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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 September 1—November 30, 1979

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U. S. DEPARTMENT OF ENERGY

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ABSTRACT

This report describes work done in the first quarter of a study of the role of coal minerals and by-product metallic wastes in coal liquefaction. Samples of Elkhorn #3 coal, SRC-II Fuel Oil Blend, Robena pyrite and magnetite, and various other minerals were acquired. SRC-II Fuel Oil Blend was distilled to obtain the 550°F+ fraction which will be used for coal liquefaction runs. The thermal stability of pyrite and other minerals was evaluated by thermal gravimetric analysis (TGA) in the presence of helium and hydrogen gases. Magnetite and zinc flue dusts (high and low zinc content) were found to be thermally stable in the inert atmosphere. Stoichiometric reduction of magnetite with hydrogen was obtained. Zinc flue dusts lost a maximum of 20% weight in the presence of hydrogen. Fly ash samples lost a maximum of 8% weight in the presence of helium and hydrogen gases. Stoichiometric reduction of Robena pyrite was observed both in helium and hydrogen gases. A pressurized thermal gravimetric reactor (PTGR) was used to determine the reactivity of the different minerals. The reduction of pyrite in the PTGR increased linearly with temperature, but the influence of hydrogen pressure was insignificant. The pyrolysis of pyrite was found to be an endothermic process, whereas oxidation of pyrite was exothermic. In batch autoclave tests, the Elkhorn #3 coal with 13.35% ash had 87% coal dissolution at 410°C and 1250 psig hydrogen pressure (at 25°C). Pyrite and several other minerals showed little improvement in naphthalene hydrogenation activity, whereas treated pyrite and pyrrhotite significantly improved this hydrogenation activity.

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 catalyst. The research program is divided into six major tasks with several subtasks within each area. An outline of the program is given below.

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

TECHNICAL PROGRESS

Task 1 Feedstock Acquisition, Preparation and Characterization

Task 1.1 Coal Feedstocks

Four drums of Elkhorn No. 3 coal from Floyd County, Kentucky, were received and sieved to -150 U.S. Mesh. Low-ash Elkhorn No. 3 coal (as reported by Pennsylvania State University Coal Data Bank) was chosen in order to minimize the baseline concentration of minerals, thereby increasing the sensitivity of the system to the effect of added materials. A sample of this coal was submitted for elemental and ash analyses and the results will be reported as they become available.

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

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

Progress - Samples of various minerals, metallic wastes, and various coal preparation plant refuse materials were received for preparation and characterization. The list of the samples along with their suppliers is given in Table 1. Pyrite and magnetite samples as received were dried at 110°C in nitrogen to determine moisture contents. The pyrite and magnetite samples were found to contain 14.5 and 6.3% moisture, respectively. Dried samples of pyrite and magnetite were sieved to different particle sizes and the different fractions were submitted for elemental, emission spectroscopy and x-ray diffraction analyses to determine whether the pyrite and magnetite contents were enriched within specific particle ranges. Screen analyses of the pyrite and magnetite samples are shown in Tables 2 and 3. The concentration of iron and the distribution of sulfur in the various fractions of the pyrite and magnetite samples

TABLE 1

Suppliers of Various Minerals and Metal
Containing By-Product Samples

Minerals

Pyrite	U. S. Steel Corporation Robena Mine Angelica, PA
Magnetite	U. S. Steel Corporation
Albanian Chrome Ore Concentrates	Interlake, Inc. Beverly, Ohio
Kaolinite ⁺ [Al ₄ Si ₄ O ₁₀ (OH) ₈]	Burgess Pigment Company P.O. Box 349 Sandersville, GA
Montmorillonite ⁺ [Al ₂ Si ₄ O ₁₀ (OH) ₂]	Georgia Kaolin Company 433 N. Broad Street Elizabeth, NJ
Apatite ⁺	Stauffer Chemical Company Westport, CT
Ilmenite ⁺ [CaPO ₄]	Pesses Company 296505 Hall St. & Cochran Solon, OH
Zircon ⁺ [ZrSiO ₄]	Chemalloy P. O. Box 350 Bryn Mawr, PA
Rutile ⁺ [TiO ₂]	Pesses Company
Gypsum ⁺ [CaSO ₄ ·2H ₂ O]	C. A. Wagner Philadelphia, PA
Feldspar ⁺ [KAlSi ₃ O ₈]	Feldspar Corporation Spruce Pine, NC
Lime ⁺ [CaO]	Pfizer Minerals Chicago, IL
Red Mud	E. I. Feld U. S. Bureau of Mines Tuscalloosa, AL

TABLE 1
(continued)

Coal Preparation Plant Refuse Materials

BEH-P-C*	Beth-Elkhorn
ICG-P-C*	Island Creek
ICG-P-F*	Island Creek
AG-P-M*	Amax
ICG-P-CM*	Island Creek
CGHI-P-CM*	Island Creek
PMC-P-C*	Pittsburg and Midway

Metal Containing By-Product Samples

Zinc Flue Dusts (low zinc and high zinc content)	Laclede Flue Dust Courtesy Dave Taschler Air Products and Chemicals, Inc. Greenville, PA
Copperas [FeSO ₄ ·7H ₂ O]	Textile Chemical Company Reading, PA
Phosphate Slime	E. I. Field
Brown Fly and Bottom Ashes*	Kentucky Utilities
Green River Fly and Bottom Ashes* (blend and high)	Kentucky Utilities
Paradise Fly and Bottom Ashes*	TVA

*Samples were supplied by Dr. Alan E. Bland of the Institute of Mining and Minerals, University of Kentucky, Lexington, Kentucky.

+Samples were supplied by Dr. James Clinton of Chemical Engineering Department, Auburn University, Auburn, Alabama

TABLE 2
Screen Analysis of Pyrite Sample

<u>Fractions</u> <u>U.S. Mesh</u>	<u>Weight %</u>
+40	8.67
40 x 80	40.19
80 x 140	35.69
140 x 220	10.81
-200	<u>4.64</u>
Total	<u>100.00</u>

TABLE 3

Screen Analysis of Magnetite Sample

<u>Fractions</u> <u>U.S. Mesh</u>	<u>Weight %</u>
+40	0.93
40 x 80	7.31
80 x 140	25.69
140 x 200	26.32
-200	<u>39.75</u>
Total	<u>100.00</u>

are given in Tables 4 and 5. Insignificant variations in total sulfur distribution in the various fractions of pyrite sample were observed with the exception of -200 mesh fraction. Similarly, the variation in sulfur distribution in the various fractions of the magnetite sample was insignificant. The various elements present in the pyrite and magnetite samples were determined by emission spectroscopy and are given in Tables 6 and 7.

The chemical form of major and minor elements present in the pyrite and magnetite samples (-200 mesh) will be determined by x-ray diffraction and the results will be reported as they become available.

The major portion of the pyrite sample was sent to Jet Pulverizer Company for grinding in an inert atmosphere (nitrogen, 99.9% -325 U.S. Mesh). The ground pyrite was returned to Air Products and placed in storage. This material will be used in future runs. Two additional 5 gallon drums of pyrite were requested from U.S. Steel's Robena Mine.

Elemental analyses of the two zinc flue dust samples (low zinc and high zinc content) are given in Table 8. The moisture contents of the low zinc and high zinc samples as received were found to be 0.39 and 0.33%, respectively. The chemical analyses of the copperas and chrome ore are given in Tables 9 and 10.

Detailed chemical analyses of the fly ash and bottom ash samples are given in Tables 11 and 12. Also, the chemical analyses of the coal preparation plant refuse materials are summarized in Table 13.

Chemical analyses of kaolinite, montmorillonite, zircon, gypsum, feldspar, and lime are summarized in Tables 14, 15, 16, 17, 18, and 19, respectively.

TABLE 4

Iron and Sulfur Distribution in the
Different Fractions of Pyrite Sample

<u>Fractions U.S. Mesh</u>	<u>Fe, Wt.%</u>	<u>Total Sulfur Wt.%</u>
+40	42.5	42.8
40 x 80	43.7	44.3
80 x 140	41.1	43.7
140 x 200	48.8	47.0
-200	50.6	35.8

TABLE 5

Iron and Sulfur Distribution in the
Different Fractions of Magnetite Sample

<u>Fractions U.S. Mesh</u>	<u>Fe, Wt.%</u>	<u>Sulfur</u>	
		<u>Pyritic, Wt.%</u>	<u>Sulfate, Wt.%</u>
40 x 80	60.3	0.39	0.09
80 x 140	63.4	0.29	0.04
140 x 200	74.6	0.32	0.04
-200	67.2	0.22	0.04

TABLE 6

Emission Spectrographic Analysis of Pyrite

<u>Fractions U.S. Mesh</u>	<u>Major Elements Greater than 1.0%</u>	<u>Minor Elements 0.01 - 1.0%</u>	<u>Trace Elements Less Than 0.01%</u>
+40	Fe	Al, Si, Ca, Na, Mn	Cr, Sr, Pb, Co, Mg, Cu, Ti, V, Ni
40 x 80	Fe	"	"
80 x 140	Fe	"	"
140 x 200	Fe	"	"
-200	Fe	Al, Si, Ca, Na, Mn, V, Ti, Cr	Sr, Pb, Co, Mg, Mo, Cu, Ni

TABLE 7

Emission Spectrographic Analysis of Magnetite

<u>Fractions</u> <u>U.S. Mesh</u>	<u>Major Elements</u>	<u>Minor Elements</u>	<u>Trace Elements</u>
40 x 80	Fe, Al	Si, Mg, V, Na, Ti, Ca, Mn, Cr	Mo, Cu, Ni, Co, Sr
80 x 140	"	"	"
140 x 200	"	"	"
-200	"	"	"

TABLE 8

Elemental Analyses* of Zinc Flue Dust Samples

<u>Elements</u>	<u>Low Zinc Sample, wt.%</u>	<u>High Zinc Sample, wt.%</u>
Al	0.3	0.35
Ca	5.0	4.8
Zn	11.6	33.6
Cu	0.18	0.17
Fe	32.1	22.5
Mg	2.3	1.41
Mn	4.8	3.0
Na	0.5	0.65
Pb	1.0	1.6
0 (by difference)	<u>42.1</u>	<u>31.9</u>
Total	100	100

*Analyses provided by Metals Recovery R&D
Air Products and Chemicals, Inc.
Greenville, PA

TABLE 9

Chemical Analysis* of Copperas (Ferrous Sulfate)

	<u>Weight %</u>
Ferrous Sulfate, FeSO_4	53.78
Iron, Fe_2O_3	0.06
Titanium, TiO_2	0.33
Magnesium Sulfate, MgSO_4	1.80
Copper, Cu	0.0004
Lead, Pb	0.0005
Water Insoluble Matter	0.28
Water of Crystallization	43.28

*Analysis provided by Quality Chemicals, Ltd.
Baltimore, Maryland

TABLE 10

Chemical Analysis* of Albanian Chrome Ore Concentrates

	<u>Weight %</u>
Chromic Oxide	49.45
Ferric Oxide	14.81
Silica	6.38
Alumina	9.23
Calcium Oxide	0.16
Magnesia	19.30
Phosphorus	0.002
Sulfur	0.005

* Analysis provided by Interlake, Inc.
Beverly, Ohio

TABLE 11
Chemical Analyses of the Fly Ash Samples

Sample	Weight %									High Temp. Ash	
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Sulfur		Moisture
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	-	96.3
16 Green River											
High	40.9	0.91	16.8	32.3	5.4	0.65	1.84	0.32	0.4	0.12	90.7
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.

TABLE 12
Chemical Analyses of the Bottom Ash Samples

Sample	Weight %									High Temp. Ash	
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Sulfur		Moisture
Brown	46.8	1.14	23.4	21.8	1.5	0.88	2.33	0.27	2.9	0.16	95.8
17 Paradise	49.8	0.93	19.8	22.6	4.01	0.86	2.24	0.38	0.11	0.04	100.8
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 13

Analyses of Coal Preparation Plant Refuse Material Samples

	<u>BEH-P-C</u>	<u>ICG-P-C</u>	<u>ICG-P-F</u>	<u>AG-D-M</u>	<u>ICF-P-CM</u>	<u>ICHI-P-CM</u>	<u>PMC-P-C</u>
Seam Source	100% Elkhorn #3	100% Elkhorn #3	100% Elkhorn #3	51% KY#11 28% Ky#13 22% Ky#12	100% KY #11	100% KY #9	53% Ky#14 47% KY#9
Volatile Matter and Fixed Carbon, wt.%	33.2	26.5	61.2	27.14	22.6	39.2	40.9
Ash, wt.%	66.8	73.5	38.8	72.9	77.4	60.81	59.10
∞ Sulfur, wt.%	3.12	8.86	3.95	6.09	8.53	9.59	12.78
<u>Major Oxides in Ash, wt.%</u>							
SiO ₂	57.3	53.4	49.2	54.0	48.3	47.8	43.0
TiO ₂	1.22	1.35	1.22	1.05	1.06	0.80	0.86
Al ₂ O ₃	23.86	21.71	23.5	20.21	19.2	15.75	17.7
Fe ₂ O ₃	10.31	18.71	16.1	15.0	26.5	27.3	23.50
MgO	1.66	1.12	1.83	1.01	0.70	1.91	1.21
CaO	0.46	0.44	2.65	2.57	1.91	2.31	3.07
K ₂ O	3.73	3.52	4.53	2.65	1.97	3.10	3.03

* Analyses provided by Dr. Alan E. Bland

TABLE 14

Chemical Analysis of Kaolinite (Burgess #10)

	<u>Weight %</u>
SiO ₂	44.8-45.3
Al ₂ O ₃	37.5-39.7
Iron Oxide	Trace
TiO ₂	1.35-2.27
Ignition Loss	13.7-14.1
Particle Size	0.5 microns

TABLE 15

Chemical Analyses of Montmorillonite Samples

	<u>Weight %</u>		
	<u>Mineral Colloid B. P.</u>	<u>Thixgel H₃</u>	<u>Hydride Px</u>
SiO ₂	55.66	64.8	45.3
Al ₂ O ₃	24.4	17.5	38.38
MgO	2.72	2.65	0.25
Fe ₂ O ₃	3.68	3.07	0.3
K ₂ O	0.21	7.01	0.4
Na ₂ O	2.62	2.75	0.27
CaO	0.72	3.12	0.5
TiO ₂	0.20	-	1.44

TABLE 16

Chemical Analyses of Zircon Samples

	<u>Weight %</u>	
	<u>Zircon 325 Mesh</u>	<u>Zircon Concentrates</u>
SiO_2	32.47	32.5
TiO_2	0.20	0.22
ZrO_2	66.61	66.65
Al_2O_3	0.30	0.31

TABLE 17

Chemical Analysis of Gypsum

	<u>Weight %</u>
CaSO_4	2.84
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	94.6
Combined H_2O	19.8
R_2O_3	0.33
SiO_2 and Insolubles	1.3
<u>Elements</u>	
Ca	23.2
S	18.8
O	54.6
H	2.3
Average Particle Size	10 microns

TABLE 18

Chemical Analyses of Two Feldspar Samples

	<u>F-20, wt.%</u>	<u>NC-4, wt.%</u>
SiO_2	68.0	68.15
Al_2O_3	19.0	18.88
Fe_2O_3	0.075	0.067
CaO	1.85	1.60
MgO	Trace	Trace
K_2O	3.75	4.50
Na_2O	7.15	6.70

TABLE 19

Chemical Analysis of Lime

	<u>Weight %</u>
CaO	94.0
MgO	0.7
SiO ₂	1.8
Al ₂ O ₃	0.4
Fe ₂ O ₃	0.1

Task 1.3 Process Solvent Sample

Progress - Twelve drums of SRC-II Fuel Oil Blend were received from The Pittsburg and Midway Coal Mining Company (PAMCO) Solvent Refined Coal Pilot Plant. The analyses of the SRC-II Fuel Oil Blend as supplied by PAMCO are given in Table 20. The Fuel Oil Blend was reported (Table 20) to have approximately 20% by weight 550°F+ fraction. Four drums of SRC-II Fuel Oil Blend were distilled in the 125 gallon batch vacuum distillation unit. The fuel oil blend was cut into two fractions--initial temperature to 550°F (obtained as overhead product) and 550°F+ (obtained as bottoms). The conditions and material balance of the distillation are given in Table 21. The 550°F+ fraction was stored at room temperature. A sample of this 550°F+ fraction was submitted for detailed analyses and the results will be reported as they become available. The distillation of the remaining eight drums is in progress.

Task 2.0 Thermal Behavior of the Minerals and Metallic Wastes

Objective - The objective of this subtask is to evaluate the stability of the minerals and metallic wastes at the coal liquefaction reaction conditions. The thermal stability will be evaluated by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) in the presence of inert helium gas. The reactivity of the material with hydrogen will be evaluated in the TGA at 1 atm and in the pressurized thermal gravimetric reactor (PTGR) at higher hydrogen pressures. See Appendix I for the design and operation of the PTGR.

Analyses - Thermal gravimetric analyses were run from room temperature to 600°C under flowing helium and hydrogen gases using Perkin-Elmer TGS-1 and DuPont 990 Thermal gravimetric analyzers. A Premco Model 50 thermal analyzer is used for DTA.

TABLE 20

Analyses of the SRC II Fuel Oil Blend *

Sp. Gravity 60/60°F	0.999	% Pyridine Insolubles	0.02
°API @ 60°F	10.14	% Conradson Carbon	0.34
Viscosity @ 100°F, cSt	4.527	% Ash	0.02
@ 210°F, cSt	1.289	% Water	trace
Pour Point, °F	-55	% Carbon	86.21
Flash Point, °F ASTM D93	160	% Hydrogen	8.64
Btu/lb	17590	% Nitrogen	0.95
Coal Tar Acid, ml/100 g	25.9	% Sulfur	0.21
		% Oxygen	3.99

<u>Distillation</u>	<u>ASTM D1160</u>	<u>ASTM D86</u>
Effective Pressure	2 mm Hg	760 mm Hg
	°F	°F
I.B.P.	---	338
5%	138	398
10%	145	412
20%	155	431
30%	168	445
40%	180	463
50%	191	480
60%	205	498
70%	221	523
80%	254	563
90%	327	669
95%	383	---
E.P.	455	700
Recovery, %	98.5	93
Residue, %	1.5	6
Lost, %	0	1

(550°F @ 77%)

*Analysis provided by Mr. R. E. Perrussel of the Pittsburg & Midway Coal Mining Co., DuPont, Washington.

TABLE 21

Distillation of SRC II Fuel Oil Blend
Conditions of the Vacuum Distillation

No. of theoretical plates	15-20
Reflux Ratio	10-1
Pressure	100 mmHg

This material was charged to the still using pressurized N₂ and the vacuum during distillation was maintained by a controlled N₂ bleed.

Material Balance:

Total Charge/Batch	=	903 lbs.
Overhead Product (550°F-)	=	672 lbs.
Bottom Product (550°F+)	=	221 lbs.
Total Recovery	=	893 lbs/98.9%
Bottom Product (550°F+)	=	24.5% of the total charge

Magnetite - The thermogram for magnetite in the presence of flowing helium is shown in Figure 1. Negligible weight loss was observed suggesting that magnetite is thermally stable up to 600°C under inert atmosphere.

The thermogram for magnetite in the presence of flowing hydrogen is also shown in Figure 1. Magnetite began losing weight (reduction of magnetite) at around 350°C; the rate of weight reduction reached its maximum at around 450°C. The reaction of magnetite with hydrogen (1) is given in Eqn. 1.

The overall weight loss at 600°C was 24%. Stoichiometrically, complete reduction of pure magnetite (Fe_3O_4) results in 27.6% weight reduction. The actual weight loss and the theoretical weight loss correspond very well (providing the impurities in the magnetite sample are accounted for in the calculation) suggesting that complete reduction of magnetite is achieved at 600°C.

Fine Flue Dust - The thermograms of low zinc and high zinc flue dust samples under flowing helium gas are shown in Figures 2 and 3. As in the case of magnetite, these two materials are thermally stable in the presence of inert gas; i.e., no weight loss upon heating in the presence of inert atmosphere.

The thermograms of low zinc and high zinc flue dust samples under flowing hydrogen are also presented in Figures 2 and 3. Both flue dusts started losing weight (reduction of flue dust) at around 350°C and continued to do so with the increase in temperature. The total reduction of flue dust samples was not achieved during the heating period. The overall weight losses for low zinc and high zinc materials at 600°C were 14.5 and 12.5%, respectively.

FIGURE 1
TGA OF MAGNETITE IN THE PRESENCE OF
HYDROGEN AND HELIUM GASES

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FIGURE 2
TGA OF ZINC FLUE DUST (LOW ZINC) IN THE PRESENCE
OF HELIUM AND HYDROGEN GASES

FIGURE 3
TGA OF ZINC FLUE DUST (HIGH ZINC) IN THE PRESENCE
OF HYDROGEN AND HELIUM GASES

The two zinc flue dust samples were reduced at 450°C under 1000 psig hydrogen pressure for 10 minutes in the PTGR (fast heating) to study the reduction of flue dusts. The low zinc and high zinc flue dust samples lost 6.3 and 4.7% weight, respectively. The corresponding weight losses (at 450°C) under flowing hydrogen (1 atm pressure) were 1.5 and 3%. The differences in the weight loss under flowing hydrogen and under pressurized hydrogen could be due to differences in pressure and heating time. The samples of zinc flue dusts before and after reduction in the PTGR will be analyzed by x-ray diffraction to determine the chemical transformations. Also, the analyses of the various products (gas and condensed liquid) obtained during reduction of the flue dust samples in the PTGR are given in Table 22. Notice that the major product of the hydrogen reduction was water; there was more than 100% error in analyzing the water content in the reaction product. Efforts are underway to locate the source of error

Green River (Blend) Fly Ash - Figure 4 shows the thermograms of Green River (blend) fly ash under flowing helium and hydrogen gases. The fly ash was found to be thermally stable under inert atmosphere (helium); whereas it started losing weight at around 300°C under flowing hydrogen. The weight loss at 600°C was observed to be 6.2%.

Green River (High) Fly Ash - The Green River (high) fly ash started losing weight at around 350°C both under flowing helium and hydrogen gases (see Figure 5). The weight losses under flowing helium and hydrogen gases at 600°C were observed to be 1.0 and 3.0%, respectively.

Brown Fly Ash - The thermograms for Brown fly ash under flowing helium and hydrogen gases are shown in Figure 6. The fly ash started losing weight at around 300°C both in helium and hydrogen gases. The weight losses under flowing helium and hydrogen gases at 600°C were found to be 1.0 and 2.3%, respectively.

TABLE 22

Reduction of Zinc Flue Dusts in PTGR

	<u>Low Zinc</u>	<u>High Zinc</u>
Temp., °C	450	450
Pressure, psig	1000	1000
Initial Weight, g	3.0	3.0
Final Weight, g	2.81	2.86
Weight Loss, g	0.19	0.14
Weight Loss, %	6.33	4.67
Gas Analyses, g water	0.02	0.0468
Liquid Analysis,* g, water	0.269	0.2845
Liquid Analysis,* g, sulfur	0.0005	0.0002
Total Recovered Product, g	0.2895	0.3315
% Recovery of Lost Weight	152.0	237.0

*Condensed in the ice trap.

FIGURE 4
TGA OF GREEN RIVER (BLEND) FLY ASH IN THE PRESENCE
OF HELIUM AND HYDROGEN GASES

FIGURE 5
TGA OF GREEN RIVER (HIGH) FLY ASH IN THE PRESENCE
OF HELIUM AND HYDROGEN GASES

FIGURE 6
TGA OF BROWN FLY ASH IN THE PRESENCE
OF HELIUM AND HYDROGEN GASES

Paradise Fly Ash - The Paradise fly ash started losing weight at around 250°C both under flowing helium and hydrogen gases (see Figure 7). The total weight losses under flowing helium and hydrogen gases at 600°C were 2.0 and 7.3%, respectively.

Copperas (Ferrous Sulfate) - The thermogram of copperas under inert atmosphere is shown in Figure 8. Notice that the sample started losing water of crystallization at around 40°C. The rate of water removal reached its maximum value at around 120°C, dropped substantially above 200°C, once again started to increase at about 500°C, and continued to do so with the increase in temperature. The water of crystallization present in the copperas (43.28%, see Table 9) was removed at 635°C. The sample was found to lose more than 44% weight at and above 640°C. This additional loss of weight (in addition to water of crystallization) at the higher temperature was due to decomposition of FeSO_4 to sulfur dioxide, sulfur trioxide, basic iron sulfate ($\text{Fe}_2(\text{SO}_4)_3$), and other products (2).

The thermogram of copperas under flowing hydrogen is shown in Figure 9. The water of crystallization (43.28%) was removed at around 470°C, considerably lower than in the case of pyrolysis. The decomposition of FeSO_4 was apparently completed at around 520°C (insignificant change in weight above 520°C). The copperas will be reduced in the PTGR to determine the weight loss and also the reduction products.

Pyrite - The pyrolysis of pyrite begins at about 500°C (3) and proceeds according to the equation:

The thermogram of pyrite under flowing helium gas is shown in Figure 10. Pyrite samples of different particle sizes were found to start losing weight at around 400°C. The samples continued to lose weight until a temperature of 640°C was reached, after which the change in weight was insignificant. Similar pyrolysis behavior of pyrite was observed by Richardson (4). It can be seen that pyrite of particle

FIGURE 7
TGA OF PARADISE FLY ASH IN THE PRESENCE
OF HELIUM AND HYDROGEN GASES

FIGURE 8
TGA OF COPPERAS IN THE PRESENCE
OF HELIUM GAS

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FIGURE 9
TGA OF COPPERAS IN THE PRESENCE
OF HYDROGEN GAS

FIGURE 10
TGA OF IRON PYRITE (MINERAL GRADE)
IN THE PRESENCE OF He GAS

sizes +40, 40 x 80, and 140 x 200 mesh showed very similar thermograms. Also, the maximum weight loss for all three samples was between 22 to 23%, which is nearly stoichiometric according to Eqn. 2. The pyrite sample of particle size -200 mesh gave an entirely different thermogram compared to the other particle size ranges. This sample started losing weight (pyrolysis) at around 400°C (same as other three particle size samples), but lost weight faster than the other three samples. Also, the maximum weight loss was found to be only 18.5% compared to 22 to 23% for others. The concentrations of total sulfur in the pyrite samples of different particle sizes are almost the same (see Table 4) except for -200 mesh fraction. The +40, 40 x 80, and 140 x 200 mesh fractions have more available sulfur for thermal distillation than -200 mesh fraction, and hence can be the cause of the above differences in weight loss. The compositions of impurities and iron compounds other than FeS_2 in the various fractions are being examined to determine if they are the cause of these differences.

Reduction of pyrite with hydrogen was reported in the literature to take place at about 500°C (3) and to proceed according to Eqn. 3.

A constant weight loss of 24% was reported in the literature at temperatures up to 500°C with no further reduction to Fe (3).

Figure 11 presents the thermogram for pyrite in the presence of flowing hydrogen. The pyrite sample started losing weight at around 320°C with maximum reduction (close to 20.0%) attained at around 600°C. Comparing the pyrolysis and reduction of pyrite (Figures 10 and 11), it was observed that pyrite was more temperature sensitive to hydrogen reduction than to pyrolysis; initial pyrite decomposition temperature was 320°C in hydrogen reduction compared to 380°C in pyrolysis. Also, the overall weight reduction was completed at about 600°C in the presence of hydrogen compared to 650°C in pyrolysis. The overall weight loss in both cases was of the same order of magnitude.

FIGURE 11
TGA OF PYRITE IN THE
PRESENCE OF HYDROGEN GAS

The reduction of -200 mesh pyrite in the presence of hydrogen gas was studied in detail in the PTGR. The PTGR was heated to the required reaction temperature and pressurized with hydrogen gas to the reaction pressure before the sample was lowered into the reaction zone. Fast heating of the sample was attained and the reduced sample was removed after the prescribed reaction time. The gaseous products were collected in a stainless steel bomb after passing them through an ice trap. The contents of the ice trap and gas products were analyzed to determine the nature of the product and to check the material balance.

Table 23 and Figure 12 show the variation in weight reduction of pyrite and the products obtained with temperature, at a constant hydrogen pressure of 1000 psig. The weight of pyrite was found to decrease linearly with the increase in reaction temperature (see Figure 12). Table 23 shows the substantial differences between the overall weight loss and the overall weight of the product recovered. Problems in obtaining a suitable material balance were noted earlier in this report. The reduced pyrite samples were submitted for total sulfur analyses to determine the sulfur removal. The sulfur removal and sulfur recovered in the product will be compared to determine the source of error in material balance as soon as the sulfur data become available.

Table 24 and Figure 13 show the variation of hydrogen pressure on pyrite reduction. Insignificant variation in weight reduction of pyrite with hydrogen pressure was observed. The reduced pyrite samples will be analyzed by x-ray diffraction to determine the chemical transformation of pyrite. Also, a portion of the reduced pyrite samples were sent to Auburn University to evaluate the effect of reduced pyrite additive on coal liquefaction.

The differential thermal analyses (DTA) of pyrite samples in helium and air are shown in Figures 15 and 16, respectively. The DTA in the presence of helium showed one minor endotherm at 87°C and one major endotherm at 620°C. The endotherm at 87°C could be due to

TABLE 23

Effect of Temperature on Pyrite (-200 Mesh) Reduction
 Reaction Time = 10 Minutes, Pressure = 1000 psig H₂

Temp. °C	Initial Weight g	Final Weight g	Weight g	Loss %	N ₂	H ₂ S	Gas Analyses, g		CO	Liquid Analyses*, g	Total Recovered Product g	% Recovery of the Lost Wt.
							H ₂ O	CH ₄		Sulfur		
400	3.0	2.50	0.50	16.67	0.0081	0.033	0.0572	-	-	0.0259	0.1242	24.8
450	3.0	2.48	0.52	17.33	0.005	0.0654	0.0289	-	-	0.0095	0.0434	8.35
500	3.0	2.43	0.57	19.0	0.021	0.0785	0.0537	-	-	0.0136	0.0883	15.5
600	3.0	2.44	0.56	18.67	0.0011	0.0595	0.0272	0.0063	0.0024	0.0133	0.1098	19.6

*Condensed in the ice trap.

FIGURE 12
EFFECT OF REACTION TEMPERATURE
ON PYRITE (-200 MESH) REDUCTION

TABLE 24

Effect of Hydrogen Pressure on Pyrite (-200 Mesh) Reduction

Reaction Time = 10 Minutes, Pressure = 1000 psig H_2

Press. 1000 psig	Initial Weight g	Final Weight g	Weight g	Loss %	N_2	H_2S	Gas Analysis, g		CO	Liquid	Analysis*, g	Total Recovered Product, g	% Recovery of the Lost Wt.
							H_2O	CH_4			Sulfur		
500	3.0	2.49	0.51	17.0	-	0.1851	0.0483	-	-		0.0006	0.2394	47.0
47 1000	3.0	2.48	0.52	17.33	0.005	0.0654	0.0289	-	-		0.0095	0.1088	21.0
1500	3.0	2.50	0.50	16.67	-	-	-	-	-		0.0009	-	-

*Condensed in the ice trap.

FIGURE 13
EFFECT OF REACTION PRESSURE ON
ON PYRITE (-200 MESH) REDUCTION

FIGURE 15
DTA OF PYRITE IN THE PRESENCE OF HELIUM

FIGURE 16
DTA OF PYRITE IN THE PRESENCE OF AIR

initial phase change, but the endotherm at 620°C is mainly due to reduction of pyrite. Contrary to the two endotherms in the presence of helium, air oxidation of pyrite showed one minor endotherm at 90°C and one major exotherm at 425°C. The exotherm is representative of air oxidation of pyrite.

Task 3 Standardization Runs and Base Case Determination

Progress - The Elkhorn #3 coal was tested for its liquefaction behavior in a small tubing-bomb reactor. The ash contents of the coal and the coal dissolution yield were measured and are presented in Table 25. The results obtained with Kentucky #9/14 coal are also presented in Table 25 for comparison. The Elkhorn coal was found to have 13.33% ash compared to 6.41% in Kentucky #9/14 coal. The dissolution yields were found to be 87 and 92% for Elkhorn #3 and Kentucky #9/14 coals, respectively. The unexpectedly high reactivity of Elkhorn #3 coal may be due to its high ash concentration. A low ash Elkhorn #3 coal sample (approximately 3%) has already been shipped to Air Products and the reactivity of this sample will be tested as it becomes available.

Task 4 Effect of Coal Minerals on Coal Liquefaction

Task 4.1 Screening Studies at Auburn

Progress - To obtain fundamental information concerning hydrogenation activity of the mineral additives (as received and treated), naphthalene was studied in a small tubingbomb reactor. The reason for choosing naphthalene was: the tetralinnaphthalene system is present in process solvent, naphthalene is readily available and easy to use in the tubingbomb reactor as well as easily analyzed by gas chromatography, hydrogenation information can be obtained rather easily in a relatively short time, and such data can help to understand the hydrogenation mechanism and the influence of various process variables.

TABLE 25

Dissolution Characteristics of Elkhorn #3 and Kentucky #9/14 Coals

Coal	Ash Content in Coal, %	Conversion to Cresol Solubles on MAF Basis, %
Elkhorn #3	13.33 $\pm$ 0.08	87.0 $\pm$ 0.6
Kentucky #9/14	6.41 $\pm$ 0.12	92.0 $\pm$ 0.1

Reaction Conditions:

Reactor = Tubing-Bomb

Coal = 3g

SRC II-Fuel Oil Solvent = 6g

Temperature = 410°C

Time = 30 min.

Agitation = 860 RPM

P = 1250 psig H₂ at 25°C

The conversion of naphthalene to tetralin and to other hydrogenated reaction products has been recognized to yield tetralin and methyl indane (5). The main hydrogen transfer reactions involved are given in Eqns. 4 and 5:

Hydrogenation Reaction

Dehydrogenation Reaction

A mixture of 10% naphthalene in hexadecane solvent was subjected to hydrogen to study the above reactions. The reaction products were vacuum filtered and analyzed by gas chromatography (G.C.) to determine the peak areas of different compounds. Specific reaction conditions of the various runs are summarized in Table 26. The hydrogenation activity of the minerals was followed by monitoring the tetralin to naphthalene (T/N) ratio. Co-Mo-Al was used as an additive in order to compare the results with no catalyst, a good catalyst and as received mineral additives. Reduced pyrite samples were prepared by precipitating ferrous chloride [$\text{FeCl}_2 + (\text{NH}_4)_2\text{S}$] and reducing pyrite with hydrogen. These reduced pyrite samples were then studied for their hydrogenation activity.

The hydrogenation activity of Co-Mo-Al catalyst and various other minerals studied is given in Table 26. As mentioned before, the hydrogenation activity is evaluated in terms of T/N ratio. Co-Mo-Al catalyst showed the highest T/N ratio, i.e., the highest hydrogenation activity. Reagent grade pyrite (Fisher Chemical Co.) and pyrrhotites prepared by pyrite reduction showed intermediate hydrogenation activity (T/N ratio in the range of 0.2 to 0.9).

TABLE 26

Effect of Additives on Conversion of Naphthalene

<u>Catalyst</u>	<u>GC Peak Area Ratio x 10³</u>						<u>T/N</u>
	<u>Surface Area (m²/g)</u>	<u>Tetralin Hexadecane</u>	<u>Naphthalene Hexadecane</u>	<u>Decalin Hexadecane</u>	<u>Dihydronaphthalene Hexadecane</u>	<u>Unknown Hexadecane</u>	
Without Treatment.	-	-	109.0	-	-	-	0.007
Blank Run	-	0.80	112.28	0.50	0.94	2.96	.063
Fe ₂ O ₃	11.27	6.49	101.95	0.46	1.37	3.38	.182
FeS ₂ (Fisher Reagent grade)	0.20	15.84	86.78	1.37	0.00	6.16	.182
FeS							
(FeCl ₂ + (NH ₄) ₂ S)	11.82	2.55	107.92	0.34	0.26	5.30	.023
(FeS ₂ + H ₂)	1.44	36.06	64.90	2.08	0.00	11.23	.555
Robena Pyrite (As Received)	1.52	2.82	102.99	0.09	0.25	0.80	.027
Robena Pyrite (-115 Mesh)		4.60	103.35	0.11	0.20	1.22	.044
Zircon (-325 Mesh)		1.55	106.22	0.32	0.77	1.64	.014
Zircon (-115 Mesh)		1.55	105.61	0.10	0.33	1.05	.014
Ilmenite (-155 Mesh)		2.28	102.44	0.02	0.27	0.34	.022
Rutile (-155 Mesh)		0.85	105.69	0.53	0.68	2.79	.008
FeSO ₄ (Dehydrated)		1.90	105.34	0.84	0.60	5.05	.018
FeSO ₄ · 7H ₂ O		1.32	109.94	0.96	1.13	12.63	.012
Robena Pyrite (-325 Mesh)		3.32	117.02	1.86	1.46	8.70	.033
Co-Mo-Al	200	75.02	23.36	1.00	0.00	2.73	3.21

Reaction Conditions: Reactor - Tubing-Bomb (17.5 ml)
 10 wt% Naphthalene in Hexadecane (6.0 g., 0.6 g of additive)
 410°C, 30 min., 1250 psig H₂ at 25°C, 860 rpm

Insignificant variation in the T/N ratio of the product obtained in the absence of additive and various other minerals (see Table 26) was observed. These minerals showed a T/N ratio very close to the blank run (T/N ratio of 0.063), indicating that these minerals are very poor catalysts/additives for hydrogenation as far as the tetralin-naphthalene system is concerned. The above results indicate that the hydrogenation activity of the pyrite could be increased by using either relatively pure pyrite or treated pyrite sample. The surface area of the reduced pyrite samples were measured to determine the influence of surface area on hydrogenation activity. No definitive relationship between surface area and hydrogenation activity could be discerned due to lack of enough data. A detailed study of the hydrogenation activity of the different mineral additives in the tetraline-naphthalene system, process solvent, and coal/oil slurry is underway.

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APPENDIX I

Pressurizable Thermogravimetric Reactor (PTGR)

A schematic diagram of the system layout is shown in Figures I.1 and I.2. The primary apparatus used in obtaining the results is a 6 gram capacity thermobalance built specifically for Air Products' laboratories by Spectrum Products, Inc. This apparatus is capable of operation at pressures up to 1500 psi and at temperatures up to 1000°C. The reactor is a 4-ft. cylindrical Haynes 188 superalloy tube with 3/4 inch i.d. and 2.5 inch o.d., 3 feet of which is heated by a Marshall tubular furnace (Model No. 1149).

Thermocouples are located along the outer tube wall, inside the furnace and inside the reactor tube. The exact locations of the thermocouples are shown in Figure I.3. The exit gas temperature upstream of the tar trap was also monitored by another thermocouple. The thermocouple just below the sample basket was used as a feedback for the heater controller to maintain constant temperature or heating rate. Process gas enters either through the top or the bottom of the reactor tube, while the purge gas can be admitted through the microbalance housing at the top and flows down the dip-tube. The gas flow rates into and out of the reactor were measured by three Brooks thermal mass flowmeters (Model 5811). FI-1 and FI-3 in Figure I.2 which measured the flowrate into and out of the reactor were calibrated with hydrogen; FI-2 which measured the flowrate down the reactor was calibrated with helium. If helium is flowing through FI-1 and FI-3, the indicated flow rate has to be multiplied by 1.5 to give the actual helium flow rate. The system pressure was measured by two pressure transducers PI-1 and PI-2 (by Setra Systems, Inc. Model 204) located at the exit gas line upstream and downstream of the tar trap respectively. The pressure difference between the inlet and exit gas line was measured by another pressure transducer PI-3 (Setra Systems, Inc. Model 228).

The 3/8 inch o.d., 5 inch long sample basket (fabricated by Newark Wire Cloth Company) can hold up to 3 gram samples. It can be lowered into or raised from the heated section of the reactor tube by a No. 40 gauge chromel wire attached

FIGURE I.1
PRESSURIZABLE THERMOGRAVIMETRIC REACTOR (PTGR)

FIGURE I.2 DETAILED PTGR SYSTEM

FIGURE I.3
THERMOCOUPLE POSITIONS IN REACTOR

to a motorized winch. The microbalance was engaged only when the basket was in its pre-determined final position inside the reactor. The exit gas line upstream of the tar trap was kept hot by heating tapes to prevent tar condensation. The pyrolysis gas was passed through the tar trap (immersed in ice) and collected either in a sampling cylinder or in the sample loops in the Valco automatic sampling unit for gas chromatograph analysis. The system pressure was maintained by a back-pressure regulator PCV-1 (Grove Valve and Regulator Company, Model S-91-W) located downstream of the tar trap.

Experimental Procedure

The PTGR has two modes of operation: the hot-start fast heating mode and the cold-start slow heating mode. In the hot-start fast heating mode, the sample in the basket was lowered rapidly into the hot reactor; the heating rate was approximately 15°C/sec. In the cold-start slow heating mode, the basket was lowered into the reactor at ambient temperature and then the reactor was heated to its final temperature; the heating rate was approximately 8°C/min.

Experimental Preparation

The PTGR system was leak-tested with helium under pressure. The microbalance transducer was checked and calibrated periodically to assure its accuracy. Before each experiment, the recorder was zeroed and spanned by means of potentiometers so that only the sample weight loss was recorded as a percentage of its original weight. The recorder was zeroed while the microbalance was engaged with an empty basket; this was done either with the reactor hot or cold. With the reactor cold, the recorder can be spanned by lowering the basket loaded with a known weight of sample (from direct weighing) into the reactor to engage the microbalance. When the reactor was hot, the recorder was spanned by using a known weight of sand in the basket instead of sample and then replacing the sand with the same weight of sample afterwards. The total percentage weight loss obtained from such thermograms agreed to within 2% of the percentage weight loss obtained from direct weighing. Three or four experiments a day were made possible with this spanning procedure. A timer could be pre-set to turn on the furnace early in the morning so that the reactor was ready at the desired temperature for experimental runs. The timer was used only when all high temperature shut-off controls were functioning. The tar trap was washed and cleaned with tetrahydrofuran (THF) after each experiment and then dried by blowing air through it.

Data Acquisition Procedure

1. Slow heating mode experiments: The basket with approximately 3 g sample was lowered into the reactor at room temperature. After purging the system with helium, the reactor was heated. The temperature, monitored by a thermocouple located immediately below the sample basket, the helium flow rate and the sample weight were continuously recorded. Gas samples were periodically collected by syringes through a septum in the heated exit line. These samples were subsequently analyzed using a Perkin-Elmer Sigma-1 gas chromatograph.
2. Fast heating mode experiments: Before heating the reactor, the system was purged with helium; when hydrogen was used, the hydrogen inlet lines were purged with hydrogen first to get rid of any trapped air before purging the system with helium. The reactor was then heated up to the operating temperature. Then the system was pressurized to the operating pressure with helium and leak-tested. The system was now ready for experimental runs in helium. The loaded sample basket was lowered rapidly into the hot reactor and held for the desired residence time. The pressure, temperature and volume of the sampling cylinder were recorded. The gas in the sampling cylinder was mixed by means of a heat gun before it was analyzed by the Perkin-Elmer Sigma-1 gas chromatograph. After the sample was cooled down, the system was depressurized and purged with helium. The basket was removed from the system and weighed. The tar trap was washed with a known volume of THF solution. The treated sample and the THF tar washings were sent to be analyzed.

A step-by-step operating procedure for a helium run and a hydrogen run is described in the next section in the PTGR operating procedure. After putting back the cleaned tar trap and replacing the full sampling cylinder with an empty one, the system was ready for the next experimental run.

3. Temperature measurement at center of sample bed: This was done only in helium at atmospheric pressure. A sub-miniature thermocouple (Omega Engineering, Inc., Catalog #SCAIN-020U-66) was embedded at the center of the sample bed. This temperature was recorded as the basket was lowered rapidly into the hot reactor with helium flowing. The microbalance

housing was opened to atmosphere for ease of feeding in the thermocouple but the reactor was purged of air by the flow of helium from the bottom of the reactor. In the slow heating mode, the system was closed after the basket was in place, and the temperature at the center of the sample bed and the gas temperature inside the reactor immediately below the basket were recorded during heat-up of the reactor.

Water Analysis

Water from the sampling cylinder was analyzed by the gas chromatograph. Water in the tar trap was washed with a known volume of tetrahydrofuran (THF). From the weight percent analyses of water in the THF washing solution and that in the "clean" THF, the volume of the THF used in the washing and from the specific gravity (0.88) of THF, the weight of water in the tar trap can be obtained.

PTGR OPERATING PROCEDURE

Helium Run Procedure

1. After spanning and zeroing the recorder, turn on the He main regulator to 1200 psig.
2. Purge system with He at atmospheric pressure (8 min. with 1 scfh flow rate). The valves (refer to Figure 2) should be as follows:

<u>CV</u>	<u>Status</u>	<u>HCV</u>	<u>Status</u>	<u>LHV</u>	<u>Status</u>
1	Open/Close*	1	Open	1	Open
2	Close	2	Open/Close	2	Open
3	Open	3	Open	3	Open/Close
4	Open	4	Close		
5	Open/Close*	5	Open		
6	Open	6	Open		
7	Open/Close*	7	Open		
8	Open/Close*	8	Open/Close*		
9	Close				
10	Close				

*Open CV1, CV5, CV7, CV8, HCV2, HCV8, LHV3 temporarily and then close them.

3. Turn on cooling water.
4. Turn on heater and heat up to desired temperature with helium purging.
5. After reaching temperature, set the dome pressure on the back-pressure regulator to the desired operating pressure.
6. After the system has reached operating pressure, purge the sampling cylinder for awhile with helium. Add ice to tar trap bath.
7. Record pressure and flow rate on data sheet.
8. Set recorder for weight monitoring:
 - (i) Switch on point 15 and print only point 15.
 - (ii) Set Point Scan on recorder to Variable (fastest) print.
 - (iii) Set chart speed to 8 inch/min.
9. Lower basket into reactor and simultaneously close LHV2.
10. Raise the basket after holding it in the reactor for the desired residence time.

11. After the calculated pressure has been reached in the sample cylinder, close LHV-1 and LHV-3.
12. Depressurize the system by closing CV3, CV4 and slowing opening up HCV8.
13. Close HCV6, HCV7 and remove sample cylinder.
14. Weight the basket and its content after letting it cool down in helium. Save the product for analysis.
15. Remove the tar trap and wash with a known quantity of THF solution. Send the THF tar trap washing and the original clean THF solution for water analysis.

Hydrogen Run Procedure

1. Set dome pressure for H_2 delivery to 1200 psig.
2. Turn on He main to 1200 psig.
3. With reactor cold, purge system with hydrogen at atmospheric pressure (8 min. with 1 scfh flow rate). The valves are as follows:

<u>CV</u>	<u>Status</u>	<u>HCV</u>	<u>Status</u>	<u>LHV</u>	<u>Status</u>
1	Close	1	Open	1	Open
2	Open	2	Close	2	Open
3	Close	3	Open	3	Open
4	Close	4	Open		
5	Close	5	Open		
6	Open	6	Open		
7	Close	7	Open		
8	Close	8	Open		
9	Close				
10	Close				

4. Purge system with helium at atmospheric pressure (8 min. with 1 scfh).
 - (i) Close CV2.
 - (ii) Open CV1, CV3, CV4, CV5.
 - (iii) Open CV7, CV8, CV10, HCV2 temporarily to purge and then close them.
 - (iv) Close HCV8 and LHV3.
5. Turn on cooling water and start heating with helium purging.
6. After reaching temperature, set back-pressure regulator's dome pressure and pressurized system to operating pressure with helium. Then check for leaks.

7. Depressurize system of helium.
 - (i) Close CV1, CV3, CV4, CV5.
 - (ii) Open CV7, CV8.
 - (iii) Slowly release back-pressure regulator dome pressure and open HCV8.
8. Set system dome pressure for H₂ inside the high pressure cell.
9. Fill tar trap bath with ice.
10. Purge system with H₂ at atmospheric pressure (8 min. with 1 scfh).
 - (i) Open CV2.
 - (ii) Open CV7, CV8, CV10 temporarily to purge and then close them.
 - (iii) Close LHV3, HCV8.

The valves should have the following status.

<u>CV</u>	<u>Status</u>	<u>HCV</u>	<u>Status</u>	<u>LHV</u>	<u>Status</u>
1	Close	1	Open	1	Open
2	Open	2	Open	2	Open
3	Close	3	Open	3	Close
4	Close	4	Open		
5	Close	5	Open		
6	Open	6	Open		
7	Open/Close	7	Open		
8	Open/Close	8	Close		
9	Close				
10	Open/Close				

11. Set back-pressure regulator dome pressure from outside of the high pressure cell.
12. After reaching operating pressure, let the system be purged with H₂ for awhile.
13. Record pressure and flow rate on data sheet.
14. Set recorder for weight monitoring (same as Step 8 in helium run procedure).
15. Lower basket into reactor and simultaneously close LHV2.
16. Raise the basket after holding it in the reactor for the desired residence time.
17. After the calculated pressure has been reached in the sample cylinder, close LHV1 and open LHV3.

18. Depressurize the system by closing CV2 and slowly opening up HCV8.
19. After depressurization, purge the system with helium before entering high pressure cell.
 - (i) Open CV1, CV3, CV4, CV5, CV7, CV8, CV10.
 - (ii) Close CV1, CV3, CV4 after purging.
20. Close HCV6, HCV7 and remove sample cylinder.
21. Weigh the basket and its content after letting it cool down in helium. Save the product for analysis.
22. Remove the tar trap and wash with THF solution (same as Step 15 in helium run procedure).

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