	2014	14	360	1669
	123-124	123-124	Sample	800	1500	1729	340	--	12	360	1583
550-850°F Solvent + 30% Elkhorn #3 Coal (Floyd County) + 10% Robena Pyrite	124-134	124-134	Line-Out	850	2000	1898	389	1714	38	354	--
	134-135	134-135	Sample	850	2000	2034	403	--	39	390	1767
	135-136	135-136	Sample	850	2000	1851	403	--	43	349	1710
101	136-146	136-146	Line-Out	850-800	2000	2052	399	1746	30	371	--
	146-147	146-147	Sample	800	2000	2058	395	1666	31	388	1761
	147-148	147-148	Sample	800	2000	1842	400	--	30	320	1637
	148-158	148-158	Line-Out	800	2500	1846	404	1684	33	369	--
	158-159	158-159	Sample	800	2500	1908	388	1822	37	345	1632
	159-160	159-160	Sample	800	2500	1794	407	--	33	398	1614
	160-170	160-170	Line-Out	800	1500	2014	390	1826	41	364	--
	170-171	170-171	Sample	800	1500	2099	360	1845	44	314	1904
	171-172	171-172	Sample	800	1500	1957	385	--	37	281	--
550-850°F Solvent + 30.6% Elkhorn #3 Coal (Latcher County) + 8.6% Robena Pyrite	172-182	172-182	Line-Out	850	2000	1912	400	1763	30	392	--
	182-183	182-183	Sample	850	2000	1908	398	1746	29.3	384	1705
	183-184	183-184	Sample	850	2000	--	400	--	29.7	--	--
	184-194	184-194	Line-Out	850-800	2000	1898	397	1751	21.0	393	--
	194-195	194-195	Sample	800	2000	1937	375	1829	24.0	372	1752
	195-196	195-196	Sample	800	2000	--	375	--	--	--	--

APPENDIX A
(continued)

Feed Slurry Designation	Hours on Sample	Balance Period	Mode	Temperature, °F	Pressure, psig	Slurry Feed Rate g/hr.	H ₂ Feed Rate, SLPH	Main Rec. Product Rate g/hr.	Condensate Rate, g/hr.	Product Gas Rate SLPH	Product Rate, g/hr.
	196-206	196-206	Line-Out	800	2500	1832	407	1798	26	402	--
	206-207	206-207	Sample	800	2500	1773	405	1715	26.2	380	1715
	207-208	207-208	Sample	800	2500	--	405	--	--	--	--
	208-218	208-218	Line-Out	800	1500	2030	415	1909	23.0	411	--
	218-219	218-219	Sample	800	1500	2036	410	1953	28.0	414	1783
	219-220	219-220	Sample	800	1500	2026	417	--	--	--	--

APPENDIX B

Robena Pyrite-Magnetite Mixture

Feed: 1.5g FeS₂
 1.5g Fe₃O₄

The reaction as presented in Eqn. 3 is:

From the equation, pyrite is the limiting reactant. The stoichiometric amount of Fe₃O₄ that can react with the 1.5g of FeS₂ is 0.97g which leaves 0.53g of Fe₃O₄ that is subjected to direct hydrogen reduction. At 450°C and 1000 psig H₂ pressure, the hydrogen reduction of Fe₃O₄, as presented by the following equation, gave only 2.67% weight reduction in the PTGR.

Using this number, the amounts of reduced pyrite, elemental iron and unreacted Fe₃O₄ that would result from the 1.5g of FeS₂ and 1.5g of Fe₃O₄ are given in Table B-1.

Table B-1
Product Distribution of Pyrite - Magnetite Reaction System

	<u>g</u>	<u>wt. %</u>
FeS	2.2	80.7
Fe ₃ O ₄	0.52	19.1
Fe	0.0064	0.20

APPENDIX C

Preparation of Reduced Pyrite

The iron sulfide or reduced pyrite (FeS) was prepared at Auburn University by sulfiding ferric oxide (Fe_2O_3) with H_2S in the presence of hydrogen gas. The ferric oxide used was red-anhydrous powder of over 99% purity and was obtained from Fisher Scientific Company. The hydrogen sulfide gas was of commercial purity obtained from Matheson Gas Company. The sulfiding reaction is given in Equation C-1.

The schematic of the apparatus used is shown in Figure C-1. A constant supply pressure of 2 psig was maintained on the H_2 and H_2S cylinders. Rotameters were used to measure the individual gas flow rates and the gas flow rates were controlled by fine metering valves to give a $\text{H}_2/\text{H}_2\text{S}$ flow ratio of 10/1. A porcelain boat containing approximately 1.25g of ferric oxide was placed in the center of 1-inch O.D. Pyrex glass tube heated by Lindberg Electric Furnace (Type 123-12). A thermocouple was installed in the center of the furnace to read and manually control the temperature. The unreacted H_2S gas was scrubbed with the use of caustic solution and the other gases were vented in the hood.

The system was checked and corrected for leaks before turning on the heat. Usually, 50-70 minutes were required to heat the furnace from room temperature to 350°C . When the temperature reached 350°C (or desired temperature), the time was marked as zero time. A reaction time of 150 minutes was used. At the end of reaction period the heat was turned off and the product was allowed to cool down rapidly to room temperature. The product was then removed, ground, and stored under an inert atmosphere of N_2 for later use as a catalyst. X-ray diffraction analysis of one of the samples showed that the material was primarily FeS, troilite and iron II sulfide.

FIGURE C-1
APPARATUS FOR FeS PREPARATION