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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 June 1—August 31, 1980

By

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Allentown, Pennsylvania

and

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U. S. DEPARTMENT OF ENERGY

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ABSTRACT

Additional data on the pyrite catalysis of Elkhorn #3 coal are presented in this report. In the previous quarter the improved conversion and product distribution were discussed. Blank runs incorporating pyrite in solvent alone showed that the hydrogenation of the solvent improved to the point that hydrogen was not depleted from the solvent whereas when solvent alone was passed through the reactor hydrogen was lost. The final solvent when pyrite was used contained 7.7% hydrogen whereas the feed solvent also contained 7.7% hydrogen. Without pyrite present the hydrogen content dropped to 7.4%. Proton distributions as determined by NMR showed essentially no change for the pyrite treated solvent whereas the no-pyrite treated solvent had a higher concentration of aromatic hydrogen which corresponds to a decrease in donor hydrogen content. The recovered solvent from the Elkhorn #3 liquefaction runs reported previously also showed the recovered solvent from pyrite catalyzed liquefaction contained less aromatic hydrogen with a significant increase in the donatable H_o concentration.

The liquefaction of Elkhorn #3 coal was significantly catalyzed by the presence of pyrite. Coal conversion, oil yield and preasphaltene conversion all increased when pyrite was added. An increase in hydrocarbon gas make accompanied by a higher hydrogen consumption were also observed. The higher activity in the presence of pyrite could be utilized by running the liquefaction step at milder conditions which would mean a lower gas make.

Although we had heard reports that sulfur elimination from the SRC was improved by use of pyrite our data showed only very small changes. Nitrogen removal from the solvent, however, was definitely observed. At 850°F nitrogen in the oil product went from 1.61 to 1.12 on adding pyrite. This increased nitrogen removal was also seen in the added ammonia yields.

Kentucky #9 coal also responded very well to the presence of pyrite. Conversions and oil yields increased while the hydrocarbon yields decreased at both temperatures that were tested, i.e., 825 and 850°F. Hydrogen consumptions also increased. Not only did the hydrogen content of the recovered solvent remain undepleted and the apparent aromaticity decreased but the boiling point of the solvent tended to increase giving a distillation curve 10-15°F higher than when pyrite was not used as solvent.

Increasing hydrogen gas rate from 20 to 40 MSCF/T coal in the presence of pyrite had beneficial effects. The yield of hydrocarbon gases went down with higher yields of oils and asphaltenes. The difference was not remarkably great for Elkhorn #3 but were much greater for Kentucky #9. These data may indicate that these reactions were not hydrogen starved. The biggest difference for Elkhorn #3 seemed to be in the increased amount of oxygen removed as water. With this went a higher hydrogen consumption. The water difference for the Kentucky #9 was quite small with the hydrogen consumption actually being less at the higher flow rate.

In the screening program the results from testing a number of materials are reported. None of the zeolites gave any significant improvement over coal itself.

The iron, molybdenum, nickel, and cobalt rich materials had significant activity, all 85-90% conversion with high oil yields. Among materials specifically reported this period the clays failed to show any significant catalytic effect.

The results of several fundamental evaluations of pyrite materials are reported here. Basic nitrogen compound (quinoline) was poisonous to naphthalene hydrogenation.

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 materials 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. Samples of two Elkhorn #3 coals from Floyd County and Letcher County, Kentucky, were found to contain high concentrations of ash which forced us to look for additional supplies of low ash Elkhorn coal for testing in our CPDU. In addition to Elkhorn coals, Kentucky #9 and numerous Ohio coals that were listed in the Third Quarterly Technical Progress Report were scheduled for testing in the program. Also, we are arranging to acquire a large sample of low ash and low pyrite coal from Illinois to be tested in this program.

The status of the procurement of the above coals is discussed below.

Elkhorn #2. A sample of washed Elkhorn #2 coal from Letcher County, Kentucky, was received. This sample was crushed and sieved to -150 U.S. Mesh and submitted for ultimate and proximate analyses. A complete chemical analysis of the coal is given in Table 1. This coal contained 6.3% ash as opposed to the other two Elkhorn #3 coals (ash content of 14.3 and 33.3%) tested earlier in the CPDU runs. The liquefaction behavior of this coal was tested in the third CPDU run and data will be presented in the next quarterly report.

Ohio Coals. Professor Savage and Professor Kneller of Ohio DOE supplied us with several seam and washed samples of Ohio coals. They also supplied us with several segmented samples of Ohio coals. A complete list of Ohio coals and how they were segmented was discussed in the Third Quarterly Technical Progress Report. Professor Kneller of the University of Toledo completed the maceral analyses of all the samples which are summarized in Tables 2 to 7.

Table 1

Analysis of Washed Elkhorn #2 Coal
Obtained from Letcher County, Kentucky

	<u>Weight %</u>
<u>Proximate Analysis</u>	
Moisture	1.55
Dry Ash	6.29
<u>Ultimate Analysis</u>	
C	77.84
H	5.24
N	1.75
S	1.08
O	7.20
<u>Distribution of Sulfur</u>	
Total Sulfur	1.08
Sulfate Sulfur	0.04
Pyrite Sulfur	0.25
Organic Sulfur	0.79

Table 2

Volume Percent (MMFB) Maceral Content of
Middle Kittanning #6 Coal Samples

	<u>CPDU- 133</u>	<u>CPDU- 126A</u>	<u>CPDU- 126B</u>	<u>CPDU- 126C</u>	<u>CPDU- 126D</u>
Sample Type	Seam Sample	Fraction I	Fraction II	Fraction III	Fraction IV
Vitrinite	91.0	90.8	89.2	91.0	84.2
Resinite	0.9	0.7	0.5	0.8	1.4
Exinite	2.6	2.4	3.4	3.1	2.1
Fusinite	1.7	2.1	2.5	2.0	3.5
Semifusinite	2.1	2.1	2.2	2.6	5.2
Sclerotinite	0.0	0.0	0.0	0.0	0.0
Micrinite	1.0	1.0	0.8	0.2	1.7
Inertodetrinite	0.7	0.9	1.4	0.3	1.4

MMFB - mineral matter free basis

Table 3

Volume Percent (MMFB) Maceral Content of
Pittsburgh #8 (Harrison County) Coal Samples

	CPDU- 137	CPDU- 127A	CPDU- 127B	CPDU- 127C	CPDU- 127D
Sample Type	Seam Sample	Fraction I	Fraction II	Fraction III	Fraction IV
Vitrinite	86.7	87.7	78.2	88.5	85.3
Resinite	3.0	2.4	2.4	2.0	2.8
Exinite	2.5	4.6	5.2	1.5	2.2
Fusinite	1.0	1.0	6.7	3.2	3.1
Semifusinite	4.7	3.4	5.4	3.6	5.9
Sclerotinite	0.6	0.2	0.4	0.4	0.2
Micrinite	1.5	0.7	1.6	0.7	0.5
Inertodetrinite	0.0	0.0	0.1	0.1	0.0

MMFB - mineral matter free basis

Table 4

Volume Percent (MMFB) Maceral Content of
Meigs #9 Coal Samples

	CPDU- 135	CPDU- 128A	CPDU- 128B	CPDU- 128C	CPDU- 128D
Sample Type	Seam Sample	Fraction I	Fraction II	Fraction III	Fraction IV
Vitrinite	81.5	87.8	73.0	86.3	80.9
Resinite	5.8	1.2	3.9	1.4	2.3
Exinite	3.6	2.1	7.0	2.4	4.4
Fusinite	3.6	3.7	6.9	4.9	7.1
Semifusinite	4.3	3.8	7.7	4.0	4.2
Sclerotinite	0.0	0.4	0.7	0.1	0.1
Micrinite	1.1	0.9	0.7	0.8	0.8
Inertodetrinite	0.0	0.1	0.1	0.1	0.2

MMFB - mineral matter free basis

Table 5

**Volume Percent (MMFB) Maceral Content of
Lower Kittanning #5 Coal Samples**

	<u>CPDU- 136</u>	<u>CPDU- 129A</u>	<u>CPDU- 129B</u>	<u>CPDU- 129C</u>
Sample Type	Seam Sample	Fraction I	Fraction II	Fraction III
Vitrinite	89.7	88.3	94.4	93.0
Resinite	0.5	0.2	0.0	0.1
Exinite	2.0	1.6	2.1	1.2
Fusinite	2.4	3.0	0.7	2.2
Semifusinite	3.5	5.1	1.8	1.5
Sclerotinite	0.0	0.0	0.0	0.0
Micrinite	1.3	1.3	0.7	1.3
Inertodetrinite	0.6	0.5	0.3	0.7

MMFB - mineral matter free basis

Table 6

**Volume Percent (MMFB) Maceral Content of
Clarion #4A Coal Samples**

	<u>CPDU- 132</u>	<u>CPDU- 128A</u>	<u>CPDU- 130A</u>	<u>CPDU- 130B</u>	<u>CPDU- 130C</u>
Sample Type	Wash Sample	Seam Sample	Fraction I	Fraction II	Fraction III
Vitrinite	83.8	86.7	83.5	80.5	89.3
Resinite	2.3	1.5	4.4	3.6	2.5
Exinite	5.3	4.3	3.0	3.7	2.3
Fusinite	3.3	3.0	1.6	3.2	2.1
Semifusinite	4.2	3.4	5.7	7.0	2.6
Sclerotinite	0.4	0.2	0.4	0.2	0.0
Micrinite	0.6	0.9	1.4	1.7	1.1
Inertodetrinite	0.1	0.0	0.0	0.0	0.1

MMFB - mineral matter free basis

Table 7

Volume Percent (MMFB) Maceral Content of
Pittsburgh #8 (Belmont County) Coal Samples

Sample Type	CPDU- 131	CPDU- 131A
	Wash Sample	Seam Sample
Vitrinite	87.3	86.9
Resinite	1.9	0.9
Exinite	2.8	2.7
Fusinite	1.1	3.7
Semifusinite	6.1	4.7
Sclerotinite	0.3	0.8
Micrinite	0.5	0.3
Inertodetrinite	0.0	0.0

MMFB - mineral matter free basis

The ash and total sulfur contents of the samples were also determined and are reported in Table 8. The variations of vitrinite, fusinite, semifusinite, total sulfur, ash, etc., in the individual seam fractions offer an opportunity to investigate their effect on coal liquefaction. The coal samples which showed wide variations within the same seam will be tested in CPDU.

The detailed analyses of Ohio coals used in the second CPDU run were received and are reported in Table 9. The Clarion #4A seam sample was obtained from one mine and the washed sample was collected from a coal preparation plant fed by two different mines. The proportion of the coals from these two mines in the washed sample is unknown. These two samples were from the same seam but from two different mines. This could be the reason that the washed sample had higher concentration of ash than the seam sample.

Professor Kneller is performing the detailed chemical analyses of the remaining Ohio coal samples and will be reported when they become available.

Task 1.2 Mineral, 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. The procurement of various minerals and metallic waste samples was by and large completed during this quarter. Large samples (approximately 50 lbs) of a number of materials which showed moderate catalytic activity in coal liquefaction in a tubing-bomb at Auburn University, for example, specularite (Fe_2O_3), red mud and flue dust, were ordered and received. These materials were tested in the CPDU for their catalytic activity.

Table 8

High Temperature Ash and Total Sulfur Contents of
Selected Samples of Ohio Coals

<u>Sample No.</u>	<u>Sample Type</u>	<u>Seam</u>	<u>% HTA</u>	<u>% Total Sulfur</u>
CPDU-133	Seam Sample	Middle Kittaning #6	11.3	5.0
CPDU-126A	Fraction I	Middle Kittaning #6	3.8	2.6
CPDU-126B	Fraction II	Middle Kittaning #6	4.3	4.2
CPDU-126C	Fraction III	Middle Kittaning #6	3.5	2.7
CPDU-126D	Fraction IV	Middle Kittaning #6	31.6	11.4
CPDU-137	Seam Sample	Pittsburgh #8	18.3	3.7
CPDU-127A	Fraction I	(Harrison County)	19.6	8.8
CPDU-127B	Fraction II	Same	15.5	2.6
CPDU-127C	Fraction III	Same	7.6	5.1
CPDU-127D	Fraction IV	Same	13.6	4.3
CPDU-135	Seam Sample	Meigs #9	14.8	7.1
CPDU-128A	Fraction I	Meigs #9	7.8	3.4
CPDU-128B	Fraction II	Meigs #9	29.5	2.7
CPDU-128C	Fraction III	Meigs #9	6.9	2.7
CPDU-128D	Fraction IV	Meigs #9	10.7	3.7
CPDU-136	Seam Sample	Lower Kittaning #5	11.3	4.8
CPDU-129A	Fraction I	Lower Kittaning #5	4.6	3.1
CPDU-129B	Fraction II	Lower Kittaning #5	3.5	3.8
CPDU-129C	Fraction III	Lower Kittaning #5	13.2	6.2
CPDU-132	Washed Sample	Clarion #4A	13.6	3.3
CPDU-134	Seam Sample	Clarion #4A	25.6	3.7
CPDU-130A	Fraction I	Clarion #4A	27.3	3.1
CPDU-130B	Fraction II	Clarion #4A	16.9	3.8
CPDU-130C	Fraction III	Clarion #4A	10.9	4.9
CPDU-131	Washed Sample	Pittsburgh #8	16.1	4.3
CPDU-131A	Seam Sample	(Belmont County)	10.9	4.7

Table 9

Analysis of Ohio Coals

	Weight %			
	Clarion #4A		Pittsburgh #8 (Belmont County)	
	CPDU-132 Washed Sample	CPDU-134 Seam Sample	CPDU-131 Washed Sample	CPDU-131A Seam Sample
<u>Proximate Analysis</u>				
Moisture	3.98	2.79	1.69	1.44
Ash	15.09	25.00	14.47	12.65
Volatile Matter	38.38	35.21	38.70	39.94
Fixed Carbon	42.55	37.00	45.14	45.97
<u>Ultimate Analysis</u>				
C	62.31	56.60	66.71	68.31
H	4.95	4.50	4.95	4.97
O	11.33	10.10	8.59	8.15
N	1.18	1.02	1.18	1.18
S	3.71	3.74	4.56	5.06
<u>Sulfur Distribution</u>				
Sulfate Sulfur	0.28	0.15	0.17	0.06
Pyrite Sulfur	1.49	1.82	2.00	2.32
Organic Sulfur	1.94	1.77	2.39	2.68

Three five gallon drums of pyrite obtained from U.S. Steel's Robena Mine were dried at 100°C and ground to -325 U.S. Mesh in nitrogen. A small sample of pyrite separated from Kentucky #9 coal, collected by Dr. David Hoover of Air Products with the help of Messrs. Don Pollock and Alan Bland of the Institute of Mining and Minerals Research of the University of Kentucky, was ground to -325 U.S. Mesh. This sample is presently being analyzed for its pyrite content. Arrangements are being made to collect a large sample of pyrite from the Kentucky #9 coal field as well as from the Ohio and Alabama coal fields. These samples of pyrite will be tested for their respective catalytic activity in coal liquefaction.

Task 1.3 Process Solvent

The product slurry from the first CPDU run CCL-25 was distilled earlier. The distillation cut points were mistakenly set at 450 and 850°F instead of the intended 550 and 850°F temperature. This recovered process solvent (450 to 850°F) was exclusively used to study the dissolution behavior of some of the Ohio coal samples in the second standardization run CCL-28. At this point a decision was made to continue using 450 to 850°F process solvent for the dissolution study of the remaining Ohio coal samples. The above decision was implemented by setting cut points at 450 and 850°F temperature for distilling the product slurry from the second CPDU run CCL-28. The recovered process solvent was stored in drums to be used exclusively for Ohio coals in future.

Ten drums of process solvent (heavy distillate) were received from the Fort Lewis SRC-II pilot plant. A sample of this solvent was submitted for detailed chemical and solvent separation analyses. The analyses are summarized in Table 10. The GC simulated distillation of the process solvent, which is presented in Table 11, showed that 6% of the material boiled below 550°F and 3% above 850°F. This process solvent was used in the third CPDU run.

Table 10

Analysis of the Process Solvent (Heavy Distillate)

<u>Fraction</u>	<u>Weight %</u>	<u>Element</u>	<u>Weight %</u>
Oil	93.8	Carbon	89.44
Asphaltene	5.0	Hydrogen	7.21
Preasphaltene	0.4	Oxygen	1.70
Residue	0.8	Nitrogen	1.10
		Sulfur	0.55

Table 11

GC Simulated Distillation of Process Solvent

<u>Weight % Off</u>	<u>Temperature °F</u>
I.B.P.	519
5	548
6	552
10	569
20	590
30	607
40	627
50	648
60	673
70	699
80	732
90	788
95	835
97	845
99	898
F.B.P.	911

The product slurry from the third CPDU run CCL-31 will be distilled to recover the 550 to 850°F process solvent to be used in future runs.

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, the starting materials for this program, under coal liquefaction conditions. The thermal stability is being evaluated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) in an inert atmosphere in the presence of helium or nitrogen. The reactivity of the materials with hydrogen will be evaluated in the TGA at atmospheric pressure and in the pressurized thermal gravimetric reactor (PTGR) at higher pressures.

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

Sphalerite (ZnS): The TGA of sphalerite under flowing hydrogen and nitrogen gases is shown in Figure 1. The material was insensitive to thermal treatment (nitrogen) as well as chemical reaction to hydrogen at temperatures up to 600°C. The material when treated with hydrogen at 450°C at 1000 psig in the PTGR no reaction was noted to be unreactive (see Table 12).

Red Oxide and Speculite: The reduction of red oxide and speculite in the PTGR was reported in the Third Quarterly Technical Progress Report. Both materials at one atmosphere were found to be thermally stable in nitrogen and were reduced completely to elemental iron in the presence of hydrogen at approximately 550°C as shown in Figures 2 and 3. At the coal liquefaction reaction temperature of 450°C at one atmosphere both red oxide and speculite were partially reduced. Similar results were noted when reducing red oxide and speculite in the PTGR.

FIGURE 1
TGA OF SPHALERITE (ZnS) IN THE PRESENCE OF
HYDROGEN AND NITROGEN GASES

Table 12

Reduction of Minerals and Metallic Wastes in the PTGR

Reaction Time = 10 Minutes, Temperature = 450°C
Pressure = 1,000 psig H₂

Sample	Initial Weight, g	Final Weight, g	Weight Loss		N ₂	Gas Analyses, %			Total Recovered Product g	% Recovery of Lost Weight
			g	%		CO ₂	H ₂ S	H ₂ O		
Albanion Chrome										
Ore Concentrate	3.00	2.98	0.02	0.67	-	-	-	-	-	-
Molybdic Oxide	3.00	2.73	0.27	9.00	-	-	0.081	0.054	0.135	50.0
Phosphate Slime	1.00	0.89	0.11	11.00	-	-	-	0.037	0.037	33.6
Sphalerite (ZnS)	3.00	2.98	0.02	0.67	-	-	-	-	-	-
Dolomite	1.00	1.00	0.00	0.00	-	-	-	-	-	-
Oil Shale	1.00	0.95	0.05	5.00	-	-	-	0.055	0.055	110.0
Red Mud	1.00	0.87	0.13	13.00	-	-	-	0.053	0.053	40.7

FIGURE 2
TGA OF RED OXIDE IN THE PRESENCE OF HYDROGEN

FIGURE 3
TGA OF SPECULITE (Fe_2O_3) IN THE PRESENCE OF HYDROGEN
AND NITROGEN GASES

Red Mud. The TGA of red mud under nitrogen (Figure 4) showed a weight loss of 12% at 700°C. This was due to loss of volatile material present in the sample. The weight loss of 27% at 650°C in the presence of hydrogen gas was due to reduction of various oxides that were present in the sample to their respective elemental form. A weight loss of 13% was noted at 450°C in the PTGR (see Table 12) which matched a corresponding weight loss of 14.5% at 450°C in the TGA.

This weight loss under process conditions can have a significant affect on the reaction conditions under continuous flow operation. Since most of the material is water, if this moisture passes through the reaction system, it can severely reduce the hydrogen partial pressure in the system. Although the initial batch tests will not likely be run in such a way to see this effect because of time limitations, subsequent continuous processing runs will be especially sensitive to this effect.

Other Materials. Albanian chrome ore concentrate discussed in the First Quarterly Technical Progress Report and dolomite were insensitive to hydrogen treatment at 450°C in the PTGR (see Table 12). So, no weight correction would be required when testing these material for their catalytic activity in coal liquefaction. Molybdic oxide and phosphate slime lost 9 and 11% weight, respectively, which was mainly due to reduction of metal oxides present in the samples. Oil shale gave 5% weight reduction mainly due to loss of volatiles.

Robena Pyrite. Robena pyrite (-200 mesh) reduced in hydrogen in the PTGR at 450°C and different pressures were discussed in the First Quarterly Technical Progress Report. The reduced samples were analyzed by x-ray diffraction to determine the nature of phases present. The result of XRD analysis, summarized in Table 13, identified the major phase in all the samples as troilite.

FIGURE 4
TGA OF RED MUD IN THE PRESENCE OF HYDROGEN
AND NITROGEN GASES

Table 13

Effect of Pressure on Reduction of
-200 Mesh Robena Pyrite in the PTGR

Reaction Time = 10 Minutes

Temperature = 450°C

Rapid Heating

<u>Pressure, psig</u>	<u>Weight Loss, Wt. %</u>	<u>XRD Analysis</u>
500	17.0	FeS (Troilite) major phase. No Fe detected. Extra unidentified lines at 3.49, 3.33 and 1.95 Å. Possible presence of pyrrhotite.
1,000	17.33	Same as above.
1,500	16.67	FeS (Troilite) major phase. No Fe detected. Extra unidentified lines at 3.50, 3.35 and 1.96 Å. Possible presence of pyrrhotite.

Task 3.0 Standardization Runs and Base Case Determination

Progress. The product distribution in the case of solvent hydrogenation and liquefaction of Elkhorn #3 coals in the presence and absence of Robena pyrite was discussed in the third quarterly progress report. Additional information concerning the above experiments was received and discussed below.

Solvent Hydrogenation. The hydrogenation of the process solvent was discussed earlier in the presence and absence of pyrite to assess the catalytic activity of Robena pyrite. It was shown earlier that pyrite catalyzed the solvent hydrogenation reaction. The hydrogen content of the oil fraction, shown in Table 14, remained constant in the presence of pyrite whereas it decreased in its absence. The sulfur content of the oil fraction decreased slightly in the presence of pyrite. The oxygen content of the oil fractions remained nearly unchanged. A slight decrease in number average molecular weight was observed on hydrogen treatment both in the presence and absence of pyrite. The molecular weight of the oil fraction obtained in the presence and absence of pyrite was similar (within the range of experimental error).

The oil fractions of the original solvent and hydrogenated solvents were analyzed by proton NMR to determine the distribution of protons as aromatic protons (H_{AR}), protons at alpha position to the aromatic ring (H_a) and protons at beta and other positions to the aromatic ring (H_o). The aromatic protons (H_{AR}) as determined by proton NMR included aromatic protons as well as phenolic protons. The donatable hydrogen in solvents is known to be mostly naphthenic type protons. However, naphthenic protons are not separable from other aliphatic protons in H_a and H_o via NMR data.

Table 14

Distribution of Elements in the Oil Fraction
of the Solvent Hydrogenation Experiments

Sample No.		25-14	25-28
<u>Feed Composition</u>	<u>Original Solvent</u>	<u>100% Solvent</u>	<u>90% Solvent + 10% Robena Pyrite</u>
Temp., °F		850	850
Pressure, psig		2,000	2,000
Hydrogen Treat Rate, wt.% Solvent		2.21	2.03
Reaction Time, Min.		61	60
Elemental Composition, wt.%			
Carbon	89.57	89.64	89.25
Hydrogen	7.72	7.40	7.74
Oxygen	1.32	1.30	1.39
Nitrogen	0.88*	1.17	1.19
Sulfur	0.51	0.50	0.44
Number Average Molecular Weight	220	198	205

* Possible error in nitrogen analysis

Proton distribution in the oil fraction of original solvent and hydrotreated solvents are computed and shown in Table 15. The distribution of protons in the original solvent and the solvent hydrotreated in the presence of pyrite was found to be identical. This suggested that the hydrogen donor capability of these two solvents would be similar. The concentration of H_a and H_o decreased and that of H_{AR} increased in the solvent hydrotreated in the absence of pyrite. This would result in a decrease in hydrogen donor capability of the generated solvent. Finally, it can be concluded that the addition of pyrite helped in solvent hydrogenation and maintained the hydrogen content of the solvent. Likewise, a tentative conclusion drawn from the proton NMR data is that solvent quality of the generated solvent is maintained in the presence of pyrite but is diminished in its absence.

Liquefaction of Floyd County Elkhorn #3 Coal. The results from the liquefaction of Floyd County Elkhorn #3 coal (14.31% ash content) studied at two different temperatures in the presence and absence of pyrite were discussed in the Third Quarterly Technical Progress Report. The product distribution and the concentration of elements in the various fractions are summarized in Tables 16 and 17. It was discussed earlier that the addition of pyrite to the coal liquefaction reaction mixture increased the conversion of coal, production of gases and benzene solubles and decreased the production of preasphaltenes. The first-order rate constant for the conversion of preasphaltene to benzene solubles is also presented in Table 16 (see Appendix C for calculation procedure). The rate constant of conversion of preasphaltene increased with increasing the reaction temperature and also with the addition of pyrite. The increase in rate constant was more pronounced with the increase in reaction temperature than with the addition of pyrite. The yield of ammonia, though too small to show in Table 16, was unchanged on increasing temperature from 800 to 850°F, however, ammonia yield increased upon addition of pyrite. The increased production of ammonia was due to improved denitrogenation in the presence of pyrite. In order to substantiate the above fact the nitrogen content of the various fractions were compared (see Table 17). The nitrogen

Table 15

**Distribution of Protons in the Oil Fraction of
the Solvent Hydrogenation Experiments**

Sample No.	25-14		25-28			
<u>Feed Composition</u>	<u>Original Solvent</u>	<u>100% Solvent</u>	<u>90% Solvent + 10% Robena Pyrite</u>			
Total Hydrogen, wt. %	7.72	7.40	7.74			
Distribution of Protons, %						
	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>
H _{AR}	3.24	42.0	3.47	46.9	3.22	41.6
H _a	2.26	29.3	1.92	26.0	2.24	28.9
H _o	2.22	28.7	2.01	27.1	2.28	29.5

H_{AR} - aromatic protons
 H_a - alpha protons
 H_o - beta and other protons

Table 16

Floyd County Elkhorn #3 Coal Liquefaction
Product Distribution

Sample No.	25-40	25-52	25-136	25-148
<u>Feed Composition</u>	<u>70% Solvent + 30% Coal</u>		<u>60% Solvent + 30% Coal + 10% Robena Pyrite</u>	
Temp., °F	850	800	850	800
Pressure, psig	2,000	2,000	2,000	2,000
Product Distribution, wt.% MAF Coal				
HC	4.2	2.4	5.3	2.0
CO, CO ₂	1.0	0.8	1.2	0.9
H ₂ S	1.3	0.9	2.8	0.9
NH ₃	0.0	0.0	0.2	0.0
Benzene Solubles	42.1	14.4	52.3	30.5
Preasphaltene	30.1	58.0	24.3	49.3
I.O.M.	18.1	20.6	10.4	13.7
Water	3.2	2.9	3.5	2.7
Conversion, %	81.9	79.4	89.6	86.3
SRC Sulfur, %	0.61	0.79	0.66	0.70
First-Order Rate Constant, hr ⁻¹				
k _p	2.14	0.39	3.05	0.96

Table 17

Elemental Distribution in the Various Fractions of
Liquefaction Product of Floyd County Coal

Sample No.	25-40	25-52	25-136	25-148
Pyrite	No	No	Yes	Yes
Temp., °F	850	800	850	800
Oil Fraction, wt.%				
C	89.05	88.86	89.12	88.59
H	7.49	7.76	7.70	7.80
O	1.79	1.24	1.76	2.02
N	1.33	1.61	0.96	1.12
S	0.34	0.53	0.49	0.47
$\bar{n}$ MW	-	214	205	213
Asphaltene Fraction, wt.%				
C	86.10	84.33	85.12	86.51
H	6.48	6.77	6.24	7.1
O	4.53	5.83	5.65	3.67
N	2.24	2.23	2.37	2.08
S	0.66	0.84	0.62	0.64
$\bar{n}$ MW	404	521	490	305
Preasphaltene Fraction, wt.%				
C	84.06	82.84	83.17	81.90
H	5.50	5.38	5.65	5.84
O	5.44	7.00	-	6.49
N	3.33	2.46	3.28	-
S	0.58	0.77	0.71	0.77
$\bar{n}$ MW	1,205	2,409	984	994

content of the oil fraction was found to decrease significantly from 1.33 to 0.96% at 850°F and from 1.61 to 1.12% at 800°F. No significant variation in the nitrogen content of asphaltenes and preasphaltenes was noted.

The oil fractions obtained from coal liquefaction runs in the presence and absence of pyrite at 800°F were further analyzed by near infrared spectroscopy (NIR) to give more information about the denitrogenation (see Table 18). The concentration of quinoline type compounds (N) decreased dramatically and that of aniline type compounds (NH_2) increased slightly. A significant increase in the concentration of decahydro- and 1,2,3,4-tetrahydroquinoline types of compounds (NH) were observed, whereas the absolute concentration remained constant. The above changes and the increase in ammonia production with the addition of pyrite are consistent with the quinoline hydrodenitrogenation mechanism shown in Figure 5. Quinoline forms an equilibrium mixture with 1,2,3,4-tetrahydroquinoline very rapidly which is consistent with the increase in the concentration of the NH group as determined by NIR and decrease in the concentration of quinoline type compounds (N). 1,2,3,4-Tetrahydroquinoline further hydrogenates to decahydroquinoline and ortho propylaniline. The formation of decahydroquinoline, which would be minor based on the relative rate constants, does not change the concentration of NH type compounds but the formation of ortho propylaniline causes a decrease in the concentration of NH type compounds and increases the concentration of NH_2 type compounds. The rates of formation and decomposition of ortho propylaniline, shown in Figure 5, are very similar causing much of the 1,2,3,4-tetrahydroquinoline to end up as nitrogen free hydrocarbons and ammonia gas. Similarly quinoline hydrogenates to 5,6,7,8-tetrahydroquinoline and decahydroquinoline and finally to nitrogen free hydrocarbons and ammonia gas. In summary, the N type compounds diminish while NH and NH_2 compound concentrations will be dependent on how far along the reaction path denitrogenation has progressed. The data in pyrite shown in Table 18 indicate that most of the N type nitrogen must end up in the ammonia form.

Table 18

**Distribution of Nitrogen Compounds in the Oil Fraction of
Coal Liquefaction Product in the Presence and Absence of Robena Pyrite**

Sample No.	25-52	25-148
Pyrite	No	Yes
Temp., °F	800	800

Distribution of Nitrogen in the Sample, wt. % Absolute

Total Nitrogen	1.61	1.12
NH	0.31	0.30
NH ₂	0.16	0.13

Functional Group Distribution, wt. % Relative

Nitrogen as N	70.8	61.6
Nitrogen as NH	19.7	26.8
Nitrogen as NH ₂	9.9	11.6

FIGURE 5
REACTION NETWORK FOR HYDRODENITROGENATION OF QUINOLINE.
REACTION CONDITIONS: 342°C, 136 ATM, PRESULFIDED Ni-Mo/
Al₂O₃ CATALYST, 0.5 WT. % CATALYST IN CARRIER OIL, 0.05 WT. % CS₂ IN
CARRIER OIL; THE NUMBERS ON THE ARROWS ARE PSEUDO-FIRST-ORDER RATE
CONSTANTS IN GRAMS OF OIL PER GRAM OF CATALYST PER MINUTE.

* S. S. SHIH, J. R. KATZER, H. KWART, AND A. B. STILES, AM.
 CHEM. SOC., DIV. PET. CHEM., PREPRINTS, 22(3) 919 (1977).

The oxygen content of the various fractions were also compared for the products obtained in the presence and absence of pyrite. The oxygen contents of oil, asphaltene and preasphaltene showed no definite trend. The oxygen contents of oil fraction increased and that of asphaltenes and preasphaltenes decreased in the presence of pyrite over no additive run at 800°F whereas totally opposite results were observed at 850°F. Oil fractions obtained from coal liquefaction reactions at 800°F in the presence and absence of pyrite were analyzed by NIR for the distribution of oxygen as ether and phenol type of compounds and the data are shown in Table 19. No change in the absolute concentration of hydroxyl functional groups was noted but a significant decrease in percent oxygen present as hydroxyl groups was observed. The concentration of oxygen as ether increased significantly with the addition of pyrite.

The oil fractions generated from the liquefaction of Floyd county Elkhorn #3 coal in the presence and absence of Robena pyrite were analyzed by NMR to determine the distribution of protons (see Table 20). The concentration of aromatic protons decreased and that of beta and other protons increased significantly with the addition of pyrite at 800 and 850°F. The concentration of alpha protons increased at 850°F and decreased at 800°F in the presence of pyrite compared to no additive run. The above data suggest that the addition of pyrite either hydrogenates the aromatic compounds or somehow promotes the production of side chains. An attempt was made at this point to identify and differentiate the chemical structure of the solvent generated in the presence and absence of Robena pyrite in coal liquefaction mixture at 800°F using Brown-Ladner structural parameters* modified by H. L. Retcofsky et al.

Brown-Ladner Calculations. The NMR, NIR, and elemental analyses of the oils were used in the Brown-Ladner equations to calculate average structural parameters for the oil molecules. The structural parameters defined by the modified Brown-Ladner equations are:

*J. K. Brown and W. R. Ladner, Fuel 39, 87 (1967).

*H. L. Retcofsky, F. K. Schweighardt, and M. Hovgh, Anal. Chem., 49, 585 (1977).

Table 19

Distribution of Oxygen Compounds in the Oil Fraction of
Coal Liquefaction Product in the Presence and Absence of Robena Pyrite

Sample No.	25-52	25-148
Pyrite	No	Yes
Temp., °F	800	800

Distribution of Oxygen in the Sample, wt. % Absolute

Total Oxygen	1.24	2.02
OH	0.64	0.66

Functional Group Distribution, wt. % Relative

O as O (ether)	48.4	67.3
O as OH (hydroxyl)	51.6	32.7

Table 20

**Distribution of Protons in the Oil Fraction of the
Coal Liquefaction Product in the Presence and Absence of Robena Pyrite**

Sample	<u>25-40</u>		<u>25-52</u>		<u>25-136</u>		<u>25-148</u>			
	Original		70% Solvent + 30%		60% Solvent					
<u>Feed Composition</u>	<u>Solvent</u>		<u>Elkhorn #3 Coal</u>		+ 30% Elkhorn #3 Coal		+ 10% Robena Pyrite			
Temp., °F		850		800		850		800		
Pressure, psig		2,000		2,000		2,000		2,000		
Total Hydrogen, wt. %	7.72	7.49		7.76		7.70		7.80		
Distribution of Protons, %										
	<u>Abs.</u>	<u>Rel.</u>	<u>Abs.</u>	<u>Rel.</u>	<u>Abs.</u>	<u>Rel.</u>	<u>Abs.</u>	<u>Rel.</u>	<u>Abs.</u>	<u>Rel.</u>
H _{AR}	3.24	42.0	3.15	42.1	3.20	41.3	3.10	40.3	3.00	38.5
H _a	2.26	29.3	2.11	28.2	2.32	29.9	2.18	28.3	2.18	27.9
H _o	2.22	28.7	2.23	29.7	2.24	28.8	2.42	31.4	2.62	33.6

H_{AR} - Aromatic protons

H_a - Alpha protons

H_o - Beta and other protons

Abs. - Absolute

Rel. - Relative

$$f_a = \frac{\frac{C}{H} - \frac{H_a^*}{X} - \frac{H_o^*}{Y}}{\frac{C}{H}} \quad (1)$$

$$\sigma = \frac{\frac{H_a^*}{X} + H_{AR}^* + \frac{H_{OH}}{H}}{\frac{H_a^*}{X} + H_{AR}^* + \frac{H_{OH}}{H}} \quad (2)$$

$$\frac{H_{AR}}{C_{AR}} = \frac{\frac{H_a^*}{X} + H_{AR}^* + \frac{H_{OH}}{H}}{\frac{C}{H} - \frac{H_a^*}{X} - \frac{H_o^*}{Y}} \quad (3)$$

where H_a^* = fractional alpha protons

H_o^* = fractional beta and higher protons

H_{AR} = fractional aromatic protons

$X = \frac{H_a}{C_a}$ atomic ratio

$Y = \frac{H_o}{C_o}$ atomic ratio

The parameter Y represents the average number of H_o hydrogen atoms on the carbon atoms that are two or more carbons away from the aromatic ring. A fixed value of 2.0 was chosen for Y in the calculation. The parameter X, the average number of hydrogen atoms on carbons alpha to an aromatic ring, was found by trial and error using equation (1) and the additional equation (4).

$$X_{BEST} = \frac{H_a^* + H_o^*}{\frac{C}{H} - \frac{C}{H} f_a} \quad (4)$$

The calculated X_{BEST} values were all in the range 2.0 ± 0.2 . The simplified equations described above assume that bridge-head hydrogens are an insignificant fraction of the total hydrogen and that all of the oxygens are attached directly to the ring, either as phenols or as cyclic ethers.

The f_a , carbon aromaticity, is defined as the ratio of aromatic carbon atoms to total carbon atoms. Since carbon atom data is not available, f_a is indirectly derived from proton data and elemental analyses using equation (1). $H_{\text{AR}}/C_{\text{AR}}$ is the ratio of hydrogen atoms at the periphery of the aromatic ring structure to the aromatic carbon atoms. This number is a useful indicator of the degree of condensation of the compounds; for example, $H_{\text{AR}}/C_{\text{AR}}$ for benzene (one ring aromatic compound), naphthalene (two ring condensed aromatic compound) and phenanthrene (three ring condensed aromatic compound)

$$\text{are } \frac{6 \text{ aromatic protons}}{6 \text{ aromatic carbons}} = 1, \frac{8 \text{ aromatic protons}}{10 \text{ aromatic carbons}} = 0.8$$

$$\text{and } \frac{10 \text{ aromatic protons}}{14 \text{ aromatic carbons}} = 0.71, \text{ respectively. Therefore, } H_{\text{AR}}/C_{\text{AR}}$$

decreases as the number of condensed aromatic rings in the compound increases. Sigma (σ) is defined as the ratio of substituents on the aromatic ring to the total available sites for the ring substitution. This provides a rough idea of the degree of aromatic ring substitutions by alkyl, naphthenic and/or phenolic, etc. Sigma (σ) for xylenes, methylnaphthalene and phenol are $2/6 = 0.33$, $1/10 = 0.1$, and $1/6 = 0.17$, respectively.

Combining the above parameters with the molecular weight data the size of aromatic ring system can be calculated assuming that the aromatic rings are ketacondensed:

$$R_a = \frac{C_{\text{AR}} - H_{\text{AR}}}{2} \cdot \frac{1}{\text{MW}} + 1 \quad (5)$$

where R_a = number of aromatic condensed ring
 C_{AR} = aromatic carbon atoms per molecule
 H_{AR} = aromatic protons atoms per molecule

The calculated values of the structural parameters for the oil fractions are tabulated in Table 21. The calculated value of f_a , carbon aromaticity, was found to decrease from 0.697 to 0.674 with the addition of pyrite to the reaction mixture. This suggest that pyrite is definitely helping to hydrogenate the aromatic ring compounds. Similarly, the degree of condensation H_{AR}/C_{AR} was found to decrease with pyrite addition; it decreased from 0.838 to 0.825. Again, the small decrease in the value of H_{AR}/C_{AR} could be due to experimental error. In order to verify whether there is a definite decrease in ring size, the value of R_a was calculated and presented in the Table 21. The calculated value of R_a showed no difference in the average ring size in the oil fractions obtained in the presence and absence of Robena pyrite. The generated oil fractions appear to contain about three ring condensed aromatic clusters on the average. The value of σ was found to increase with the addition of pyrite indicating the increase in the degree of substitution by alkyl, naphthenic and/or phenolic, etc. The increase in the value of H_o (Table 20) suggests the substitutions are mainly due to alkyl groups. Comparing the values for the starting solvent (original solvent) and solvent generated after reaction (Table 21) it can be seen that the aromaticity, H_{AR}/C_{AR} , and average ring size decreases and degree of substitution (σ) increases with the reaction in the presence and absence of pyrite.

Second Standardization Run

The second standarization run (CCL-28) carried out during the month of April was designed to study the liquefaction behavior of Kentucky #9 coal at two different temperatures in the presence and absence of Robena pyrite. The liquefaction behavior of run-of-mine and washed Ohio coals was also studied. The run lasted for 150 hours during which 11 different samples were taken and submitted for detailed

Table 21

Brown-Ladner Structural Parameters for the Oil Fractions

Sample		<u>25-52</u>	<u>25-148</u>
		70% Solvent + 30% Elkhorn	60% Solvent + 30% Elkhorn #3 Coal + 10% Robena Pyrite
Feed Composition	<u>Original Solvent</u>	<u>#3. Coal</u>	<u>Robena Pyrite</u>
Temp., °F	-	800	800
Pressure, psig	-	2,000	2,000
f_a	0.702	0.697	0.674
σ	0.271	0.287	0.294
H_{AR}/C_{AR}	0.834	0.838	0.825
R_a	3.23	3.12	3.13

analyses. The complete operating data for this run were reported in the Third Quarterly Technical Progress Report. A summary of the sample numbers and process conditions is given in Table 22. Complete analytical and work-up data for some of the samples of run CCL-28 are presented in Appendix A.

Liquefaction of Kentucky #9 (Pyro) Coal. The conversion of Kentucky #9 (Pyro) coal, studied at two different temperatures (see Table 23) was found to decrease slightly with an increase in temperature from 825 to 850°F. Hydrocarbon gases, H_2S and water production were found to increase with increasing reaction temperature from 825 to 850°F; hydrocarbon gas, H_2S and water production increased from 3.2 to 5.0%, 1.4 to 1.7% and from 4.0 to 6.5%, respectively. Significant differences in the production of oil, asphaltene and preasphaltene were noted with an increase in temperature. At 825°F the major portion of coal ended up in the asphaltene and preasphaltene fractions as shown in Table 23. An oil production of approximately 8% was noted at 825°F. Increasing the reaction temperature from 825 to 850°F increased the conversion of preasphaltenes to asphaltenes, oils and gases. The oil fraction increased two fold from 8 to 15%. A slight increase in asphaltene formation from 26 to 30% was noted, but a significant decrease in preasphaltene formation from 47 to 28% was observed. Also, as temperature increased the hydrogen consumption increased, as calculated by elemental hydrogen balance, from 1.34 to 1.51%. The increase in hydrogen consumption was mainly due to increased hydrocarbon gases, oil, and water formation; 0.02, 0.14 and 0.02 wt.% hydrogen based on maf coal were due to increased production of gases, oils and water, respectively.

Data on the concentration of the elements in the various fractions summarized in Table 24 show that the oil fraction lost a significant amount of hydrogen both at 825 and 850°F compared to the hydrogen content of the original solvent. Insignificant differences in the hydrogen contents of asphaltene and preasphaltene fractions were noted at the two temperatures. The number average molecular weight

Table 22

Summary of Process Conditions
For Run Number CCL-28

<u>Sample No.</u>	<u>Coal</u>	<u>Temp., °F</u>	<u>Pressure, psig</u>	<u>Reaction Time, Minutes</u>	<u>Solvent/Coal/Pyrite By Weight</u>	<u>Hydrogen Feed Rate, MSCF/T</u>
28-11	Kentucky #9	825	2,000	37	70/30/0	19.78
28-22	Kentucky #9	850	2,000	37	70/30/0	20.61
28-35	Kentucky #9	825	2,000	35	60/30/10	21.54
28-46	Kentucky #9	850	2,000	35	60/30/10	21.83
28-56	Kentucky #9	850	2,000	37	60/30/10	45.89
28-71	Elkhorn #3	850	2,000	35	63.6/27.3/9.1	47.20
28-84*	Ohio	850	2,000	36	70/30/0	19.60
28-96*	Ohio	850	2,000	37	70/30/0	20.32
28-110*	Ohio	850	2,000	37	70/30/0	20.82
28-123*	Ohio	850	2,000	37	70/30/0	19.97

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

*450-850°F cut of product from first standardization run

Table 23

Liquefaction Behavior Of Kentucky #9 Coal

Sample No.	28-11	28-22
Feed	70% Solvent/30% Coal	
Temp., °F	825	850
Pressure, psig	2,000	2,000
Hydrogen Treat Rate MSCF/T	19.78	20.61
Residence Time, Min.	37	37
Product Distribution, Wt.% MAF Coal		
HC	3.2	5.0
CO, CO ₂	0.5	0.6
H ₂ S	1.4	1.7
NH ₃	0.0	0.0
Oil	7.9	15.3
Asphaltene	26.6	30.0
Preasphaltene	47.0	28.1
Insoluble Organic Matter (I.O.M.)	9.4	12.8
Water	4.0	6.5
Conversion, % MAF	90.6	87.2
Hydrogen Consumption, Wt.% MAF		
Total	1.34	1.51
Gas	0.69	0.47
Solvent	0.65	1.04

Table 24

Elemental Distribution In The Various Fractions Of
Liquefaction Product Of Kentucky #9 Coal

Sample No.	Original Solvent	28-11	28-22
Temp., °F.	-	825	850
Oil Fraction, Wt.%			
C	89.57	89.52	89.53
H	7.72	7.46	7.30
O	1.32	1.54	1.65
N	0.88	0.92	0.96
S	0.51	0.56	0.56
$\bar{n}$ MW	220	290	204
Asphaltene Fraction, Wt.%			
C	-	85.83	86.19
H	-	6.42	6.41
O	-	4.30	4.35
N	-	2.49	2.20
S	-	0.95	0.86
$\bar{n}$ MW	-	341	342
Preasphaltene Fraction, Wt.%			
C	-	83.74	83.94
H	-	5.46	5.39
O	-	5.99	6.03
N	-	2.40	2.42
S	-	1.38	1.17
$\bar{n}$ MW	-	1,583	1,772

of the oil fraction was considerably higher at 825 than 850°F; whereas, no difference was noted for the asphaltene fraction. A slightly higher $\bar{n}$ MW was observed for the preasphaltene obtained at 850°F than 825°F. The sulfur contents of the oil fraction obtained at both the temperatures were identical with lower sulfur contents in the asphaltene and preasphaltene at 850°F than 825°F. This is indicative of increased desulfurization at higher temperature. Insignificant variations in the oxygen and nitrogen contents of the oil, asphaltene and preasphaltene fractions were noted at both the temperatures.

The simulated distillations (D-2887) of the oil fractions of the product obtained at two different temperatures are shown in Figure 6. No significant differences were noted 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 825°F.

The oil fractions were analyzed by NIR to determine the distribution of nitrogen and oxygen compounds and the data are shown in Table 25. No significant differences in the distribution of nitrogen and oxygen compounds were noted with the change in reaction temperature. The NMR data are summarized in Table 26. Lower concentrations of alpha and other protons were found in the generated oil fraction than the original oil fraction. This would mean lower solvent quality for the generated oil fractions than the original solvent. The Brown-Ladner structural parameters were calculated and are summarized in Table 27. The aromaticity of the solvent was found to increase with the reaction temperature. No definite trend was observed in the variation of degree of substitution (σ) and condensation (H_{AR}/C_{AR}). Although H_{AR}/C_{AR} decreased considerably from the value of the original solvent, no change in the average number of condensed aromatic rings was noted. The original solvent and generated solvents were found to have three or more condensed aromatic rings.

FIGURE 6
EFFECT OF REACTION TEMPERATURE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM LIQUEFACTION OF KY #9 COAL

Table 25

Distribution Of Nitrogen And Oxygen Compounds
In Oil Fractions Of Coal Liquefaction Product

Sample No.	28-11		28-22	
Temp., °F	825		850	
Total Nitrogen, Wt.%	0.92		0.96	
Total Oxygen, Wt.%	1.54		1.65	
Distribution of Nitrogen, %	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>
N as N	0.54	58.7	0.60	62.5
N as NH	0.35	38.0	0.33	34.4
N as NH ₂	0.03	3.3	0.03	3.1
Distribution of Oxygen, %				
O as O	0.89	57.8	0.96	58.2
O as OH	0.65	42.2	0.69	41.8

Table 26

Distribution Of Protons In The Oil Fractions

Sample No.	Original Solvent		28-11		28-22	
Temp., °F			825		850	
Total Hydrogen, Wt. %	7.72		7.46		7.30	
Distribution of Protons, %	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>
H _{AR}	3.24	42.0	3.27	43.8	3.30	45.2
H _a	2.26	29.3	2.08	27.9	2.09	28.6
H _o	2.22	28.7	2.11	28.3	1.91	26.2

Table 27

Modified Brown-Ladner Structural Parameters
For The Oil Fractions

Sample	Original Solvent	28-11	28-22
Temp., °F		825	850
Pressure, psig		2,000	2,000
f_a	0.702	0.722	0.733
σ	0.271	0.259	0.264
H_{AR}/C_{AR}	0.834	0.809	0.800
R_a	3.23	3.23	3.24

Liquefaction of Kentucky #9 (Pyro) Coal in the Presence of Robena Pyrite. The liquefaction of Kentucky #9 coal was studied at two different temperatures in the presence of Robena pyrite and the results are summarized in Table 28. Coal conversion was similar at the two different temperatures, but significant differences were found in hydrocarbon gas production, product distribution and hydrogen consumption. Hydrocarbon gases, CO , CO_2 , NH_3 and water production were found to increase with increasing reaction temperature from 825 to 850°F; hydrocarbon gas and ammonia production increased from 2.9 to 4.9% and from 0.0 to 0.3%, respectively. Increasing the temperature from 825 to 850°F increased the conversion of both asphaltenes and preasphaltenes to oils and gases; the oil production increased from 24 to 35% and asphaltenes and preasphaltenes decreased from 28 to 20 and 31 to 26%, respectively. Also, an increase in temperature increased the hydrogen consumption from 2.2 to 2.9 wt.% on the basis of MAF coal. The increase in hydrogen consumption (0.7%) was due mainly to increased hydrocarbon gases and oils formation: 0.09% was due to increased gas formation; 0.6% was due to the additional oil formation; the balance, i.e., 0.02 wt.% on the basis of MAF coal, was due to the change in the amounts of residue and water.

The distribution of elements in the various fractions is summarized in Table 29. The hydrogen contents of the oil fractions obtained from the coal liquefaction runs were found to be identical to that of starting solvent. Increasing reaction temperature from 825 to 850°F increased the hydrogen content of both the asphaltene and preasphaltene fractions. The number average molecular weights of the oil, asphaltene, and preasphaltene fractions were observed to decrease with increasing temperature. No significant differences were noted in the nitrogen contents of oil, asphaltenes and preasphaltenes. With increasing temperature from 825 to 850°F, the sulfur contents changed as follows: the oils remained unchanged, the asphaltenes decreased from 1.28 to 0.95% and the preasphaltenes increased from 1.36 to 1.68%. The oxygen contents of all the three

Table 28

Liquefaction Behavior Of Kentucky #9 Coal
In The Presence Of Robena Pyrite

Sample No.	28-35	28-46
Feed	60% Solvent/30% Coal/10% Robena Pyrite	
Temp., °F	825	850
Pressure, psig	2,000	2,000
Hydrogen Treat Rate MSCF/T	21.54	21.83
Residence Tim, Min.	35	35
Product Distribution, Wt.% MAF Coal		
HC	2.9	4.9
CO, CO ₂	0.6	0.7
H ₂ S	0.6	0.4
NH ₃	0.0	0.3
Oil	23.9	34.9
Asphaltene	28.2	19.8
Preasphaltene	31.5	25.6
I.O.M.	6.7	7.4
Water	5.6	5.9
Conversion, % MAF	93.3	92.6
Hydrogen Consumption, Wt.% MAF		
Total	2.16	2.90
Consumed from Gas	2.12	2.88
Consumed from Solvent	0.04	0.02
Consumed by Pyrite	0.50	0.50

Table 29

Elemental Distribution In The Various Fractions
Of Liquefaction Product Of Kentucky #9 Coal
In The Presence Of Robena Pyrite

Sample No.	Original Solvent	28-35	28-46
Temp., °F	-	825	850
Oil Fraction, Wt.%			
C	89.57	88.82	89.05
H	7.72	7.70	7.71
O	1.32	1.79	1.74
N	0.88	1.14	1.03
S	0.51	0.54	0.47
$\bar{n}$ MW	220	212	208
Asphaltene Fraction, Wt.%			
C	-	83.99	85.39
H	-	6.31	6.83
O	-	6.16	4.41
N	-	2.26	2.42
S	-	1.28	0.95
$\bar{n}$ MW	-	698	557
Preasphaltene Fraction, Wt.%			
C	-	82.45	83.52
H	-	5.62	5.69
O	-	7.49	5.76
N	-	2.40	2.53
S	-	1.36	1.68
$\bar{n}$ MW	-	1,878	1,426

fractions decreased with reaction temperature; the oils decreased from 1.79 to 1.74%, the asphaltenes decreased from 6.16 to 4.41%, and the preasphaltenes decreased from 7.49 to 5.76%.

The simulated distillation of the oil fractions obtained at two different temperatures is shown in Figure 7. The oil fractions were found to have identical initial and final boiling points. The oil fraction obtained at 850°F showed slightly lower quantity of higher boiling point compounds than the oil fraction obtained at 825°F.

The distribution of nitrogen and oxygen compounds in the oil fractions summarized in Table 30 showed some improvement in the denitrogenation of oil fraction with increasing reaction temperature. The improvement in denitrogenation was verified by a decrease in concentration of N type compounds (pyridine, quinoline, etc.) and an increase in that of NH and NH₂ type compounds. Also, a slight increase in production of NH₃ was noted at 850°F over 825°F as shown in Table 28. Slight improvement in deoxygenation of various fractions was also noted.

The distribution of protons was found to be unaffected by reaction temperature as shown in Table 31. The concentration of H_{AR} was found to be lower and that of H_a and H_o higher in the generated oil fractions compared to the original solvent. This is indicative of higher solvent quality of generated oils than the original solvent. Lower aromaticity and higher degree of substitution by alkyl or other groups was found for generated solvents than the original solvent. Although the value of H_{AR}/C_{AR} decreased considerably with increasing reaction temperature, no change in the average number of condensed aromatic rings was noted (see Table 32). The original solvent and generated solvents were found to have on the average three or more condensed aromatic rings.

FIGURE 7
EFFECT OF REACTION TEMPERATURE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM LIQUEFACTION OF KY #9
COAL IN THE PRESENCE OF ROBENA PYRITE

Table 30

Distribution Of Nitrogen And Oxygen Compounds
In Oil Fraction Of Coal Liquefaction Product
In The Presence Of Robena Pyrite

Sample No.	28-35		28-46	
Temp., °F	825		850	
Total Nitrogen, Wt. %	1.14		1.03	
Total Oxygen, Wt. %	1.79		1.74	
Distribution of Nitrogen, %	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>
N as N	0.85	74.6	0.71	68.9
N as NH	0.26	22.8	0.25	24.3
N as NH ₂	0.03	2.6	0.07	6.8
Distribution of Oxygen, %				
O as O	1.00	55.9	0.90	51.7
O as OH	0.79	44.1	0.84	48.3

Table 31

Distribution of Protons in the Oil Fractions
Obtained in the Presence of Robena Pyrite

Sample No.	Original Solvent		28-46		28-56	
Temp., °F	-		825		850	
Total Hydrogen, wt. %	7.72		7.71		7.76	
Distribution of Protons, %	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>
H _{AR}	3.24	42.0	2.96	38.5	2.98	38.7
H _a	2.26	29.3	2.42	31.5	2.35	30.5
H _o	2.22	28.7	2.32	30.0	2.38	30.8

Table 32

Modified Brown-Ladner Structural Parameters for the Oil
Fractions Obtained in the Presence of Robena Pyrite

Sample No.	Original Solvent	28-35	28-46
Temp., °F	-	825	850
f_a	0.702	0.685	0.693
σ	0.271	0.306	0.290
H_{AR}/C_{AR}	0.834	0.834	0.804
R_a	3.23	3.26	3.27

Effect of Robena Pyrite on Kentucky #9 Coal Liquefaction. Liquefaction of coal in the presence of Robena pyrite at 825°F increased the coal conversion from 91 to 93% (see Table 33). The preasphaltenes conversion increased significantly as shown by a decrease in concentration from 47 to 32%. The added coal and preasphaltene conversion ended up in the oil, gases and water fractions; the oil fraction increased by a factor of three from 8 to 24%. The addition of pyrite also increased the hydrogen consumption based on elemental hydrogen balance from 1.34 to 2.16 wt.% MAF coal. 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 oils, gases and water yields.

The liquefaction of coal in the presence and absence of Robena pyrite at 850°F is also shown in Table 33. Again the addition of pyrite increased the conversion of coal and formation of oil, water and hydrocarbon gases; oil production went up from 15 to 35%. Slight improvement in preasphaltenes conversion from 29 to 26% was noted, but asphaltenes production decreased significantly from 30 to 20%. On the contrary, at 825°F significant conversion of preasphaltenes was observed. The possible explanation for this behavior could be that preasphaltene conversion was very sensitive to temperature (see Table 33), whereas asphaltene conversion was not and an external catalyst like pyrite was required to convert it to oils and hydrocarbon gases. The first-order rate constants for the conversion of asphaltene and preasphaltene are also presented in Table 33. The rate constants were calculated assuming sequential reaction path and the calculation procedure is described in detail in Appendix C. The rate constants for the conversion of asphaltene and preasphaltene increased with increasing the reaction temperature and also with the addition of pyrite. The reaction rate for conversion of asphaltene increased significantly with the addition of pyrite; it increased from 0.25 to 0.83 at 825°C and from 0.46 to 1.47 at 850°C, respectively. Significant increase in reaction rate of conversion of preasphaltene was also observed. These observations were consistent with the hypothesis that preasphaltene conversion

Table 33

Comparison of Kentucky #9 Coal Liquefaction
in the Presence and Absence of Robena Pyrite

Sample No.	28-11	28-35	28-22	28-46
Temp., °F	825	825	850	850
Pyrite	No	Yes	No	Yes
Production Distribution, wt.% MAF Coal				
HC	3.2	2.9	5.0	4.9
CO, CO ₂	0.5	0.6	0.6	0.7
H ₂ S	1.4	0.6	1.7	0.4
NH ₃	0.0	0.0	0.0	0.3
Oil	7.9	23.9	15.3	34.9
Asphaltene	26.6	28.2	30.0	19.8
Preasphaltene	47.0	31.5	28.8	25.6
I.O.M.	9.4	6.7	12.8	7.4
Water	4.0	5.6	6.5	5.9
Conversion	90.6	93.3	87.2	92.6
Hydrogen Consumption, wt.% MAF				
Total	1.34	2.16	1.51	2.90
Consumed from Gas	0.69	2.12	0.47	2.88
Consumed from Solvent	0.65	0.04	1.04	0.02
Consumed by Pyrite	-	0.50	-	0.50
First-Order Rate Constants, hr ⁻¹				
k _a	0.25	0.46	0.83	1.47
k _p	1.17	2.53	2.78	3.57

was very sensitive to temperature, whereas asphaltene conversion required an external catalyst. The addition of pyrite increased the hydrogen consumption from 1.51 to 2.90 wt.% MAF coal at 850°F. The increased hydrogen consumption was due mainly to reduce pyrite to FeS and increased production of oils and asphaltenes.

The simulated distillation of the oil fractions obtained with and without the use of pyrite at 825 and 850°F are shown in Figures 8 and 9. The oil fractions obtained with and without pyrite were shown to have similar initial and final boiling points but very different boiling point distribution. The oils obtained with pyrite were found to contain consistently higher boiling point compounds compared to oils generated without pyrite as shown in Figures 8 and 9.

The distribution of elements in the various fractions obtained in the presence and absence of pyrite at 825 and 850°F are shown in Table 34. The oil fractions obtained in the absence of pyrite had considerably lower hydrogen content than the ones obtained in the presence of pyrite. The hydrogen content of oil fractions obtained in the presence of pyrite was similar to that of starting solvent. This lead to the conclusion that the oil hydrogen content was depleted in the absence of pyrite, whereas it was maintained in its presence. The hydrogen contents of asphaltenes and preasphaltenes obtained with pyrite were also found generally to be higher than the ones without pyrite. Higher nitrogen, oxygen and sulfur contents of all the fractions were also noted with pyrite than without pyrite.

The distribution of nitrogen and oxygen compounds present in the oil fractions are shown in Table 35. The concentration of pyridine, quinoline, etc. type of compounds were found to increase and that of NH type compounds decrease with the addition of pyrite. The decrease in the concentration of NH type compounds was probably due to hydrogenation of NH to NH_2 type compounds and finally to ammonia.

FIGURE 8
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTIONS
OBTAINED FROM COAL LIQUEFACTION RUNS AT 825°F

FIGURE 9
COMPARISON OF SIMULATED DISTILLATION OF OIL FRACTIONS
OBTAINED FROM COAL LIQUEFACTION RUNS AT 850°F

Table 34

Elemental Distribution in the Various Fractions of
Liquefaction Product of Kentucky #9 Coal in the
Presence and Absence of Robena Pyrite

Sample No.	Original	28-11	28-35	28-22	28-46
Temp., °F	Solvent	825	825	850	850
Pyrite	-	No	Yes	No	Yes
Oil Fraction, wt.%					
C	89.57	89.52	88.82	89.53	89.05
H	7.72	7.46	7.70	7.30	7.71
O	1.32	1.54	1.79	1.65	1.74
N	0.88	0.92	1.14	0.96	1.03
S	0.51	0.56	0.54	0.56	0.47
$\bar{n}$ MW	220	208	212	204	208
Asphaltene Fraction, wt.%					
C	-	85.83	83.99	86.19	85.39
H	-	6.42	6.31	6.41	6.83
O	-	4.30	6.16	4.35	4.41
N	-	2.49	2.26	2.20	2.42
S	-	0.95	1.28	0.86	0.95
$\bar{n}$ MW	-	341	698	342	557
Preasphaltene Fraction, wt.%					
C	-	83.74	82.45	83.94	83.52
H	-	5.46	5.62	5.39	5.69
O	-	5.99	7.49	6.03	5.76
N	-	2.40	2.40	2.42	2.53
S	-	1.38	1.36	1.17	1.68
$\bar{n}$ MW	-	1583	1878	1772	1426

Table 35

Distribution of Nitrogen and Oxygen Compounds in Oil Fractions of Coal
Liquefaction Product Obtained in the Presence and Absence of Robena Pyrite

Sample No.	28-11		28-35		28-22		28-46	
Temp., °F	825		825		850		850	
Pyrite	No		Yes		No		Yes	
Total Nitrogen, Wt. %	0.92		1.14		0.96		1.03	
Total Oxygen, Wt. %	1.54		1.79		1.65		1.74	
Distribution of Nitrogen, %	Absolute	Relative	Absolute	Relative	Absolute	Relative	Absolute	Relative
N as N	0.54	58.7	0.85	74.6	0.60	62.5	0.71	68.9
N as NH	0.35	38.0	0.26	22.8	0.33	34.4	0.25	24.3
N as NH ₂	0.03	3.3	0.03	2.6	0.03	3.1	0.07	6.8
Distribution of Oxygen, %								
O as O	0.89	57.8	1.00	55.9	0.96	58.2	0.90	51.7
O as OH	0.65	42.2	0.79	44.1	0.69	41.8	0.84	48.3

This route is supported by the fact that increased production of NH_3 was noted with pyrite (see Table 33). No definite trend was observed in the case of oxygen compounds.

Higher concentration of H_{AR} in the oil fractions obtained without pyrite and lower values in oil fractions obtained with pyrite were observed as compared to the original solvent (see Table 36). This indicated that more and more aromatic hydrocarbons were hydrogenated with pyrite. The concentrations of H_a and H_o protons were found to decrease without pyrite while they increased with pyrite. This was indicative of increased production of side chain and hydrogenated aromatic compounds. The solvent quality, estimated by the concentration of H_a , improved for the solvent generated in the presence of pyrite and declined for the ones generated in its absence. The Brown-Ladner structural parameters for the oil fractions are calculated and are listed in Table 37. The aromaticity, f_a , of the oils obtained without pyrite was higher and of the oils obtained with pyrite was lower than the original solvent. This was also supported by higher value of H_{AR} without pyrite and lower with pyrite. The increase in the value of H_o with pyrite was also verified by increased degree of substitution (σ). Although some variation in the degree of condensation ($\text{H}_{\text{AR}}/\text{C}_{\text{AR}}$) was observed with and without pyrite, no significant change in the average number of aromatic rings (R_a) was observed. The average number of condensed aromatic rings in the original and generated oils was found to be three or more.

The above results showed that addition of Robena pyrite to Kentucky #9 coal increased coal dissolution, promoted solvent hydrogenation, increased oil production and improved solvent quality.

Effect of Hydrogen Flow Rate on Liquefaction of Elkhorn #3 and Kentucky #9 Coals in the Presence of Robena Pyrite. In the liquefaction experiments on Elkhorn #3 and Kentucky #9 coals in the presence of pyrite discussed earlier in this report, a hydrogen flow rate of approximately 22 MSCF/T was used. By gas chromatographic analysis

Table 36

Distribution of Protons in the Oil Fractions Obtained
in the Presence and Absence of Robena Pyrite

Sample No.	Original Solvent		28-11		28-35		28-22		28-46	
Temp., °F	-		825		825		850		850	
Pyrite	-		No		Yes		No		Yes	
Total Hydrogen, Wt. %	7.72		7.46		7.70		7.30		7.71	
Distribution of Protons, %	Absolute	Relative	Absolute	Relative	Absolute	Relative	Absolute	Relative	Absolute	Relative
H _{AR}	3.24	42.0	3.27	43.8	2.96	38.5	3.30	45.2	2.98	38.7
H _a	2.26	29.3	2.08	27.9	2.42	31.5	2.09	28.6	2.35	30.5
H _o	2.22	28.7	2.11	28.3	2.32	30.0	1.91	26.2	2.38	30.8

Table 37

**Brown-Ladner Structural Parameters for the Oil Fractions
Obtained in the Presence and Absence of Pyrite**

Sample No.	Original Solvent	28-11	28-35	28-22	28-46
Temp., °F		825	825	850	850
Pyrite	-	No	Yes	No	Yes
f_a	0.702	0.722	0.685	0.733	0.693
σ	0.271	0.259	0.306	0.264	0.290
H_{AR}/C_{AR}	0.834	0.809	0.834	0.800	0.804
R_a	3.23	3.23	3.26	3.24	3.27

the exit gas was found to contain more than 80% hydrogen in these runs indicating that more than enough hydrogen gas was present in the reaction. By increasing the hydrogen flow rate a measure of the impact of available hydrogen and increased hydrogen partial pressure on the consumption of hydrogen gas during coal liquefaction reaction was examined. A hydrogen flow rate close to 45 MSCF/T (more than twice the flow rate previously used) was employed to study these effects.

Floyd County Elkhorn #3 Coal. The results of liquefaction of Elkhorn #3 coal at two different hydrogen flow rates in the presence of pyrite are compared in Table 38. Conversion of coal was found to be unchanged with increasing hydrogen flow rate. The hydrocarbon gases, CO, CO₂, and H₂S production decreased with increasing hydrogen flow rate. Significant increase in water production was noted with higher hydrogen flow rate. Preasphaltene conversion and oil and asphaltene production were increased with increasing hydrogen flow rate. The hydrogen consumption was also found to increase from 2.53 to 2.85 wt.% MAF coal with increasing flow rate.

The distribution of elements in the various fractions is summarized in Table 39. The hydrogen content of all the fractions increased with increasing hydrogen flow rate. The oxygen content of various fractions decreased with increasing hydrogen flow rate as shown in Table 39. The reduction in oxygen content as a matter of fact verified by increased production of water. Nitrogen content of oil fraction increased from 0.96 to 1.05% with increasing hydrogen flow rate, whereas it decreased from 2.37 to 2.22% and 3.28 to 2.60% for the asphaltene and preasphaltene fractions, respectively. Sulfur contents of oil and asphaltene fractions decreased slightly but that of preasphaltenes increased from .71 to 0.89% with increasing hydrogen flow rate.

Table 38

**Effect of Hydrogen Flow Rate on Liquefaction of
Elkhorn #3 Coal in the Presence of Robena Pyrite**

Sample No.	25-136	28-71
H ₂ Flow Rate, MSCF/T	21.9	47.2
Feed Composition	60% Solvent/30% Coal/10% Pyrite	63.6% Solvent/27.3% Coal/9.1% Pyrite
Temp., °F	850	850
Residence Time, Min.	41	35
Pressure, psig	2000	2000
Product Distribution, wt.% MAF Coal		
HC	5.3	3.1
CO, CO ₂	1.2	0.8
H ₂ S	2.8	0.4
NH ₃	0.2	0.3
Oil	41.0	42.1
Asphaltene	11.3	18.5
Preasphaltene	24.3	18.8
I.O.M.	10.4	9.9
Water	3.5	6.1
Conversion, %	89.6	90.1
Hydrogen Consumption, wt.% MAF		
Total	2.53	2.85
Consumed from Gas	2.49	2.88
Consumed from Solvent	0.04	(0.03)
Consumed by Pyrite	0.50	0.50

() means negative value

Table 39

Distribution of Elements in Various Fractions of
Elkhorn #3 Coal Liquefaction Product at Two Different Hydrogen Flow Rates

Sample No.	25-136	28-71
H ₂ Flow Rate, MSCF/T	21.9	47.2
Temp., °F	850	850
Oil Fraction, wt.%		
C	89.12	89.3
H	7.70	7.73
O	1.76	1.52
N	0.96	1.05
S	0.49	0.40
$\bar{n}$ MW	205	208
Asphaltene, wt.%		
C	85.12	86.69
H	6.24	7.43
O	5.65	3.09
N	2.37	2.22
S	0.62	0.56
$\bar{n}$ MW	490	498
Preasphaltene, wt.%		
C	83.17	84.19
H	5.65	5.68
O	-	5.37
N	3.28	2.60
S	0.71	0.89
$\bar{n}$ MW	984	1649

Above results show that increased hydrogen flow rate did not alter conversion of Elkhorn #3 coal, but increased conversion of preasphaltenes, increased production of oils and asphaltenes, further hydrogenated the oils, asphaltenes and preasphaltenes, and helped in deoxygenation of the product.

Kentucky #9 Coal. The effect of hydrogen flow rate on liquefaction of Kentucky #9 coal is shown in Table 40. The conversion of coal increased and the production of hydrocarbon gases, NH_3 and water decreased with increasing hydrogen flow rate. The production of preasphaltene decreased from 26 to 20% with increasing hydrogen flow rate. Significant increase in oil production, from 35 to 41% was noted with increasing flow rate. The hydrogen consumption was found to decrease from 2.90 to 2.61 wt.% MAF coal with increasing hydrogen flow rate.

The distribution of elements in the various fractions is tabulated in Table 41. Insignificant change in the hydrogen contents of oils, asphaltenes and preasphaltenes was observed with increasing hydrogen flow rate (see Table 41). The oxygen and sulfur contents of all the fractions were lower at high hydrogen flow rate indicating improved desulfurization and deoxygenation with increasing hydrogen flow rate. Insignificant variation in nitrogen contents of all the fractions was noted. The number average molecular weight was consistently lower for all the fractions obtained at higher hydrogen flow rate.

The distribution of nitrogen and oxygen compounds in the oil fractions are shown in Table 42. The concentration of quinoline type compounds was found to increase with higher hydrogen flow rate. Other than that no significant differences were noted. The concentration of oxygen compounds like ethers was found to decrease with increasing hydrogen flow rate; it decreased from 0.90 to 0.67%. This was indicative of improved deoxygenation. The NMR data for the oil fractions obtained at two different hydrogen flow rates are shown in Table 43 and they are found to be similar.

Table 40

Effect of Hydrogen Flow Rate on Liquefaction of
Kentucky #9 Coal in the Presence of Robena Pyrite

Sample No.	28-46	28-56
H ₂ Flow Rate, MSCF/T	21.8	45.9
Feed Composition	60% Solvent/30% Coal/10% Pyrite	
Temp., °F	850	850
Residence Time, Min.	35	37
Product Distribution, wt.% MAF Coal		
HC	4.9	3.4
CO, CO ₂	0.7	0.7
H ₂ S	0.4	2.7
NH ₃	0.3	0.0
Oil	34.9	41.3
Asphaltene	19.8	22.5
Preasphaltene	25.6	20.2
I.O.M.	7.4	4.1
Water	5.9	5.1
Conversion, %	92.6	95.9
Hydrogen Consumption, wt.% MAF		
Total	2.90	2.61
Consumed from Gas	2.88	2.70
Consumed from Solvent	0.02	(0.09)
Consumed by Pyrite	0.50	0.50

() means negative value

Table 41

Distribution of Elements in Various Fractions of
Kentucky #9 Coal Liquefaction Product at Two Different Hydrogen Flow Rates

Sample No.	28-46	28-56
H ₂ Flow Rate, MSCF/T	21.8	45.9
Temp., °F	850	850
Oil Fraction, wt.%		
C	89.05	89.05
H	7.71	7.76
O	1.74	1.49
N	1.03	1.23
S	0.47	0.47
$\bar{n}$ MW	208	208
Asphaltene, wt.%		
C	85.39	85.99
H	6.83	6.40
O	4.41	4.40
N	2.42	2.38
S	0.95	0.83
$\bar{n}$ MW	557	423
Preasphaltene, wt.%		
C	83.52	84.11
H	5.69	5.57
O	5.76	5.52
N	2.53	2.66
S	1.68	1.07
$\bar{n}$ MW	1426	1142

Table 42

Distribution of Nitrogen and Oxygen Compounds in the
Oil Fractions Obtained at Two Different H₂ Flow Rates

Sample No.	28-46		28-56	
H ₂ Flow Rate, MSCF/T	21.8		45.9	
Temp., °F	850		850	
Total Nitrogen, wt.%	1.03		1.23	
Total Oxygen, wt.%	1.74		1.49	
Distribution of Nitrogen, %	Absolute	Relative	Absolute	Relative
N as N	0.71	68.9	0.91	74.0
N as NH	0.25	24.3	0.26	21.1
N as NH ₂	0.07	6.8	0.06	4.9
Distribution of Oxygen, %				
O as O	0.90	51.7	0.67	45.0
O as OH	0.84	48.3	0.82	55.0

Table 43

Distribution of Protons in the Oil Fractions
Obtained at Two Different Hydrogen Flow Rates

Sample No.	28-46		28-56	
H ₂ Flow Rate, MSCF/T	21.8		45.9	
Temp., °F	850		850	
Total Hydrogen, wt.%	7.71		7.76	
Distribution of Protons, %	<u>Absolute</u>	<u>Relative</u>	<u>Absolute</u>	<u>Relative</u>
H _{AR}	2.98	38.7	2.96	38.2
H _a	2.35	30.5	2.31	29.8
H _o	2.38	30.8	2.49	32.0

The simulated distillation of the oil fractions obtained at two different hydrogen flow rates is shown in Figure 10. The oil fraction obtained at high hydrogen flow rate was shown to have higher initial and final boiling points. Also, it was found to contain higher amounts of high boiling point compounds.

The above results indicated that the use of high hydrogen flow rate in liquefaction of Kentucky #9 coal increased coal and preasphaltene conversion, improved oil production and helped in deoxygenation of product.

The liquefaction of Elkhorn #3 and Kentucky #9 coals at two different hydrogen flow rates showed improved conversion of preasphaltenes, oil production and solvent hydrogenation with increasing hydrogen flow rate. Similar trends, for example, increased oil yield, decreased SRC production and improved conversion of coal, were shown by The Pittsburg and Midway Coal Mining Co.* (PAMCO). Based on the above facts, we established that hydrogen flow rate changed the product distribution. A major impact of changing hydrogen flow rate would be on the effective hydrogen partial pressure in the reactor. The increase in hydrogen flow rate would ultimately increase the effective hydrogen partial pressure. In another study, PAMCO** showed that increasing total pressure in the reactor increased the oil yield and decreased the SRC production. All the above facts lead to the conclusion that the coal liquefaction product distribution was very sensitive to the hydrogen partial pressure and the desired product slate could be achieved by manipulating either the total pressure or hydrogen flow rate.

*Solvent Refined Coal (SRC) Process, Quarterly Technical Progress Report prepared by The Pittsburg and Midway Coal Mining Co. for U.S. Dept. of Energy (FE/496-141), December, 1977.

**Solvent Refined Coal (SRC) Process, Quarterly Technical Progress Report prepared by PAMCO for U.S. Dept. of Energy (FE/496-143), January, 1978.

FIGURE 10
EFFECT OF HYDROGEN FLOW RATE ON SIMULATED DISTILLATION
OF OIL FRACTIONS OBTAINED FROM LIQUEFACTION OF KY #9
COAL IN THE PRESENCE OF ROBENA PYRITE

Task 4.0 Effect of Minerals on Coal Liquefaction

Auburn University has continued to screen a number of materials for their catalytic activity toward coal liquefaction. In the previous Quarterly Technical Progress Report the results from testing of a number of minerals were reported. Another group, rutile, illite, zircon and calcite, gave slightly lower activity but conversions and yields were still greater than coal alone.

In this report results from another series of runs at Auburn University are presented. In previous work some of the mineral materials showed a slight detrimental effect on coal conversion. The test results reported here as shown in Table 44 also contain some examples in which the mineral additive has a retarding effect on coal conversion.

Zeolites. Both synthetic X and mordenite zeolites caused a decrease in coal conversion. From a conversion level of 77% for the pure coal, adding these two zeolites reduced conversion to 72 and 69%, respectively. Slight change in preasphaltene production was noted. X-zeolite and mordenite addition to coal liquefaction reaction mixture improved the production of oil from 16 to ~20 percent which was mainly due to increased conversion of asphaltenes. The addition of chabazite did not alter the conversion of coal but significantly increased the production of oil at the expense of asphaltenes. The catalytic activity of chabazite was moderate compared to Robena pyrite.

Clays. Kaolinite and montmorillonite did not improve the conversion of coal (see Table 44) although both of these clay materials increased the conversion of asphaltenes to oils. Oil production increased from 16 (no-additive run) to 32 and 29% and asphaltenes decreased from 48 (no-additive run) to 33 and 34% with the addition of kaolinite and montmorillonite, respectively. The addition of these clays

Table 44

Catalytic Activity of Various Minerals in Coal Liquefaction

<u>Additive</u>	<u>None</u>	<u>Robena Pyrite</u>	<u>X-Type Molecular Sieve</u>	<u>Mordenite</u>	<u>Chabazite</u>
Experiment Number	AP-91	AP-95	AP-152	AP-150	AP-151
Oil, %	16	39	20	22	28
Asphaltene, %	48	44	33	33	35
Preasphaltene, %	13	7	19	14	13
I.O.M., %	23	10	28	31	24
Conversion, %	77	90	72	69	76

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

Reaction Conditions: Temperature - 450°C
 Pressure - 1,250 psig H₂ at 25°C
 Time - 60 Minutes

Reactor: Tubing-Bomb
 Volume - 46.3 ml.

Table 44
(continued)

Catalytic Activity of Various Minerals in Coal Liquefaction

<u>Additive</u>	<u>Albanian Chrome Ore Concentrate</u>	<u>Red Oxide (Fe₂O₃)</u>	<u>Speculite (Fe₂O₃)</u>	<u>Molybdic Oxide</u>	<u>Silica*</u>
Experimental No.	AP-148	AP-147	AP-149	AP-138	AP-121
Oil, %	33	39	40	58	25
Asphaltene, %	34	36	35	29	37
Preasphaltene, %	13	11	11	2	13
I.O.M., %	20	14	14	11	25
Conversion, %	80	86	86	89	75

*Received from Fisher Scientific Company.

Table 44
(continued)

Catalytic Activity of Various Minerals in Coal Liquefaction

<u>Additive</u>	<u>Gypsum</u>	<u>Magnetite</u>	<u>Kaolinite</u>	<u>Montmo- rillonite</u>
Experimental No.	AP-123	AP-120	AP-137	AP-119
Oil, %	34	36	37	29
Asphaltene, %	36	36	33	34
Preasphaltene, %	13	14	13	12
I.O.M., %	17	14	22	25
Conversion, %	83	86	78	75

showed an improvement in oil production considerably less than that with pyrite. The catalytic activity of silica, shown in Table 44, was also found to be similar to that of montmorillonite.

Gypsum and Chromium Ore. Both Gypsum and Albanian chrome ore concentrate (see First Quarterly Technical Progress Report for analysis) showed slightly improved catalytic activity compared to x-zeolites, mordenite and clay materials. The conversion of coal and production of oil with these two additives were generally higher but not comparable to the ones with pyrite.

Iron Ores. The addition of magnetite and iron oxide (Fe_2O_3) significantly increased the conversion of coal from 77% in the case of no-additive run to 86% with these two additives (see Table 44). Similarly, the production of oil was higher than the no additive case and comparable to that with pyrite. Lower asphaltene and higher preasphaltene production were noted compared to that obtained with pyrite.

Molybdcic Oxide. Molybdcic oxide, shown in Table 44, gave similar conversion of coal to that with pyrite. The production of oil with molybdcic oxide was considerably higher than with pyrite.

Diatomaceous Earth (Filter Aid). The catalytic activity of low and high temperature treated filter aid was evaluated in coal liquefaction reaction. The addition of heat treated filter aid did not change the conversion of coal compared to no-additive run (see Table 45). It increased the conversion of asphaltenes such that oil production increased from 16 to 36% and asphaltenes decreased from 48 to 31 percent with the addition of filter aid. No differences in the product distribution were noted with the different pretreated filter aid materials as shown in Table 45.

Table 45

Effect of Diatomaceous Earth (Filter Aid) on Coal Liqefaction

Additive	None	Filter Aid		
Heat Treatment				
Temperature, °C	-	800	510	Low Temp. Ash
Experiment No.	AP-91	AP-124	AP-127	AP-130
Oil, %	16	36	36	37
Asphaltene, %	48	31	31	30
Preasphaltene, %	13	12	11	10
I.O.M., %	23	21	22	23
Conversion, %	77	79	78	77

Reaction Mixture: 3 g Elkhorn #3 coal
 6 g Solvent
 1 g Additive

Reaction Conditions: Temp. - 450°C

Pressure - 1,250 psig H₂ at 25°C

Time - 60 Minutes

Reactor - Tubing-Bomb (46.3 ml? volume)

Quartz - A sample of quartz received from Sawyer Research Products was tested for its catalytic activity in coal liquefaction reaction. The result of the experiment reported in the Third Quarterly Technical Progress Report showed significant increase in the production of oil. The above result was based on only one experiment and we are not sure about the validity of the data. Quartz is basically a form of silica (SiO_2) and the addition of silica to coal liquefaction reaction mixture did not show any catalytic activity (see Table 44). Duplicate runs are needed to explain the differences in the activity of quartz and silica.

Quartz-Effect of Particle Size. Quartz of different particle sizes (5, 10, 15 and 30 microns) were received from Pennsylvania Glass Sand Corporation to evaluate the effect of quartz and its particle size in coal liquefaction. The results of the above experiments are summarized in Table 46. The addition of this particular quartz was shown to be detrimental to coal liquefaction reaction. The coal conversion and asphaltene production were severely hampered by the addition of this quartz. Also, different particle size quartz were shown to have similar activity.

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

A number of metallic wastes and metal-containing by-products were screened for their catalytic activity toward coal liquefaction and the results were reported in the Third Quarterly Technical Progress Report. Zinc flue dust, phosphate slime and red mud showed significant improvement in conversion of coal and production of benzene solubles. Two samples of zinc flue dust with varying concentration of zinc and iron were tested and they showed very similar activity. These results showed no relationship between the catalytic activity and the concentration of zinc in the samples. Also, the presence of iron in addition to zinc in the samples showed no definite advantage.

Table 46

Effect of Particle Size of Quartz on Coal Liquefaction

Additive	None	Quartz			
		5 Microns	10 Microns	15 Microns	30 Microns
Experiment No.	AP-91	AP-176	AP-177	AP-178	AP-179
Oil, %	16	18	19	16	16
Asphaltene, %	48	32	31	30	32
Preasphaltene, %	13	14	17	16	17
I.O.M., %	23	36	33	38	35
Conversion, %	77	64	67	62	65

Reaction Mixture: 3 g Elkhorn #3 coal

6 g Solvent

1 g Additive

Reaction Condition: Temp. - 450°C

Pressure - 1,250 psig at 25°C

Time - 60 Minutes

Reactor - Tubing-Bomb (46.3 ml.)

However, iron when added to the coal liquefaction reaction mixture alone or in the form of either pyrite or iron oxide showed significant improvement in conversion of coal and production of benzene solubles. The above results suggest that iron if chemically bonded to zinc apparently loses its catalytic activity in coal liquefaction. More work is in progress to study the synergistic effect of iron in coal liquefaction reaction.

In this report results from another series of runs at Auburn University are presented. In the previous work most of the metallic waste materials showed either slight or significant effect on conversion of coal. All the materials reported here (see Table 47) also showed significant effect on conversion of coal. The addition of flue dust, copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and super alloy and alnico grindings to coal liquefaction reaction mixture significantly improved the conversion of coal and asphaltenes and the production of oil. The concentration of iron in various metallic wastes reported in the Third Quarterly Technical Progress Report was used as a measure to correlate their catalytic activity and no definite trend was observed. Once again, iron when added to the coal liquefaction reaction mixture as a pure compound showed higher catalytic activity than when it was added as a complex compound of various elements.

Effect of Fly Ashes. The catalytic activity of various fly ashes in coal liquefaction reaction was evaluated and the data are shown in Table 48. The addition of Brown and Green River fly ashes to coal liquefaction reaction was found to be detrimental to conversion of coal (see Table 48). The addition of Paradise fly ash did not change the conversion of coal, but it significantly improved the oil and asphaltene production. The oil production increased from 14 to 28% and asphaltenes from 31 to 36% with the addition of different fly ashes. The chemical analyses of different fly ashes given in Table 49 were checked to find out the possible reasons for the above differences. No definite trend could be seen to supplement

Table 47

Catalytic Activity of By-Products Waste Material in Coal Liquefaction

<u>Additive</u>	<u>None</u>	<u>Super Alloy Grindings</u>	<u>Alnico Grindings</u>	<u>Flue Dust</u>	<u>FeSO₄·7H₂O</u>
Experiment No.	AP-91	AP-134	AP-133	AP-139	AP-136
Oil, %	16	35	39	48	46
Asphaltene, %	48	39	40	37	38
Preasphaltene, %	13	13	9	7	10
I.O.M., %	23	13	12	8	6
Conversion, %	77	87	88	92	96

Reaction Mixture: Coal - 3 g (Floyd County Elkhorn #3)

Solvent - 6 g

Additive - 1 g

Temp. - 450°C

Pressure - 1,250 psig H₂ at 25°C

Time - 60 Minutes

Reactor - Tubing-Bomb (46.3 ml. volume)

Table 48

Effect of Fly Ashes on Coal Liquefaction

<u>Additive</u>	<u>None</u>	<u>Brown Fly Ash</u>	<u>Green River Fly Ashes Blend</u>	<u>High</u>	<u>Paradise Fly Ash</u>
Experiment No.	AP-91	AP-157	AP-159	AP-160	AP-158
Oil, %	16	14	23	24	28
Asphaltene, %	48	32	35	31	36
Preasphaltene, %	13	22	14	14	14
I.O.M., %	23	32	28	31	22
Conversion, %	77	68	72	69	78

Reaction Mixture: Coal - 3 g Elkhorn #3

Solvent - 6 g

Additive - 1 g

Reaction Conditions: Temp. - 450°C

Pressure - 1,250 psia H₂ at 25°C

Time - 60 Minutes

Reactor - Tubing-Bomb (46.3 ml.)

Table 49

Chemical Analyses of the Fly Ash Samples

Weight Percent

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Sulfur	Mois- ture	High Temp. Ash
Brown	51.9	1.4	29.1	11.6	1.1	1.25	3.3	0.4	0.49	0.32	96.7
Paradise	42.9	1.2	18.5	29.6	2.3	0.85	2.92	0.56	0.99	-	96.7
Green River											
High	40.9	0.91	16.8	32.3	5.4	0.65	1.84	0.32	0.4	0.12	09.7
Blend	48.1	0.74	14.8	32.2	1.56	0.52	1.62	0.22	0.20	0.21	94.0

*Analyses provided by Dr. Alan E. Bland of the Institute of Mining and Minerals,
University of Kentucky, Lexington, Kentucky.

the above data. The surface area of the fly ashes will be determined to correlate it to the variation in their activity in coal liquefaction reaction.

Effect of Bottom Ashes. The catalytic activity of various bottom ashes in coal liquefaction reaction was studied and is shown in Table 50. The catalytic activity of the bottom ashes was found to be in the following order: Green River > Brown > Paradise. The catalytic activity of these bottom ashes could be correlated to the variation in their sulfur content shown in Table 51. The highest sulfur content ash gave highest activity and vice versa. The surface area of these ashes will be determined to explain further the variation in their catalytic activity in coal liquefaction reaction.

Effect of Low and High Temperature Ashes of SRC Filter Cake Residue. The SRC filter cake residue was ashed at low temperature (LTA) and at two different high temperatures and then used as additives in coal liquefaction experiments. The addition of various ashes, shown in Table 52, improved the conversion of coal; it increased from 77 to 83 percent. The different ashes also catalyzed the conversion of asphaltenes to oils and the highest catalytic activity was obtained with LTA of filter cake residue.

The SRC filter cake residue obtained from Wilsonville pilot plant contained few percent of diatomaceous earth used as a filter aid to improve the performance of the filtration process. The catalytic activity of the filter aid was discussed earlier and it was shown that the addition of filter aid to coal liquefaction reaction mixture had no effect on increasing the conversion of coal but it significantly enhanced the production of oil. The LTA of filter cake residue was shown to increase the conversion of coal and production of oil compared to no-additive run. The catalytic activity of filter cake residue was much higher than that of filter aid. This indicated that filter aid was not solely responsible for the catalytic activity of filter cake residue. More work is required to quantify this statement.

Table 50

Effect of Bottom Ashes on Coal Liquefaction

	<u>None</u>	<u>Paradise</u> <u>Bottom Ash</u>	<u>Brown</u> <u>Bottom Ash</u>	<u>Green River</u> <u>Bottom Ash</u>
Experiment No.	AP-91	AP-163	AP-162	AP-164
Oil, %	16	21	29	38
Asphaltene, %	48	31	33	34
Preasphaltene, %	13	15	13	14
I.O.M., %	23	33	25	14
Conversion, %	77	67	76	86

Reaction Mixture: Coal - 3 g Elkhorn #3

Solvent - 6 g

Additive - 1 g

Reaction Conditions: Temp. - 450°C

Pressure - 1,250 psig H₂ at 25°C

Time - 60 Minutes

Reactor - Tubing-Bomb (46.3 ml.)

Table 51

Chemical Analyses of the Bottom Ash Samples

Weight Percent

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Sulfur	High	Ash
										Mois- ture	
Paradise	49.8	0.93	19.8	22.6	4.01	0.86	2.24	0.38	0.11	0.04	100.8
Brown	46.8	1.14	23.4	21.8	1.5	0.88	2.33	0.27	2.9	0.16	95.8
Green River	49.75	1.09	20.7	23.7	1.63	0.79	2.22	0.30	3.28	0.60	85.3

*Analyses provided by Dr. Alan E. Bland

Table 52

**Catalytic Activity of Low and High Temperature Ashes of
SRC Filter Cake Residue**

Additive	None	Filter Cake Residue		
		800	510	LTA
Ashing Temp., °C	-			
Experiment No.	AP-91	AP-113	AP-115	AP-129
Oil, %	16	35	38	46
Asphaltene, %	48	34	36	29
Preasphaltene, %	13	13	10	8
I.O.M., %	23	18	16	17
Conversion, %	77	82	84	83

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent
1 g Additive

Reaction Condition: Temp. - 450°C
Pressure - 1,250 psig H₂ at 25°C
Time - 60 Minutes
Reactor - Tubing-Bomb

Effect of Low and High Temperature Ashes of Kerr-McGee Ash Concentrate.

The K-M ash concentrate was treated in the same way filter cake residue was and used as additives in coal liquefaction experiments. The ashes of K-M ash concentrate were more reactive than that of filter cake residue (see Table 53). Again, the addition of ashes increased the dissolution of coal and conversion of asphaltenes to oils. The highest oil production once again was obtained with LTA of Kerr-McGee ash concentrate.

Effect of Various Coal Preparation Plant Waste Materials. Various coal preparation plant waste materials were collected from plants processing different eastern and western Kentucky seam coals. A list of these waste materials and their chemical compositions were described in the First Quarterly Technical Progress Report. These materials were oxidized at 500°C for 2 hours in air and then used as additives in coal liquefaction experiments. The results of these experiments are described in Table 54. The addition of these waste materials on the average increased the dissolution of coal and the conversion of asphaltenes to oils. However, no definite relationship between production of oil and the chemical constituents of the various waste materials was found.

Catalytic Activity of Commercial Fe_2O_3 Catalysts. The catalytic activity of reagent grade iron oxide (Fe_2O_3) was studied and reported in the Third Quarterly Technical Progress Report. At that time it was reported that the addition of Fe_2O_3 significantly increased the conversion of coal as well as production of oil; coal conversion and oil production were reported to be 98 and 50 percent, respectively. This tremendous increase in conversion of coal and production of oil showed the potential of Fe_2O_3 as one of the most important candidates for disposable catalyst study.

In order to study the catalytic activity of Fe_2O_3 in detail, the catalyst division of Air Products (Houdry) was contacted and was requested to supply commercially available iron oxide catalyst. They supplied us several iron oxide catalysts supported on either

Table 53

**Catalytic Activity of Low and High Temperature Ashes of
Kerr-McGee Ash Concentrate**

Additive Ashing Temp., °C	None -	K-M Ash Concentrate		
		800	510	LTA
Experiment No.	AP-91 _a	AP-111	AP-112	AP-132
Oil, %	16	41	42	50
Asphaltene, %	48	36	34	31
Preasphaltene, %	13	10	10	8
I.O.M., %	23	13	14	11
Conversion, %	77	87	86	89

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent
1 g Additive

Reaction Condition: Temp. - 450°C
Pressure - 1,250 psig H₂ at 25°C
Time - 60 Minutes
Reactor - Tubing-Bomb

Table 54

Catalytic Activity of Various Coal Preparation Plant Waste Materials in Coal Liquefaction

Coal Preparation Plant Waste from:

Eastern Kentucky Coals

Western Kentucky Coals

Additive	None	BEH-P-C	ICG-P-C	ICG-P-F	AG-P-M	ICF-P-CM	ICH1-P-CM	PMC-P-C
Experiment Number	AP-91	AP-184	AP-185	AP-186	AP-188	AP-189	AP-190	AP-191
Oil, %	16	22	35	38	34	31	38	35
Asphaltene, %	48	33	33	31	32	34	31	33
Preasphaltene, %	13	29	13	15	15	15	13	16
I.O.M., %	23	16	19	16	19	20	18	16
Conversion, %	77	84	81	84	81	80	82	84

Reaction Mixture: 3 g Elkhorn #3 Coal
 6 g Solvent
 1 g Additive (oxidized at 550°C for 2 hours in air)

Reaction Condition: Temp. - 450°C
 Pressure - 1,250 psig H₂ at 25°C
 Time - 60 Min.
 Reactor - Tubing-Bomb

fly ash or silica with varying concentration of iron oxide (either in the pure form or obtained from U.S. Steel). A list of various Fe_2O_3 catalysts supplied by Air Products (Houdry) is given in Table 55. These materials were added to coal liquefaction reaction to study their catalytic activities and the results are shown in Table 56. Increasing the concentration of iron oxide from 25 to 75 percent, changing the source of iron oxide (pure versus obtained from U.S. Steel) and the support (fly ash versus pure silica) and calcining or not calcining did not show any definite trend. Conversion of coal and production of oil were significantly lower in all the cases compared to the ones obtained with reagent grade Fe_2O_3 . The lower activity of these catalyst could be due to inhibition effect of fly ash and silica on the activity of Fe_2O_3 . Fly ashes and silica have already been shown earlier, Tables 46 and 48, to have detrimental effect on coal liquefaction.

Table 55

Chemical Composition of Various Fe₂O₃ Catalysts

<u>Number</u>	<u>Source of Fe₂O₃</u>	<u>Support</u>	<u>Heat Treatment</u>
705x8-5x1	25% Pure	75% Fly Ash	Calcined
813x1-1x4	75% Pure	25% Fly Ash	Calcined
831x1-1	75% Pure	25% Fly Ash	Not Calcined
705x9-3x2	25% U.S. Steel	75% Fly Ash	Calcined
705x9-3	25% U.S. Steel	75% Fly Ash	Not Calcined
814x1-1x12	50% U.S. Steel	50% Fly Ash	Calcined
705x16-1x6	25% U.S. Steel	75% Silica	Calcined
705x16-1	25% U.S. Steel	75% Silica	Not Calcined
814x3-2x2	50% U.S. Steel	50% Silica	Calcined

Table 56

Catalytic Activity of Various Fe₂O₃ Catalysts

Catalyst	705x8-5x1 25% Fe ₂ O ₃ on Fly Ash Calcined	813x1-1x4 75% Fe ₂ O ₃ on Fly Ash Calcined	813x1-1 75% Fe ₂ O ₃ on Fly Ash Not Calcined
Experiment Number	AP-167	AP-165	AP-161
Oil, %	34	29	34
Asphaltene, %	31	33	30
Preasphaltene, %	15	20	17
I.O.M., %	17	18	19
Conversion, %	83	82	81

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent
1 g Catalyst

Reaction Condition: Temp. - 450°C
Time - 60 Minutes
Pressure - 1,250 psig H₂ at 25°C
Reactor - Tubing-Bomb

Table 56
(continued)

Catalytic Activity of Various Fe_2O_3 Catalysts

Catalyst	705x9-3x2 25% U.S. Steel Fe_2O_3 on Fly Ash Calcined	705x9-3 25% U.S. Steel Fe_2O_3 on Fly Ash Not Calcined	814x1-1x12 50% U.S. Steel Fe_2O_3 on Fly Ash Calcined
Experiment Number	AP-175	AP-169	AP-173
Oil, %	31	34	39
Asphaltene, %	32	32	31
Preasphlatene, %	14	13	16
I.O.M., %	23	21	14
Conversion, %	77	79	86

Table 56
(continued)

Catalytic Activity of Various Fe_2O_3 Catalysts

Catalyst	705x16-1x6 25% U.S. Steel Fe_2O_3 on Silica Calcined	705x16-1 25% U.S. Steel Fe_2O_3 on Silica Not Calcined	814x3-2x2 50% U.S. Steel Fe_2O_3 on Silica Calcined
Experiment Number	AP-168	AP-166	AP-174
Oil, %	34	36	40
Asphaltene, %	32	31	31
Preasphlatene, %	13	13	12
I.O.M., %	21	20	17
Conversion, %	79	80	83

Table 57

Comparison of the Catalytic Activity of Iron Oxide,
and Robena Pyrite in Coal Liquefaction

Additive	<u>Fe₂O₃</u>	<u>Robena</u>
Experiment Number	AP-89	AP-81
Surface Area, m ² /g	11.0	0.8
Oil, %	50	39
Asphaltene, %	41	44
Preasphaltene, %	7	7
I.O.M., %	2	10
Conversion, %	98	90

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent
1 g Additive

Reaction Condition: Temp. - 450°C
Pressure - 1,250 psig H₂ at 25°C
Time - 60 Minutes
Reactor - Tubing-Bomb

Effect of In-Situ Sulfiding of Red Mud. The catalytic activity of and sulfided iron oxide in coal liquefaction was found to be slightly less active than the original material. An experiment was then designed to study the effect of in-situ sulfiding of iron oxide in coal liquefaction reaction. Red mud alone and red mud with elemental sulfur were added to the coal liquefaction reaction mixture and studied for their catalytic activity and the results are summarized in Table 58. The original red mud and in-situ sulfided red mud showed almost similar activity within the limits of experimental error. Once again no definite advantage was seen by sulfiding iron oxide outside or in-situ in coal liquefaction reaction.

Effect of Robena Pyrite Particle Size. Two different particle size Robena pyrite -325 and -200 U.S. Mesh were studied for their catalytic activity in coal liquefaction and the results are shown in Table 59. The higher particle size pyrite (-200 mesh) was shown to be slightly less active in improving conversion of coal but seemed to be more active in producing oil than -325 mesh pyrite. The variation in the product distribution was well within the limits of experimental error and hence no definite conclusion could be drawn. More work is presently underway to study the effect of wide variation in particle size of pyrite on coal liquefaction.

Effect of Pyrrhotite/Reduced Pyrite. Robena pyrite (-200 U.S. Mesh) was treated in the PTGR at different reaction temperatures and pressures in the presence of hydrogen for 10 minutes to prepare samples of pyrrhotite/reduced pyrite. The reaction conditions for the hydrogen reduction of the pyrite are listed in Table 60. These samples were then analyzed by x-ray diffraction to determine the form of iron sulfide and all of them were found to be troilite (FeS). The original pyrite and these samples were then tested for their catalytic activity in coal liquefaction and the results are summarized in Table 61. No significant variation in the catalytic activity of pyrite or reduced pyrites was noted. The reduced

Table 58

Effect of In-Situ Sulfiding of Fe_2O_3 on Coal Liquefaction

Additive	Red Mud + Elemental Sulfur	
	<u>Red Mud</u>	
Experiment Number	AP-84,85	AP-135
Oil, %	53	51
Asphaltene, %	33	37
Preasphaltene, %	7	7
I.O.M., %	7	5
Conversion, %	93	95

Reaction Mixture: 3 g Elkhorn #3 Coal
 6 g Solvent
 1 g Additive
 1 g Sulfur

Reaction Condition: Temp. - 450°C
 Pressure - 1,250 psig H_2 at 25°C
 Time - 60 Minutes
 Reactor - Tubing-Bomb

Table 59

Effect of Particle Sizes of Robena Pyrite on Liquefaction of Coal

Additive Experiment Number	-200 Mesh <u>Robena Pyrite</u> AP-131	-325 Mesh <u>Robena Pyrite</u> AP-81
Oil, %	46	39
Asphaltene, %	31	44
Preasphaltene, %	9	7
I.O.M., %	14	10
Conversion, %	86	90

Reaction Mixture: 3 g Elkhorn #3 Coal
 6 g Solvent
 1 g Additive
 1 g Sulfur

Reaction Condition: Temp. - 450°C
 Pressure - 1,250 psig H₂ at 25°C
 Time - 60 Minutes
 Reactor - Tubing-Bomb

Table 60

Reduction of Robena Pyrite (-200 U.S. Mesh) in the PTGR

<u>Sample No.</u>	<u>Temp., °C</u>	<u>Hydrogen</u>		<u>Time, Min.</u>
		<u>Pressure, psig</u>		
CH001	400	1000		10
CH002	450	1000		10
CH003	500	1000		10
CH004	600	1000		10
CH005	450	1500		10
CH006	450	500		10

Charge: 3 g of Robena Pyrite

Table 61

**Catalytic Activity of Robena Pyrite (-200 Mesh)
and Reduced Robena Pyrite (FeS) in Coal Liquefaction**

Additive	Robena Pyrite	Reduced Robena Pyrite					
	(-200 Mesh)	CH001	CH002	CH003	CH004	CH005	CH006
Experiment No.	AP-131	AP-141	AP-142	AP-143	AP-144	AP-145	AP-146
Oil, %	46	41	41	41	42	40	42
Asphaltene, %	31	35	34	31	32	34	34
Preasphaltene, %	9	10	11	11	10	10	10
I.O.M., %	14	14	14	17	16	16	14
Conversion, %	86	86	86	83	84	84	86

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent
1 g Additive

Reaction Condition: Temp. - 450°C
Pressure - 1,250 psig H₂ at 25°C
Time - 60 Minutes
Reactor - Tubing-Bomb

pyrites studied above were all produced by gas medium reduction of Robena pyrite. The liquid medium reduction of Robena pyrite (-325 U.S. Mesh) was carried out in run number CCL-25 as part of the program involving study of catalytic activity of Robena pyrite in solvent hydrogenation. The solid residue from the sample CCL-25-28 was separated by filtration to recover the reduced pyrite. This sample was analyzed by x-ray diffraction and identified as $\text{FeS}_{1.099}$. This sample was then used as an additive in coal liquefaction reaction to study its catalytic activity and the results are tabulated in Table 62. Both reduced pyrite (pyrrhotite) and pyrite were shown to have very similar catalytic activity. Slight differences observed in the product distribution were well within the range of experimental error.

The catalytic activity of reduced pyrite (FeS), pyrite (FeS_2), synthetic pyrite (FeS_2) and pyrrhotite ($\text{FeS}_{1.099}$) in coal liquefaction were shown to be similar. This information lead us to a very important phase in disposable catalyst study. Based on the above data it would be most desirable to use reduced pyrite or pyrrhotite as a catalyst for coal liquefaction reaction instead of pyrite. The use of pyrite would increase the consumption of process hydrogen (hydrogen used to reduce pyrite) and increase the production of hydrogen sulfide gas which has to be scrubbed out resulting in increased capital investment.

Effect of Concentration of Robena Pyrite. The addition of Robena pyrite to coal liquefaction reaction mixture was shown to increase coal conversion and oil production. The concentration of pyrite used in the above experiment was 33 percent by weight of the coal. This was rather high and impractical in a real sense. The concentration of Robena pyrite was varied in coal liquefaction reaction to study its effect and the experimental results are shown in Table 63 and Figure 11. The conversion of coal and production of asphaltene and oil were found to increase with increasing the amount of pyrite added. The increase in conversion of coal and production of oil were very sensitive to addition of pyrite at lower concentration

Table 62

Comparison of the Catalytic Activity of Robena
Pyrite (-325 U.S. Mesh) and Pyrrhotite ($\text{FeS}_{1.099}$) in Coal Liquefaction

Additive	<u>Robena Pyrite</u>	<u>Pyrrhotite ($\text{FeS}_{1.099}$)</u>
Experiment Number	AP-81	AP-96
Oil, %	39	41
Asphaltene, %	44	40
Preasphaltene, %	7	9
I.O.M., %	10	10
Conversion, %	90	90

Reaction Mixture: 3 g Elkhorn #3 Coal
 6 g Solvent
 1 g Additive

Reaction Condition: Temp. - 450°C
 Pressure - 1,250 psig H_2 at 25°C
 Time - 60 Minutes
 Reactor - Tubing-Bomb

Table 63

Effect of Concentration of Robena Pyrite in Coal Liquefaction

Concentration of Pyrite, g	0.0	0.25	0.5	1.0	1.5	2.0
Experiment Number	AP-91	AP-122	AP-125	AP-118	AP-126	AP-128
Oil, %	16	37	46	46	59	62
Asphaltene, %	48	38	33	39	24	26
Preasphalente, %	13	9	7	7	7	6
I.O.M., %	23	16	14	8	10	6
Conversion, %	77	84	86	92	90	94

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent

Reaction Condition: Temp. - 450°C
Pressure - 1,250 psig H₂ at 25°C
Time - 60 Minutes
Reactor - Tubing-Bomb

FIGURE 11
EFFECT OF CONCENTRATION OF ROBENA PYRITE
ON COAL LIQUEFACTION

level. Beyond certain concentration level, for example 0.5g of pyrite, there was no pronounced effect of adding more pyrite to coal liquefaction mixture.

Effect of Concentration of Pyrrhotite ($\text{FeS}_{1.099}$). Table 64 and Figure 12 show the effect of changing concentration of pyrrhotite in coal liquefaction reaction mixture. Like pyrite the conversion of coal and production of oil were found to increase with increasing amounts of pyrrhotite with no pronounced improvement resulting from adding more than 0.25g of pyrrhotite to the reaction mixture.

X-Ray Deffraction Analysis of Added Minerals Before and After the Coal Liquefaction Reaction (Auburn University).

The objective of this work was to analyze various minerals and metallic wastes and identify their basic chemical structure. After using these materials in coal liquefaction reaction, the residue material from coal liquefaction reaction, containing these added catalysts, were again analyzed by x-ray powder diffraction to determine any mineral alteration that occurred during the liquefaction reaction.

The mineral alteration could be of three types; 1. recrystalization, 2. decrystalization, and 3. dehydration. Recrystalization is normally involved with rearrangement of the internal structure of the mineral caused by either heat or pressure or both; for example, transformation of pyrite to pyrrhotite and hematite to magnetite etc. Decrystalization is the disruption of a structure and gives an amorphous product which is difficult to analyze by x-ray diffraction and can be identified only as a reduced intensity of the diffraction peaks. Dehydration is the loss of water without a disruption of the crystal structure. This effect is most commonly observed in clays and zeolites.

Table 64

Effect of Concentration of Pyrrhotite ($\text{FeS}_{1.099}$) on Coal Liquefaction

Concentration of Pyrrhotite, g	0.0	0.1	0.25	1.0
Experiment No.	AP-91	AP-153	AP-140	AP-96
Oil, %	16	25	42	41
Asphaltene, %	48	33	33	40
Preasphaltene, %	13	16	13	9
I.O.M., %	23	26	12	10
Conversion, %	77	74	88	90

Reaction Mixture: 3 g Elkhorn #3 Coal
6 g Solvent

Reaction Condition: Temp. - 450°C
Pressure - 1,250 psig H_2 25°C
Time - 60 Minutes
Reactor - Tubing-Bomb

FIGURE 12
EFFECT OF CONCENTRATION OF PYRRHOTITE ($\text{FeS}_{1.099}$)
ON LIQUEFACTION OF COAL

Experimental Method. The minerals and metallic wastes were analyzed by x-ray powder diffraction method using Phillips x-ray diffractometer. A sample size of 100 mg ground to -200 mesh was mounted on a glass slide as an acetone slurry. The diffraction pattern was corrected for any dilution effect by organic and mineral residues.

Progress. Eleven disposable catalysts analyzed by x-ray powder diffraction before and after the coal liquefaction reaction are shown in a list given in Table 65 of various materials tested and the changes observed. The pyrite was found to form pyrrhotite. No major changes were noted with other minerals. The transformation of alpha Fe_2O_3 to gamma Fe_2O_3 in coal liquefaction reaction was very surprising. It was thought that iron oxide would react with the hydrogen sulfide gas formed during the reaction to produce iron sulfide. More work is needed to confirm the above analysis.

Effect of Minerals and Metal-Containing Wastes on Coal Liquefaction - Continuous Stirred Tank Reactor Study

The third CPDU run (CCL-31) was carried out during the months of July and August. Based on the tubing-bomb runs several minerals and metallic wastes were chosen as specified in the program to test their catalytic activity in CPDU. The objectives of this run were (1) to study the solvent hydrogenation in the absence of catalyst; (2) to study the solvent hydrogenation activity of zinc sulfide, specularite (Fe_2O_3), red mud and flue dust; (3) to study the dissolution behavior of Elkhorn #2 coal; (4) to evaluate the effect of Robena pyrite concentration on liquefaction of Elkhorn #2 and Elkhorn #3 coals; and (5) to test the catalytic activity of zinc sulfide, specularite, red mud and flue dust in the liquefaction of Elkhorn #3 coal. A detailed summary of the operating data of the runs is given in Appendix B. The analytical results of the run CCL-31 will be reported as they become available.

Table 65

X-Ray Diffraction Analyses of Minerals Before and After the
Coal Liquefaction Reaction

<u>Minerals</u>	<u>Original Chemical Form</u>	<u>Chemical Form After Coal Liquefaction Reaction</u>
Robena Pyrite	Major Phase, FeS_2	Pyrrhotite Fe_{1-x}S
Pyrrhotite	Major Phase, $\text{FeS}_{1.099}$	Pyrrhotite Fe_{1-x}S
Fe_2O_3	Fe_2O_3	Fe_2O_3
Red Mud	Major Phase, Fe_2O_3	Amorphous (not detected)
Laclede Fly Ash	ZnO , $(\text{Zn}, \text{Mn}) \text{Fe}_2\text{O}_4$	Unidentified
Rutile	TiO_2	Amorphous (not detected), Anatase
ZnS	Major Phase Sphalerite ZnS	Amorphous, Wurtzite ZnS
Quartz	SiO_2	No Change
Calcite	CaCO_3	No Change
LTA of Elkhorn #3 Coal	Kaolinite, mica, pyrite, gypsum, etc.	Pyrrhotite, anhydrite

Appendix A

Fractional and Elemental Compositions of the CCL-28 Product Liquids

	FR	C	H	O	N	S	Ash	Sum	MW
CCL-28-11 PL		84.16	6.68	3.18	1.37	0.90	3.71	100.00	290
O	67.6	89.52	7.43	1.54	1.92	0.56	-	100.00	208
A	13.5	85.83	6.42	4.30	2.49	0.95	-	100.00	341
P	12.7	83.74	5.46	5.99	2.40	1.38	1.03	100.00	1583
R	6.2	28.53	1.65	5.08	0.77	5.01	63.62	104.66	-
Sum	100.0								
RCV	98.8								
CCL-28-22 PL		83.73	6.55	2.14	1.21	1.17	5.19	100.00	243
O	68.21	89.53	7.30	1.65	0.96	0.56	-	100.00	204
A	14.15	86.19	6.41	4.35	2.20	0.86	-	100.00	342
P	7.56	83.94	5.39	6.03	2.42	1.17	1.04	100.00	1772
R	10.08	18.04	1.26	4.77	0.53	7.65	74.18	106.43	-
Sum	100.0								
RCV	99.44								

Appendix A

(Continued)

	FR	C	H	O	N	S	Ash	Sum	MW
CCL-28-35 PL		75.14	6.12	2.60	1.22	3.58	11.34	100.00	320
O	63.8	88.82	7.70	1.79	1.14	0.54	-	100.00	212
A	13.3	83.99	6.31	6.16	2.26	1.28	-	100.00	698
P	8.7	82.45	5.62	7.49	2.40	1.36	0.68	100.00	1878
R	14.2	12.32	0.80	4.27	0.27	20.37	75.34	113.37	-
Sum	100.0								
RCV	101.00								

Appendix A

(Continued)

	FR	C	H	O	N	S	Ash	Sum	MW
CCL-28-46 PL	-	-	-	-	-	-	-	-	-
O	66.8	89.05	7.71	1.74	1.03	0.47	-	100.00	208
A	11.0	85.39	6.83	4.41	2.42	0.95	-	100.00	557
P	7.1	83.53	5.69	5.76	2.53	1.68	0.81	100.00	1426
R	15.1	11.13	0.81	3.28	0.27	20.65	80.16	116.30	-
Sum	100.00								
RCV	99.57								
CCL-28-56 PL		76.55	6.45	2.73	1.22	3.01	10.03	100.00	253
O	69.09	89.05	7.76	1.49	1.23	0.47	-	100.00	208
A	11.82	85.99	6.40	4.40	2.38	0.83	-	100.00	423
P	5.70	84.11	5.57	5.52	2.66	1.07	-	100.00	1142
R	13.39	10.7	0.75	3.74	0.24	20.01	80.20	115.64	-
Sum	100.00								
RCV	99.86								

Appendix A

(Continued)

	FR	C	H	O	N	S	Ash	Sum	MW
CCL-28-71 PL		79.24	6.64	2.49	1.15	2.44	9.18	100.00	271
O	70.60	89.30	7.73	1.52	1.05	0.40	-	100.00	208
A	10.40	86.69	7.43	3.09	2.22	0.56	-	100.00	498
P	4.70	84.19	5.68	5.37	2.60	0.89	1.27	100.00	1649
R	14.30	15.07	0.97	4.65	0.25	17.66	76.40	115.00	-
Sum	100.00								
RCV	100.00								

PL = Product Liquid

O = Oil

A = Asphaltene

P = Preasphaltene

R = Residue

RCV = Recovery

FR = Solvent Fractions

Appendix B

RUN CCL-31 SUMMARY OF OPERATING DATA

Feed Slurry Designation	Hours on Stream	Balance Period	Mode	Temp., °F	Pressure, psig	Slurry Feed Rate, g/hr.	H ₂ Feed Rate, SLPH	Main Rec. Rate, g/hr.	Product Drum Rate, g/hr.	Conden-Sate Rate, g/hr.	Product Gas Rate, SLPH
Solvent . (550-850 F)	0-9 9-10	0-9 9-10	Line-Out Sample	850 850	2000 2000	1752 1746	218 206	1659 1655	- 1671	29.4 18.4	206 178
Creosote Oil	10-23	Leak in the low pressure side. Changed rupture disc of main receiver.									
Solvent + 10% Robena Pyrite	23-25 25-30 30-31 31-44	10-12 12-13	Line-Out Line-Out	850 850	2000 2000	1897 -	258 -	1893 -	1660 -	- -	170 -
		System pressure increased to 2250 psig. Research control valve problem.									
		Leak in the low pressure side. Unit was shut down to locate the leak.									
	44-54 54-56	13-23 23-24	Line-Out Sample	850 850	2000 2000	1797 1818	236 240	1684 -	1682 1646	7.2 6.5	164 155
	56-64	Moyno pump leak. Problem with Annin valve.									
	64-72 72-73	24-33 33-34	Line-Out Sample	850 850	2000 2000	- 1787	235 246	1765 1972	1722 -	3.2 3.4	192 200
	73-77	No data taken.									
Solvent + 10% Speculite (Fe ₂ O ₃)	77-85 85-86	35-44 44-45	Line-Out Sample	850 850	2000 2000	1722 1652	251 240	- -	1647 1550	8.9 10.4	188 170
Creosote Oil	86-105	B&L pump failure. Annin valve not functioning well. Mayno pump leaking. No data taken.									
Solvent +10% Red Mud	105-113 113-114	45-54 54-55	Line-Out Sample	850 850	2000 2000	1764 1786	240 217	1623 -	1767 1538	26.8 22.0	189 164
	114-115	55-56	Changing batch.								
Solvent + 10% Flue Dust	115-124 124-125	56-65 65-66	Line-Out Sample	850 850	2000 2000	1776 1818	239 235	1784 -	1763 1814	10.0 11.8	185 175
	125-126	66-67	Changing batch								
70% Solvent + 30% Elkhorn #3 Coal	126-139 139-140	67-80 80-81	Line-Out Sample	850 850	2000 2000	1779 1772	332 285	1696 1694	1731 1908	14.2 20.3	228 228
	140-141	81-82	Changing batch.								

Appendix B
(continued)

Feed Slurry Designation	Hours on Stream	Balance Period	Mode	Temp., °F	Pressure, psig	Slurry Feed Rate, g/hr.	H ₂ Feed Rate, SLPH	Main Rec. Rate, g/hr.	Product Drum Rate, g/hr.	Condensate Rate, g/hr.	Product Gas Rate, SLPH
67.5% Solvent + 30% Elkhorn #3 Coal + 2.5% Robena Pyrite	141-151	82-92	Line-Out	850	2000	1725	427	1655	1611	25.5	292
	151-152	92-93	Sample	850	2000	1544	417	2025	1500	29.0	275
Creosote Oil	152-155	93-96	Line-Out	850	2000	1977	382	1690	1600	-	-
	155-156	96-97	Feed pump (B&L) not working properly.								
	156-171	Corrected all the problems.									
	171-172	97-98	Switch back to feed slurry.								
65% Solvent + 30% Elkhorn #3 Coal + 5% Robena Pyrite	172-182	98-108	Line-Out	850	2000	1800	412	1772	1811	37.0	265
	182-183	108-109	Sample	850	2000	1882	426	-	1916	41.1	267
	183-186	109-112	Line-Out	850	2000	1909	380	1850	1880	43.4	244
	186-187	112-113	Sample	850	2000	1953	353	1673	1897	30.2	240
Creosote Oil	187-198	Replaced main receiver rupture disc.									
	198-200	Switch batch.									
70% Solvent + 30% Elkhorn #2 Coal	200-214	113-127	Line-Out	825	2000	1927	332	1769	1903	19.3	257
	214-215	127-128	Sample	825	2000	1633	351	-	2139	18.4	286
	215-225	128-138	Line-Out	850	2000	1819	345	1720	1734	28.6	172
	225-226	138-139	Sample	850	2000	1915	332	-	1879	26.0	202
	226-235	139-148	Line-Out	850	2000	1916	685	1729	1830	-	592
	235-236	148-149	Sample	850	2000	2025	689	-	1822	19.3	560
	236-238	149-151	Switch batch.								
	238-247	151-160	Line-Out	850	2000	1837	427	1758	1748	29.4	323
30% Elkhorn #2 Coal + 2.5% Robena Pyrite	247-248	160-161	Sample	850	2000	1921	408	-	1770	19.2	254
	248-249	Switch batch.									
65% Solvent + 30% Elkhorn #2 Coal + 5% Robena Pyrite	249-262	161-174	Line-Out	850	2000	1851	391	1779	1828	30.0	259
	262-263	174-175	Sample	850	2000	1836	375	1908	1693	34.0	242
	263-264	175-176	Switch batch.								

Appendix B

(continued)

Feed Slurry Designation	Hours on Stream	Balance Period	Mode	Temp., °F	Pressure, psig	Slurry Feed Rate, g/hr.	H ₂ Feed Rate, SLPH	Main Rec. Rate, g/hr.	Product Drum Rate, g/hr.	Condensate Rate, g/hr.	Product Gas Rate, SLPH
60% Solvent + 30% Elkhorn #2 Coal + 10% Robena Pyrite	264-273	176-185	Line-Out	825	2000	1871	406	1829	1839	29.5	210
	273-274	185-186	Sample	825	2000	1852	393	-	1766	31.3	240
	274-283	186-195	Line-Out	850	2000	1859	396	1804	1807	37.5	243
	283-284	195-196	Sample	850	2000	1922	377	1857	1812	41.5	228
	284-293	196-205	Line-Out	850	2000	1817	775	1754	1773	32.3	620
	293-294	205-206	Sample	850	2000	1791	819	-	1703	37.8	596
	294-295	Switch batch.									
	295-297	206-208	Line-Out	No data taken because of failure of feed recycle loop pump.							
	297-315	Replace feed recycle loop pump with Sand Piper pump.									
	315-325	208-218	Line-Out	825	2000	1739	431	1782	1823	28.0	358
	325-326	218-219	Sample	825	2000	1747	432	2043	1961	24.5	335
	326-329	219-223	Line-Out	850	2000	-	-	-	-	-	-
	329-356	Problems with B&L pump and Annin valve. Switch to creosote oil. Fixed charge tank and feed recycle loop pumps.									
	356-366	223-233	Line-Out	850	2000	1838	406	1950	1758	26.8	348
	366-367	233-234	Sample	850	2000	1747	419	-	1749	29.2	372
	367-371	234-238	Flush the system with high flow rate of creosote oil.								
	371-379	Main receiver rupture disc replaced. Blockage of Annin valve cleaned.									
60% Solvent + 30% Elkhorn #3 Coal + Speculite (Fe ₂ O ₃)	379-388	238-247	Line-Out	825	2000	1827	382	1695	1770	42.1	335
	388-389	247-248	Sample	825	2000	1786	386	-	1788	24.0	307
	389-398	248-257	Line-Out	850	2000	1790	420	1863	1720	46.0	339
	398-399	257-258	Sample	850	2000	1859	391	1690	1688	43.0	314
	399-404	Switch batch.									
60% Solvent + 30% Elkhorn #3 Coal + 10% Red Mud	404-413	258-267	Line-Out	825	2000	1758	391	1798	1772	47.2	302
	413-414	267-268	Sample	825	2000	1873	426	-	1731	53.3	312
	414-423	268-277	Line-Out	850	2000	1797	416	1798	1742	50.0	315
	423-424	277-278	Sample	850	2000	1810	423	-	1687	57.3	318
	424-425	Switch batch.									

Appendix B

(continued)

<u>Feed Slurry Designation</u>	<u>Hours on Stream</u>	<u>Balance Period</u>	<u>Mode</u>	<u>Temp., °F</u>	<u>Pressure, psig</u>	<u>Slurry Feed Rate, g/hr.</u>	<u>H₂ Feed Rate, SLPH</u>	<u>Main Rec. Rate, g/hr.</u>	<u>Product Drum Rate, g/hr.</u>	<u>Conden- Sate. Rate, g/hr.</u>	<u>Product Gas Rate, SLPH</u>
60% Solvent + 30% Elkhorn #3 Coal + 10% Flue Dust	426-428	278-281	Line-Out	825	2000	1774	420	1565	1610	-	383
	428-491	Problems with Annin valve. Back pressure regulator failed.									
	491-510	281-300	Line-Out	825	2000	1898	398	1872	1865	36.0	264
	510-511	300-301	Sample	825	2000	1953	421	-	1860	37.0	260
	511-521	301-311	Line-Out	850	2000	1840	412	1817	1794	41.0	264
	521-522	311-312	Sample	850	2000	1915	412	-	1786	42.8	250

Appendix C

Calculation of Reaction Rate Constants

The reaction rate constants for conversion of asphaltene and preasphaltene were calculated assuming sequential reaction, for example,

where k_c , k_p , and k_a are first-order rate constants for the conversion of coal, preasphaltene and asphaltene, respectively. The rate expression could be written as follows:

$$k_c C_i t = C_i - C_o \quad (C-1)$$

$$k_c C_o t - k_p P_o t = P_o - P_i \quad (C-2)$$

$$k_p P_o t - k_a A_o t = A_o - A_i \quad (C-3)$$

$$\text{and} \quad k_a A_o t = O_o - O_i \quad (C-4)$$

where t = nominal residence time, hr.

C = concentration of coal, g/hr.

P = concentration of preasphaltene, g/hr.

A = concentration of asphaltene, g/hr.

O = concentration of oil, g/hr.

and subscript i and o refer to inlet and outlet, respectively.

Rearranging the equations C-1 to C-4, we get

$$k_a = \frac{O_o - O_i}{A_o t} \quad (C-5)$$

$$k_p = \frac{(A_o - A_i) + (O_o - O_i)}{P_o t} \quad (C-6)$$

C-1

Equations C-5 and C-6 were used to calculate the first-order reaction rate constants for the conversion of asphaltene and preasphaltene.