Enthalpy Measurements on a Syncrude from a Western Kentucky Coal

A.J. Kidnay, R.R. Fleckenstein, H. Omid and V.F. Yesavage

Chemical and Petroleum-Refining Engineering Department
Colorado School of Mines
Golden, Colorado 80401

ABSTRACT

Enthalpy measurements over the range 65 to 700 F and 100 to 1500 psia were made on a coal-derived liquid using a Freon 11 reference calorimeter. The coal liquid was produced from a western Kentucky coal using the Char-Oil-Energy-Development (COED) process, and was analyzed by the Bartlesville Energy Research Center (BERC/RI-75/12, November, 1975) prior to the measurements.

INTRODUCTION

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.

The research program is divided into three major 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,

(2) enthalpy measurements on samples of well-defined coal-derived liquids, and

(3) preparation of engineering correlations for the measured enthalpy data, and comparison with representative data for petroleum and petroleum fractions.

The work reported here is one part of item 2, that is a complete set of enthalpy measurements on a whole (unfractionated) sample of liquid derived from a western Kentucky coal by the COED process.

RESULTS AND DISCUSSION

The liquid used in this work was analyzed by the ERDA Bartlesville Energy Research Center, and the results of their work are available. (G. P. Sturm, Jr., P. W. Woodward, J. W. Vogh, S. A. Holmer, J. E. Dooley, "Analyzing Syncrude from Western Kentucky Coal," BERC/RI-75/12).

The samples used in the calorimetric are from the same lot used by BERC in its characterization studies. The sample was prepared by filtering with Whatman, quality number 1, filter paper before being charged to the system. The enthalpy of the sample was measured along four different isobars (100, 500, 1000, 1500 psia) with the calorimeter inlet temperature varying over the range of 122-705^{o}F. The data are presented in the accompanying table and figures.

The outlet temperature was corrected to the base of 65^{o}F using the heat capacity at this temperature as found from the measured enthalpy vs. temperature curve (CP = 0.44 Btu/lb^{o}F). This correction never amounted to more than 0.3 Btu/lbm. The outlet pressure was corrected to a reference of 1 atm. using the Kesler-Lee correlations (Lee, B. I. and Kesler, M. G., AIChE Journal, 21, 510 (1975); Kesler, M. G. and Lee, B. I., Hydrocarbon Processing, 55, No. 3, 153, (1976)). The pressure corrections are shown in the table.

From the figures it can be seen that for the Western Kentucky syncrude the enthalpy was not a significant function of pressure at high pressures (500 to 1500 psia) where the sample was essentially a liquid at all temperatures. At the lowest pressure of 100 psia where significant vaporization occurs at higher temperatures, the enthalpy is greater at lower pressures (100 psia versus 500 psia).

During the enthalpy measurements, what appeared to be thermal cracking was often observed at pressures above 500 psia and at inlet temperatures above 600^{o}F. The cracked fluid foamed into the collection tube, appeared to be less viscous and changed to a lighter color. The foaming was believed to be the result of a large volume of gas produced by cracking of the sample. An obnoxious odor was also associated with the cracked sample. The cracked-sample enthalpy measurements were higher than the values for the uncracked material possibly due to vapor entrainment. One possible explanation for the cracking is a catalytic effect due to the stainless steel wall of the preheater bath coil. Several modifications were tried in order to correct the problem, including replacing the coil, and more gradual preheating of the oil without much success. A major difficulty is the apparent randomness of occurance of the cracking. On some runs, the sample cracks and foaming is observed while on others it does not. Several operations are under consideration which could reduce or eliminate decomposition, including hydrogen sulfide flushing of the coil to poison catalytic surface sites, and deaeration of the sample after every run to prevent oxidation reactions. However, until some more definitive conclusions can be drawn, our present operating policy at high temperatures is to complete runs until foaming and sample decomposition occurs. At such time, the system is drained and refilled with fresh sample.

Gas chromatograms of the sample in the system were taken periodically. Chromatograms of the uncracked material showed the same characteristic peaks; however, those of the cracked sample showed small compositional changes in the low temperature boiling range.

ACKNOWLEDGEMENTS

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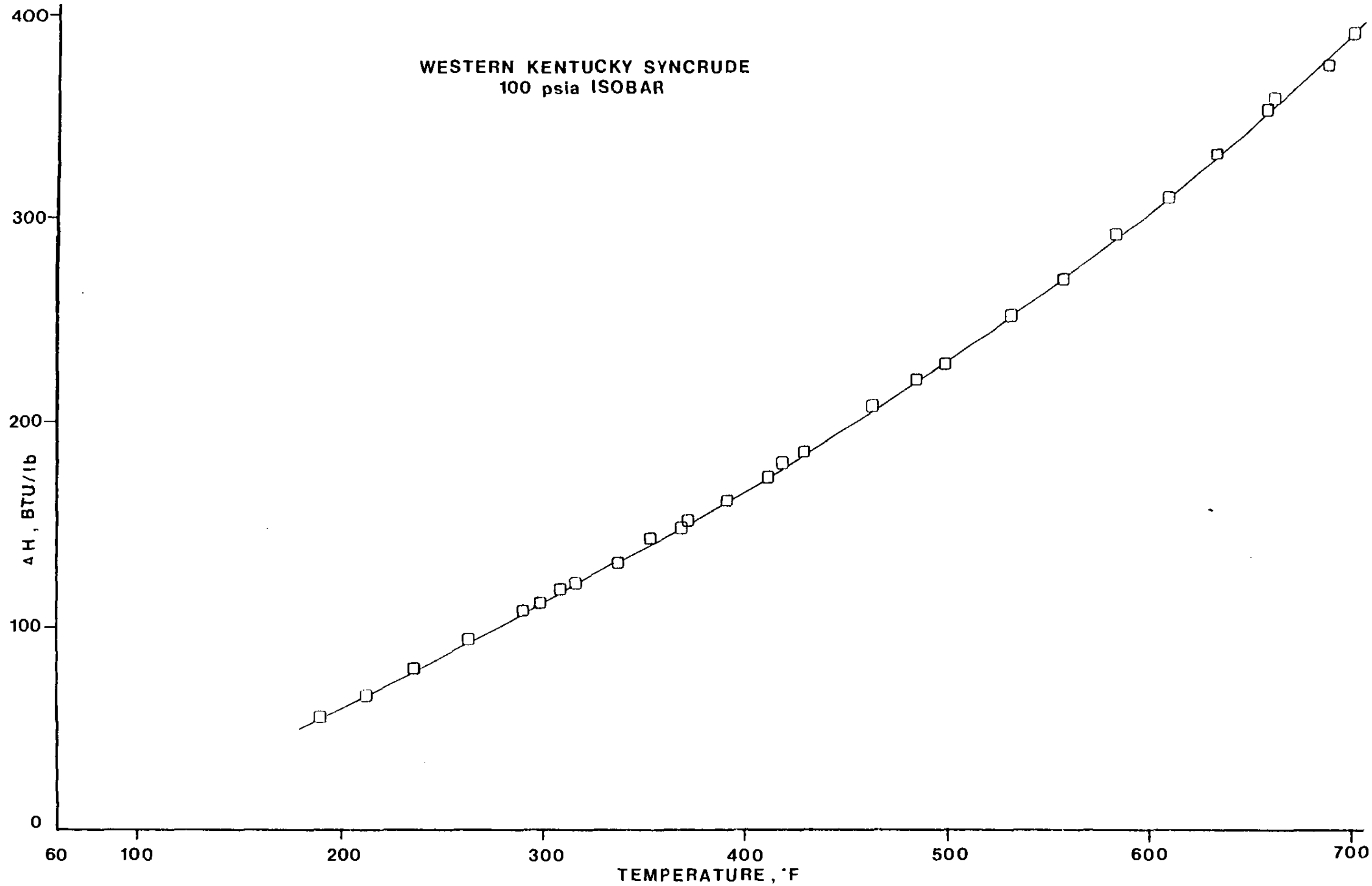
The coal-derived liquid sample used in this work was furnished by Mr. C. J. Thompson, Bartlesville Energy Research Center.

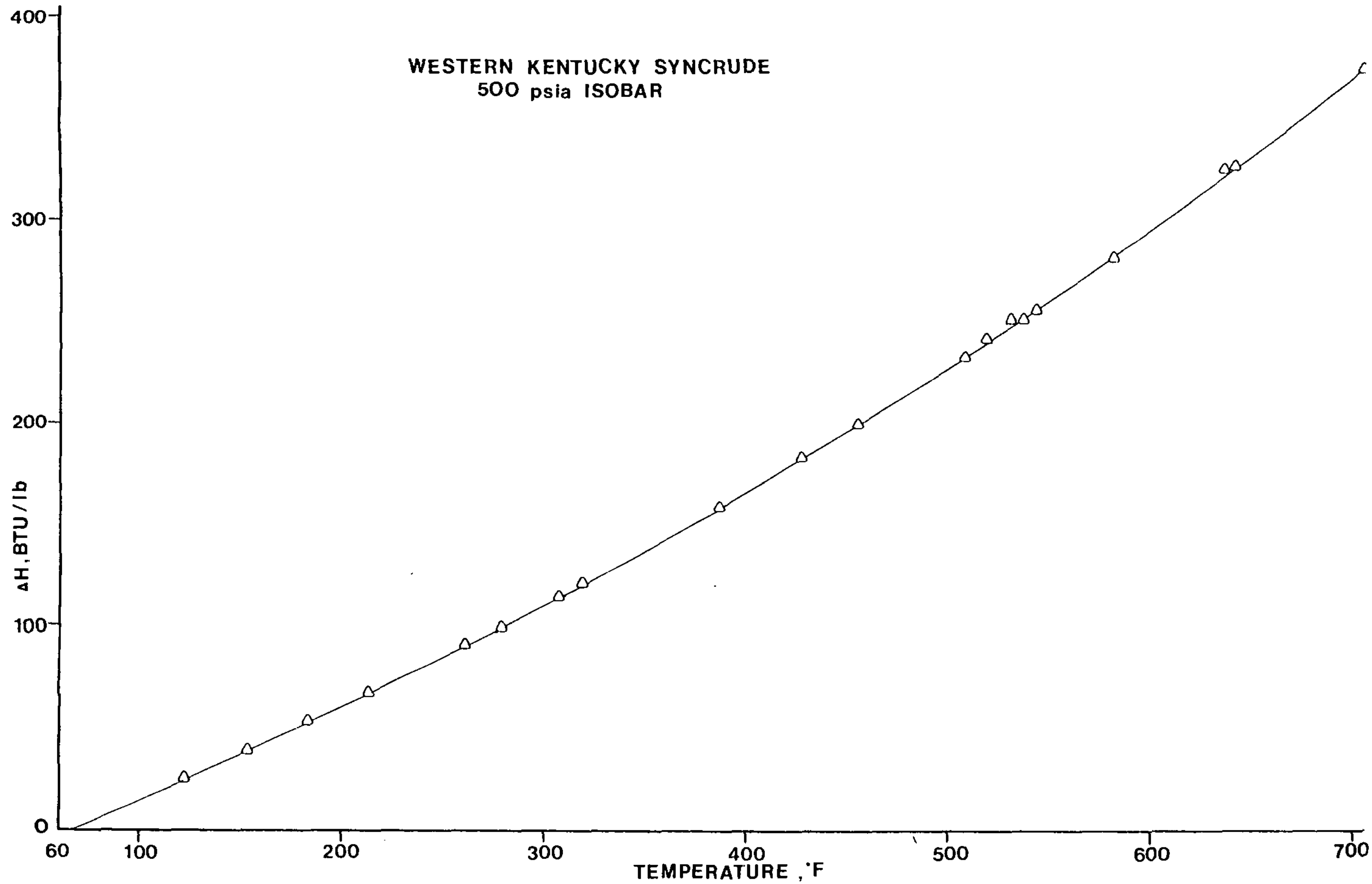
WESTERN KENTUCKY SYNCRUDE ENTHALPY DATA

Run No.	Temperature, °F Inlet	Pressure, psia Inlet	Pressure, psia Out	ΔH experimental Btu/lb	Pressure Correction Btu/lb	ΔH corrected Btu/lb
1	190.1	106	20	55.7	-0.005	55.7
2	213.4	105	20	65.3	-0.005	65.3
30	237.1	106	20	78.5	-0.005	78.5
29	264.1	105	20	92.5	-0.005	92.5
28	290.6	105	20	107.1	-0.005	107.1
3	298.7	102	27	110.7	-0.012	110.7
27	308.9	132	56	119.1	-0.040	119.1
4	316.3	101	26	121.3	-0.011	121.3
5	337.2	101	27	132.7	-0.012	132.7
7	352.4	104	37	142.6	-0.022	142.6
23	367.3	100	21	148.6	-0.006	148.6
8	371.2	105	38	151.1	-0.022	151.1
9	390.7	104	38	161.6	-0.023	161.6
10	411.1	103	30	173.0	-0.014	173.0
24	418.2	100	20	179.5	-0.006	179.5
11	429.5	103	33	184.9	-0.018	184.9
12	462.0	103	22	207.0	-0.007	207.0
14	483.7	105	30	220.2	-0.014	220.2
15	498.8	101	21	227.7	-0.006	227.7
16	531.6	102	22	251.2	-0.007	251.2
17	556.9	102	21	269.3	-0.006	269.3
18	583.6	102	21	290.7	-0.006	290.7
19	608.9	106	21	308.5	-0.006	308.5
20	633.9	104	22	331.4	-0.006	331.4
26	657.9	105	32	354.2	-0.016	354.2
21	662.0	104	23	358.4	-0.008	358.4
22	689.1	100	20	376.3	-0.005	376.3
25	700.9	104	32	391.0	-0.017	391.0

WESTERN KENTUCKY SYNCRUDE ENTHALPY DATA

Run No.	Temperature, °F Inlet	Pressure, psia Inlet	Pressure, psia Out	ΔH experimental BTU/lb	Pressure Correction BTU/lb	ΔH corrected BTU/lb
40	122.0	500	346	25.1	-0.32	24.8
39	154.4	502	379	39.4	-0.35	39.0
38	183.6	499	378	52.9	-0.35	52.5
37	213.3	498	279	66.9	-0.25	66.6
36	261.5	503	384	90.9	-0.36	90.5
35	280.2	507	415	99.7	-0.39	99.3
34	306.2	505	416	115.0	-0.39	114.6
33	307.0	505	417	114.5	-0.39	114.1
41	319.6	500	424	121.0	-0.40	120.6
42	387.6	504	424	159.1	-0.39	158.7
64	427.9	494	369	182.6	-0.34	182.3
43	455.8	505	423	199.1	-0.39	198.7
45	507.7	500	408	232.6	-0.38	232.2
49	518.1	508	438	241.8	-0.41	241.4
44	531.1	508	424	251.4	-0.39	251.0
50	537.2	495	436	251.7	-0.41	251.3
46	544.1	498	394	256.9	-0.37	256.5
47	582.3	498	405	282.7	-0.38	282.3
66	636.7	498	419	326.0	-0.39	325.6
65	641.8	500	397	327.0	-0.37	326.6
67	705.4	495	418	376.5	-0.39	376.1
55	246.7	996	911	83.7	-0.86	82.8
54	288.9	995	913	106.3	-0.87	105.4
56	332.7	1003	920	127.3	-0.87	126.4
57	384.2	1000	921	156.3	-0.87	155.4
58	441.8	1001	922	192.7	-0.87	191.8
68	268.8	1492	1379	95.9	-1.32	94.6
62	344.6	1501	1411	141.2	-1.35	139.8
63	345.7	1498	1411	135.3	-1.35	133.9
69	391.3	1490	1386	162.7	-1.32	161.4
61	415.2	1498	1439	174.7	-1.37	173.3
59	471.8	1498	1437	205.7	-1.37	204.3
60	472.3	1498	1435	209.4	-1.37	208.0
70	541.3	1487	1368	255.5	-1.30	254.2
71	608.8	1486	1382	301.2	-1.32	299.9
72	640.0	1482	1386	324.1	-1.32	322.8
73	676.6	1494	1408	355.4	-1.34	354.1
74	693.1	1487	1408	367.6	-1.34	366.3


WESTERN KENTUCKY SYNCRUDE
100 psia ISOBAR
ΔH, BTU/lb
0
100
200
300
400
TEMPERATURE, °F
60
100
200
300
400
500
600
700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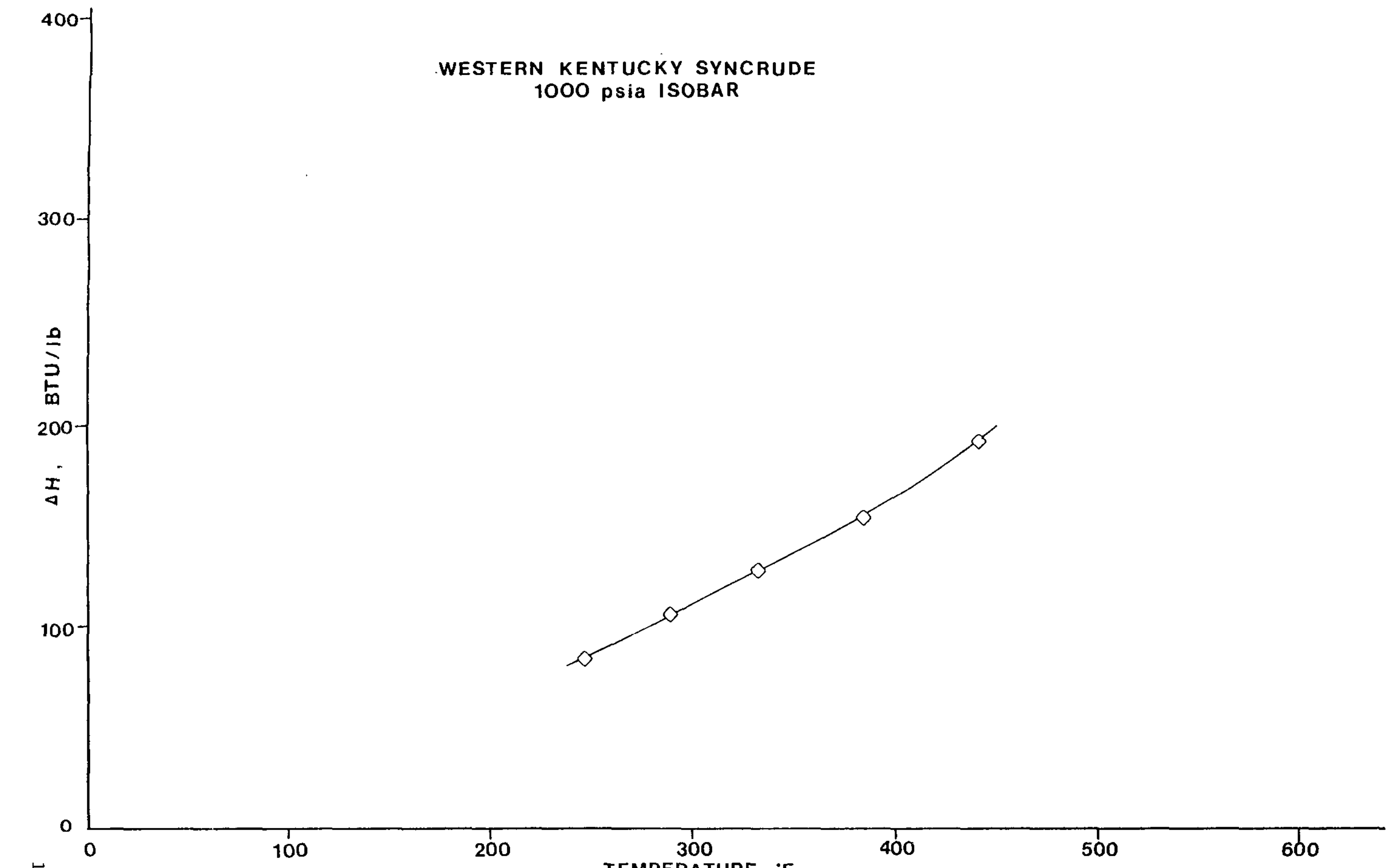
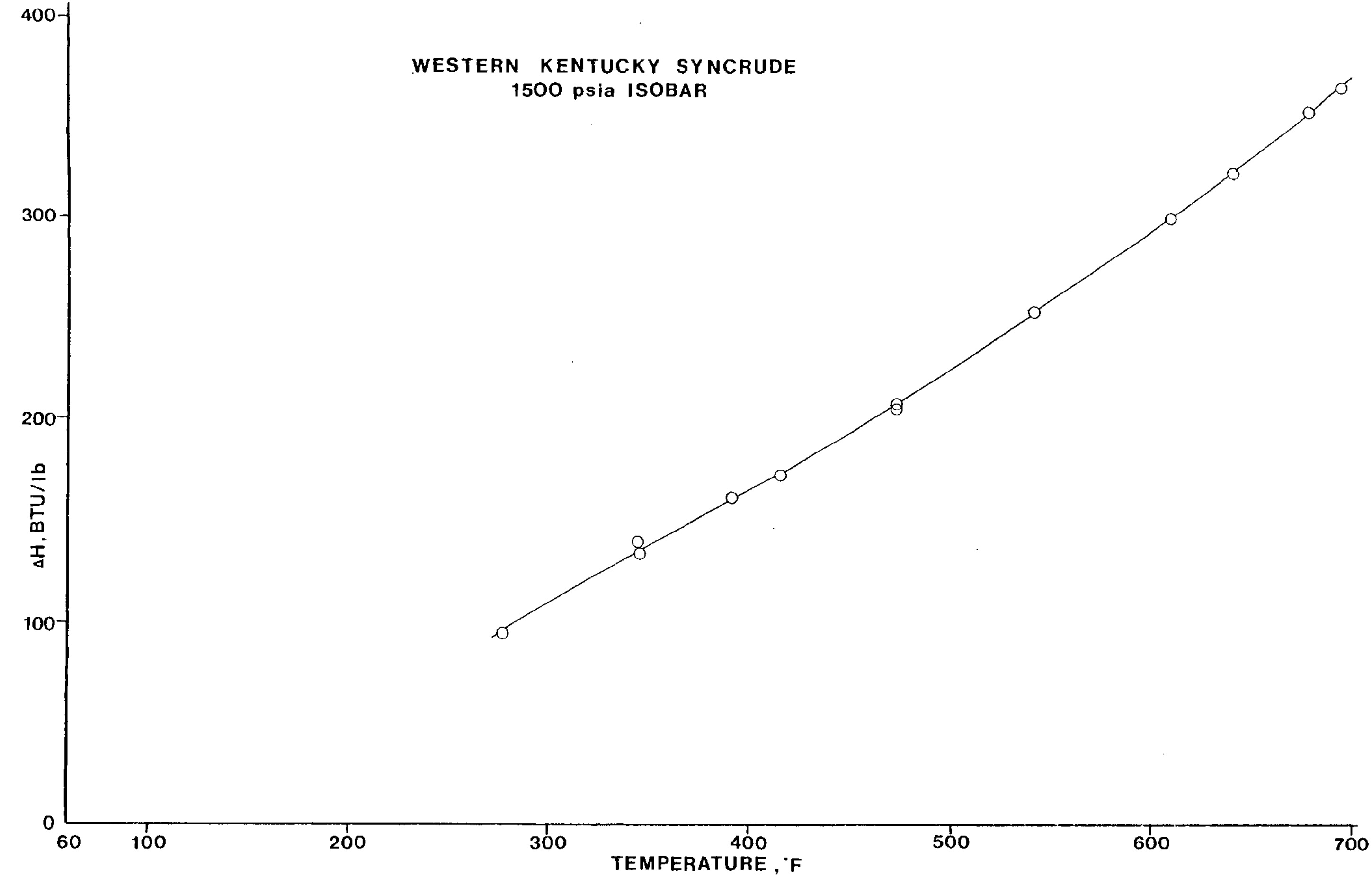
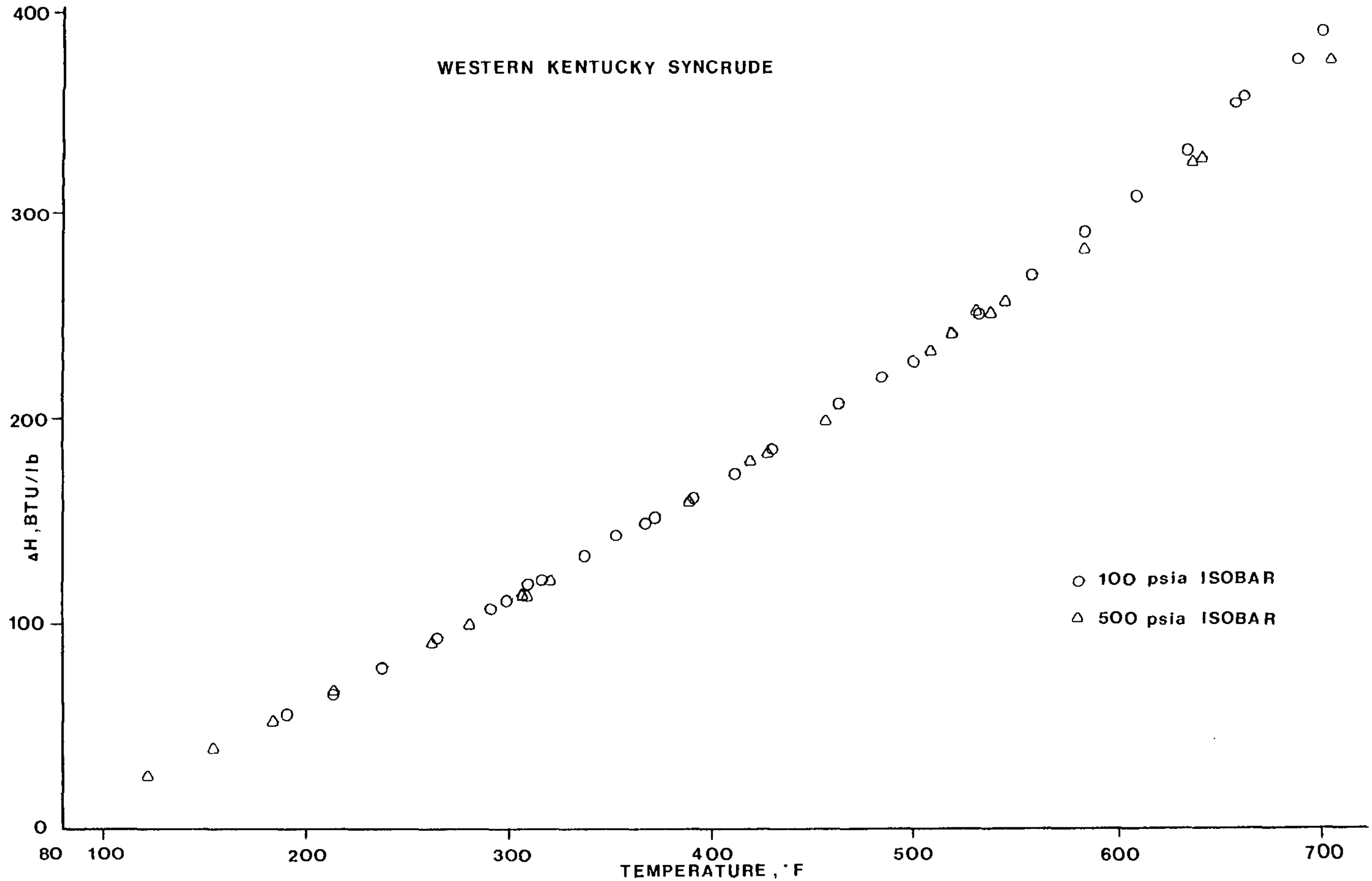
500 psia ISOBAR
ΔH, BTU/lb
0
100
200
300
400
60
100
200
300
400
500
600
700
TEMPERATURE, °F


WESTERN KENTUCKY SYNCRUDE
1000 psia ISOBAR
ΔH, BTU/lb
400
300
200
100
0
0
100
200
300
400
500
600
TEMPERATURE, °F


WESTERN KENTUCKY SYNCRUDE
1500 psia ISOBAR
ΔH, BTU/lb
0
100
200
300
400
60
100
200
300
400
500
600
700
TEMPERATURE, °F



WESTERN KENTUCKY SYNCRUDE
○ 100 psia ISOBAR
△ 500 psia ISOBAR
ΔH, BTU/lb
0
100
200
300
400
80
100
200
300
400
500
600
700
TEMPERATURE, °F