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ENTHALPY MEASUREMENT OF COAL-DERIVED LIQUIDS

Quarterly Technical Progress Report

for the Period July - September 1977

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I.

II. ABSTRACT

On June 24, 1975, work was initiated on a 36 month contract for experimental enthalpy measurements on coal-derived liquids. The principal investigators on the program are Dr. Arthur J. Kidnay and Dr. V. F. Yesavage, Department of Chemical and Petroleum-Refining Engineering, Colorado School of Mines, Golden, Colorado.

During the ninth quarter, experimental measurements were made on a distillate from a coal-derived liquid sample produced with the Synthoil process. The measurements extend from 155 to 742 ^{o}F at pressures of 150, 200, 500, 1000, and 1500 psia. Enthalpy measurements were also started on a naphtha cut from a coal-derived liquid produced by the SRC-I process. These naphtha measurements are approximately 60% complete, and will be reported in the next quarterly report.

III. OBJECTIVE AND SCOPE OF WORK

Thermodynamic property research is justly recognized as invaluable by process and design engineers in the petroleum, chemical, and allied industries. Calorimetric measurements of specific heats or enthalpies, pressure density-temperature measurements, and phase equilibrium determination, for pure fluids or complex mixtures, are all essential in the optimum design of both physical and chemical processing units.

Coal-derived liquids are a new and vital class of industrial compounds, but have thermodynamic properties that are largely unknown and, presently, unpredictable. The objective of this research is to measure one of the most important thermodynamic properties, the enthalpy, for representative coal-derived liquids over the pressure and temperature regions most likely to be encountered in both liquefaction and processing systems.

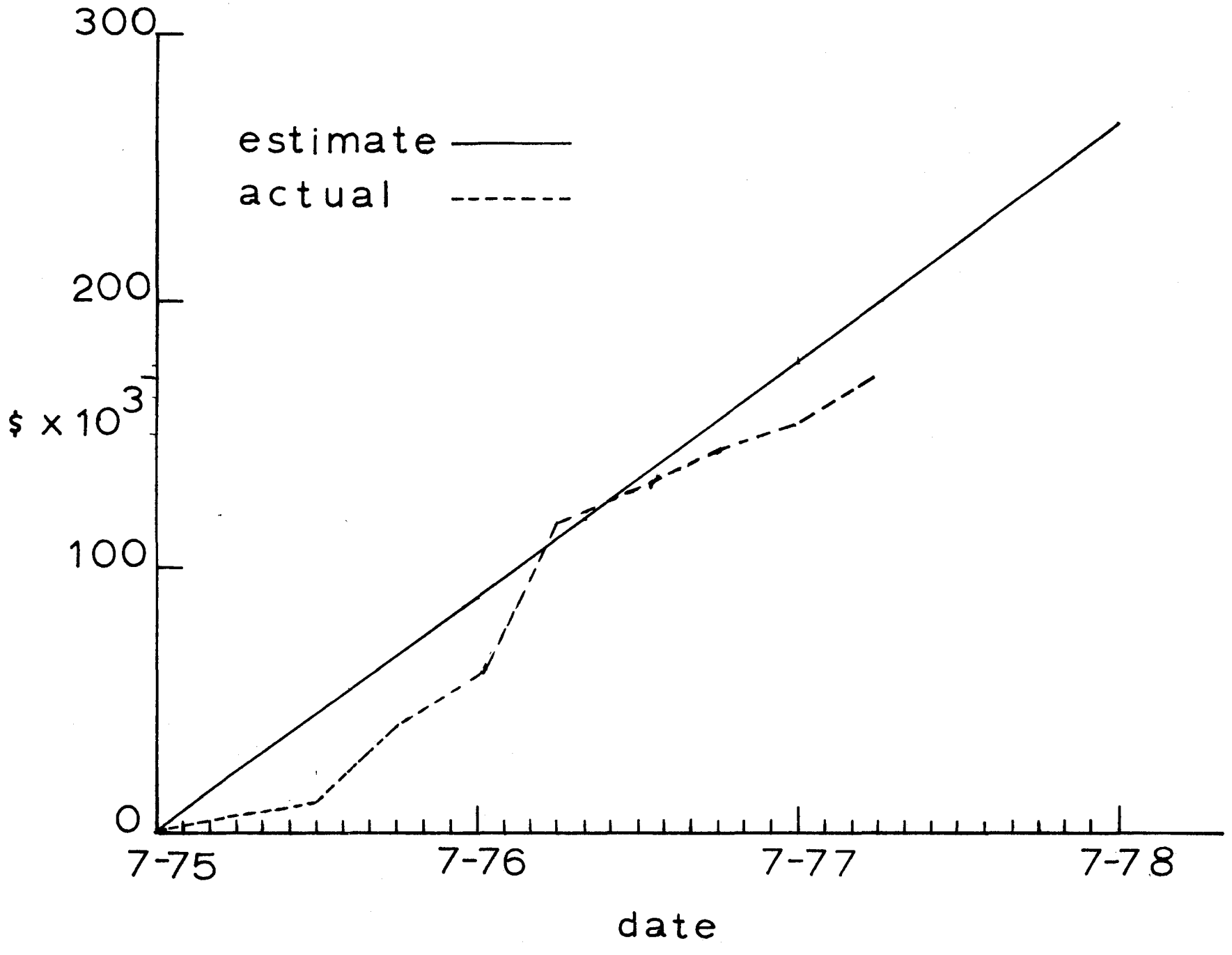
PROJECT PLAN & PROGRESS

TASK	WORK STATEMENT	1975 7 9 11	1976 1 3 5 7 9 11	1977 1 3 5 7 9 11	1978 1 3 5
1	CALORMETRIC DESIGN & FABRICATION				
2	CALORIMETRIC EVALUATION				
3	ENTHALPY MEASUREMENTS ON COAL-DERIVED LIQUIDS				
4	PREPARATION OF ENTHALPY CORRELATIONS				
5	COMPARISON WITH PETROLEUM				
6	ENTHALPY MEASUREMENTS ON SELECTED MIXTURES				
7	LIASON WITH ERDA BARTLESVILLE				
8	ERDA CONSULTATION & ADVICE				

WORK IN PROGRESS

SCHEDULED WORK

EARLY START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200
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The research is divided into three major program areas:

I) Design, construction, and evaluation of a freon boil off calorimeter for temperatures of 70 to 700°F and pressures to 2000 psig.

II) Enthalpy measurements on approximately 10 samples of coal-derived liquids. The samples for measurement will be selected after consultation with the ERDA Bartlesville Energy Research Center.

III) Preparation of engineering correlations for the measured enthalpy data, and comparison with representative data for petroleum and petroleum fractions.

V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

This section of the progress report contains a discussion of the eight tasks comprising the program.

Design and Fabrication of a Flow Calorimeter for Measuring Enthalpies of Coal Liquids to 700°F and 2000 psig

This phase of the program is finished. The calorimeter was fully described in the fifth quarterly progress report.

Evaluation and Standardization of the Calorimeter

This phase of the program is finished. Results for water and n-heptane are presented in the sixth and seventh quarterly progress reports.

Enthalpy Measurements on Coal-Derived Liquids

During the past quarter runs were made on a distillate that was prepared from a "Synthoil" product oil. The "Synthoil" product oil was obtained from Dr. Paul M. Yavorsky of the Pittsburgh Energy Research Center. Data reported by the Pittsburgh Energy Research Center on the "Synthoil" is presented in Table I. As obtained the "Synthoil" sample was a tar like substance which

TABLE 1

Data for 1-5 Gallon Sample of FB-59 Centrifuge SYNTHOIL
Sent to A. Kidnay, Colorado School of Mines, on May 24, 1977

This SYNTHOIL product was made from a blend of Kentucky bituminous coal. Analysis of this coal and its source follows:

	Kentucky Coal
Proximate Analysis, wt pct	
Moisture	6.1
Ash	15.5
Volatile matter	36.3
Fixed carbon	42.1
Ultimate Analysis, wt pct	
Moisture	6.1
Ash	15.5
Carbon	60.3
Hydrogen	4.9
Nitrogen	1.2
Oxygen, by difference	12.8
Sulfur	5.3
as sulfate	0.58
as pyrite	2.69
as organic	2.03
Coal Source	
A blend from Kentucky seams 9, 11, 12, and 13; Ohio County, Western Kentucky. The seams are all mined together.	

Conditions of Run FB-59 were 4,000 psig, 450° C, feeding 35 pct coal slurry in lined-out, coal-derived oil at 25 lb per hour. This oil was produced, using our nominally 1/2 ton/day unit with a 28-ft-long fixed-fed reactor.

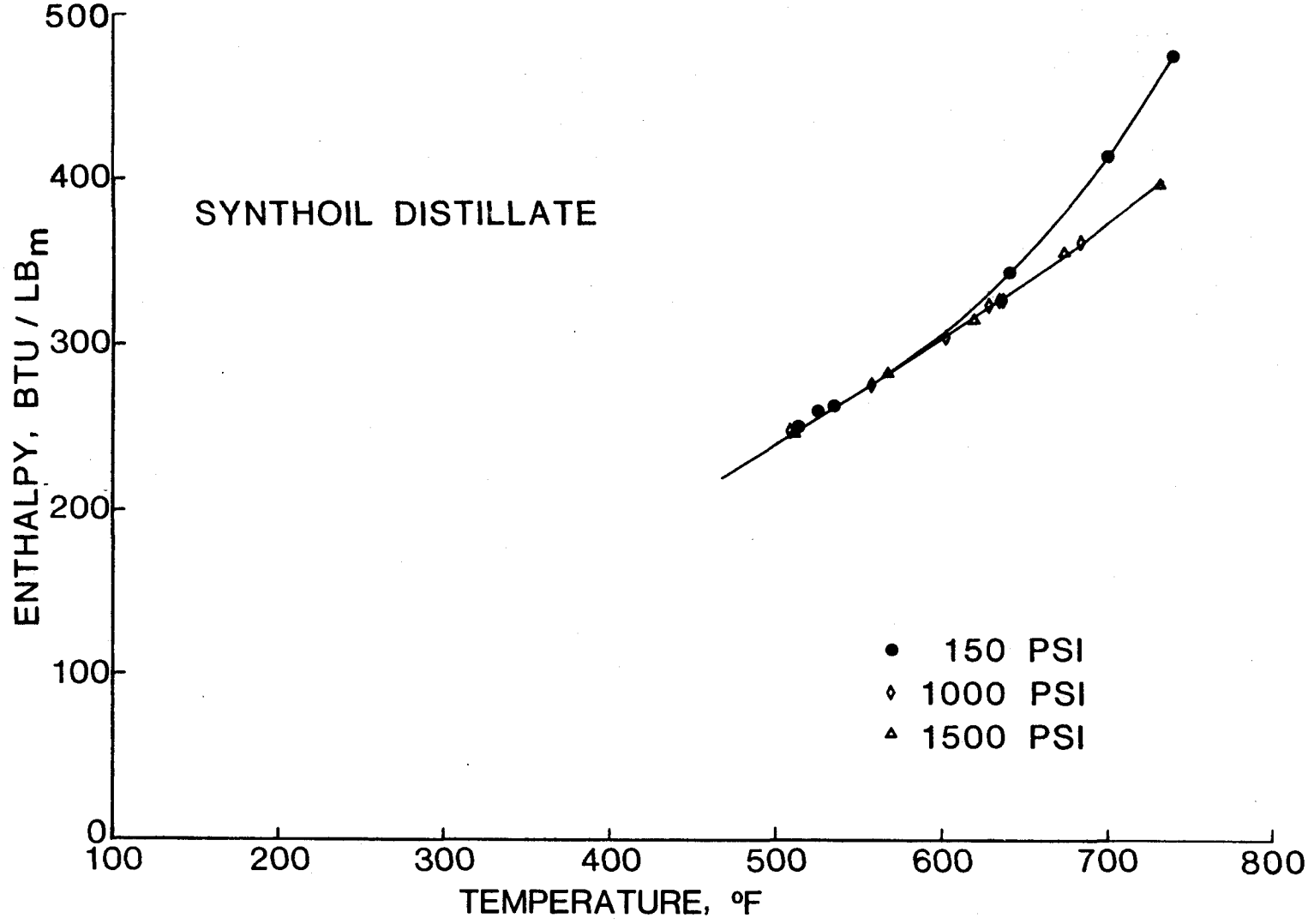
Analyses typical of this SYNTHOIL product sample (Run FB-59) follow:

S in product, wt pct	0.4
Ash in product, wt pct	.7
Viscosity of product, SSF at 180° F	26.5
Specific gravity of product	1.100
Solvent Analysis (wt pct) (Ash-free)	
Organic benzene insols	1.8
Asphaltenes	23.5
(Pentane insols from benzene sols)	
Oils	74.7
(Pentane sols from benzene sols)	

was too viscous for use as a calorimeter sample. Thus an atmospheric cut (cut point ≈520°F @ 760 mm Hg) was prepared from the "Synthoil" using the same batch distillation procedure described in the last quarterly progress report. No vacuum cut was taken. Losses associated with the distillation were negligible (less than 0.36 wt %). An overall material balance is presented in Table 2. The atmospheric cut was light, transparent, golden-brown in color which darkened with the passage of time. The residue (cut point > 520°F at 760 mm Hg) was a black viscous material which became a solid at room temperature. An ASTM distillation and API gravity measurement were performed on the atmospheric cut as an initial step of characterization and the results are presented in Table 3.

The distillate was charged to the system and data were measured from 155 to 742°F at 150, 200, 500, 1000, and 1500 psia. At the very high temperatures, a slight foaming in the sample was noted, but this did not appear to effect the enthalpy. The data are presented in Table 4 and Figures 1 and 2. The figures illustrate how pressure effects the enthalpy. Low pressure and high temperature data show the transition from liquid to the two-phase region. The 500, 1000, and 1500 psia isobars show the effect of temperature on the enthalpy of the liquid.

Enthalpy measurements have also been made on an SRC-I naptha that was obtained from the Pittsburgh and Midway Coal Mining Company. At present measurements on this sample are about two thirds complete. Results will be reported in detail for this sample in the next progress report after the measurements are completed.


SYNTHOIL DISTILLATE
ENTHALPY, BTU / LBm
TEMPERATURE, °F
0
100
200
300
400
500
100
200
300
400
500
600
700
800
150 PSI
1000 PSI
1500 PSI

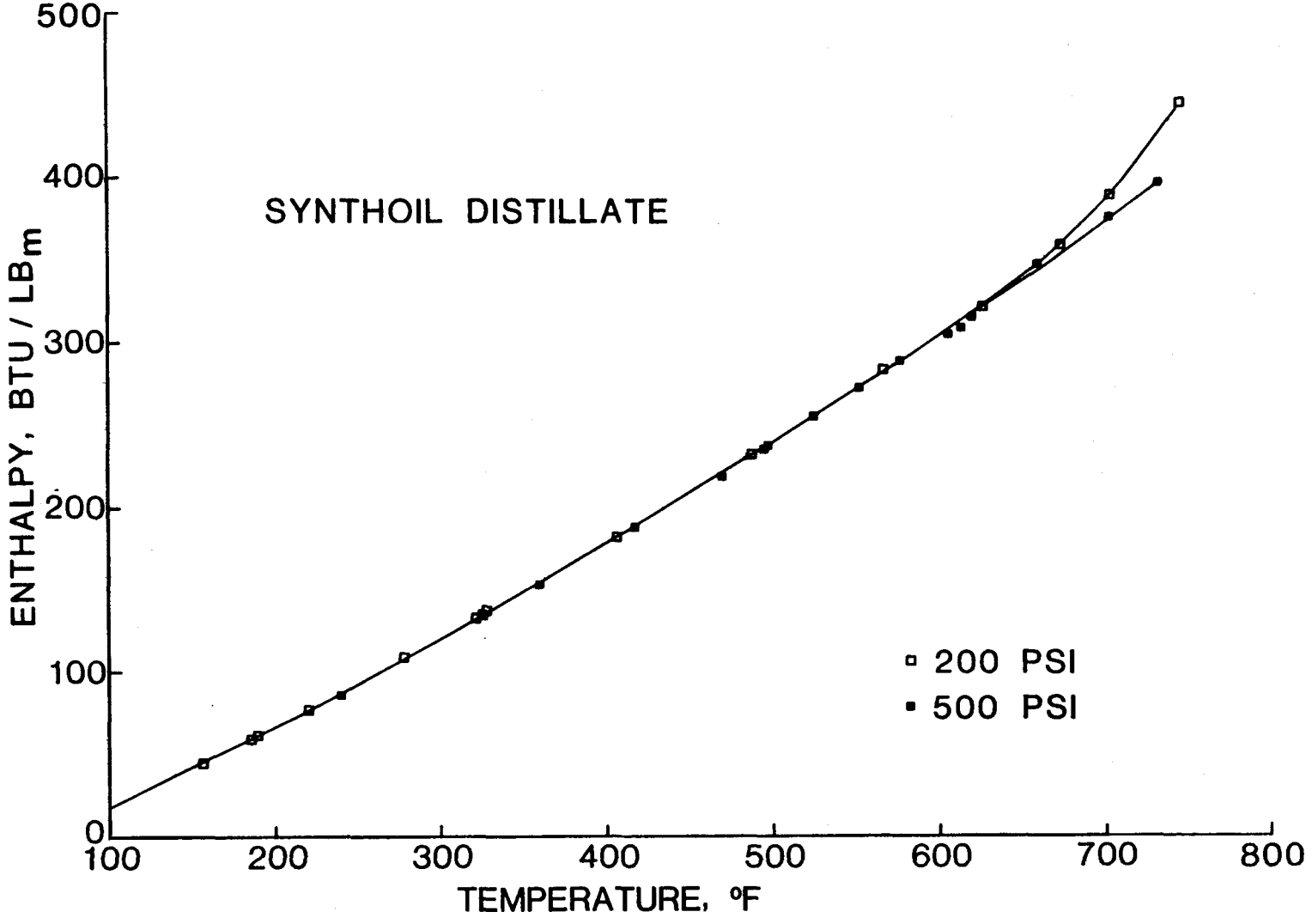

SYNTHOIL DISTILLATE
ENTHALPY, BTU / LBm
TEMPERATURE, °F
200 PSI
500 PSI
0
100
200
300
400
500
100
200
300
400
500
600
700
800

TABLE 2

Overall Material Balance (Synthoil)

Total "Crude" charged	=	15,865.17 gm
Products:		
Atmospheric Distillation (≈620 mm Hg) (cut point ≈ 610°F @ 760 mm Hg)	=	4,034.91 gm
Residue (610°F+ @ 760 mm Hg)	=	11,773.70 gm
TOTAL PRODUCTS	=	15,808.61 gm
Loss	=	56.56 gm
	=	0.357%

TABLE 3

Characterization of Synthoil Distillate

ASTM Distillation

% Recovered (By Volume)	Temp., ^{o}F * @ 0.81 ATM.	Temp., ^{o}F @ 1.0 ATM.	(Fig. 5A-15 API Data Book)
IBP	196	208	
10	404	420	
20	420	435	
30	436	450	
40	449	465	
50	466	480	
60	487	504	
70	506	525	
80	536	555	
90	590	605	
End Point	618	635	

(7.0 ml. were left at the bottom of the distilling flask.)

* Ambient pressure of Golden, Colorado.

Measured ^{o}API of Synthoil Distillate = 13.2^{o}API.

TABLE 4

Synthoil Distillate

Enthalpy Data

150 psia Run No.	Temperature °F Inlet	Pressure, psia Inlet	Outlet	ΔH, exp., Btu/lb_m	Pressure Correction Btu/lb_m	ΔH Corrected Btu/lb_m
32	471.6	150	18	222.9	0.32	223.2
33	513.4	152	18	250.2	0.32	250.5
54	526.1	148	18	260.0	0.32	260.3
34	535.8	148	18	263.0	0.32	263.3
35	588.9	150	18	298.9	0.32	299.2
53	621.7	150	18	326.3	0.32	326.6
36	629.7	150	18	331.5	0.32	331.8
55	640.4	148	18	343.7	0.32	344.0
37	662.1	150	20	359.1	0.32	359.4
39	700.8	151	43	414.0	0.32	414.3
40	738.1	151	44	474.3	0.32	474.6

TABLE 4

Synthoil Distillate

Enthalpy Data

200 psia Run No.	Temperature ^{o}F Inlet	Pressure, psia Inlet	Outlet	ΔH, exp., Btu/lb_m	Pressure Correction Btu/lb_m	ΔH Corrected Btu/lb_m
16	155.5	203	23	44.4	.43	44.8
15	185.6	202	24	58.7	.43	59.1
13	189.4	199	22	60.6	.43	61.0
14	219.4	201	24	75.9	.43	76.3
12	237.8	202	23	86.3	.43	86.7
11	276.7	201	23	107.7	.43	108.1
1	321.6	200	24	132.9	.43	133.3
10	323.4	196	23	134.5	.43	134.9
9	324.8	199	24	134.7	.43	135.1
3	358.5	199	23	154.0	.43	154.4
2	359.7	200	24	153.9	.43	154.3
4	405.7	188	24	182.4	.43	182.8
5	439.7	200	24	203.2	.43	203.6
6	485.8	200	24	232.1	.43	232.5
7	523.7	200	24	256.0	.43	256.4
8	565.9	199	24	283.5	.43	283.9
41	624.1	200	90	321.6	.43	322.0
42	672.0	199	191	358.6	.43	359.0
43	700.9	200	90	388.5	.43	388.9
44	742.2	200	90	444.2	.43	444.6

TABLE 4

Synthoil Distillate

Enthalpy Data

500 psia Run No.	Temperature ^{o}F Inlet	Pressure, psia Inlet	Outlet	ΔH, exp., Btu/lb_m	Pressure Correction Btu/lb_m	ΔH Corrected Btu/lb_m
17	358.3	498	331	154.0	1.13	155.1
18	415.9	499	331	188.2	1.13	189.3
19	469.5	500	330	220.7	1.13	221.8
21	493.0	501	350	236.7	1.13	237.8
20	495.5	498	334	239.0	1.13	240.1
24	524.3	501	352	256.4	1.13	257.5
25	550.0	498	352	272.5	1.13	273.6
26	575.2	500	350	288.7	1.13	289.8
27	602.2	500	350	306.6	1.13	307.7
45	612.8	500	363	315.2	1.13	316.3
23	619.9	497	352	318.5	1.13	319.6
46	658.7	501	370	347.7	1.13	348.8
47	700.7	500	371	375.6	1.13	376.7
48	729.4	495	372	397.6	1.13	398.7

TABLE 4

Synthoil Distillate

Enthalpy Data

1000 psia Run No.	Temperature ^{o}F Inlet	Pressure, psia Inlet	Outlet	ΔH, exp., Btu/lb_m	Pressure Correction Btu/lb_m	ΔH Corrected Btu/lb_m
28	510.5	1000	862	248.9	2.28	251.2
29	558.2	1000	860	277.6	2.28	279.9
30	602.1	1000	857	307.6	2.28	309.9
49	627.6	1000	878	326.9	2.28	329.2
50	634.1	1009	877	329.4	2.28	331.7
31	636.7	1002	856	329.5	2.28	331.8
51	683.3	1006	878	364.1	2.28	366.4

TABLE 4

Synthoil Distillate

Enthalpy Data

1500 psia Run No.	Temperature ^{o}F Inlet	Pressure, psia Inlet	Outlet	ΔH, exp., Btu/lb_m	Pressure Correction Btu/lb_m	ΔH Corrected Btu/lb_m
56	512.5	1503	1328	247.1	3.43	250.5
57	567.8	1496	1327	283.0	3.43	286.4
58	619.0	1502	1344	316.8	3.43	320.2
59	673.2	1495	1346	356.3	3.43	359.7
60	732.5	1500	1357	396.0	3.43	399.4

Comparison of Heat Capacities

A comparison of our heat capacity data for the Western Kentucky Syncrude was made with values as reported by D. R. Douslin, W. D. Good, S. H. Lee, et. al., "Thermodyanmics of Coal Liquids," BERC/QPR-76/3. Results are presented in Table 5. Although a direct comparison cannot be made in the data because of the differences in the fractions (cut points), the heat capacities generally compared well. As is evident from the table, heat capacities are in good agreement at low temperatures. At the higher temperatures where compositional effects are pronounced due to vaporization, the heat capacities differ considerably from those reported by D. R. Douslin, et. al.

Table 5

Comparison of Heat Capacity Data

Temp. ^{o}F	Western Kentucky Syncrude Light Distillate	(Douslin) Light	(Douslin) Middle	(Douslin) Residue
148	0.47	0.49	0.46	--
306	0.52	0.59	0.53	--
500	0.65	--	0.62	--
	Western Kentucky Syncrude Whole Oil			
153	0.45	--	0.46	0.44
300	0.54	--	0.53	0.51
457	0.67	--	0.61	0.59

Comparison of Coal-Derived Liquid Enthalpies with Petroleum-Liquid Enthalpies

No work was done on this task during the quarter.

Correlation of Enthalpy Data for Coal-Derived Liquids

No work was done on this task during the quarter.

Enthalpy Measurements on Selected Mixtures

This is an optional task, and no work has been initiated or is planned at the present time.

Liaison

No work during this quarter.

VI. CONCLUSIONS

Experimental measurements are reported for a distillate from a coal-derived liquid obtained using the Synthoil process. The measurements cover the region 155 to 742^{o}F at pressures of 150, 200, 500, 1000, and 1500 psia. Measurements were also initiated on a naphtha sample produced by the SRC-I process. These measurements are approximately 60% complete, and will be reported in full in the next quarterly progress report.