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

Technical Progress Report for the Period March 1—May 31, 1980

By

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June 1980

Work Performed Under Contract No. AC22-79ET14806

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U. S. DEPARTMENT OF ENERGY

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ABSTRACT

This report describes work done in the third quarter of a study of the role of coal minerals and by-product metallic wastes in coal liquefaction. Samples of washed Elkhorn #3 coal (Floyd County), Kentucky #9 coal (Pyro Mine) and various Ohio coals, several minerals and metallic by-products wastes were acquired. Some of the minerals and metallic by-product wastes which showed improved activity in coal liquefaction were also acquired in large quantities to be tested in the coal process development unit (CPDU). Distillation of product slurry from the first standardization run CCL-25 was performed to obtain additional process solvent to be used in subsequent coal liquefaction runs. A new supply of ten drums of process solvent has been requested from Fort Lewis SRC-II pilot plant.

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. Stoichiometric reduction (24.6% weight loss) of ZnO was obtained at about 660°C; whereas, no weight loss was observed at 450°C in the PTGR at 1000 psig hydrogen pressure. ZnO continued to lose weight at temperatures above 660°C due to volatilization of elemental zinc. Zinc oxide was observed to be thermally stable in air. The reduction of ZnO in hydrogen gas verified our earlier work on zinc flue dusts. Montmorillonite and apatite lost the water of hydration upon hydrogen treatment at 450°C and 1000 psig pressure. Gypsum lost two waters of hydration and there was slight decomposition of gypsum at 450°C and 1000 psig hydrogen pressure. Bornite was partially reduced and quick lime, ilmenite, rutile, molybdenite, alnico grindings and super alloy grindings were found to be insensitive to hydrogen treatment at 450°C and 1000 psig pressure. Flue dust was reduced to its corresponding elemental form at the same hydrogen treatment conditions. DTA of copperas showed endotherms due to removal of water of hydration and exotherms due to decomposition of FeSO_4 . Complete reduction of iron oxide (Fe_2O_3) was not achieved at 450°C and 1000 psig in ten minutes reaction time.

The gas phase hydrogen reduction of Robena pyrite in the PTGR at 1000 psig pressure, ten minutes reaction time and various reaction temperatures resulted in the production of troilite (FeS). There was some formation of elemental iron depending on the reaction temperature. Liquid phase reduction of Robena pyrite at 850°F and 2000 psig hydrogen pressure in process solvent yielded pyrrhotite ($\text{FeS}_{1.099}$).

The 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. The catalytic activity of Robena pyrite was measured in terms of product distribution (production of gases, oil, asphaltene, preasphaltene, residue, etc.) and hydrogen consumption. Robena pyrite was found to catalyze solvent hydrogenation and coal liquefaction reactions. The addition of pyrite resulted in higher yields of hydrocarbon gases, ammonia and water over a non-additive run. Pyrite also catalyzed the conversion of preasphaltene and asphaltene to oil and gases and increased the hydrogen consumption. The hydrogen content of the oil fraction was found to be maintained in the presence of pyrite; whereas, it was depleted in its absence. In short, the addition of pyrite improves coal conversion, increases production of benzene solubles and gases and maintains the solvent hydrogen content.

A number of minerals were screened for catalytic activity toward coal liquefaction in a tubing-bomb reactor. The catalytic activity of the minerals was assessed by comparing the product distributions both in the presence of minerals and their absence. The use of a Bronson Sonifier was initiated in March to accelerate and improve the solvent separation technique. The addition of lime to the reaction mixture practically killed the liquefaction reaction. The addition of dolomite, rutile, illite, quartz, zircon, and calcite to the reaction mixture showed no significant improvement over that of a no additive run. The addition of zinc oxide and ilmenite showed slight improvement. Robena pyrite and Co-Mo-Al showed significant improvement in coal conversion and production of benzene solubles and gases. Iron oxide (Fe_2O_3) gave the highest conversion of coal and production of benzene solubles among all the minerals tested so far.

Several metallic wastes and metal-containing by-products were also tested for their catalytic activity in coal liquefaction. The addition of high and low zinc flue dusts and oil shale had practically no advantage over a non-additive run. Robena pyrite and red mud showed significant improvement in coal conversion and production of benzene solubles. There seemed to be no significant difference in the activity of Robena pyrite and pyrrhotite ($\text{FeS}_{1.099}$), which was produced from Robena pyrite. Red mud showed the highest catalytic activity among all the metallic wastes and metal-containing by-products tested so far. The catalytic activity of red mud is probably due to the fact that iron oxide (Fe_2O_3), shown earlier to have the highest activity, is present in the sample as a major compound.

The second standardization run (CCL-28) was carried out during the month of April. The run was designed to study the liquefaction behavior of Kentucky #9 coal in the presence and absence of Robena pyrite. Also, the liquefaction behavior of run-of-mine and washed Ohio coals was studied.

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 are being 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

The program plan specified testing of several different coals and the use of a low ash, low pyrite Elkhorn #3 in the screening tests. Since the beginning of our program the interest of Ohio DOE in evaluating the SRC yields from Ohio coals offered an opportunity of including Ohio coals in our program. Numerous channel samples have been supplied by Ohio DOE through Professor William A. Kneller of University of Toledo and Professor Robert Savage of Ohio University. This program is supporting extensive evaluation of those coals by Professor Kneller at the University of Toledo.

The status of the coal selection and procurement is discussed below.

Elkhorn #3. A sample of Elkhorn #3 coal, obtained from Letcher County, Kentucky, was crushed and sieved to -200 U.S. Mesh and submitted for ultimate and proximate analyses. The ground coal was found to contain 33.34% ash. A complete chemical analysis of the coal is given in Table 1. This sample of coal was studied for its liquefaction behavior in the first CPDU run (CCL-25). A sample of washed Elkhorn #3 coal was obtained from Floyd County through the assistance of the Institute of Mining and Minerals, University of Kentucky. This sample should have the same general petrography as the original unwashed Floyd County Elkhorn #3 sample but also have a reduced ash and pyrite level.

Kentucky #9. The ultimate and proximate analyses of a sample of Kentucky #9 coal obtained from the Pyro mine is shown in Table 2. This coal has been evaluated in the second CPDU run and data will be presented in the next quarterly report.

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

	<u>Weight %</u>
<u>Proximate Analysis</u>	
Moisture	1.80
Dry Ash	33.34
<u>Ultimate Analysis</u>	
C	52.88
H	3.67
N	0.95
S	1.63
O	7.73

Table 2
Analysis of Kentucky #9 Coal Obtained
from Pyro Mine, Kentucky

	<u>Weight %</u>
<u>Proximate Analysis</u>	
Moisture	1.60
Volatile	36.13
Fixed Carbon	48.90
Dry Ash	13.10
<u>Ultimate Analysis</u>	
C	70.42
H	4.76
N	1.50
S	3.30
O	6.07
<u>Distribution of Sulfur</u>	
Total Sulfur	3.30
Sulfate Sulfur	0.10
Pyrite Sulfur	1.60

Ohio Coals. Professor Savage and Professor Kneller of Ohio DOE supplied us with a number of Ohio coals representing a wide range of total sulfur, pyrite sulfur and ash contents (see Table 3). Seam samples from six mines and two washed samples from coal preparation plants associated with two of those mines were obtained. The seam samples from five of the mines were further segmented into samples by layers (Figures 1-5). The individual seam fractions offer an opportunity to investigate the variation of indigeneous pyrite and minerals on the liquefaction of coal from the same seam.

Professor Kneller at the University of Toledo is in the process of completing the ultimate and proximate analyses of the above mentioned Ohio coals.

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 and their sources is given in Table 4. Three additional five gallon drums of pyrite were obtained from U.S. Steels' Robena Mine. This sample will be dried at 110°C and ground to -325 U.S. mesh in nitrogen.

Large quantities (approximately 100 pounds) of lime, feldspar, rutile and zinc sulfide were ordered. These materials will be tested in our CPDU for their catalytic activity.

Table 3
List of Ohio Coal Samples

<u>Sample No.</u>	<u>Seam No.</u>	<u>County</u>	<u>Sample Type/Fraction</u>	<u>Comment</u>
CPDU-133	Middle Kittaning #3	Muskingum	Composite Seam Sample	See Figure 1
CPDU-126-A			Fraction I	
CPDU-126-B			Fraction II	
CPDU-126-C			Fraction III	
CPDU-126-D			Fraction IV	
CPDU-137	Pittsburgh #8	Harrison	Composite Seam Sample	See Figure 2
CPDU-127-A			Fraction I	
CPDU-127-B			Fraction II	
CPDU-127-C			Fraction III	
CPDU-127-D			Fraction IV	
CPDU-135	Meigs #9	Harrison	Composite Seam Sample	See Figure 3
CPDU-128-A			Fraction I	
CPDU-128-B			Fraction II	
CPDU-128-C			Fraction III	
CPDU-128-D			Fraction IV	
CPDU-136	Lower Kittaning #5	Holmes	Composite Seam Sample	See Figure 4
CPDU-129-A			Fraction I	
CPDU-129-B			Fraction II	
CPDU-129-C			Fraction III	
CPDU-132	Clarion #4A	Vinton	Washed Seam Sample	See Figure 5
CPDU-134			Composite Seam Sample	
CPDU-130-A			Fraction I	
CPDU-130-B			Fraction II	
CPDU-130-C			Fraction III	
CPDU-131	Pittsburgh #8	Belmont	Washed Seam Sample	
CPDU-131A			Composite Seam Sample	

FIGURE 1.
SPLIT OF MIDDLE KITTANING #6 COAL SEAM

FIGURE 2.
SPLIT OF PITTSBURGH #8 SEAM

FIGURE 3.
SPLIT OF MEIGS #9 SEAM

FIGURE 4.
SPLIT OF LOWER KITTANING #5 SEAM

SEAM: LOWER KITTANING #5

FIGURE 5.
SPLIT OF CLARION #4A SEAM

SEAM: CLARION #4A

Table 4
Suppliers of Various Minerals and Metal-
Containing By-Product Samples

Dolomite
[CaMg(CO₃)]

David New Minerals
Providence, Utah

Potassium Carbonate
[K₂CO₃]

Fisher Scientific Co.

Sodium Carbonate
[Na₂CO₃]

Fisher Scientific Co.

Oil Shale

John Ward Smith
Manager, Div. of Resource
Characterization
U.S. Department of Energy
Laramie Energy Technology Center
P.O. Box 3395
University Station, Wyoming 82071

Zinc Oxide

J. T. Baker Chemical Co.

A sample of oil shale was received in a single piece. It was broken into 1/8 inch or smaller pieces and then cooked in air at 400°C for six hours to release the oil. The material was then extracted with tetrahydrofuran (THF) to remove the released oil. The residue was then dried and ground to -115 U.S. mesh. The dried ground powder was tested for its catalytic activity.

The chemical analysis of phosphate slime was provided by Auburn University and is presented in Table 5. Potassium carbonate, sodium carbonate and zinc oxide were 99% pure materials.

Task 1.3 Process Solvent

The product slurry from the first standardization run CCL-25 was distilled to recover the process solvent to be used in the second standardization run. The distillation cut points were mistakenly set at 450 and 850°F instead of the intended 550 and 850°F temperature. The GC simulated distillation of the distilled solvent, presented in Table 6, showed that eight and thirty-three percent of the material boiled below 450 and 550°F, respectively. On solvent separation the recovered solvent was found to be mainly oil (pentane soluble). The elemental analysis of the solvent is presented in Table 7.

Five drums of solvent, received from Fort Lewis SRC-II pilot plant, turned out to be the IBP-550°F cut rather than the 550-850°F heavy distillate material we are using as process solvent in this program. We are trying to make arrangements for returning the drums to Fort Lewis in order to avoid the disposal expense. A new supply of ten drums has been requested.

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 is being evaluated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) in the presence of helium or nitrogen.

Table 5
Chemical Analysis of Phosphate Slime

	<u>Weight %</u>
CaO	16.2
P ₂ O ₅ Equivalent	12.0
MgO	2.9
Fe ₂ O ₃	3.4
SiO ₂	36.5
Na ₂ O	0.3
K ₂ O	0.8
F	1.5
C	1.0
CO ₂	2.3
S	0.2
Loss on Ignition 500°C	10.3

Table 6
Simulated Distillation of 450-850°F
Process Solvent (F.O.B. #3)

<u>Weight % Off</u>	<u>Temperature °F</u>
I.B.P.	406
5%	444
8%	451
10%	459
20%	512
30%	543
33%	551
40%	573
50%	596
60%	614
70%	636
80%	666
90%	697
95%	725
99%	784
F.B.P.	805

Table 7
Elemental Analysis of 450-850°F
Process Solvent (F.O.B. #3)

<u>Element</u>	<u>Weight %</u>
Carbon	89.84
Hydrogen	7.20
Oxygen	1.29
Nitrogen	1.12
Sulfur	<u>0.50</u>
	99.95
 Molecular Weight	 177

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.

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.

Zinc Oxide - Zinc oxide on analysis by TGA started losing weight at around 450°C in the presence of hydrogen gas as shown in Figure 6. The stoichiometric reduction (24.6% weight loss) of ZnO was obtained at about 660°C. The sample continued to lose weight at temperatures above 660°C. The excess loss in weight (more than stoichiometric amount) was due to volatilization of zinc. Similar results were obtained by reducing ZnO in the PTGR at 450 and 1000°C and 1000 psig hydrogen pressure. ZnO lost approximately 60% of the initial weight in just ten minutes; whereas no weight loss was observed at 450°C as shown in Table 8. So, if ZnO is to be reduced to Zn, the reduction temperature used should be in between 450-660°C to assure the reduction of ZnO and to avoid volatilization of elemental zinc. The reduction of ZnO sample verified earlier work of hydrogen reduction of zinc flue dusts where no reduction of ZnO was reported at 450°C. Furthermore, no weight correction due to reduction of ZnO would be necessary if it is used as an additive in coal liquefaction under normal operating conditions.

The DTA of ZnO in the presence of air showed no significant features up to 550°C (see Figure 7) indicating the sample was thermally stable.

Chrome Ore Concentrate - The DTA of chrome ore concentrate in the presence of air showed no significant activity over the temperature range used in this study (see Figure 8).

FIGURE 6.
TGA OF ZINC OXIDE IN THE PRESENCE OF HYDROGEN

Table 8
Reduction of Zinc Oxide in PTGR

Temp., °C	1000	450
H ₂ Pressure, psig	1000	1000
Reaction Time, min.	10	10
Initial Weight, g	3.00	3.00
Final Weight, g	1.20	3.00
Weight Loss, g	1.80	0.00
Weight Loss, %	60.0	0.0

FIGURE 7.
DTA OF ZINC OXIDE IN THE PRESENCE OF AIR

FIGURE 8.
DTA OF CHROME ORE CONCENTRATE
IN THE PRESENCE OF AIR

Quick Lime - Quick lime in the presence of air showed no apparent thermal activity up to 550°C. The apparent broad exotherm shown in Figure 9 was due to non-linearity of the base line. Under hydrogen pressure quick lime did not reduce at 450°C as shown in Table 9.

Feldspar - The DTA of feldspar in air showed no thermal activity (see Figure 10).

Molybdic Oxide - No thermal activity was observed in the presence of air as shown in Figure 11.

Mordenite and Chabozite - The thermograms of mordenite and chabozite (Figures 12 and 13) showed no thermal activity in the presence of air.

X-Type Molecular Sieve - The thermogram of x-type molecular sieve showed a broad and pronounced endotherm starting at room temperature and continuing to about 350°C (see Figure 14). The endotherm was due to loss of adsorbed water. The weight loss of the material will be determined by TGA and a necessary weight correction will be employed when using it in coal liquefaction run.

Reduced Pyrite (obtained from CPDU run CCL-25) - A very strong exotherm in the range of 280 to 405°C was observed in the DTA in the presence of air. The exotherm shown in Figure 15 was due to oxidation of reduced pyrite to iron oxide. The DTA of reduced pyrite showed the exotherm in the same temperature range as that of pyrite.

Flue Dust - The broad exotherm shown in the DTA in the presence of air (Figure 16) was due to oxidation of various metals present in the sample. The hydrogen reduction of flue dust showed a weight loss of seven percent at 450°C and 1000 psig pressure. The major weight loss was due to the reduction of oxides to their corresponding reduced states. The results of hydrogen reduction of flue dust are tabulated in Table 9.

FIGURE 9.
DTA OF QUICK LIME (CaO) IN THE PRESENCE OF AIR

Table 9
Reduction of Minerals and Metallic Wastes in the PTGR
 Reaction Time = 10 Minutes, Temperature = 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	CO ₂	H ₂ O		
Montmorillonite (Thixogel #3)	3.00	2.53	0.47	15.6	0.0045	--	0.0564	0.0609	13.0
Montmorillonite (Hydrite PX1672)	1.50	1.47	0.03	2.0	--	--	--	--	--
Montmorillonite (Colloid BP1673)	3.00	2.75	0.25	8.3	--	--	0.0744	0.0744	29.8
Apatite (Monocalcium Phosphate)	3.00	2.82	0.18	2.7	--	--	0.0035	0.0035	1.9
Apatite (Dicalcium Phosphate)	3.00	2.79	0.21	2.8	--	--	0.0656	0.0656	31.2
2 Apatite (Tricalcium Phosphate)	3.00	2.69	0.31	10.3	--	--	0.0446	0.0446	14.4
Quick Lime	3.00	3.00	--	--	--	--	--	--	--
Gypsum	3.00	2.41	0.59	19.7	0.0025	0.0562	0.0497	0.1084	18.4
Bornite	3.00	2.81	0.19	6.3	0.0022	0.0017	0.0317	0.0356	10.8
Ilmenite	3.00	2.91	0.09	3.0	--	--	--	--	--
Rutile	3.00	3.00	0.00	0.0	--	--	--	--	--
Illite	3.00	2.90	0.10	3.3	--	--	--	--	--
Molybdenite	3.00	3.00	0.00	0.0	--	--	--	--	--
Flue Dust	3.00	2.78	0.22	7.3	0.0033	--	0.0496	0.0529	24.1
Alnico Grindings	3.00	2.96	0.04	1.3	--	--	--	--	--
Super Alloy Grindings	3.00	3.00	0.00	0.0	--	--	--	--	--

FIGURE 10.
DTA OF FELDSPAR IN THE PRESENCE OF AIR

FIGURE 11.
DTA OF MOLYBDIC OXIDE IN THE PRESENCE OF AIR

FIGURE 12.
DTA OF MORDENITE IN THE PRESENCE OF AIR

FIGURE 13.
DTA OF CHABOZITE IN THE PRESENCE OF AIR

FIGURE 14.
DTA OF X-TYPE MOLECULAR SIEVE
IN THE PRESENCE OF AIR

FIGURE 15.
DTA OF REDUCED PYRITE IN THE PRESENCE OF AIR

FIGURE 16.
DTA OF FLUE DUST IN THE PRESENCE OF AIR

Super Alloy and Alnico Grindings - The DTA's in air of super alloy and Alnico grindings are shown in Figures 17 and 18. The samples showed definite exotherm due to oxidation of the metals. Since the oxidation is a surface process, the broad peaks are due to lack of rapid oxygen transfer below the surface.

The hydrogen reduction of the above two grindings at 450°C and 1000 psig was carried out in the PTGR. The samples were found to be insensitive to hydrogen reduction as shown in Table 9. This is possibly due to presence of metals in the samples in the reduced form.

Copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) - The DTA of copperas run to 550°C in the presence of air showed endotherms that were due to loss of water at around 75 and 130°C and exotherms that were due to decomposition and oxidation of FeSO_4 at 220°C (see Figure 19). The sample after cooling was run again. Most of the endotherms and exotherms disappeared as shown in Figure 19. Another sample was heated to just below 220°C to remove the water of crystallization and then cooled to room temperature. Again on heating to 200°C, most of the endotherm disappeared as shown in Figure 20. Clearly all the water of crystallization was lost by 200°C without decomposing the material.

Montmorillonite - Three different samples of montmorillonite were hydrogen reduced at 450°C and 1000 psig pressure. The samples showed weight losses ranging from two to ten percent. The weight loss was mainly due to either removal of water from the samples or reduction of samples. Water was the major compound determined in the gas product as reported in Table 9. The montmorillonite by itself is insensitive to hydrogen reduction at 450°C.

Apatite (Monocalcium, Dicalcium, and Tricalcium Phosphate) - The hydrogen reduction results of apatite are shown in Table 9. The weight loss ranging from two to ten percent was due to loss of water of hydration. The apatite by itself is insensitive to hydrogen reduction at 450°C.

FIGURE 17.
DTA OF SUPER ALLOY GRINDINGS
IN THE PRESENCE OF AIR

FIGURE 18.
DTA OF ALNICO GRINDINGS IN THE PRESENCE OF AIR

FIGURE 19.
DTA OF COPPERAS ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) IN THE PRESENCE OF AIR

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

Ilmenite, Rutile, Illite, and Molybdenite - All of these samples are insensitive to hydrogen reduction at 450°C as shown in Table 9.

Gypsum - The TGA of gypsum discussed in the second quarterly progress report, showed a weight loss of approximately 19% (stoichiometric loss of water of hydration). The hydrogen reduction of gypsum at high hydrogen pressure shown in Table 9 also gave a weight loss of about 19 percent. A large portion of weight loss is due to removal of water of hydration and the balance due to decomposition of gypsum.

Bornite - The hydrogen reduction of bornite shown in Table 9 gave a six percent weight loss. The weight is mainly due to the reduction of oxides to their corresponding reduced form.

Bottom Ashes - The hydrogen reduction of bottom ashes (taken from power plants in Kentucky) was carried out in the PTGR. The samples lost weight ranging from one to 14 percent as presented in Table 10. The major compounds found in the gas phase were methane and water. Brown and paradise bottom ashes lost insignificant weight (maximum of three percent); whereas Green River bottom ash lost approximately 14 percent weight. The above observations suggest that Green River bottom ash is more hydrogen sensitive than brown and paradise bottom ashes.

Red Oxide and Speculite (commercial Fe_2O_3) - The DTA's of speculite and red oxide in the presence of air are shown in Figures 21 and 22, respectively. The DTA of speculite showed a very minor endotherm at around 340°C, possibly due to volatilization of the impurities present in the sample. The DTA of red oxide showed a small exothermic elevation at around 350°C. This was due to oxidation of residual iron in the sample.

Table 10

Reduction of Bottom Ashes in the PTGR

Reaction Time = 10 Minutes, Temperature = 450°C

Pressure = 1000 psig, H₂

<u>Sample</u>	<u>Initial Weight, g</u>	<u>Final Weight, g</u>	<u>Weight Loss</u>		<u>Gas Analyses, g</u>			<u>Total Recovered Product, g</u>	<u>% Recovery of Lost Wt.</u>
			<u>g</u>	<u>%</u>	<u>N₂</u>	<u>CH₄</u>	<u>H₂O</u>		
37 Brown Bottom Ash	3.00	2.92	0.02	2.7	0.0031	0.0032	0.0426	0.0489	61
Paradise Bottom Ash	3.00	2.96	0.04	1.3	--	--	--	--	0
Green River Bottom Ash	3.00	2.58	0.42	14.0	0.0043	0.0078	0.0519	0.0640	15

FIGURE 21.
DTA OF SPECULITE (Fe_2O_3) IN THE PRESENCE OF AIR

FIGURE 22.
DTA OF RED OXIDE (Fe_2O_3) IN THE PRESENCE OF AIR

Both samples were hydrogen reduced in the PTGR at 450°C and 1000 psig pressure. Red oxide and specularite showed a weight loss of 21 and 16 percent, respectively as shown in Table 11. The stoichiometric reduction of Fe_2O_3 to elemental iron results in 30 percent weight loss. This suggested that complete reduction of iron oxide to elemental iron was not achieved in both cases. The samples will be treated in the TGA in the presence of hydrogen gas to determine the temperature at which complete reduction of Fe_2O_3 occurs.

Robena Pyrite - Robena pyrite (-325 mesh) was hydrogen reduced in the PTGR at 1000 psig at different temperatures. The results of the reduction were discussed in the second quarterly progress report. The samples of Robena pyrite reduced at different reaction temperatures were analyzed by x-ray diffraction to determine the nature of the phases present. The results of XRD analysis, summarized in Table 12, identified the major phase in all the samples as troilite. No positive identification of pyrrhotite was observed.

Robena Pyrite-Red Oxide Mixture - The possibility of generating reduced pyrite by reacting a mixture of pyrite and red oxide (Fe_2O_3) in the PTGR was explored. The individual and coupled reactions would be as follows:

Experimentally a 50-50 mixture by weight of pyrite and red oxide (1.33/1.00 mole ratio) was treated at 450°C and 1000 psig hydrogen pressure in the PTGR. The sample lost approximately 19 percent weight which is far below the 28.3 percent weight loss required for complete reduction of pyrite to reduced pyrite and red oxide to elemental iron. Part of the lower weight loss is due to the impurities present in both pyrite and red oxide samples. Theoretically, if the reaction proceeded by Equation 3, a weight loss of

Table 11

Reduction of Iron Oxides in the PTGR

Reaction Time = 10 Minutes, Temperature = 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	CO ₂	H ₂ O		
Red Oxide (Fe ₂ O ₃)	3.00	2.36	0.64	21.3	0.0027	0.0096	0.0721	0.0844	13
Speculite (Fe ₂ O ₃)	3.00	2.51	0.49	16.3	0.0024	0.0068	0.0346	0.0438	9

Table 12
Reduction of -325 Mesh Robena Pyrite in the PTGR

Reaction Time = 10 Minutes

H₂ Pressure = 1000 psig

Rapid Heating

<u>Reaction Temperature, °C</u>	<u>Weight loss, wt%</u>	<u>XRD Analysis</u>
400	21.3	FeS (troilite) major phase. No Fe detected. One extra line at 3.34Å probably due to pyrrhotite.
450	23.0	FeS (troilite) major phase. No Fe detected. Possible presence of pyrrhotite (less than in the sample treated at 400°C) extra lines at 3.35, 3.03, and 1.95Å were not identified.
500	24.0	FeS (troilite) major phase. No Fe detected. Extra unidentified lines at 3.33, 3.38, 3.02, 5.14, and 1.95Å. Possible presence of pyrrhotite.
600	23.3	FeS (troilite) major phase. Possible presence of pyrrhotite and elemental Fe. Unidentified lines at 5.14, 3.33 and 1.95Å.
700	25.0	FeS (troilite) major phase. Possible presence of pyrrhotite and Fe. Unidentified lines at 5.18, 3.36 and 1.95Å.
800	25.0	FeS (troilite) major phase. Possible presence of pyrrhotite and Fe. Unidentified lines at 3.33, 2.85 and 1.95Å.

8.5 percent would have resulted. The treated material was analyzed by XRD and FeS (troilite) and elemental iron were identified as ^{the} major phases. Two extra very weak unidentified lines were also observed. Further work is in progress to quantify the amount of FeS and Fe in the sample and to determine whether there was any reaction between red oxide and pyrite.

Coal Preparation Plant Waste Materials - The TGA of the various coal preparation plant waste materials were studied in the presence of air. The samples showed a weight loss ranging from 35 to 68 percent as shown in Figures 23, 24, and 25. The weight loss was primarily due to oxidation of the organic material present in the samples. The purpose of this study was to determine the oxidation temperature required to remove the organic phase and the weight percent ash present in the samples. The temperature required for complete oxidation was observed to be greater than 500°C. These waste materials will be oxidized in the presence of air and the catalytic activity of the original material along with ash of the original material will be tested in coal liquefaction.

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 summary of the sample numbers and process conditions are given in Table 13. The complete operating data is given in Appendix A.

Feed and Product Analysis - The feed and product slurries were solvent-separated into four fractions: (1) pentane-soluble material (oil), (2) pentane-insoluble and benzene-soluble material (asphaltene), (3) benzene-insoluble and pyridine soluble material (preasphaltene), and (4) pyridine-insoluble material. The latter contains insoluble organic material (IOM) and mineral residue. The solvent separation

FIGURE 23.
TGA OF HENDRIX/BETH-ELKHORN COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 24.
TGA OF GUND/ISLAND CREEK COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

FIGURE 25.
TGA OF FIES/ISLAND CREEK COAL PREPARATION PLANT
WASTE MATERIAL IN THE PRESENCE OF AIR

Table 13

Summary of Process Conditions for Run Number CCL-25

<u>Sample No.</u>	<u>Temp., °F</u>	<u>Pressure, psig</u>	<u>Reaction Time, Min.</u>	<u>Solvent/Coal/Pyrite</u>	<u>Hydrogen Feed Rate</u>
25-14	850	2000	61	100/0/0	2.21 wt.% Solvent
25-28	850	2000	60	90/0/10	2.03 wt.% Solvent
25-40*	850	2000	38	70/30/0	19.9 MSCF/T
25-52*	800	2000	38	70/30/0	18.2 MSCF/T
25-88 ⁺	850	2000	40	70/30/0	21.9 MSCF/T
25-100 ⁺	800	2000	39	70/30/0	20.8 MSCF/T
25-136*	850	2000	41	60/30/10	20.1 MSCF/T
25-148*	800	2000	38	60/30/10	19.9 MSCF/T
25-184 ⁺	850	2000	41	60.8/30.6/8.6	22.1 MSCF/T
25-196 ⁺	800	2000	41	60.8/30.6/8.6	22.1 MSCF/T

Solvent - 550-850°F cut of SRC-II Fuel Oil Blend

* Elkhorn #3 coal from Floyd County (14.31% Ash)

+ Elkhorn #3 coal from Latcher County (34.34% Ash)

scheme is described in Appendix B. Each fraction was further subjected to detailed elemental analysis as well as to nuclear magnetic resonance spectroscopy (NMR), near infrared analysis and simulated distillation (ASTM D2886). Product gases were analyzed by on-line gas chromatography up to C_4 hydrocarbon gases including other non-hydrocarbon gases (H_2S , NH_3 , CO , CO_2 , etc.). The product water was a combination of the condensed water collected at the unit plus the amount calculated by assuming the water vapor exiting the process unit was in equilibrium with the condensed water.

Products from the process unit were sampled as gases, light condensate, and the main receiver product slurry. The light condensate was a mixture of water and oil and was analyzed to determine the percentages of each in the mixture. The quantity of light oil was extremely small based on main receiver product. The elemental analysis of the light oil was assumed to be the same as that of heavier oil fraction obtained from solvent-separation. Complete analytical and work-up data for run CCL-25 are presented in Appendix C.

Solvent Hydrogenation - The hydrogenation of the process solvent was studied in the presence and absence of pyrite to assess the catalytic activity of Robena pyrite. Table 14 summarizes the process conditions and product distribution for the solvent hydrogenation runs. The first column of Table 14 presents the analysis of the starting solvent; whereas, the other two columns present solvent hydrogenation in the presence and absence of pyrite. The treatment of solvent in the absence of pyrite resulted in slight shift in product distribution from low molecular weight species (oil and asphaltene) to higher molecular weight species (preasphaltene); the preasphaltene fraction increased from 0.4 to 3.3 percent. Also, there was net hydrogen loss from the solvent; the hydrogen content of the oil fraction decreased from 7.72 to 7.40 percent as shown in Table 15. Hydrogen loss can be accounted for by the production of light hydrocarbon (HC) gases.

Table 14
Product Distribution for 550-850°F
Cut of SRC-II Fuel Oil Blend Process Solvent Hydrogenation Runs

Sample No.		25-14	25-28
Feed Composition	Original Solvent	100% Solvent	90% Solvent + 10% Robena Pyrite
Temp., °F	--	850	850
Pressure, psig	--	2000	2000
Hydrogen Treat Rate, wt% solvent	--	2.21	2.03
Reaction Time, min.	--	61	60
Product Distribution, Wt.%			
HC	--	0.9	1.8
CO, CO ₂	--	0.3	0.2
H ₂ S	--	0.2	0.2
NH ₃	--	0.01	0.4
Oil	90.8	87.3	92.9
Asphaltene	8.9	7.6	3.2
Preasphaltene	0.4	3.3	0.7
Insoluble Organic Material	0.0	0.2	0.0
Water	--	0.1	0.8
Hydrogen Consumption, Wt.% Solvent	--	(0.2)	0.5

() - means negative value

Oil - pentane solubles

Asphaltene - pentane insolubles, benzene solubles

Preasphaltene - benzene insolubles, pyridine solubles

Insoluble Organic Material - pyridine insolubles

Table 15
Hydrogen Concentration in Feed and Product of
Solvent Hydrogenation Runs

Sample No.	25-14	25-28
Feed	550°F + Solvent	550°F + Solvent + 10% Pyrite
Hydrogen Content, Wt. %		
Oil Fraction		
Start	7.72	7.72
Finish	7.40	7.74
Asphaltene Fraction		
Start	--	--
Finish	6.58	6.76

Solvent treatment in the presence of Robena pyrite showed a net solvent hydrogenation. There was a shift in product distribution from high molecular weight compounds to lower molecular weight material; the asphaltene fraction decreased from 8.9 to 3.2 percent. The hydrogen content of the oil fraction was maintained at its original value of 7.72% with a net consumption of hydrogen.

Comparing hydrogenation of solvent in the presence and absence of pyrite, it can be seen that addition of pyrite resulted in higher yield of hydrocarbon gases, ammonia, and water. The hydrogen content of oil fraction was not only maintained but also improved in the case of pyrite (see Table 15); whereas oil fraction lost hydrogen in the absence of pyrite. The hydrogen content of asphaltene fraction was also found to be higher in the presence of pyrite than its absence (see Table 15). The consumption of hydrogen was considerably higher in the presence of pyrite than its absence. A part of the additional hydrogen consumed in the case of Robena pyrite addition was due to reduction of pyrite to reduced pyrite. Back calculating the amount of hydrogen required to reduce the added pyrite, it was found to be 0.14 percent by weight of the solvent. This showed that if the hydrogen consumed by pyrite reduction was subtracted from total hydrogen consumption, hydrogen would still be consumed. This net hydrogen consumption was due to hydrocarbon gases, hydrogen sulfide, ammonia, solvent hydrogenation, and water production.

Product distribution calculation, when Robena pyrite was used, assumed that the pyrite was totally converted to reduced pyrite (FeS). In order to verify this important assumption, the solid residue from the sample CCL-25-28 was separated by filtration and analyzed by x-ray diffraction to determine the form of pyrite. No unreacted pyrite was detected and the sample pattern gave a very good match with pyrrhotite 11C which is $\text{FeS}_{1.099}$. Therefore, the assumption of complete reduction of pyrite to reduced pyrite was a valid one and will not create any significant error in calculation.

The simulated distillations of the oil fractions of the original solvent and treated solvent in the presence and absence of pyrite are shown in Figure 26. Notice that the solvent treated in the presence and absence of pyrite showed lower boiling point distribution compared to the original solvent. It is very difficult to make a quantitative decision about distribution of compounds in the oil fraction from simulated distillation data. It is quite evident that solvent treated in the pyrite has lower boiling point distribution compared to the solvent treated in the absence of pyrite.

Coal Liquefaction - Two different Elkhorn #3 coals, one from Floyd County (14.31% ash content) and the other from Letcher County (34.34% ash content), were liquefied both alone and in the presence of Robena pyrite. The results are discussed below.

Liquefaction of Floyd County Coal - The liquefaction of Floyd County Elkhorn #3 coal was studied at two different temperatures and the results are summarized in Table 16. Coal conversion was found to be almost similar at two different temperatures, but significant differences were found in gas production, product distribution and hydrogen consumption. Hydrocarbon gases, CO, CO₂, H₂S, NH₃, and water production were found to increase with increasing reaction temperature from 800 to 850°F; hydrocarbon gas production increased from 2.4 to 4.2 percent and the benzene soluble fraction increased from 14 to 42 percent. At 800°F the major portion of the coal ended up in the preasphaltene fraction as shown in Table 16. Increasing the temperature to 850°F increased the conversion of preasphaltenes to the benzene soluble fraction and to gases. Also, the increase in temperature increased the hydrogen consumption from 0.5 to 1.4 percent. The increase in hydrogen consumption was mainly due to increased gas formation and conversion of preasphaltene to the benzene soluble fraction; 0.4 percent of this increase was due to increased gas formation and 0.6 percent was accounted for in conversion of preasphaltenes to the benzene soluble fraction.

FIGURE 26.
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTIONS
OF ORIGINAL SOLVENT AND HYDROTREATED SOLVENT

Table 16
Liquefaction Behavior of Floyd County Elkhorn #3 Coal

Sample No.	25-40	25-52
Feed	70% Solvent/30% Coal	
Temperature, °F	850	800
Pressure, psig	2000	2000
Hydrogen Treat Rate, MSCF/T	19.9	18.2
Residence Time, min.	38	38
Product Distribution, Wt.% MAF Coal		
HC	4.2	2.4
CO, CO ₂	1.0	0.8
H ₂ S	1.3	0.9
NH ₃	0.0	0.0
Benzene Solubles	42.1	14.4
Preasphaltene	30.1	58.0
Insoluble Organic Matter (IOM)	18.1	20.6
Water	3.2	2.9
Conversion, % MAF	81.9	79.4
Hydrogen Consumption, Wt.% MAF		
Total	1.40	0.51
Gas	0.82	0.61
Solvent	0.58	(0.10)

() - means negative value

$$\text{Solvent H}_2 \text{ Consumption} = \frac{(\text{Oil H}_2)_{\text{in}} - (\text{Oil H}_2)_{\text{out}}}{\text{Wt. MAF Coal}} \times 100$$

Table 17 summarizes the distribution of hydrogen in feed oil and various product. The oil fraction lost significant amount of hydrogen at 850°F; whereas, the hydrogen content of oil was found to be more than the starting value at 800°F. Some differences in hydrogen content of asphaltene and preasphaltene fractions were also noted. The production of SRC and SRC sulfur content are listed in Table 18. The difference in SRC yield is due to the difference in the benzene soluble fraction. Also, SRC sulfur content decreased from 0.79 to 0.61 percent as temperature increased from 800 to 850°F.

The simulated distillation distribution of the oil fractions of the product obtained at two different temperatures are shown in Figure 27. There was no apparent differences in the initial and final boiling points of the two oil fractions. The oil fraction obtained from coal liquefaction at 850°F showed a slightly larger quantity of higher boiling point compounds than the oil fraction obtained at 800°F.

Liquefaction of Floyd County Coal in the Presence of Robena Pyrite -

The liquefaction of Floyd County Elkhorn #3 coal in the presence of Robena pyrite was studied at two different temperatures. The results, tabulated in Table 19, show significant differences in product distribution at two different temperatures. Coal conversion was similar at the two temperatures but the yield of hydrocarbon gases, CO, CO₂, H₂S, NH₃, and water increased with temperature. The most significant differences were in the distribution between the benzene soluble and preasphaltene fractions. At 800°F most of the dissolved coal ended up in the preasphaltene fraction. As reaction temperature increased so did the conversion of preasphaltenes to benzene solubles and hydrocarbon gases; the preasphaltene fraction decreased from 49 to 24% and benzene solubles increased from 30 to 52 percent. The increase in temperature not only increased benzene solubles but also increased the hydrogen consumption. The total hydrogen consumption increased from 1.7 to 2.5 percent. The increase in hydrogen consumption was due mainly to increased

Table 17
Hydrogen Concentration in Feed and Product

Sample No.	25-40	25-52
Reaction Temperature, °F	850	800
Hydrogen Content, Wt.%		
Feed Oil	7.72	7.72
Product:		
Oil	7.49	7.76
Asphaltene	6.48	6.77
Preasphaltene	5.50	5.38

Table 18
SRC Production and its Sulfur Content

Sample No.	25-40	25-52
Reaction Temperature, °F	850	800
Product Distribution, Wt.% MAF		
Asphaltene	14.8	17.6
Preasphaltene	30.2	58.0
Total (SRC)	45.0	75.6
SRC Sulfur, Wt.%	0.6	0.8

FIGURE 27.

EFFECT OF REACTION TEMPERATURE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM COAL LIQUEFACTION RUNS

Table 19
Liquefaction Behavior of Floyd County Elkhorn #3
Coal in the Presence of Robena Pyrite

Sample No.	25-136	25-148
Feed	60% Solvent/30% Coal/ 10% Pyrite	60% Solvent/30% Coal/10% Pyrite
Temp., °F	850	800
Pressure, psig	2000	2000
Hydrogen Treat Rate, MSCF/T	21.9	20.8
Residence Time, Min.	41	38
Product Distribution, Wt.% MAF Coal		
HC	5.3	2.0
CO, CO ₂	1.2	0.9
H ₂ S	2.8	0.9
NH ₃	0.2	0.0
Benzene Solubles	52.3	30.5
Preasphaltene	24.3	49.3
Insoluble Organic Matter	10.4	13.7
Water	3.5	2.7
Conversion, % MAF	89.6	86.3
Hydrogen Consumption, Wt.% MAF		
Total	2.53	1.65
Consumed by Gas	2.49	1.82
Consumed by Solvent	0.04	(0.17)
Consumed by Pyrite	0.50	0.50

() - means negative value

gas formation: 0.1% is due to increased gas formation and 0.8% is accounted for increased production of benzene solubles. Table 20 summarizes the distribution of hydrogen in feed oil and various products. The hydrogen content of oil fractions at two different reaction temperatures was either maintained or increased at the two reaction temperatures. The hydrogen contents in asphaltene and preasphaltene products were higher at 800°F than at 850°F. The SRC sulfur contents were not significantly different as shown in Table 21. The higher production of SRC at 800 than 850°F was due to the lower production of benzene solubles fraction.

The boiling point distribution curves for the oil fractions obtained at 800 and 850°F as presented in Figure 28 show a crossover at the 30% point. The average boiling point of the first 30% obtained at 850°F was lower than the oil obtained at 800°F; whereas the last 70% showed the opposite result.

Effect of Pyrite on Floyd County Elkhorn #3 Liquefaction -

Liquefaction in the presence of Robena pyrite at 850°F increased the coal conversion from 82 to 90 percent (see Table 22). There was a net increase of preasphaltene conversion to benzene solubles and gases; the benzene solubles increased from 42 to 52 percent and gas formation increased from 6.5 to 9.5 percent. The added coal conversion ended up in the benzene solubles and gases. The addition of pyrite increased the hydrogen consumption from 1.40 to 2.53 percent. A part of the increased hydrogen consumption, 0.5 wt.%, was consumed in reducing the added pyrite. The remaining increased hydrogen consumption went to increase the yields of gases and benzene solubles. A significant observation was that oil hydrogen content was depleted in the absence of pyrite; whereas it was maintained in its presence (see Table 22). The pyrite was assumed to be totally reduced to iron sulfide (FeS) in computing product distribution. From the above results it can be concluded that pyrite catalyses the oil and gas production and helps in rehydrogenation of process solvent at 850°F.

Table 20
Hydrogen Concentration in Feed and Product

Sample No.	25-136	25-148
Reaction Temperature, °F	850	800
Hydrogen Content, Wt.%		
Feed Oil	7.72	7.72
Product:		
Oil	7.70	7.80
Asphaltene	6.24	7.10
Preasphaltene	5.65	5.84

Table 21
SRC Production and Its Sulfur Content

Sample No.	25-136	25-148
Reaction Temperature, °F	850	800
Product Distribution, Wt.% MAF		
Asphaltene	10.9	39.8
Preasphaltene	24.1	48.6
Total (SRC)	35.0	88.4
SRC Sulfur, Wt.%	0.7	0.7

FIGURE 28.
EFFECT OF REACTION TEMPERATURE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM COAL LIQUEFACTION RUNS
IN THE PRESENCE OF ROBENA PYRITE

Table 22
Comparison of Floyd County Coal Liquefaction in the
Presence and Absence of Robena Pyrite

Sample No.	25-40	25-136	25-52	25-148
Temp., °F	850	850	800	800
Pyrite	No	Yes	No	Yes
Product Distribution, Wt.% MAF Coal				
HC	4.2	5.3	2.4	2.0
CO, CO ₂	1.0	1.2	0.8	0.9
H ₂ S	1.3	2.8	0.9	0.9
NH ₃	0.0	0.2	0.0	0.0
Benzene Solubles	42.1	52.3	14.4	30.5
Preasphaltene	30.1	24.3	58.0	49.3
I.O.M.	18.1	10.4	20.6	13.7
Water	3.2	3.5	2.9	2.7
Conversion	81.9	89.6	79.4	86.3
SRC Sulfur, %	0.61	0.68	0.79	0.71
Hydrogen Consumption, Wt.% MAF				
Total	1.40	2.53	0.51	1.65
Consumed by Gas	0.82	2.49	0.61	1.82
Consumed by Solvent	0.58	(0.04)	(0.10)	(0.17)
Consumed by Pyrite	--	0.50	--	0.50
Oil Hydrogen Content, Wt.%				
Start	7.72	7.72	7.72	7.72
Finish	7.49	7.70	7.76	7.80

() - means negative value

The simulated distillation of the fraction obtained with and without the use of pyrite at 850°F are shown in Figure 29. The oil fraction obtained with pyrite showed slightly lower I.B.P., F.B.P. and had lower boiling point compounds compared to oil generated without pyrite.

The liquefaction of coal in the presence and absence of Robena pyrite at 800°F is shown in Table 22 (sample numbers 25-52 and 25-148). The addition of pyrite to the reaction mixture at 800°F improved the coal conversion from 79 to 86%. It also increased the conversion of preasphaltene. Both the increased amounts of converted coal and preasphaltenes resulted in more benzene solubles.

The hydrogen consumption increased from 0.5 to 1.7 percent on addition of pyrite. The additional consumed hydrogen went to reduction of pyrite and formation of more benzene solubles. Also the hydrogen content of the oil fraction in the presence of pyrite improved; whereas, it suffered depletion in the absence of pyrite. This verifies that pyrite catalyses solvent hydrogenation. The simulated distillations of the oil fractions obtained with and without pyrite at 800°F are compared in Figure 30. The results are very similar to those obtained at 850°F. About 30% of the oil obtained with the use of pyrite had higher boiling point distribution than the oil obtained without the use of pyrite. The trend was opposite for the remaining 70% of the oil fraction.

These results show that addition of Robena pyrite to Floyd County Elkhorn #3 coal increases coal dissolution, promotes solvent hydrogenation and improves conversion of preasphaltenes to benzene solubles and gases.

Liquefaction of Letcher County Kentucky Elkhorn #3 Coal - The results of liquefaction of Letcher County Elkhorn #3 coal at two different temperatures are summarized in Table 23. Coal conversion increased from 62 to 72 percent as temperature increased from 800 to 850°F. Hydrocarbon gas production also increased with temperature.

FIGURE 29.
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTION OBTAINED
FROM COAL LIQUEFACTION RUNS AT 850° F

FIGURE 30.
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTIONS OBTAINED
FROM COAL LIQUEFACTION RUNS AT 800° F

Table 23
Liquefaction Behavior of Letcher County
Elkhorn #3 Coal

Sample No.	25-88	25-100
Feed	70% Solvent/30% Coal	
Temp., °F	850	800
Pressure, psig	2000	2000
Hydrogen Treat Rate, Mscf/T	20100	19900
Residence Time, Min.	39.7	39.3
Product Distribution, Wt.% MAF Coal		
HC	6.8	2.4
CO, CO ₂	1.3	1.0
H ₂ S	0.8	0.7
NH ₃	0.0	0.0
Benzene Solubles	15.9	17.2
Preasphaltene	44.8	38.6
I.O.M.	28.4	37.7
Water	2.0	2.4
Conversion, % MAF	71.6	62.3
Hydrogen Consumption, Wt. % MAF		
Total	0.47	0.14
Consumed by Gas	0.14	(0.09)
Consumed by Solvent	0.33	0.23

() - means negative value

No significant differences were found in the production of benzene solubles and preasphaltenes. Hydrogen consumption increased from 0.14 to 0.47 percent as reaction temperature increased. The increased hydrogen consumption was mainly due to higher hydrocarbon gas production and coal conversion.

The distribution of hydrogen in feed oil and various products are given in Table 24. The oil fraction lost some hydrogen at both the temperatures, but the loss was greater at 850°F than 800°F. Also, the hydrogen contents of the asphaltenes and preasphaltenes were higher at the lower temperature (800°F). The SRC sulfur content was found to be considerably lower at 850 than at 800°F (0.5% at 850°F compared to 0.8% at 800°F) as shown in Table 25. The simulated distillations of the oil fractions obtained at two different temperatures are shown in Figure 31. The oil fraction obtained at 850°F showed a higher boiling point distribution than the oil at 800°F. This is probably due to a higher proportion of higher molecular weight oil generated from the coal at 850°F than 800°F.

Liquefaction of Letcher County Coal in the Presence of Robena Pyrite -

The liquefaction of Letcher County Elkhorn #3 coal was studied at 800 and 805°F in the presence of Robena pyrite. The results are tabulated in Table 26. The coal conversion was found to increase from 75 to 91 percent with increase in temperature from 800 to 850°F. The yield of hydrocarbon gases and benzene solubles increased and hydrogen consumption increased with temperature. The hydrogen consumption increased from 1.8 to 3.1 percent. The increase in hydrogen consumption was mainly due to increased hydrocarbon gas production and coal conversion. The hydrogen content of the oil fraction decreased at 850°F and remained unchanged at 800°F as shown in Table 27. The hydrogen contents of other fractions were higher at 800 than 850°F. The SRC sulfur was almost identical at the two temperatures as shown in Table 28.

Table 24
Hydrogen Content in Feed and Product

Sample No.	25-88	25-100
Hydrogen Content, Wt.%		
Feed Oil	7.72	7.72
Product:		
Oil	7.61	7.65
Asphaltene	6.29	6.71
Preasphaltene	5.20	5.54

Table 25
SRC Production and Its Sulfur Content

Sample No.	25-88	25-100
Product Distribution, Wt.% MAF		
Asphaltene	39.4	20.5
Preasphaltene	44.8	38.6
Total (SRC)	84.2	59.1
SRC Sulfur, Wt.%	0.5	0.8

FIGURE 31.
EFFECT OF REACTION TEMPERATURE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM COAL LIQUEFACTION RUNS

Table 26
Liquefaction Behavior of Letcher County Elko #3
Coal in the Presence of Robena Pyrite

Sample No.	25-184	25-196
Feed	60.8% Solvent/30.6% Coal/8.6% Pyrite	
Temp., °F	850	800
Pressure, psig	2000	2000
Hydrogen Treat Rate, Mscf/T	22100	22100
Residence Time, Min.	41	41
Product Distribution, Wt.% MAF Coal		
HC	6.2	2.2
CO, CO ₂	1.3	1.0
H ₂ S	6.8	5.2
NH ₃	0.6	0.8
Benzene Solubles	45.6	24.8
Preasphaltene	27.0	38.8
I.O.M.	8.7	24.9
Water	3.8	2.3
Conversion, % MAF	91.3	75.1
Hydrogen Consumption, Wt.% MAF		
Total	3.13	1.79
Consumed by Gas	2.79	1.79
Consumed by Solvent	0.34	0.00
Consumed by Pyrite	0.55	0.55

() - means negative value

Table 27
Hydrogen Concentration in Feed and Product

Sample No.	25-184	25-196
Temperature, °F	850	800
Hydrogen Content, Wt.%		
Feed Oil	7.72	7.72
Product:		
Oil	7.60	7.72
Asphaltene	6.35	8.02
Preasphaltene	5.34	5.89

Table 28
SRC Production and Its Sulfur Content

Sample No.	25-184	25-196
Temperature, °F	850	800
Product Distribution, Wt.% MAF		
Asphaltene	14.2	22.1
Preasphaltene	27.0	38.8
Total (SRC)	41.2	60.9
SRC Sulfur, %	0.5	0.6

The boiling point distribution as determined by simulated distillation for the oil fractions obtained at 800 and 850°F are shown in Figure 32. The two curves are identical in the lower boiling range, but the oil fraction obtained at 850°F shows more material in the higher boiling point range.

Effect of Pyrite on Letcher County Elkhorn #3 Liquefaction - In the presence of Robena pyrite at 850°F coal conversion increased significantly as shown in Table 29. Coal conversion increased from 72 to 91 percent. There was a significant increase in conversion of preasphaltenes to benzene solubles. The increased coal conversion ended up in more benzene solubles. The addition of pyrite increased hydrogen consumption from 0.5 to 3.1 weight percent. The increase in hydrogen consumption was due to pyrite reduction, increased coal conversion and increased gas and benzene solubles yield. The hydrogen content of the oil fractions were almost the same (see Table 29). The simulated distillations of the oil fractions of the runs in the presence and absence of pyrite at 850°F are shown in Figure 33. The addition of pyrite shifted the curve towards higher boiling point materials.

The effect of Robena pyrite on coal liquefaction at 800°F is also summarized in Table 29. Again, the addition of pyrite resulted in higher coal conversion and higher production of benzene solubles and gases. The increased coal conversion ended up in higher benzene solubles. The preasphaltenes remained unaffected by pyrite. The sulfur content of SRC decreased from 0.8 to 0.6% on addition of pyrite. Also, pyrite increased the hydrogen consumption from 0.1 to 1.8 percent; the increased hydrogen consumption was due to pyrite reduction, higher gas and benzene soluble yield and improved coal conversion. The hydrogen content of the oil fraction remained at the original level with pyrite; whereas, it decreased without pyrite. The simulated distillations of the oil fractions presented in Figure 34 did not show any significant difference.

FIGURE 32.
EFFECT OF REACTION TEMPERATURE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM COAL LIQUEFACTION RUNS
IN THE PRESENCE OF ROBENA PYRITE

Table 29
Comparison of Letcher County Coal Liquefaction in the
Presence and Absence of Robena Pyrite

Sample No.	25-88	25-184	25-100	25-196
Temp., °F	850	850	800	800
Pyrite	No	Yes	No	Yes
Production Distribution, Wt.% MAF Coal				
HC	6.8	6.2	2.4	2.2
CO, CO ₂	1.3	1.3	1.0	1.0
H ₂ S	0.8	6.8	0.7	5.2
NH ₃	0.0	0.6	0.0	0.8
Benzene Solubles	15.9	45.6	17.2	24.8
Preasphaltene	44.8	27.0	38.6	38.8
I.O.M.	28.4	8.7	37.7	24.9
Water	2.0	3.8	2.4	2.3
Conversion	71.6	91.3	62.3	75.1
SRC Sulfur, Wt.%	0.5	0.5	0.8	0.6
Hydrogen Consumption, Wt.% MAF				
Total	0.47	3.13	0.14	1.79
Consumed by Gas	0.14	2.79	(0.09)	1.79
Consumed by Solvent	0.33	0.34	0.23	0.00
Consumed by Pyrite	--	0.55	--	0.55
Oil Hydrogen Content, Wt.%				
Start	7.72	7.72	7.72	7.72
Finish	7.61	7.60	7.65	7.72

() - means negative value

FIGURE 33.
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTIONS
OBTAINED FROM COAL LIQUEFACTION RUNS AT 850° F

FIGURE 34.
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTIONS
OBTAINED FROM COAL LIQUEFACTION RUNS AT 800° F

Finally, the addition of pyrite improves coal conversion, increases production of benzene solubles and gases and maintains the solvent hydrogen content.

The second standardization run (CCL-28) was carried out during the month of April. The run was designed to study the liquefaction behavior of Kentucky #9 coal at two different temperatures in the presence and absence of Robena pyrite. Also, the liquefaction behavior of run-of-mine and washed Ohio coals was studied. The run lasted for 150 hours during which 11 different samples were taken and submitted for detailed analyses. A detailed summary of the operating data of the runs is given in Appendix D. The analytical results of the standardization runs will be reported as they become available.

Task 4.0 Effect of Coal Minerals on Coal Liquefaction

A number of minerals were screened at Auburn University for catalytic activity toward coal liquefaction in their tubing-bomb reactor. Conversion and product distribution data were generated using a solvent separation technique. The method was quite similar to that described in Appendix B except that the original frozen material was not sonicated in pentane. Without a sonicator the process was slow and mixing appeared to be less than satisfactory. In order to speed up the separation procedure and to assure proper mixing, the use of a Bronson Sonifier was initiated in March. The results of the tests with the sonifier showed significantly higher oil extraction compared to the previous manual mixing technique. In order to check the two mixing techniques, one product slurry was divided into two portions and separated using the two different mixing techniques. The results are summarized in Table 30. The residue and preasphaltene fractions were the same by the two methods. However, more oil was extracted when using the sonifier than by manual mixing, but the sum of oils and asphaltenes was the same in both cases. The shift to a higher oil yield occurred at the expense of the asphaltene fraction. Similar observation was made in other runs. Therefore, the sum of oil and asphaltene fractions, referred to in this report as benzene solubles, was

Table 30
Comparison of Solvent Separation Methods

	Weight, %	
	<u>Manual Separation</u>	<u>Sonifier Aided Separation</u>
Oil	11	32
Asphaltene	42	22
Preasphaltene	12	14
Residue	35	32

Oil - pentane solubles

Asphaltene - pentane insolubles, benzene solubles

Preasphaltene - benzene insolubles, methylene chloride/10% methyl alcohol solubles

Residue - methylene chloride/10% methyl alcohol insolubles

employed in the comparison of the catalytic activity of the various minerals. The use of either technique would give identical comparisons. In order to be consistent, the sonifier aided mixing technique will be used in future work. The solvent separation technique used at Auburn University is described in detail in Appendix E.

The catalytic activity of various minerals in coal liquefaction was studied and the results are summarized in Table 31. The addition of lime to the reaction mixture practically killed the liquefaction reaction; coal conversion was only 8 percent. The addition of dolomite, bornite, feldspar, sodium carbonate, potassium carbonate, apatite, rutile, illite, quartz, zircon, and calcite to the reaction mixture gave product distributions similar to that of the no additive run. There was slight variation in coal conversion and production of benzene solubles, but the variation was within the limits of experimental error. The addition of ilmenite and zinc oxide slightly improved coal conversion and production of benzene solubles, but improvement was marginal. The addition of Robena pyrite and Co-Mo-Al to the reaction mixture increased the coal conversion and benzene soluble fraction considerably. A major portion of the increased coal conversion was converted to benzene soluble fraction. Also, there was some conversion of preasphaltenes to benzene solubles. The addition of iron oxide (Fe_2O_3) to the reaction mixture gave the highest conversion of coal and benzene soluble production among all the minerals tested so far. Almost all of the increased conversion ended up in the benzene soluble fraction. Also, Fe_2O_3 improved conversion of preasphaltenes to benzene solubles.

Comparison of Auburn University and Air Products Results - The coal liquefaction data in the batch autoclave (Auburn University) and the CSTR (Air Products) show no significant difference in conversion of coal in the presence and absence of pyrite as shown in Table 32. Major differences were found in product distribution. Auburn University data did not include gas and water analyses

Table 31.

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

<u>Additive</u>	<u>None</u>	<u>Lime</u>	<u>Dolomite</u>	<u>Bornite</u>	<u>Feldspar</u>	<u>Na₂CO₃</u>	<u>Apatite (Ca₃PO₄)</u>	<u>K₂CO₃</u>
Experiment Number	AP-91	AP-95	AP-101	AP-86	AP-97	AP-108	AP-106	AP-110
Benzene Solubles, %	64	-4	57	61	64	65	65	65
Preasphaltene, %	13	12	17	12	16	8	12	6
I.O.M., %	23	92	26	27	20	27	23	29
Conversion, %	77	8	74	73	80	73	77	71

Reaction Mixture: Coal - 3g (Floyd County Elkhorn #3)
 Solvent - 6g
 Additive - 1g

Reaction Conditions: Temperature - 450°C
 Pressure - 1250 psig H₂ at 25°C
 Time - 60 Minutes

Reactor: Tubing-Bomb
 Volume - 46.3 ML

Preasphaltene - benzene insolubles, methylene chloride/10% methyl alcohol solubles

I.O.M. - insoluble organic material

Table 31
(continued)

<u>Additive</u>	<u>Rutile</u>	<u>Illite</u>	<u>Quartz</u>	<u>Zircon</u>	<u>Calcite</u>	<u>Ilmenite</u>	<u>ZnO</u>	<u>Robena Pyrite</u>	<u>Co-Mo-Al</u>	<u>Reagent Grade Fe₂O₃</u>
Experiment Number	AP-92	AP-99	--	AP-102	AP-98	AP-105	AP-100	AP-81	Average of AP-88, AP-90	AP-89
Benzene Solubles, %	66	67	67	67	68	71	73	83	85	91
Preasphaltene, %	14	14	13	15	15	13	11	7	9	7
I.O.M., %	20	19	20	18	17	16	16	10	6	2
Conversion, %	80	81	80	82	83	84	84	90	94	98

Table 32
Comparison of Auburn University (AU) and
Air Products (AP) Data

Source	AU	AP	AU	AP
Run No.	AP-91	CCL-25-40	AP-81	CCL-25-136
Temperature, °F	850	850	850	850
H ₂ Pressure, psig	1250 at 25°C	2000	1250 at 25°C	2000
Additive	None	None	Robena Pyrite	Robena Pyrite
Time, Min.	60	40	60	40
Product Distribution, Wt.% MAF Coal				
Gases	--	6.5	--	9.5
Benzene Solubles	64	42.1	83	52.3
Preasphaltene	13	30.1	7	24.3
I.O.M.	23	18.1	10	10.4
Water	--	3.2		3.5
Conversion, %	77	81.9	90	89.6

which made comparison of the product distribution very difficult. The differences in product distribution could be due to difference in reaction time. However, both Auburn University and Air Products data confirmed an increase in benzene soluble production and coal conversion with the addition of Robena pyrite.

Task 5.0 Effect of Metallic Wastes and Metal-Containing By-Products on Coal Liquefaction

Progress - A number of metallic wastes and metal-containing by-products were investigated for their catalytic activity in coal liquefaction at Auburn University in their tubing-bomb reactor. The results are summarized in Table 33. Addition of high and low zinc flue dusts and oil shale had particaly no advantage over non-additive run. Phosphate slime, reduced Robena pyrite (obtained from CPDU run no. CCL-25-28), Robena pyrite and red mud showed significant improvement in coal conversion (coal conversion increased from 77 to 90 percent) and production of benzene solubles (benzene solubles increased from 64 to greater than 80 percent). There seemed to be no significant difference in the activity of reduced Robena pyrite and Robena pyrite. The difference in the activity of the two materials was within the limits of experimental error. So the preliminary data indicates that there is no apparent advantage as far as product distribution is concerned in reducing the Robena pyrite and then using it as a catalyst instead of using Robena pyrite straight. Red mud showed the highest catalytic activity among all the metallic wastes and metal-containing by-products tested so far.

Table 33

Catalytic Activity of Metallic Waste and Metal-Containing By-Products

<u>Additive</u>	<u>None</u>	<u>Oil Shale</u>	<u>High Zinc Flue Dust</u>	<u>Low Zinc Flue Dust</u>	<u>Phosphate Slime</u>	<u>Reduced Robena Pyrite</u>	<u>Robena Pyrite</u>	<u>Red Mud</u>
Experiment No.	AP-91	AP-104	AP-93	AP-94	AP-107	AP-96	AP-81	Average of AP-84 and AP-85
Product Distribution, % MAF								
Benzene Solubles, %	64	64	68	70	80	81	83	86
84 Preasphaltene, %	13	16	12	14	12	9	7	7
I.O.M., %	23	20	20	16	8	10	10	7
Conversion, %	77	80	80	84	92	90	90	93

Reaction Mixture: Coal - 3g (Floyd County Elkhorn #3)
 Solvent - 6g
 Additive - 1g

Reaction Conditions: Temperature - 450°C
 Pressure - 1250 psig H₂ at 25°C
 Time - 60 Minutes

Reactor: Tubing-Bomb
 Volume - 46.3 ML.

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
CS	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	1339
	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	1788	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
	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	--
	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

Solvent Separation Procedure for Coal Conversion Products

It is the purpose of this procedure to provide a rapid and precise fractionation of the gross coal conversion product into four (4) subfractions defined by their solubility.

- A) Oils - Pentane Solubles
- B) Asphaltenes - Pentane Insoluble/Benzene Soluble
- C) Preasphaltenes - Pyridine Soluble/Benzene Insoluble
- D) Residue - Pyridine insoluble

This procedure is carried out at room temperature $25^{\circ}\text{C} \pm 3^{\circ}$, under nitrogen gas pressure, using solvents of the highest quality available. The sample may be liquid, solid or a mixture, with less than 1% material boiling below 150°C .

Equipment Required:

1. Branson Model 350 Sonicator with 3/4" horn
2. Millipore 142 mm pressure filter with 300 ml capacity #XX40-047-00, with 142 mm filter, 54, FSLW-01420
3. Round bottom distilling flasks - 500 ml, 250 ml, 2 each
4. Rotovapor R, Fisher Scientific #9-548-151 (1979)
5. Vacuum pump and trap
6. Nitrogen-Gas (0-20 psi adjustable) pressure filter feed
Nitrogen-Gas (0-20 psi adjustable) rotovapor feed
Nitrogen-liquid (1-2L) freeze sample (dewar)
7.
 - a) n-Pentane -
 - b) Benzene - Grade of solvent depends upon ultimate
 - c) Pyridine - use of sample subfractions Pesticide,
 - d) Methanol - Distilled in Glass, or HPCL grade
8. Fume hood 150-200 cfm air rate exchange
9. Cooling water or heater exchange for rotovapor condenser

10. Balance to read weights $\pm$ 0.005 grams or better with maximum load 200 grams.

Safety Features:

Solvents must be used only under the fume hood and transferred from bottle to flask by hand pump. Gloves to protect workers hands, and overalls for laboratory work. Clean-up of spills on hands can be completed with Go-Jo, waterless hand-cleaner, mild scrubbing and water wash (warm). All normal safety precautions must be observed during the full operation.

Sampling Handling:

The sample chosen for this procedure must be representative of the process unit output. Great care must be given to the isolation of approximately 50 grams of gross product.

The sample once chosen must be kept free of air (oxygen), heat and light. Store samples not ready for separation at 4°C under a blanket of nitrogen. Hot samples may be taken in 316 stainless steel bottles (DuPont #03226, 235 ml 61 x 140 mm with screw cap). Samples may be warmed to 65°C in the cans and stirred or shaken to induce good mixing just prior to taking a 5 gram actual work-up sample.

Procedure

The laboratory equipment is prepared in the following order:

- a) Ultrasonic unit with 3/4" horn adjusted and cleaned with methylene chloride.
- b) Millipore filter put in place after taking weight of dry filter element. Ensure that all O-rings fit well with no leaks (test with n-pentane under 10 psi). Use Teflon tape (3/4") to wrap screw fittings and seals.

- c) Prepare rotovapor-bath temperature at 55-60°F for n-pentane; nitrogen flow rate should just cause 1/4-1/2" dimple in liquid of 250 ml flask.
- d) Cooling liquid for rotovapor condenser should be 10°C if heater exchanger used -10°C with MeOH.

Step 1 Tare a 150 ml heavy wall Pyrex beaker; add 5 grams read to ± 0.005 grams of the desired coal-derived sample. Add approximately 100 ml of liquid nitrogen slowly to the beaker to maintain a quiet solution. Total volume of liquid nitrogen used may exceed 500 ml.

Step 2 With a Pyrex glass stirring rod (3/8-1/2") Pyrex, grind the now frozen sample to a fine powder. Requires 5-8 minutes. [no large (1/16") lumps]. Fill with more liquid nitrogen to maintain at least 30 ml volume while grinding.

Step 3 Allow the liquid nitrogen to evaporate to just above the solid mixture. Add with moderate (micro-probe 1/8"/power level 3) sonication 100 ml of n-pentane. Some stirring may be required - keep tools out of beaker while sonic power is on. Sonicate for 5 minutes at level 5 power.

Step 4 Allow mixture to settle (1-2 minutes) decant supernatant into filter unit, refill beaker with n-pentane and sonicate again for 3-5 minutes. Allow decant liquid to filter into a 250 ml flask - do not allow filter to dry from this time onwards.

Step 5 Repeat Step 4 twice for a total of 300 ml n-pentane. If catch flask fills transfer to rotovapor and begin to remove n-pentane under nitrogen at 60°C. Transfer the solids with small portions (25-50 ml) of pentane.

Do not discard beaker -- hold for additional transfer of solvents to filter. This assures removal of maximum amount of material - reduces loss.

Step 6 Filter the solids, adding nitrogen pressure (5-10 psi) if needed. Add new pentane via original beaker as needed for a total of 2 L. This amount can be recollected from rotovapor unit during the continuous solvent removal steps.

Step 7 Continue solvent filtering (up to 2 L) until the filtrate is a very light yellow/green. At the end of the pentane extraction, with 25 ml pentane in the filter, add 100 ml benzene and continue as in Step 6 for 2.5 L. The new filtrate is collected in a new 500 ml flask (tare). Continue to transfer filtrate to rotovapor - waterbath temperature 75°C. Nitrogen flow rate 1/2" dimple.

Step 8 The pentane solubles from steps 6 and 7 should be held on rotovapor for 2 minutes past the last drop of condensed pentane is in the catch flask. Remove, clean and dry outside of the flask containing the oils (reddish) and weigh. From difference on tare:

Yield of oils:-----grams

Step 9 The benzene extraction is carried out in a similar fashion as in Steps 6-8. The benzene solubles are removed from rotovapor when 10-20 ml of solution remain. The flask is swirled in liquid nitrogen to evenly coat 2/3 inner flask and freeze the solution in place. Quickly transfer flask to vacuum line (1 mm Hg) with trap and allow flask to stand unheated to freeze dry the benzene (sublime) in about 1 hour.

Yield of asphaltenes-----grams

Step 10 After the last benzene extraction begin to add pyridine and continue extraction as in steps 6-8. Remove the solvent at 90°C under 1/4-1/2" nitrogen dimple. Two liters of pyridine are required. The last wash should be pure methanol (100 ml), followed by nitrogen gas at 5 psi for 10 minutes. As the pyridine is just nearly removed (5-10 ml) stop and add 10-15 ml benzene. Swirl flask to mix contents and freeze-dry as in Step #9 for one hour. If pyridine odor remains, add 20 mL benzene and re-freeze dry.

Yield of preasphaltenes-----grams

Step 11 The residue will dry in-place. Stop nitrogen, gently remove filter and weigh.

Yield of residue-----grams

<u>Step 12</u>	Oils	<u>A</u>
	Asphaltenes	<u>B</u>
	Preasphaltenes	<u>C</u>
	Residue	<u>D</u>
	$A + B + C + D = \text{Total recovered}$	

Original mass of sample = MS.

MS - total recovered = net loss or gain.

If gain of weight is observed solvent is present in oils or other fraction.

If loss of weight is observed oils have volatile matter.

Add net loss to mass of oils (A + net loss) and calculate over material recovery.

Report:		Recovered	Corrected	%
	Oils	A	A + net loss	_____
	Asphaltenes	B	B	_____
	Preasphaltenes	C	C	_____
	Residue	<u>D</u>	<u>D</u>	_____
	Total Recovered		MS	100%

APPENDIX C

Fractional and Elemental Compositions of the CCL-25 Product Liquids

		FR	C	H	O	N	S	Ash	Sum	MW
CCL-25-14	PL		89.0	7.28	1.82	1.20	0.47	0.23	100.00	206
	O	88.60	89.64	7.40	1.30	1.17	0.50	--	100.00	198
	A	7.80	80.99	4.68	--	--	--	--	--	--
	P	3.40	--	--	--	--	--	--	--	--
	R	0.20	--	--	--	--	--	--	--	--
	Sum	100.0								
	RCV	98.8								
CCL-25-28 93	PL		82.82	7.28	1.32	0.97	0.46	7.14	100.00	203
	O	88.0	89.25	7.74	1.39	1.19	0.44	--	100.00	205
	A	3.0	84.0	6.76	--	--	0.64	--	--	--
	P	1.0	--	--	--	--	--	--	--	--
	R	8.0	4.55	0.41	3.54	0.33	31.61	85.58	126.02	
	Sum	100.00								
	RCV	99.60								
CCL-25-40	PL		82.22	6.67	2.82	1.17	0.98	6.15	100	238
	O	71.34	89.05	7.49	1.79	1.33	0.34	--	100	--
	A	10.20	86.10	6.48	4.53	2.24	0.66	--	100	404
	P	8.00	84.06	5.50	5.44	3.33	0.58	1.10	100	1205
	R	10.46	30.44	1.88	5.18	0.78	5.01	56.71	100	--
	Sum	100.00								
	RCV	98.06								

PL = Product Liquid

O = Oil

A = Asphaltene

P = Preasphaltene

R = Residue

RCV = Recovery

FR = Solvent Fractions

APPENDIX C

(continued)

		FR	C	H	O	N	S	Ash	Sum	MW
CCL-25-52	PL		82.88	6.71	2.89	1.20	0.79	5.52	99.99	276
	O	63.28	88.86	7.76	1.24	1.61	0.53	--	100	214
	A	10.80	84.33	6.77	5.83	2.23	0.84	--	100	521
	P	15.00	82.84	5.38	7.00	2.46	0.77	1.55	100	2409
	R	10.93	34.54	1.97	5.85	0.87	3.05	53.72	100.00	
	Sum	100.01								
	RCV	99.9								
CCL-25-88	PL		78.73	6.32	2.36	1.12	0.86	10.60	100	279
	O	59.0	89.83	7.61	1.24	0.83	0.49	--	100	215
	A	14.0	87.03	6.29	4.20	1.97	0.51	--	100	394
	P	9.0	82.35	5.20	5.26	4.17	0.56	2.46	100	1210
	R	18.0	18.75	1.13	5.30	0.35	1.88	72.59	100	
	Sum	100.0								
	RCV	99.6								
CCL-26-100	PL		73.42	5.88	2.86	0.96	0.73	16.16	100	302
	O	58.2	89.16	7.65	1.87	0.86	0.47	--	100	204
	A	9.5	85.61	6.71	4.85	2.23	0.59	--	100	309
	P	7.2	83.49	5.54	6.88	2.39	0.85	0.85	100	1527
	R	25.1	19.16	1.24	4.83	0.43	1.63	74.89	102.18	
	Sum	100.0								
	RCV	99.7								
CCL-25-136	PL		74.34	6.24	2.47	0.95	2.59	13.41	100	278
	O	67.6	89.12	7.70	1.76	0.96	0.49	--	100	205
	A	8.6	85.12	6.24	5.65	2.37	0.62	--	100	490
	P	6.6	83.17	5.65		3.28	0.71	--		984
	R	17.20	17.06	1.00	4.19	0.39	12.64	74.70	109.98	
	Sum	100.00								
	RCV	99.6								

APPENDIX C
(continued)

		FR	C	H	O	N	S	Ash	Sum	MW
CCL-25-148	PL		75.09	6.39	2.85	1.05	3.10	11.51	100	283
	O	53.8	88.59	7.8	2.02	1.12	0.47	--	100	213
	A	16.1	86.51	7.1	3.67	2.08	0.64	--	100	305
	P	13.0	81.90	5.84	6.49	4.04	0.77	0.10	100	994
	R	17.1	18.99	1.18	4.78	0.74	15.80	70.91	111.40	
	Sum	100.0								
	RCV	99.0								
CCL-25-184	PL		77.30	6.54	2.53	1.12	1.11	11.40	100	
	O	66.34	88.50	7.60	2.29	1.17	0.44	--	100	208
	A	8.91	86.09	6.35	4.59	2.43	0.54	--	100	454
	P	5.94	82.84	5.34	6.15	2.79	0.59	2.30	100	1239
	R	18.81	15.52	0.99	4.40	0.39	5.89	72.81	100.0	
	Sum	100.0								
	RCV	100.0								
CCL-25-196	PL		69.61	5.74	3.37	0.92	1.85	18.52	100	
	O	57.0	87.87	7.72	2.64	1.32	0.45	--	100	209
	A	10.0	86.01	8.02	3.52	1.81	0.63	--	100	566
	P	8.0	81.02	5.89	5.68	3.55	0.69	3.18	100	1284
	R	25.0	16.99	1.27	5.49	0.34	6.04	76.21	106.34	
	Sum	100								
	RCV	99.8								

APPENDIX D

RUN CCL-28: 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.	Product Drums Rate g/hr.	Condensate Rate g/hr.	Product Gas Rate SLPH
550-850°F Solvent + 30% Kentucky #9 Coal (Pyro)	0- 10	0- 10	Line-Out	825	2000	1832	339	1788	1830	--	442
	10- 11	10- 11	Sample	825	2000	1772	360	--	1714	32.6	452
	11- 21	11- 21	Line-Out	850	2000	1805	348	1715	1740	--	424
	21- 22	21- 22	Sample	850	2000	1863	340	--	1784	45.2	430
550-850°F Solvent + 30% Kentucky #9 Coal (Pyro) + 10% Robena Pyrite	22- 34	22- 34	Line-Out	825	2000	1985	400	1900	1900	--	424
	34- 35	34- 35	Sample	825	2000	1990	390	--	1878	94.0	420
	36- 45	36- 45	Line-Out	850	2000	2008	410	1845	1843	--	410
	45- 46	45- 46	Sample	850	2000	2129	402	--	1856	47.5	393
550-850°F Solvent + 27.3% Elkhorn #3 Coal + 9.1% Robena Pyrite	46- 55	46- 55	Line-Out	850	2000	1887	810	1773	1770	--	815
	55- 56	55- 56	Sample	850	2000	1874	820	--	1750	38.1	803
	56- 70	56- 70	Line-Out	850	2000	1962	780	1802	1811	--	815
	70- 71	70- 71	Sample	850	2000	1973	796	--	1863	42.3	837
450-850°F Solvent + 30% SOJ #4A Washed Coal	71- 81	71- 81	Line-Out	850	2000	1880	344	1839	1823	--	390
	81- 82	81- 82	Sample	850	2000	1852	343	--	1794	32.3	398
	82- 83	82- 83	Line-Out	850	2000	1921	346	--	--	--	382
	83- 84	83- 84	Sample	850	2000	1900	351	--	1605	--	360
450-850°F Solvent + 30% SOJ #4A Seam Coal	84- 93	84- 93	Line-Out	850	2000	1840	349	1800	1747	--	407
	93- 94	93- 94	Sample	850	2000	1818	345	1752	1688	37.9	398
	94- 95	94- 95	Line-Out	850	2000	1827	345	--	--	--	--
	95- 96	95- 96	Sample	850	2000	--	350	--	1674	--	400
450-850°F Solvent + 30% North American #8 Washed Coal	96-107	96-107	Line-Out	850	2000	1819	350	1802	1753	--	423
	107-108	107-108	Sample	850	2000	1814	345	--	1731	31.4	--
	108-109	108-109	Line-Out	850	2000	1837	--	--	--	--	400
	109-110	109-110	Sample	850	2000	--	370	--	1775	--	--
450-850°F Solvent + 30% North American #8 Seam Coal	110-120	110-120	Line-Out	850	2000	1840	360	1774	1783	--	400
	120-121	120-121	Sample	850	2000	1854	354	--	1716	23.9	420
	121-122	121-122	Line-Out	850	2000	--	340	1663	--	--	400
	122-123	122-123	Sample	850	2000	1864	331	--	1716	--	--
450-850°F Solvent + 30% Elkhorn #3 Coal	0- 8	0- 8	Line-Out	850	2000	1853	354	1771	1745	--	433
	8- 9	8- 9	Sample	850	2000	1903	348	--	1751	32.6	--
	9- 12	9- 12	Line-Out	850	2000	1869	349	1792	1766	--	416
	12- 13	12- 13	Sample	850	2000	1895	341	--	--	--	--

APPENDIX E

Solvent Separation Procedure Used at Auburn University

I. Obtaining Sample Weight

1. Weight filter paper, beaker, and three 500 ml flasks.
2. Place filter paper into filter (readings to .001 g are presently used).
3. Transfer reaction mixture from tubing-bomb to beaker. Carefully scrape the inside of the bomb and caps to remove all the sample as is possible practically. Do not include drops on the outside edges which may be contaminated with sealing material.
4. Presently two steel balls are used in the tubing-bombs to aid mixing. Remove the steel mixing balls from the mixture in the beaker after stirring well.
5. Wipe off any sample on the top half of the inside of the beaker.
6. Weigh the beaker and sample to obtain sample weight. (The time between step 3 and 5 should be as short as practical because some of the sample is volatile.) The volatile components and oil are calculated from the sample weight less the other components and thus after weighing some loss of volatiles does not affect the analysis.

II. Extraction Procedures

Pentane Extraction of Oils

1. Pour 40 to 50 ml pentane into the sample and with a spatula stir the mixture well. Wipe as much as possible of the material adhering to the spatula into the bottom of the beaker.

2. Pour the liquid into two 100 ml centrifuge tubes and centrifuge for 3 to 5 minutes at 500 to 700 rpm. Place a lid (rubber stopper) lightly on the centrifuge tubes before centrifuging. Before centrifuging, wash the remaining mixture in the beaker and beaker walls with pentane from a wash bottle. This liquid also is poured into the centrifuge tubes before centrifuging.
3. After centrifuging pour the fluid directly into the pressure filter and catch the fluid in one of the 500 ml flasks.
4. Spread out the mixture remaining in the flask on the bottom of the flask to facilitate the crushing in step 6 below. Any material remaining on tools (spatula, glass rod, etc.) should be carefully protected and included in the separation procedure at the appropriate time determined by the operator.
5. Fill the beaker with liquid nitrogen and immerse a glass stirring rod (1/2" to 1") with a flat end. Allow the mixture to stop boiling violently before proceeding with step 6.
6. Crush the frozen sample to a fine powder under the liquid nitrogen. Five to ten minutes of crushing is required.
7. Allow the liquid N₂ to evaporate to just above the sample. Place a cap on the beaker to minimize splatter loss. The cap may be a funnel cut to allow the sonicator tip to be immersed in the fluid. Material which splatters on the cap, upper part of the beaker, or on the sonifier should be recovered.
8. Place the beaker quickly under the sonifier and turn on the sonifier.
9. Pour enough pentane into the beaker after the sonifier is turned on so that the sonifier tip will be immersed at least 1/2 inch.
10. Sonicate at level 5 on the "output control" for five minutes.

11. Let the mixture settle for approximately 2 minutes after removing from the sonifier.
12. Pour the liquid into two 100 ml centrifuge tubes and centrifuge for 3 to 4 minutes (700 rpm). (Allow the solid material to remain in the beaker.)
13. After centrifuging, pour the fluid into the filter.
14. Repeat steps 9-13 twice more (three sonications in all). On the last step allow the solid material to pour into the centrifuge tubes. Wash the material from the beaker thoroughly with pentane, pouring the entire mixture into the centrifuge tubes.
15. Centrifuge for 3 to 4 minutes and pour the fluid into the filters. See step 19 below for the completion of the use of the pressure filter.

Benzene Extraction of Asphaltenes

16. Pour about 20 ml benzene into each of the centrifuge tubes. Stir with a glass rod (1/4" to 3/8" diameter) and pour into the original beaker. Remove as much of the material from the tubes into the beaker as possible practically. Care should be exercised so that material is not spilled.
17. Sonicate the benzene in the beaker for 3 to 5 minutes at "output control" level 3. Use a benzene wash bottle to wash material remaining on the sonicator into the beaker. Pour all the material, liquid and solid, into the centrifuge tubes using a benzene wash bottle as required.
18. Centrifuge for 4 to 5 minutes.

19. To complete the PENTANE soluble portion collection apply pressure to the filter if any liquid remains in the filter. Wash the insides of the pressure filter with pentane and pressure it through. Repeat. Remove the pentane catch flask and place a clean flask for the collection of asphaltenes. Use a little benzene to wash the filter and filter paper. A few drops will begin to collect in the clean flask.
20. Pour the liquid from the centrifuge in step 18 into the pressure filter. The solid material should remain in the centrifuge tubes.
21. Pour some benzene into the beaker and scrape the material remaining on the sides of the beaker into the benzene. Wash other tools upon which any quantity of sample remains into the benzene in the flask. The tools will include glass rods, spatula, sonifier tip, etc. used above after the extraction procedures were begun.
22. Pour the benzene from the beaker into the centrifuge tubes. Wash any loose material in the beaker into the centrifuge tubes. Stir the material in the centrifuge tubes vigorously with the glass rods used in step 15.
23. Centrifuge.
24. Pour the liquid from step 22 into the pressure filter.
25. Repeat steps 21-23 one more time.

Methylene Chloride (90% by volume) - Methyl Alcohol (10% by Volume)

Extraction of Preasphaltenes

26. Repeat steps 15 through 24, but with the Methylene Chloride-Methyl Alcohol mixture rather than benzene. Step 19 will refer to completing the benzene soluble portion collection rather than the "pentane soluble portion" collection.

27. On the last step wash all of the material from the centrifuge tubes into the pressure filter. It will probably take about one hour under 10 lbs pressure to push the liquid through the filter.

III. Removing Solvents from the Respective Fractions

Removing Pentane on Rotovap

1. The flask may be rotated slowly (on the lowest Rotovap setting). Rotovap bath temperature should be 60°C; a small flow of nitrogen should be directed into the oil flask. No stop cock grease is used.
2. Leave the flask on two minutes after pentane ceases to form on the cooling coils. (Drops may still remain on the coils but will not be increasing in size.) Cooling coils are approximately at 0°C. Place a clean flask on the rotovap to avoid condensing Rotovap bath vapors on the cooling coils.
3. Allow the flask now containing oils only to set at room temperature for one half hour then weigh to obtain weight of oils.

Removing Benzene

1. Rotovap bath temperature 75°C (Up to 90°C is acceptable). A medium nitrogen flow rate is required.
2. Do not evaporate the last 10 to 20 ml of benzene. This is freeze dried as follows:
 - a. Swirl the flask in liquid nitrogen to evenly coat the inside two thirds of the flask.

- b. Attach immediately to a vacuum pump. A trap immersed in liquid nitrogen is necessary to collect the benzene. The trap is positioned between the flask and the pump. The pump should be exhausted to a hood. The freeze drying requires approximately 1 hour.
3. After freeze drying, dry the outside of the flask as necessary, let set at room temperature for 15 minutes and weigh to obtain the weight of asphaltenes. The appearance of the asphaltenes should be a medium to light tan and obviously dry. If not dry, then repeat the freeze drying step.

Removing Methylene Chloride - Methyl Alcohol

1. Rotovap bath temperature 60°C to 90°C.
2. A low nitrogen flow rate is required; too high a flow rate will result in blowing some of the dry preasphaltenes out of the flask.
3. When the preasphaltene is completely dry, remove the flask, dry the outside, allow to set at room temperature for one half hour and weigh to obtain weight of preasphaltene.

IV. Obtaining the Weight of Residue

1. The residue containing the insoluble organic matter (I.O.M.), coal minerals, and any insoluble material added will accumulate on the filter paper. Carefully remove this material along with the filter paper on to a watch glass. Recover any material adhering to the filter parts. Allow the material to air dry (breaking the material apart will help). After drying (one half hour is generally sufficient if the material is broken into small pieces) weigh to obtain the amount of residue.

V. Sample Weights

1. In spite of repeated scraping and washing with various solvents there will be some small amount of material remaining on the beaker, centrifuge tubes, sonicator tip, filter walls, and tools. This is unavoidable, however, reasonable effort should be made to minimize the loss.
2. The weights of the various fractions are calculated from the fraction plus flask weight less the flask weight.
3. Though the oils amount is weighed, the actual oil value used is obtained by subtracting the sum of the asphaltene, preasphaltene, and residue weights from the original sample weight. The assumption is that if the sum of the four fractions is less than the sample weight, that volatile components from the oil were lost. This assumes that the amount of material lost in 1. is small.