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ENTHALPY MEASUREMENT OF COAL-DERIVED LIQUIDS

Quarterly Technical Progress Report

for the Period April-June, 1978

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II. ABSTRACT

On June 24, 1975, work was initiated on a 36 month contract for experimental enthalpy measurements on coal-derived liquids. The contract has recently been extended to 42 months. 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 twelfth quarter of the program, experimental measurements were completed on a middle distillate furnished by Pittsburg and Midway Coal Mining Company. A total of 52 enthalpy measurements were made covering the ranges 157 to 675^{o}F and 130 to 1000 psia.

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, unpredicitable. 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.

The research is divided into three major program areas:

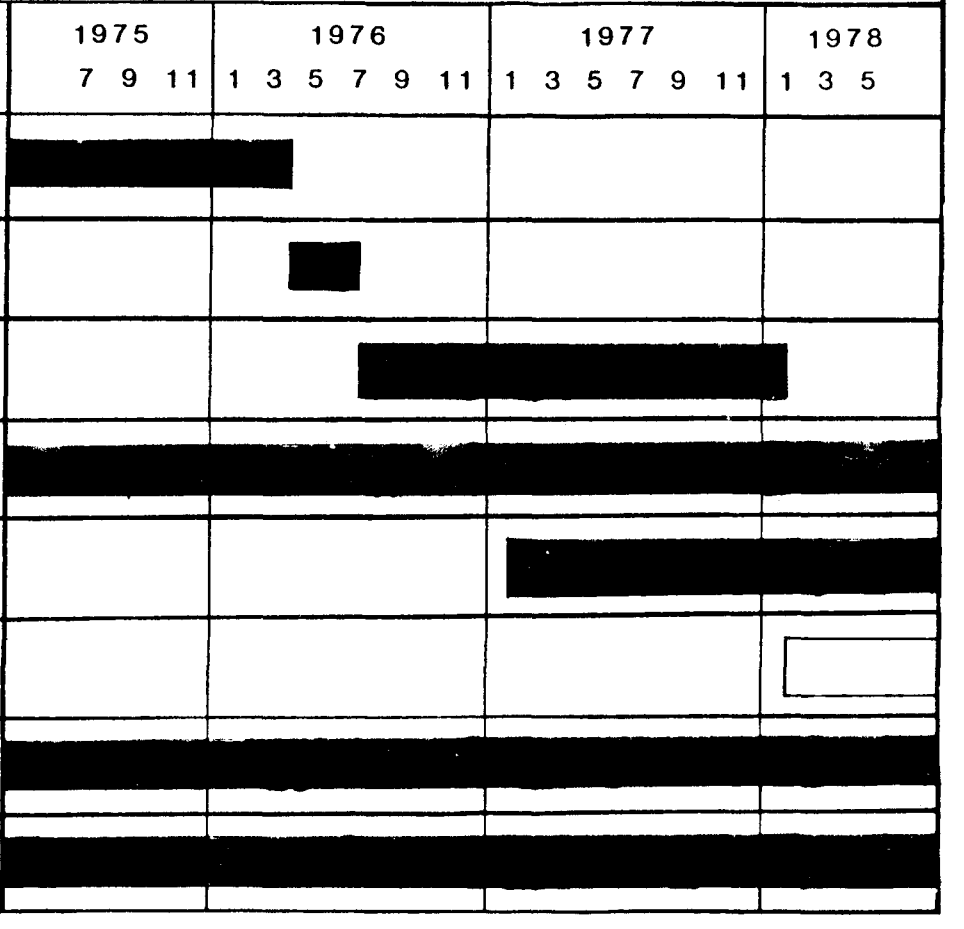
1) Design, construction, and evaluation of a freon boil off calorimeter for temperatures of 70 to 700^{o}F and pressures to 2000 psig.

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

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

PROJECT PLAN & PROGRESS

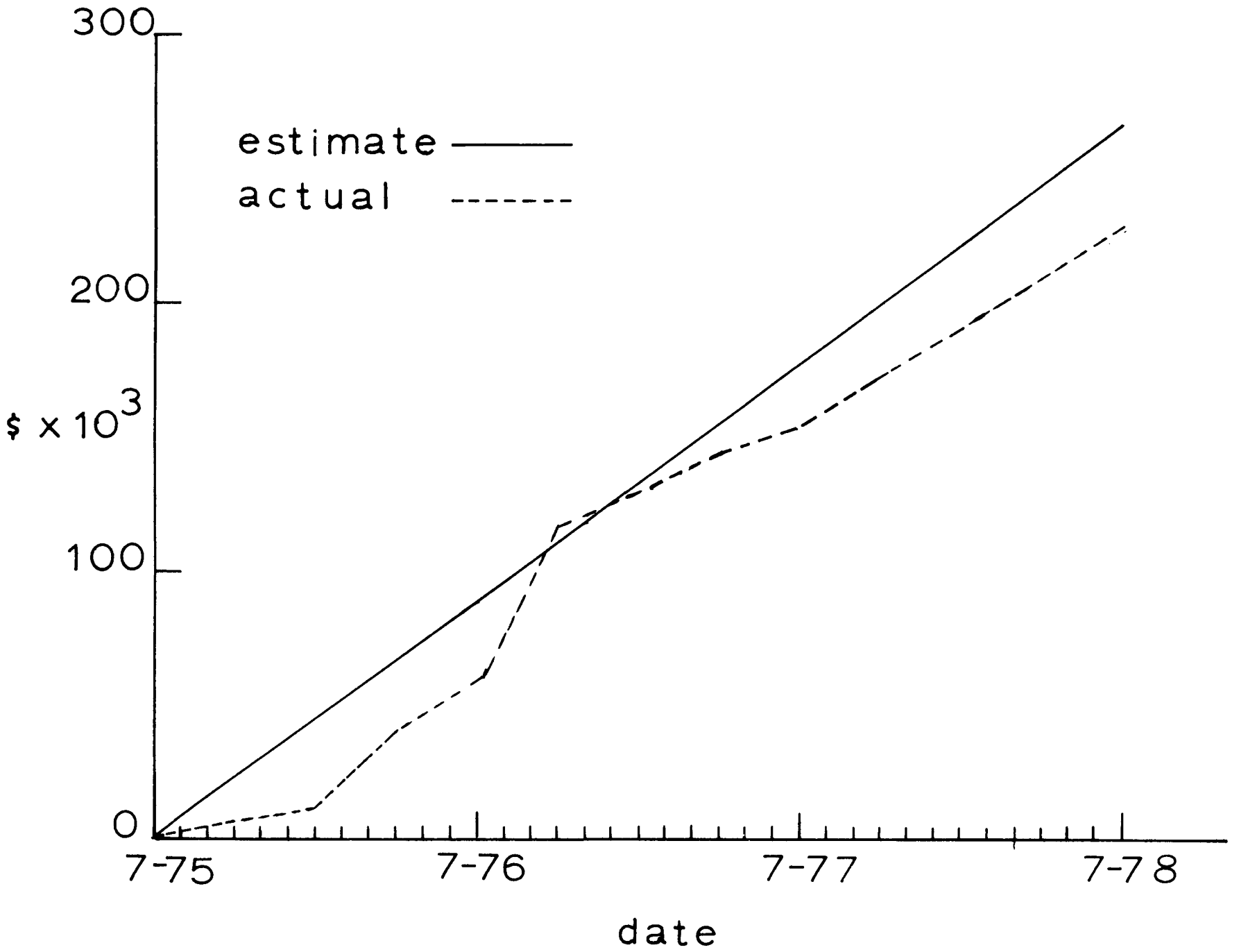
TASK	WORK STATEMENT
1	CALORMETRIC DESIGN & FABRICATION
2	CALORIMETRIC EVALUATION
3	ENTHALPY MEASUREMENTS ON COAL-DERIVED LIQUIDS
4	PREPARATION OF ENTHALPY CORRELATIONS
5	COMPARISON WITH PETROLEUM
6	ENTHALPY MEASUREMENTS ON SELECTED MIXTURES
7	LIASON WITH ERDA BARTLESVILLE
8	ERDA CONSULTATION & ADVICE



WORK IN PROGRESS

SCHEDULED WORK

EARLY START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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 this quarter, enthalpy measurements were completed on a middle distillate sample furnished by the Pittsburg and Midway Coal Mining Co. The sample was produced from a Kentucky coal at the P & M DuPont Washington pilot plant using the Solvent Refined Coal process. Some physical property data for the material are presented in Table 1.

The data gathering process was disappointingly slow for the quarter, due to severe operational problems caused by the thermal instability of the middle distillate. At moderate pressures (on the order of 150 psig) and at temperatures greater than 500°F severe coking problems quickly developed in the preheater coil and final heater assembly. This coking forced frequent shut-downs, disassemblies, and cleanup of the apparatus, a process involving several days of work at each occurrence. These operational problems are much the same as those encountered with the SRC-1 naphtha sample, as discussed in the 11th quarterly report.

The complete set of enthalpy measurements for the middle distillate are presented in Table 2 and the accompanying figure.

TABLE 1

Middle Distillate Sample (#878)

Furnished by: Pittsburg and Midway Coal Mining Co.
Solvent Refined Coal Pilot Plant
Dupont, Washington

Coal source: Kentucky

Sp. Gravity 60/60°F 0.976

Kin. Vis. @ 77°F _____
@100°F 36.49
@210°F 6.96

Distillation: D-86 **@** ATM Pressure

Initial Boiling Point	354 °F	**70%**	456 °F
5%	390 °F	**80%**	468 °F
10%	400 °F	**90%**	485 °F
20%	413 °F	**95%**	500 °F
30%	418 °F	**End Point**	532 °F
40%	428 °F	**Recovery**	98 %
50%	437 °F	**Residue**	2 %
60%	435 °F	**Lost**	— %

Elementals :	**% Carbon** 85.53	%	_____
	% Hydrogen 9.05	%	_____
	% Nitrogen 1.32	%	_____
	% Sulfur 0.15	%	Two Runs
	% Oxygen _____	%	_____

TABLE 2

#878 Middle Distillate (Pittsburg & Midway Coal Mining Co.)

ENTHALPY DATA

130 Psia Isobar

Run No.	Temp., °F Inlet	Pressure, Psia Inlet	Outlet	ΔHexpt. Btu/lb$_m$	Press. Correction Btu/lb$_m$	ΔH corrected Btu/lb$_m$
31 (1)	436.0	129	13	199.5	0.00	199.5
40 (1)	524.1	131	57	250.6	0.10	250.7
39 (*)	604.2	130	54	310.0	0.09	310.1
41 (*)	613.9	131	57	327.3	0.10	327.4
42 (*)	642.9	131	53	375.5	0.09	375.6
38	665.8	128	54	437.5	0.09	437.6
150 Psia Isobar						
8 (1)	157.1	159	61	42.3	0.11	42.4
7 (1)	185.6	150	62	57.1	0.11	57.2
6 (1)	217.9	149	53	71.3	0.09	71.4
5 (1)	255.7	150	38	93.2	0.06	93.3
14 (1)	268.2	151	20	99.7	0.02	99.7
1 (1)	280.2	150	20	105.9	0.04	105.9
15 (1)	315.7	157	20	126.3	0.02	126.3
2 (1)	326.8	151	28	132.9	0.04	132.9
3 (1)	372.9	151	28	158.6	0.04	158.6
12 (1)	399.7	152	96	175.1	0.175	175.3
4 (1)	424.9	149	28	190.2	0.04	190.2
62 (1)	441.0	150	12	202.0	0.00	202.0
9 (1)	444.3	155	29	200.0	0.05	200.1
63 (1)	486.1	151	12	228.1	0.00	228.1
66 (1)	490.8	150	12	229.7	0.00	229.7
46 (1)	511.8	151	57	243.5	0.10	243.6
64 (1)	525.0	149	12	254.3	0.00	254.3
57 (1)	533.6	150	12	259.3	0.00	259.3
48 (1)	535.4	153	40	258.4	0.06	258.5
67 (1)	548.2	150	12	266.0	0.00	266.0
45 (1)	565.5	147	66	279.7	0.12	279.8
68 (1)	579.6	150	12	285.1	0.00	285.1

TABLE 2

#878 Middle Distillate (Pittsburg & Midway Coal Mining Co.)

ENTHALPY DATA

150 Psia Isobar (Contd.)

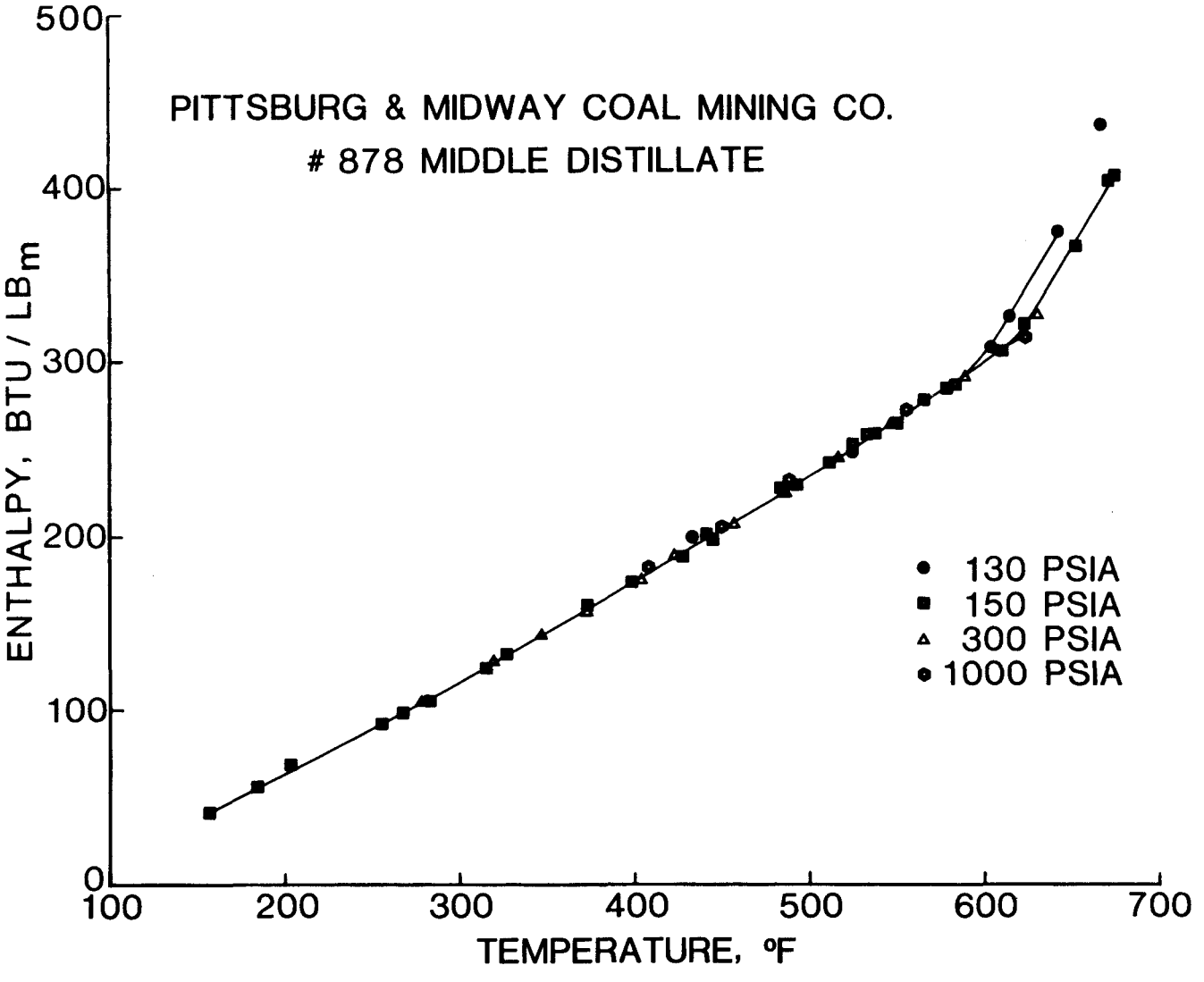
Run No.	Temp., °F Inlet	Pressure, Psia Inlet	Outlet	ΔHexpt. Btu/lb$_m$	Press. Correction Btu/lb$_m$	ΔH corrected Btu/lb$_m$
69 (1)	582.1	151	12	287.1	0.00	287.1
73 (1)	609.6	149	12	308.3	0.00	308.3
70 (*)	622.5	149	12	322.7	0.00	322.7
65 (*)	652.6	150	12	367.0	0.00	367.0
75 (*)	671.8	149	54	404.6	0.09	404.7
71 (*)	674.9	150	12	409.3	0.00	409.3
300 Psia Isobar						
17 (1)	279.1	299	167	106.6	0.34	106.9
18 (1)	318.9	300	159	128.8	0.325	129.1
19 (1)	346.9	300	152	144.3	0.30	144.6
20 (1)	372.6	299	152	159.2	0.30	159.5
21 (1)	403.0	302	153	175.8	0.30	176.1
23 (1)	424.7	299	190	189.8	0.39	190.2
24 (1)	456.0	298	189	207.4	0.39	207.8
27 (1)	485.2	300	217	225.6	0.45	226.1
28 (1)	515.9	303	216	246.3	0.45	246.8
29 (1)	545.7	303	214	265.2	0.44	265.6
30 (1)	588.1	301	214	291.4	0.44	291.8
52 (*)	630.6	300	192	327.7	0.40	328.1
1000 Psia Isobar						
32 (1)	408.5	995	923	182.7	1.00	183.7
33 (1)	450.3	999	923	206.5	1.00	207.5
34 (1)	488.6	997	915	229.8	0.98	230.8
35 (1)	516.7	1000	916	246.1	0.98	247.1
36 (1)	555.8	1002	917	271.0	0.99	272.0
37 (1)	623.5	998	910	315.0	0.97	316.0

TABLE 2

#878 Middle Distillate (Pittsburg & Midway Coal Mining Co.)

The reference temperature and pressure are 1 atm. and 65^{o}F.

(l) = liquid phase
(*) = two phase region
(v) = vapor phase


PITTSBURG & MIDWAY COAL MINING CO.
878 MIDDLE DISTILLATE
ENTHALPY, BTU / LBm
TEMPERATURE, °F
0
100
200
300
400
500
100
200
300
400
500
600
700
130 PSIA
150 PSIA
300 PSIA
1000 PSIA

Enthalpy measurements are presently underway on a naphtha sample (#1046) also furnished by Pittsburg and Midway Coal Mining Co. Unfortunately, the coking problems associated with the middle distillate are also occurring with the naphtha sample. The complete set of enthalpy measurements for the naphtha will be presented in the next quarterly progress report.

Correlation of Enthalpy Data for Coal-Derived Liquids

During this quarter, the correlation proposed by P.K. Huang (Characterization and Thermodynamic Correlations for Undefined Mixtures, Ph.D. Thesis, Pennsylvania State University, 1977) was applied to several of the fluids in our enthalpy data bank. The results of this work are summarized in Table 3.

Some additional property measurements on the fluids of Table 3 were also carried out at the Colorado School of Mines. These results are summarized in Tables 4-7.

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

Comparisons are available in the tenth quarterly progress report (October-December 1977).

Enthalph Measurements on Selected Mixtures

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

Liaison

No work during this quarter.

Consultation and Advice to DOE

No work during this quarter.

TABLE 3

Use of the Huang Correlation for Enthalpy Prediction

Coal-Derived Liquid	Progress Report Containing the Experimental Data	Average Error, BTU/lb_m (experimental-correlation)
Western Kentucky Whole Oil (COED Process)	#7 (January-March 1977)	5.5
Western Kentucky Distillate (COED Process)	#8 (April-June 1977)	4.0
Utah Distillate (COED Process)	#8 (April-June 1977)	11.1
Kentucky Distillate (Synthoil Process)	#9 (July-September 1977)	32.4

TABLE 4

Asphaltenes Content

Coal Liquid	Wt. % Asphaltenes
Western Kentucky Whole Oil (COED Process)	0.406
Western Kentucky Distillate (COED Process)	0.161
Utah Distillate (COED Process)	0.519
Kentucky Distillate (Synthoil Process)	0.865

TABLE 5

Carbon-Hydrogen-Nitrogen Analysis

Coal-Liquid	Wt. % C	Wt. % H	Wt. % N	C/H
Western Kentucky Whole Oil (COED Process)	73.48 (±2.47)	8.35 (±0.62)	1.26 (±0.01)	0.73
Western Kentucky Distillate (COED Process)	88.12 (±0.02)	11.06 (±0.04)	1.08 (±0.13)	0.64
Utah Distillate (COED Process)	87.91 (±0.05)	10.81 (±0.07)	1.48 (±0.07)	0.64
Kentucky Distillate (Synthoil Process)	81.01 (±2.65)	8.84 (±0.1€)	1.96 (±0.02)	0.77

± is the standard deviation for three separate runs for each sample.

Note that the accuracy of the instrument under normal operating conditions is ± 0.3%. The major sources of error during the runs are incomplete combustion of the sample and spent catalytic sites in the combustion tube.

TABLE 6

Total Sulfur Content

Coal-Liquid	Total Sulfur, Wt. %
Western Kentucky Whole Oil (COED Process)	0.04
Western Kentucky Distillate (COED Process)	0.00
Utah Distillate (COED Process)	0.00
Kentucky Distillate (Synthoil Process)	0.13

TABLE 7

Refractive Index

Coal-Liquid	Avg. n_d^{20}
Western Kentucky Whole Oil (COED Process)	1.5186
Western Kentucky Distillate (COED Process)	1.4997
Utah Distillate (COED Process)	1.4992
Kentucky Distillate (Synthoil Process)	1.5400

VI. CONCLUSIONS

Enthalpy measurements were completed for a middle distillate sample furnished by the Pittsburg & Midway Coal Mining Co. A total of 52 measurements were made, covering the ranges 157 to 675°F and 130 to 1000 psia.

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