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# ENTHALPY MEASUREMENT OF COAL-DERIVED LIQUIDS

Combined Quarterly Technical Progress Reports, April—June 1979 and July—September 1979

By
A. J. Kidnay
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September 15, 1980
Date Submitted

Work Performed Under Contract No. AC22-79ET13395

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U. S. DEPARTMENT OF ENERGY

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# Enthalpy Measurement of Coal-Derived Liquids

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## Abstract

Enthalpy measurements on a coal-derived naphtha and middle distillate, both produced by the SRC-II process, were made using flow calorimetry. The accuracy of the measurements, as reported by Omid (2), was within ± 1% of the measured enthalpy differences, $\Delta H$.

Experimental data for the Naphtha were obtained over a pressure range of 100-300 psia and temperatures from $148^{\circ}$ to $456^{\circ}F$. The Middle Distillate enthalpy measurements were made in the pressure and temperature ranges of 130-1000 psia, and $157^{\circ}$-$675^{\circ}F$, respectively.

The methods of prediction of enthalpy developed for petroleum fractions were unsatisfactory when applied to the above data. These results were then compared with the earlier work of Omid (2), Sharma (3), and Andrew (4), and a negative bias was observed in the predicted enthalpy values for several of the coal-liquids. Based on these results, it was theorized that the high experimental enthalpy values for coal-liquids were due to an energy of association attributed, primarily, to hydrogen-bonding effects.

The petroleum-fraction enthalpy correlations were then tested on the experimental data for pure compounds, both associating and non-associating. The predicted values compared very well with the experimental results for non-associating model compounds. However, for associating model compounds the predicted enthalpy values were considerably lower than their experimental data. This served to confirm the basic premise that the high experimental enthalpy values, for model compounds and coal liquids, were a direct consequence of an energy of association attributed, primarily, to hydrogen-bonding effects.

## 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-denity-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 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 200 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.

## Detailed Description of Technical Progress

# PART I

# ENTHALPY MEASUREMENTS ON COAL-DERIVED LIQUIDS

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## EQUIPMENT AND PROCEDURE

The equipment used in this study is a reference-fluid boil-off flow calorimeter similar to that originally developed by Nelson and Holcomb (24) and previously described by McConnell (1), and Yesavage, et al, (15). Figure 1 shows a detailed drawing of the calorimeter, while the schematic diagram of the flow system is presented in Figure 2. The first law of thermodynamics when applied to a flow calorimeter, with negligible potential and Kinetic energy effects, reduces to (3)

$$(\Delta H)_x = \frac{Q-W}{M} \qquad (1)$$

where,

$(\Delta H)_x$ = enthalpy difference/unit mass of the fluid between the outlet and inlet conditions at a constant overall composition, $x$,

$Q$ = net rate of heat transfer to the fluid,

$W$ = net rate of work output, and

$M$ = mass flow rate of the "test" fluid.

For a boil-off calorimeter ($W = 0$):

$$Q = -M_r \lambda_r - q \qquad (2)$$

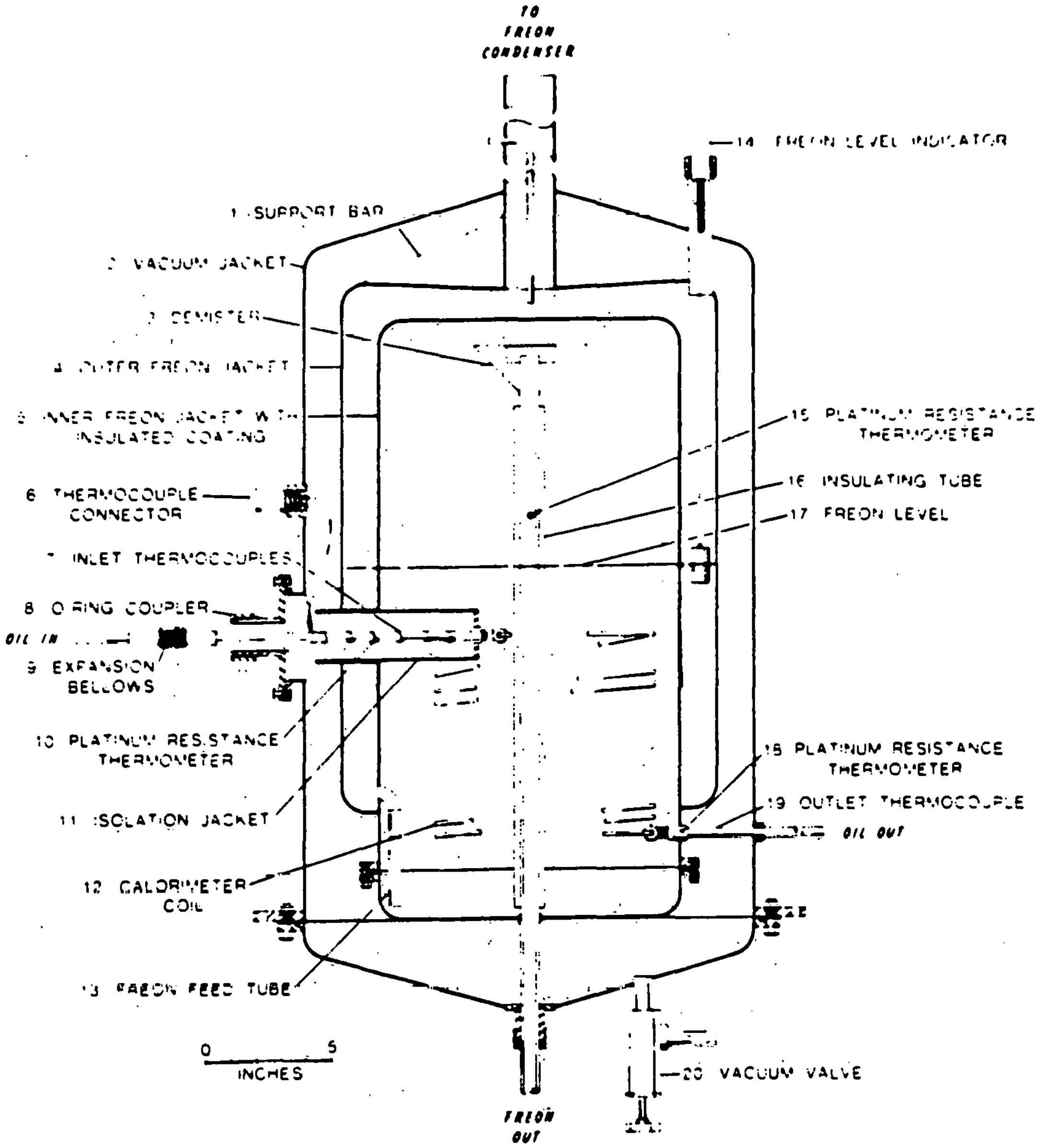

FIGURE 1 FLOW CALORIMETER

where, $M_r$ = mass flow rate of the reference fluid boiling off,

$\lambda_r$ = latent heat of vaporization of the reference fluid, and

$q$ = heat loss from the calorimeter reference fluid system, or heat flow from ambient ($80^{\circ}F$) to the Freon 11 @ $65^{\circ}F$.

Hence, equation (1) becomes $(\Delta H)_x = - \frac{M_r \lambda_r}{M} - \frac{q}{M}$

$$\text{or,} \quad H_{(T,P)} - H_{(65^{\circ}F,P)} = \frac{M_r \lambda_r}{M} + \frac{q}{M} \qquad (3)$$

The heat loss term represents a limitation in the accuacy of a measurement but, as is apparent, it is inversely proportional to flow rate. Thus, in order to minimize the heat loss effects, most of the calorimetry facilities (as with this one) have been designed to operate at flow rates in the order of one gallon per hour (24, 26).

The final results consist of enthalpy variations with temperature (reference temperature = $65^{\circ}F$) along different isobars. The outlet pressures of the "test" fluid were all corrected to a reference pressure of 1 atmosphere.

In the two-phase region, the experimentally determined enthalpies represent the total enthalpy of the vapor-liquid mixture having an overall composition the same as that of the original sample. These results are useful in the process design of heat transfer equipment; however, a knowledge of vapor-liquid equilibria is also required in the design of mass transfer equipment.

The calorimeter, as shown in Figure 1, is "constructed of 304 stainless steel except where it is in contact with the sample oil, where 316 stainless steel is used. The inner chamber constitutes the boiling bath. The 35 foot long coil 1/8 inch outside diameter stainless steel tubing provides more than adquate heat transfer area to cool the sample down to within 1°F of the Freon 11 bath. The Freon vapors that boil off from the inner chamber travel through the demister before leaving the calorimeter. The demister removes entrained liquid from the exit stream allowing only the vapor to leave. The middle chamber contains boiling Freon. It acts as an insulating barrier by eliminating any temperature difference between the inner chamber and its surroundings. It also increases the capacity of the calorimeter for holding freon since the two chambers are connected by the Freon feed tube. The outer chamber is evacuated by the vacuum system to provide a pressure of less than $7 \times 10^{-4}$ mm." (1).

The flow system, Figure 2, was designed to handle corrosive, relatively unstable coal-derived liquids. The layout of the piping was dictated by the possibility of two-phase

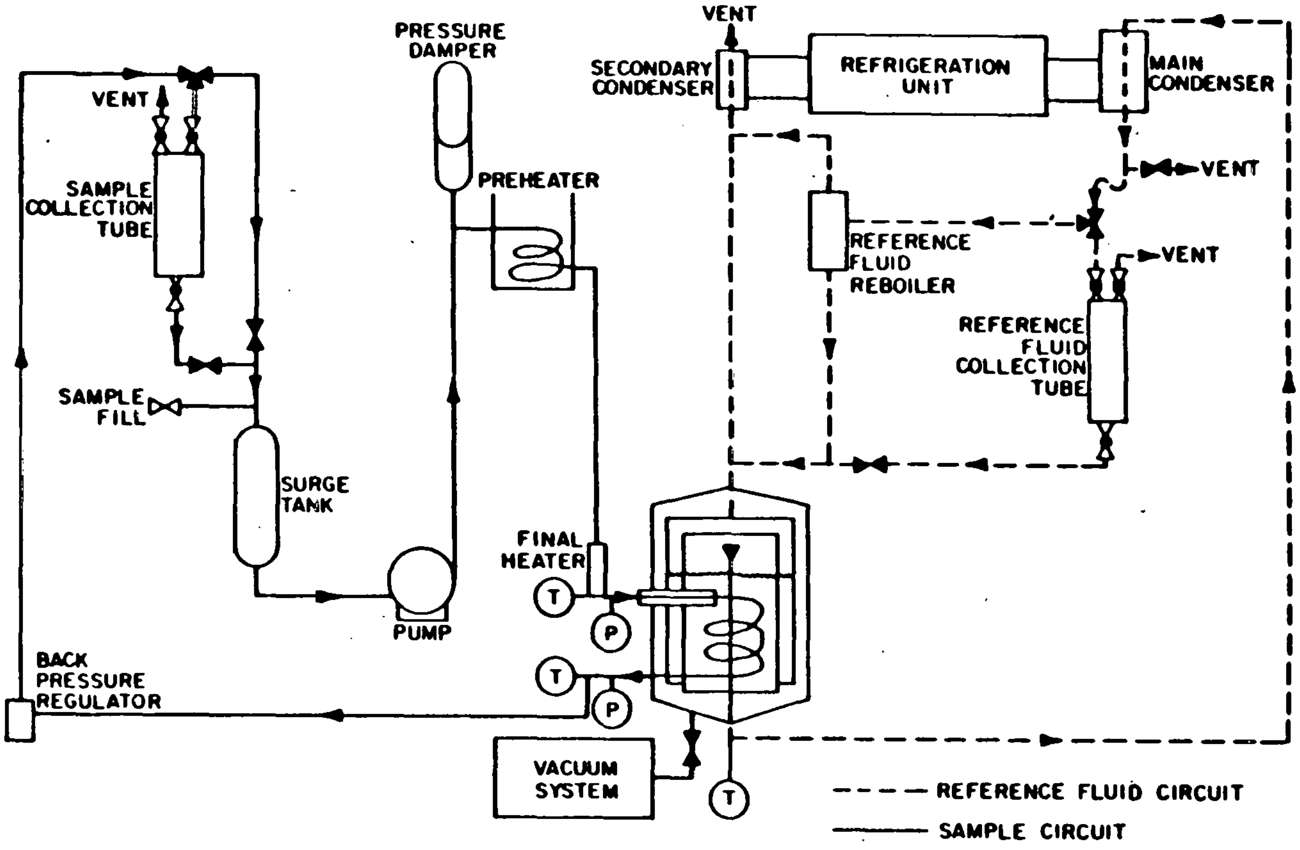

FIGURE 2

Flow Diagram of Experimental Apparatus for the Measurement of Enthalpy flow developing at high temperatures as well as the expected small amount of some of the samples. This called for a constant downward movement of the sample after heating, to prevent trapping of the liquid in low spots, thus minimizing the possibility of any compositional changes that might otherwise take place. Also, because of the limitation of small amounts of some of the samples, the shortest possible piping was used. For virtually all of the system, 1/8" outside diameter (0.035" wall thickness) 316 stainless steel tubing was used.

The sample is pumped from the surge tank by means of a Milton-Roy dual diaphragm pump. The dual diaphragm evens out the pump pulsations because of its double-action. The sample then flows through an in-line 60μ filter to remove any solids that might be present in order to prevent clogging up of the lines. A damper consisting of two 300 cc cylinders, in which the oil comes into contact with nitrogen, is installed down stream of the in-line filter to absorb the force of the pump stroke and cushion the liquid system against pressure surges. The sample is then preheated gradually, to minimize sample decomposition, in a fluidized-bed preheater bath. The sample flows through a 25-foot coil installed in the bath to provide an adequate heat transfer area. Air is injected at the bottom of the bath in order to fluidize the fused alumina sand to produce a safe heat transfer medium.

The inlet and outlet pressures of the calorimeter are measured with two bourdon tube gauges. The inlet and outlet temperatures are measured with in-line platinum resistance thermometers. A rod-type final heater controlled by a Proportional-Integral-Derivative controller, using an in-line thermocouple, sets the inlet temperature of the fluid to the calorimeter. A back pressure regulator is used to maintain the system pressure with the pressure being set by pressurized nitrogen. The sample fluid is then returned to the surge tank or sent to the collection tube by means of a three-way valve.

The Freon 11 boiled off from the inner calorimeter chamber as a result of heat transfer with the sample fluid, passes through a demister before entering a heated tube leading to the main condenser. An in-line platinum resistance thermometer, upstream of the heated tube, measures the Freon vapor outlet temperature. The tube is heated to prevent the condensation of the vapor before it reaches the main condenser. The condensed vapor from the main condenser flows past a vent, through a vapor trap, and on to a three-way valve whereby it can be directed to either the return heater or the collection tube. The return heater is used to heat the subcooled liquid Freon to its saturation temperature, allowing it to enter the calorimeter.

The Freon boiled off from the outer chamber of the calorimeter is condensed in the small condenser, along with vapors from the return heater, and returned to the calorimeter.

The layout of the Freon 11 lines was influenced by the gravity forced flow from the main condenser, minimization of pipe length, the low boiling point of Freon and room dimensions.

The platinum resistance thermometers used for the measurement of the inlet and outlet oil temperatures were custom made, 100 ohm nominal resistance, units sheathed in 316 stainless steel. The thermometer outputs were measured with a Fluke digital volt/ohm meter. Calibration over the temperature range of interest was accomplished with a Leeds and Northrup 8167-25-B platinum thermometer which was in turn calibrated by the manufacturer on IPTS-68. The temperature measurements are believed accurate to ± 0.1°F. The inlet and outlet pressures were measured with Heise gauges, calibrated by the manufacturer, with an accuracy of ± 2 psi. The weights of Freon and oil collected during an experimental measurement were determined to ± 0.05 gm on a Mettler analytical balance.

The evaluation of the calorimeter consisted of 33 measurements on compressed liquid water over a pressure range of 179-1529 psia and a temperature range of 196-551°F by Omid (2) and comparing the data obtained with that in the literature (27). The calorimeter was further evaluated by Sharma (3) using n-heptane as the test fluid in order to obtain enthalpy data across a liquid-vapor phase transformation. This was deemed necessary since the measurements done earlier on water were all in the compressed liquid region. The high heat of condensation of water makes operation with a steam or steam + liquid water inlet stream impractical with the present calorimeter (1, 2 ). In general, the accuracy of the calorimeter was determined to be ± 0.5% of the measured enthalpy difference, $\Delta H$.

A major concern during operation with coal derived liquids is the occurrence of sample decomposition at high temperatures. To determine the significance of decomposition at higher temperatures on the enthalpy measurements, low temperature runs were repeated after high temperatures were attained. In general, the low temperature runs obtained before and after heating up the sample were in agreement. At times, however, the runs differed indicating decomposition.

This generally occurred together with system pressure build-up from coking or a change in appearance of the sample. When this occurred, the sample in the system was replaced. As a check of the continued reliability of the system, runs with n-heptane were generally repeated whenever the sample was replaced. The n-heptane data were always in agreement with previous results.

## ENTHALPY MEASUREMENTS ON COAL-DERIVED LIQUIDS

A brief discussion of the enthalpy measurements attempted on two coal-liquids (a naphtha and a middle distillate cut ) is presented below.

### 1046 Naphtha

This material was produced by the Pittsburg and Midway Coal Mining Company at their DuPont, Washington pilot plant using the SRC-II process. The sample was used as received.

Liquid phase enthalpy measurements in the temperature range of 148$^{0}$ - 459$^{0}$F, along 100, 200 and 300 psia isobars are presented in Table 1 and Figure 3.

The outlet temperature was corrected to the base of 65$^{0}$F using the heat capacity at this temperature as found from the measured enthalpy vs temperature curve. This correction never amounted to more than 0.5 Btu/$lb_m$. The outlet pressure was corrected to a reference of 1 atm. using the Kesler-Lee correlation (9, 28). The pressure corrections are shown in the table and detailed calculations have been presented by Sharma (3).

From Figure 3 it can be seen that the liquid phase enthalpy is not a significant function of the pressure.

No enthalpy data in the two-phase or the vapor regions could be obtained at the isobars attempted due to severe operational problems caused by the thermal instability of

## Table 1

## #1046 Naphtha

## ENTHALPY DATA

<u>100 Psia Isobar</u>

| Run No. | Temp., °F Inlet | Pressure, Psia Inlet | Pressure, Psia Outlet | ΔHexpt. Btu/$lb_m$ | Press. Correction Btu/$lb_m$ | ΔH Corrected Btu/$lb_m$ |
|---|---|---|---|---|---|---|
| 1 (ℓ) | 208.1 | 100 | 56 | 74.9 | .10 | 75.0 |
| 2 (ℓ) | 209.7 | 101 | 56 | 75.5 | .10 | 75.6 |
| 43 (ℓ) | 232.4 | 100 | 74 | 90.6 | .14 | 90.7 |
| 3 (ℓ) | 234.4 | 101 | 56 | 90.0 | .10 | 90.1 |
| 5 (ℓ) | 256.6 | 101 | 48 | 103.0 | .07 | 103.1 |
| 44 (ℓ) | 258.4 | 98 | 69 | 104.3 | .14 | 104.4 |
| 73 (ℓ) | 279.2 | 100 | 82 | 115.2 | .22 | 115.4 |
| 45 (ℓ) | 282.2 | 100 | 68 | 119.2 | .13 | 119.3 |
| 6 (ℓ) | 285.2 | 103 | 48 | 119.5 | .09 | 119.6 |
| 74 (ℓ) | 291.1 | 99 | 84 | 122.4 | .23 | 122.6 |
| 53 (ℓ) | 295.1 | 100 | 20 | 126.4 | .03 | 126.4 |
| 49 (ℓ) | 301.1 | 100 | 48 | 131.5 | .09 | 131.6 |
| 75 (ℓ) | 306.1 | 99 | 85 | 133.1 | .23 | 133.3 |
| 50 (ℓ) | 310.6 | 100 | 40 | 137.4 | .05 | 137.5 |
| 47 (ℓ) | 324.3 | 101 | 70 | 146.0 | .14 | 146.1 |
| 76 (ℓ) | 334.7 | 100 | 85 | 150.9 | .23 | 151.1 |
| 77 (ℓ) | 348.3 | 100 | 89 | 161.7 | .25 | 162.0 |
| **200 Psia Isobar** | | | | | | |
| 56 (ℓ) | 255.9 | 201 | 139 | 101.5 | .40 | 101.9 |
| 64 (ℓ) | 272.9 | 199 | 180 | 111.2 | .54 | 111.7 |

## Table I (cont.)

## #1046 Naphtha

## ENTHALPY DATA

300 Psia Isobar

| Run No. | Temp., °F Inlet | Pressure, Psia Inlet | Pressure, Psia Outlet | $\Delta H_{expt.}$ Btu/lb$_m$ | Press. Correction Btu/lb$_m$ | $\Delta H$ Corrected Btu/lb$_m$ |
|---|---|---|---|---|---|---|
| 26 (ℓ) | 143.2 | 302 | 198 | 41.3 | .61 | 41.9 |
| 27 (ℓ) | 171.5 | 301 | 208 | 54.3 | .61 | 54.9 |
| 28 (ℓ) | 185.0 | 300 | 208 | 61.9 | .61 | 62.5 |
| 11 (ℓ) | 200.8 | 299 | 12 | 69.9 | 0 | 69.9 |
| 15 (ℓ) | 213.8 | 300 | 274 | 79.6 | .86 | 80.5 |
| 16 (ℓ) | 242.1 | 290 | 261 | 95.7 | .82 | 96.5 |
| 17 (ℓ) | 264.8 | 297 | 251 | 109.3 | .78 | 110.1 |
| 18 (ℓ) | 289.0 | 303 | 247 | 124.2 | .77 | 125.0 |
| 19 (ℓ) | 296.6 | 300 | 268 | 128.8 | .84 | 129.6 |
| 20 (ℓ) | 328.3 | 302 | 269 | 147.6 | .85 | 148.5 |
| 21 (ℓ) | 329.3 | 306 | 274 | 148.4 | .86 | 149.3 |
| 22 (ℓ) | 340.5 | 302 | 265 | 154.7 | .83 | 155.5 |
| 23 (ℓ) | 369.1 | 301 | 265 | 173.3 | .83 | 174.1 |
| 54 (ℓ) | 385.6 | 299 | 264 | 181.5 | .83 | 182.3 |
| 24 (ℓ) | 393.7 | 302 | 265 | 188.4 | .83 | 189.2 |
| 29 (v) | 408.9 | 301 | 246 | 201.1 | .77 | 201.9 |
| 25 (v) | 424.5 | 302 | 265 | 209.4 | .83 | 210.2 |
| 30 (v) | 434.7 | 301 | 247 | 223.7 | .77 | 224.5 |
| 32 (v) | 458.9 | 301 | 245 | 231.6 | .76 | 232.4 |

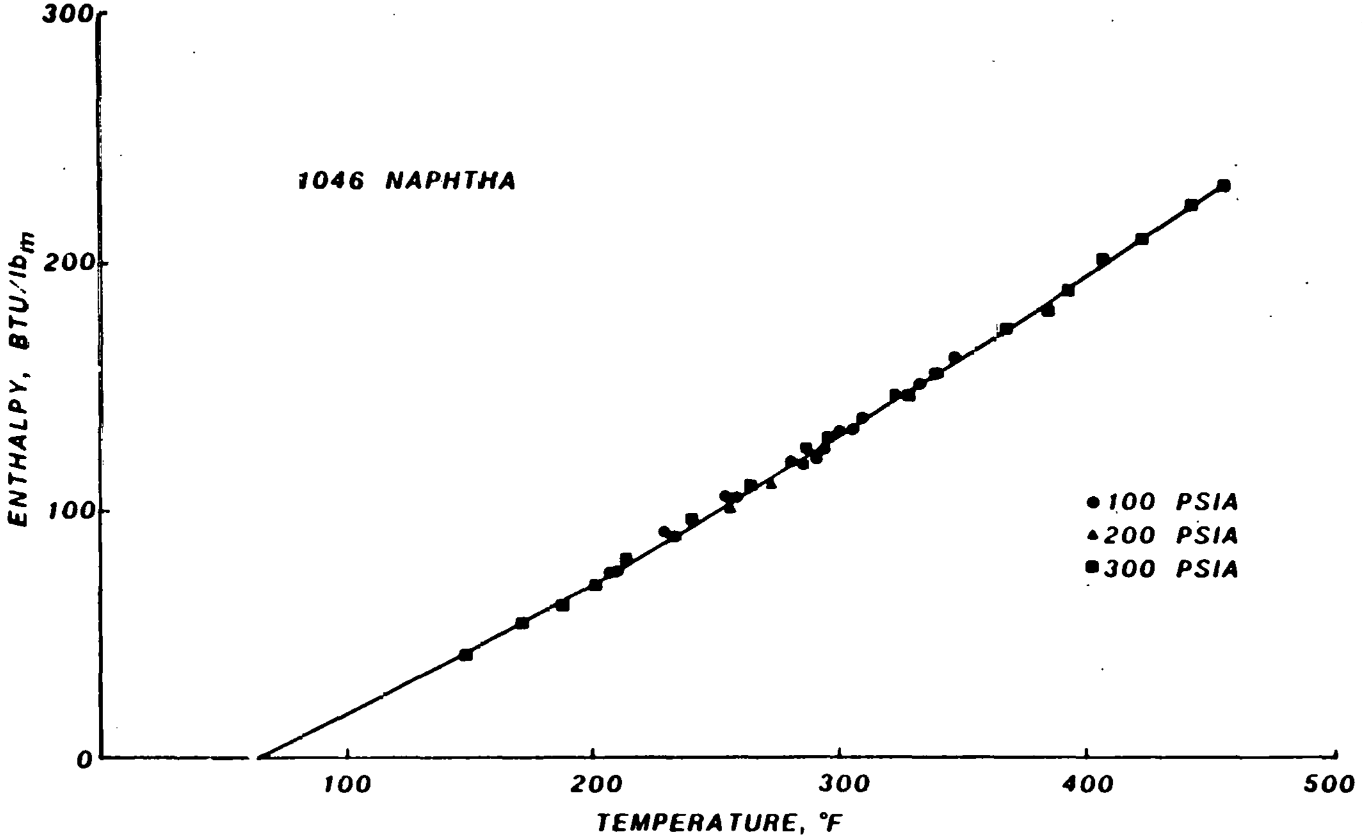

Figure 3. Enthalpy as a Function of Temperature for the 1046 Naphtha

the sample. Severe "coking" or polymerization, due to compositional changes, occurred in the sample lines and the preheater, resulting in frequent shut-downs, and replacement of the affected equipment. Repeated attempts at obtaining enthalpy data in the two-phase and the vapor regions by charging fresh samples to the system were unsuccessful.

## Middle Distillate

This sample was also furnished by the Pittsburg and Midway Coal Mining Company and was produced from a Kentucky coal at their DuPont, Washington pilot plant using the SRC-II process.

Enthalpy measurements, in the temperature range of 157° - 675°F along 130, 150, 300 and 1000 psia isobars, on the middle distillate cut were obtained and are presented in Table 2 and Figure 4.

The outlet temperature and pressure were corrected to 65°F and 1 atm respectively, using the same procedure as outlined for the 1046 Naphtha sample.

Severe operational problems were caused by the thermal instability of the sample. At moderate pressures (on the order of 150 psia), and at temperatures greater than 500°F, severe plugging problems quickly developed in both the preheater and final heater, forcing frequent shut-downs

## Table 2

## Middle Distillate

## ENTHALPY DATA

**130 Psia Isobar**

| Run No. | Temp., °F Inlet | Pressure, Psia Inlet | Pressure, Psia 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 | 123 | 54 | 437.5 | 0 09 | 437.6 |

**150 Psia Isobar**

| Run No. | Temp., °F Inlet | Pressure, Psia Inlet | Pressure, Psia Outlet | ΔHexpt. Btu/$lb_m$ | Press. Correction Btu/$lb_m$ | ΔH Corrected Btu/$lb_m$ |
|---|---|---|---|---|---|---|
| 8 (1) | 157.1 | 153 | 61 | 42.3 | 0 11 | 42.4 |
| 7 (1) | 185.6 | 150 | 62 | 57.1 | 0.1[illegible] | 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 | 15[illegible] | 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 | 0.02 | 202.0 |

## Table 2 (cont.)

## Middle Distillate

## ENTHALPY DATA

150 Psia Isobar (cont.)

| Run No. | Temp., $^oF$ Inlet | Pressure, Psia |  | ΔHexpt. Btu/$lb_m$ | Press. Correction Btu/$lb_m$ | ΔH Corrected Btu/$lb_m$ |
|---|---|---|---|---|---|---|
|  |  | Inlet | Outlet |  |  |  |
| 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 |
| 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 |

## Table 2 (cont.)

## Middle Distillate

**300 Psia Isobar** — **ENTHALPY DATA**

| Run No. | Temp., °F Inlet | Pressure, Psia Inlet | Pressure, Psia Outlet | ΔHexpt. Btu/lb$_m$ | Press. Correction Btu/lb$_m$ | ΔH Corrected Btu/lb$_m$ |
|---|---|---|---|---|---|---|
| 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 |

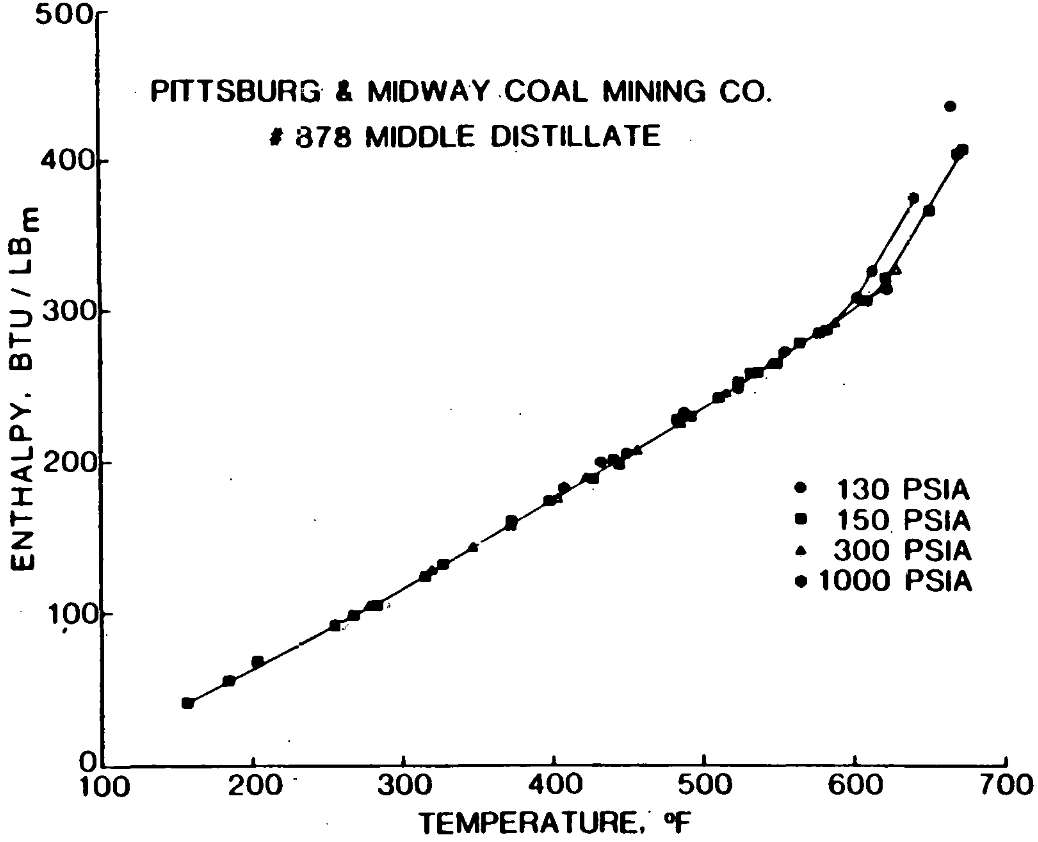

Figure 4. Enthalpy as a Function of Temperature for the Middle Distillate

and replacement of both the sample and the affected equipment. These operational problems were much the same as those encountered with the 1046 Naphtha sample.

As can be seen from Figure 4, some two-phase data was obtained for this sample at pressures of 130 and 150 psia. However, repeated attempts at obtaining enthalpy data in the two phase and the vapor regions, at the higher isobars, by charging fresh samples to the system, were unsuccessful.

# PREVIOUS EXPERIMENTAL WORK

Enthalpy measurements on several coal-derived liquids were undertaken as part of the enthalpy program at the Colorado School of Mines. Furthermore, enthalpy data was also taken for four pure compounds as part of a continuing effort to develop a predictive technique for enthalpies of coal-derived liquids. Table 3 gives the temperature and pressure range of all the data for the various systems studied along with the appropriate references.

There have also been some other enthalpy measurements of associated compounds and mixtures of associated compounds reported in the literature and these are presented in Table 4 along with the relevant temperature and pressure ranges as well as the appropriate references.

## Table 3

## ENTHALPY DATA FOR THE VARIOUS SYSTEMS STUDIED

| System Studied | References | Approximate Temperature Range, °F | Approximate Pressure Range, PSIA |
|---|---|---|---|
| Utah Light Distillate | Sharma (3) | 129-722 | 60-1500 |
| Western Kentucky Syncrude | Omid, (2) | 122-705 | 100-1500 |
| Western Kentucky Light Distillate | Omid, (2) | 119-756 | 60-500 |
| Synthoil Distillate | Andrew, (4) | 155-742 | 150-1500 |
| SRC-I Naphtha | Yesavage, et al. (11) | 159-719 | 30-1500 |
| Benzene | Hinman, (5) | 230-670 | 70-1000 |
| m-Xylene | Halla, (7) | 140-730 | 50-1500 |
| 1-methylnaphthalene | Holliman, (6) | 224-740 | 75-470 |
| m-Cresol | Hinman, (5) | 210-750 | 200-1500 |

## TABLE 4

### Liquid Heat Capacity/Enthalpy Data for Associated and Mixtures of Associated Compounds as Reported in the Literature

| System Studied | References | Approximate Temperature Range, °K | Approximate Pressure Range, PSIA |
|---|---|---|---|
| Methyl Alcohol<br>(Liquid heat capacity) | Kelley (12), Parks (13)<br>Carlson and Westrum (14) | 181-320 | Saturation Pressure |
| N-Propanol (Enthalpy) | Kubicek & Eubank (15) | 422-555 | 75-900 |
| i-Propanol (Enthalpy) | Ginnings & Corruccini(16) | 273-473 | Saturated Liquid |
| Ethyl Alcohol<br>(Liquid Heat Capacity) | Williams & Daniels (17) | 300-330 | Saturated Liquid |
| 2-Methylpropan-1-ol | Counsell, et al. (18) | 175-355 | Saturated Liquid |
| Pentan-1-ol<br>(Liquid Heat Capacity) | Counsell, et al. (18) | 200-389 | Saturated Liquid |
| Butan-2-ol<br>(Liquid Heat Capacity) | Andon, et al (19) | 188-345 | Saturated Liquid |
| Phenol<br>(Liquid Heat Capacity) | Andon, et al. (20) | 317-356 | Saturated Liquid |
| m-Cresol<br>(Liquid Heat Capacity) | Andon, et al (21) | 285-400 | Saturated Liquid |
| p-Cresol<br>(Liquid Heat Capacity) | Andon, et al (21) | 308-400 | Saturated Liquid |
| Butyl Alcohol<br>(Liquid Heat Capacity) | Counsell, et al. (22) | 395-453 | Ideal Gas State |
| n-Pentanol (Enthalpy) | Thinh, et al. (23) | 450-599 | 150-1500 |
| N-Hexanol (Enthalpy) | Thinh, et al. (23) | 522-616 | 200-1500 |

# PART II

# CORRELATION OF ENTHALPY DATA

## PETROLEUM CORRELATIONS

As an initial stage in the effort to correlate enthalpy data for coal-derived liquids, the experimental enthalpies were compared with the predicted enthalpies using correlations developed for petroleum fractions. However, it is to be noted that the conditions under which the coal liquids are formed and the hydrocarbon type distribution often differ radically from those of the petroleum fractions. This could prove to be a severe limitation on the usefulness of petroleum correlations to predict enthalpies of coal liquids. Moreover, a mixing rule with a pure component correlation cannot be applied to undefined mixtures of hydrocarbons such as coal liquids.

The correlations considered were the Johnson-Grayson correlation (8) as presented in the API data book, and the Kesler-Lee correlations (9, 28) which are an improvement over the former. These correlations and others have been discussed in detail by Fleckenstein (10). Briefly, however, all the correlations follow basically the same procedure for predicting the enthalpies. First, empirical equations at reference state pressure are determined for estimating the liquid and vapor phase heat capacities, as well as the heat of vaporization, as functions of temperature. The enthalpy of the liquid phase is determined by integrating the liquid phase specific heat equation between the reference temperature and the temperature of the liquid. If the fluid exists in the vapor phase, the liquid phase heat capacity is integrated between the reference and the normal boiling point, the heat of vaporization is added, and the vapor phase heat capacity equation integrated between the normal boiling point and the temperature of the fluid. The pressure correction term, for deviation from the reference pressure, is then added to compensate for the effect of pressure on the enthalpy. Often the effect of pressure on a liquid that exists below 1000 psia, is neglected.

The following equation is a mathematical representation of the above steps:

$$H = \int_{T_o}^{T_b} (C_p)_L \, dT + \int_{T_b}^{T} (C_p)_v \, dT + H_{p.c.} + \Delta H_v \quad (4)$$

where,

$H$ = enthalpy relative to $T_o$, Btu/lbm

$T_o$ = reference temperature,

$T_b$ = normal boiling point temperature,

$(C_p)_L$ = liquid phase heat capacity @ reference pressure,

$(C_p)_v$ = vapor phase heat capacity @ reference pressure,

$Hp.c$ = pressure correction term to compensate for the effect of the system's pressure on enthalpy,

$T$ = system temperature, (which is higher than $T_b$ for a gas), and

$\Delta H_v$ = latent heat of vaporization.

The correlations mentioned earlier use the ASTM distillation results and the API gravity as properties for characterizing the sample. From the ASTM distillation and the API gravity, properties such as true boiling curve, mean average boiling point, molecular weight, and pseudocritical properties, which are required for the correlation, are computed using charts in the API data book and the equations given by Kesler and Lee (9, 28). In both of these correlations, ideal gas and low pressure liquid enthalpies are presented as a function of temperature for different values of the characterizing variable. The affect of pressure on enthalpy can be obtained using corresponding states enthalpy departures which are also presented.

The results of application of these correlations to predict enthalpies of coal-liquids and pure compounds are presented in the following section.

# APPLICATION OF PETROLEUM CORRELATIONS TO PREDICT ENTHALPIES OF COAL LIQUIDS AND PURE COMPOUNDS

## Coal Liquids

The Johnson-Grayson (8) and Lee-Kesler (9, 28) correlations were used to predict the enthalpy values of the SRC-I Naphtha, the 1046 Naphtha, and the Middle Distillate cut. Comparisons of these methods were then made with the experimental data for the above-mentioned coal liquids. The calculations were performed in both the liquid and vapor phases and the detailed results are tabulated in Tables 1-3 of Appendix I. Figures 5-8 present some of these results graphically. The methods of prediction cannot be used directly for enthalpy calculations in the two phase region since experimental vapor-liquid equilibrium data are not available. For the liquid data points, the low pressure liquid enthalpy curves of Johnson-Grayson or Kesler-Lee were used to calculate the enthalpies. The small effect of pressure on liquid enthalpy was neglected. In the SRC-I naphtha comparisons it was necessary to use the ideal gas enthalpy and corresponding states enthalpy departures for the calculations. Details of the calculation procedure have been given by Sharma (3). In fact, it should be noted that liquid enthalpies can always be

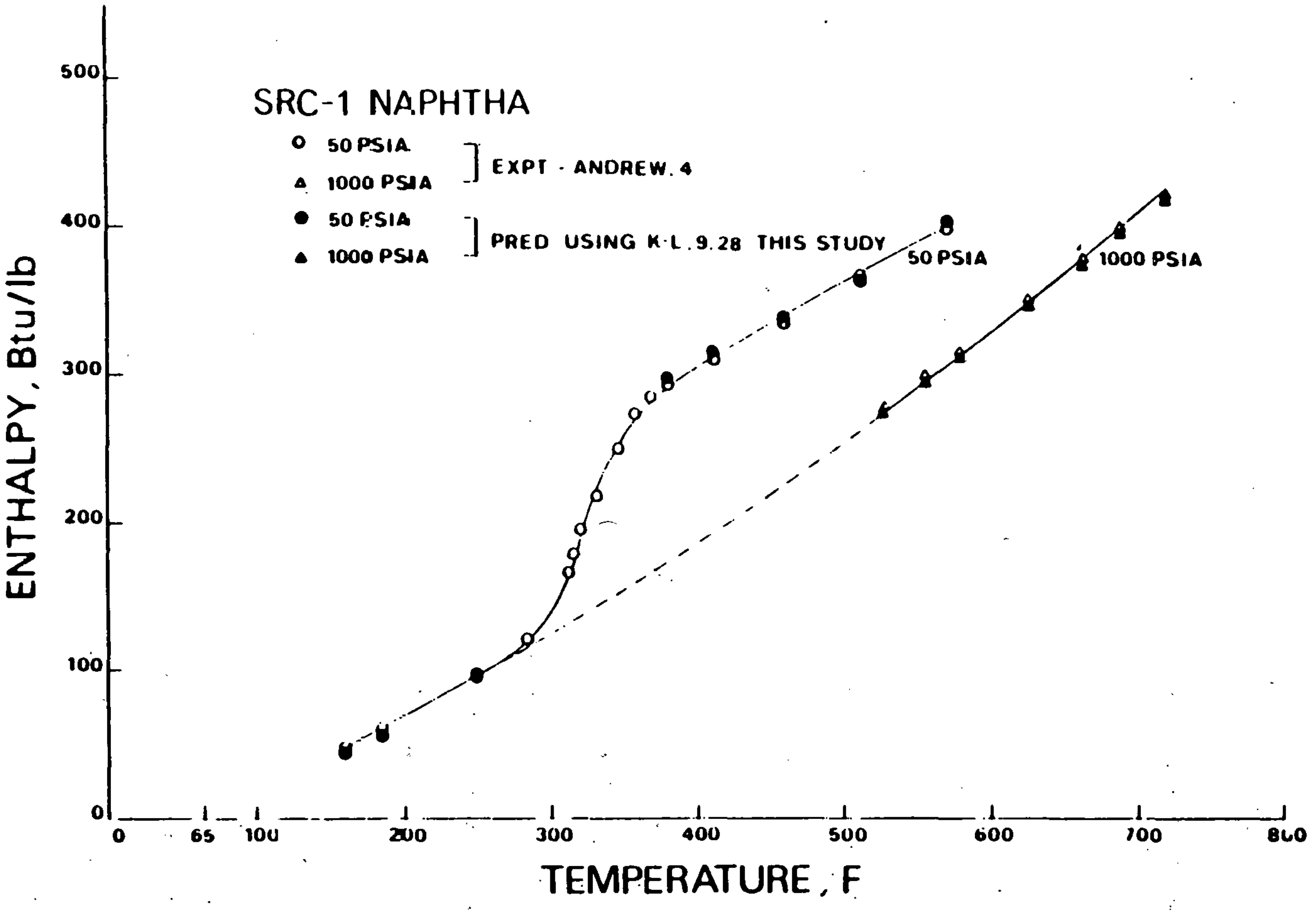

Figure 5. A Comparison Between the Experimental and Predicted Enthalpy Values for SRC-I Naphtha

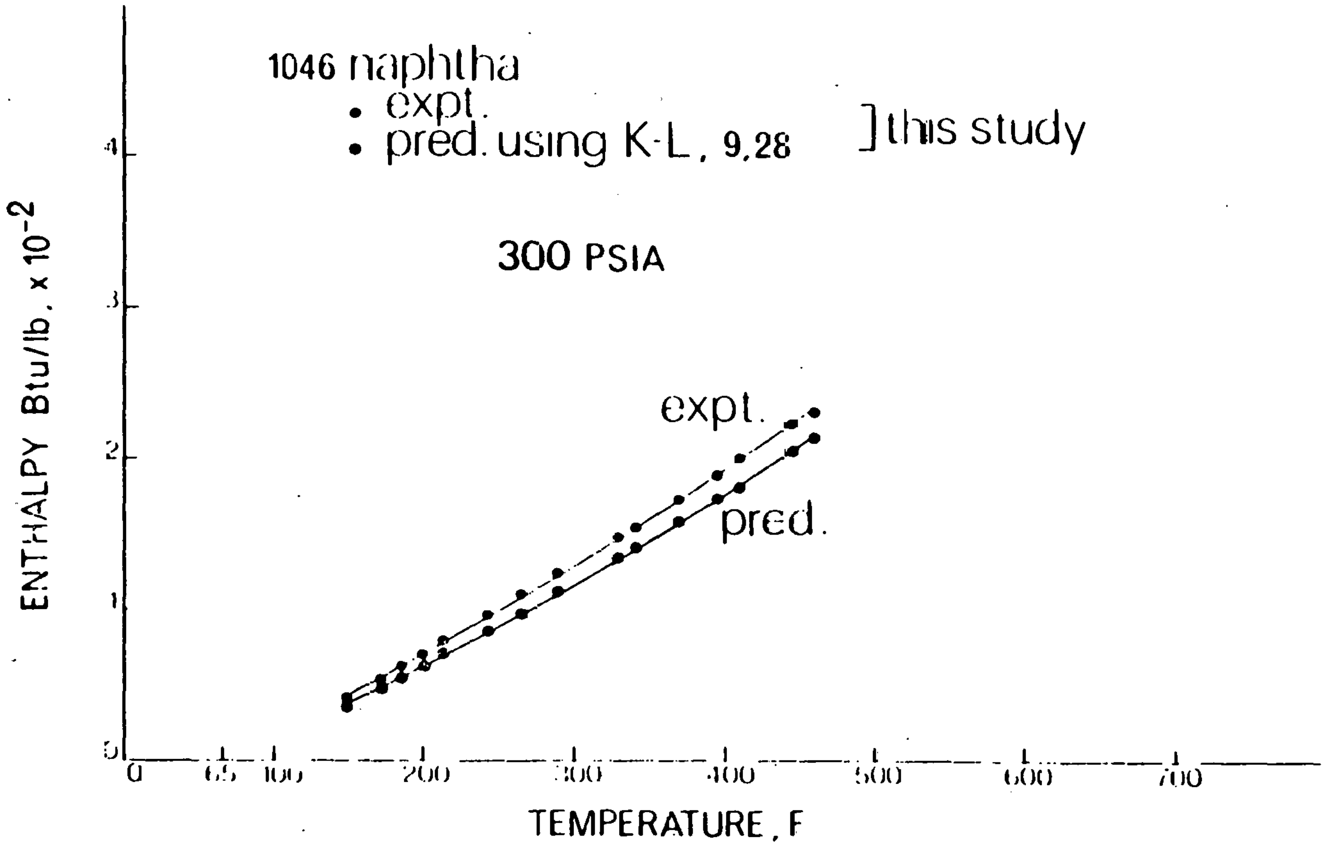

Figure 6. A Comparison Between the Experimental and Predicted Enthalpy Values for the 1046 Naphtha

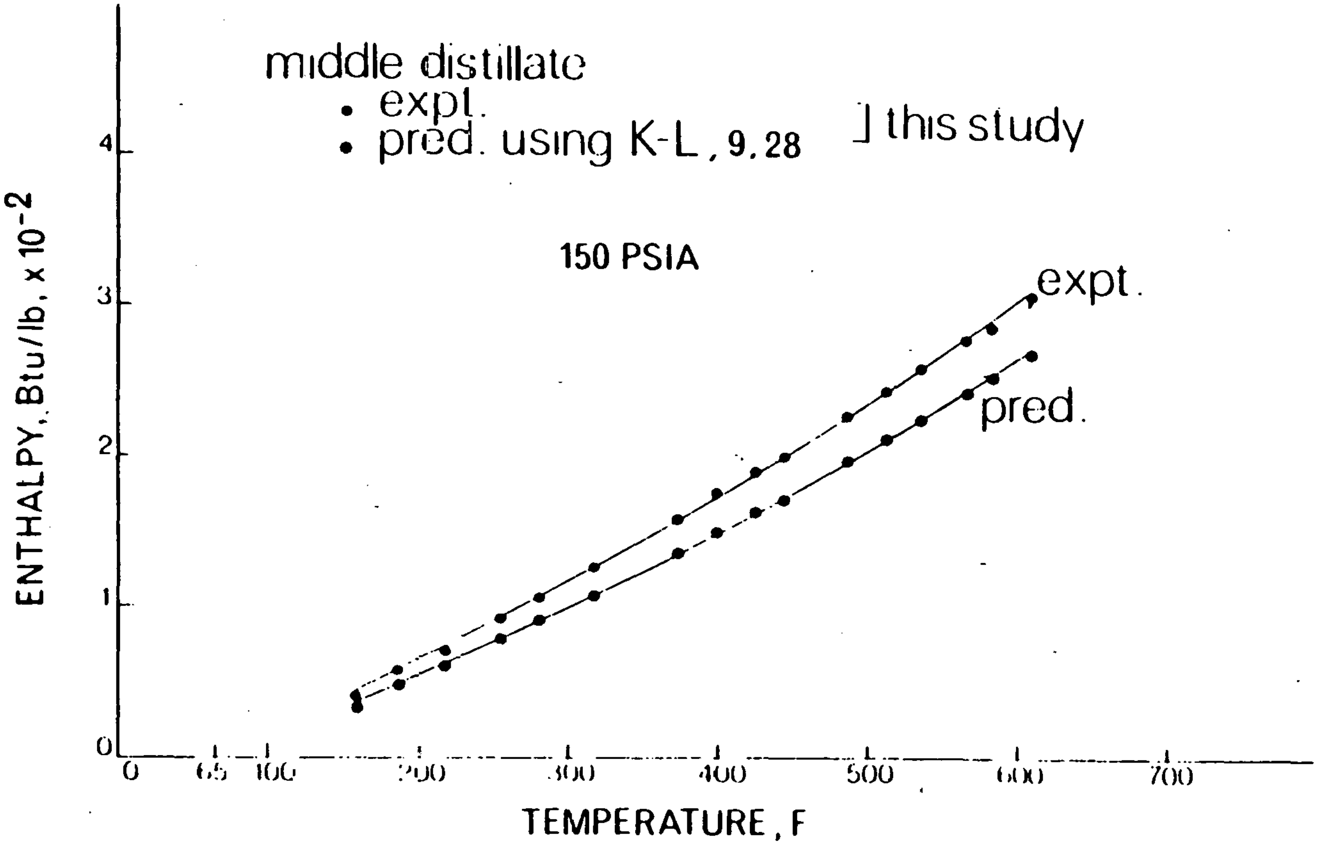

Figure 7. A Comparison Between the Experimental and Predicted Enthalpy Values for the Middle Distillate at the 150 PSIA Isobar

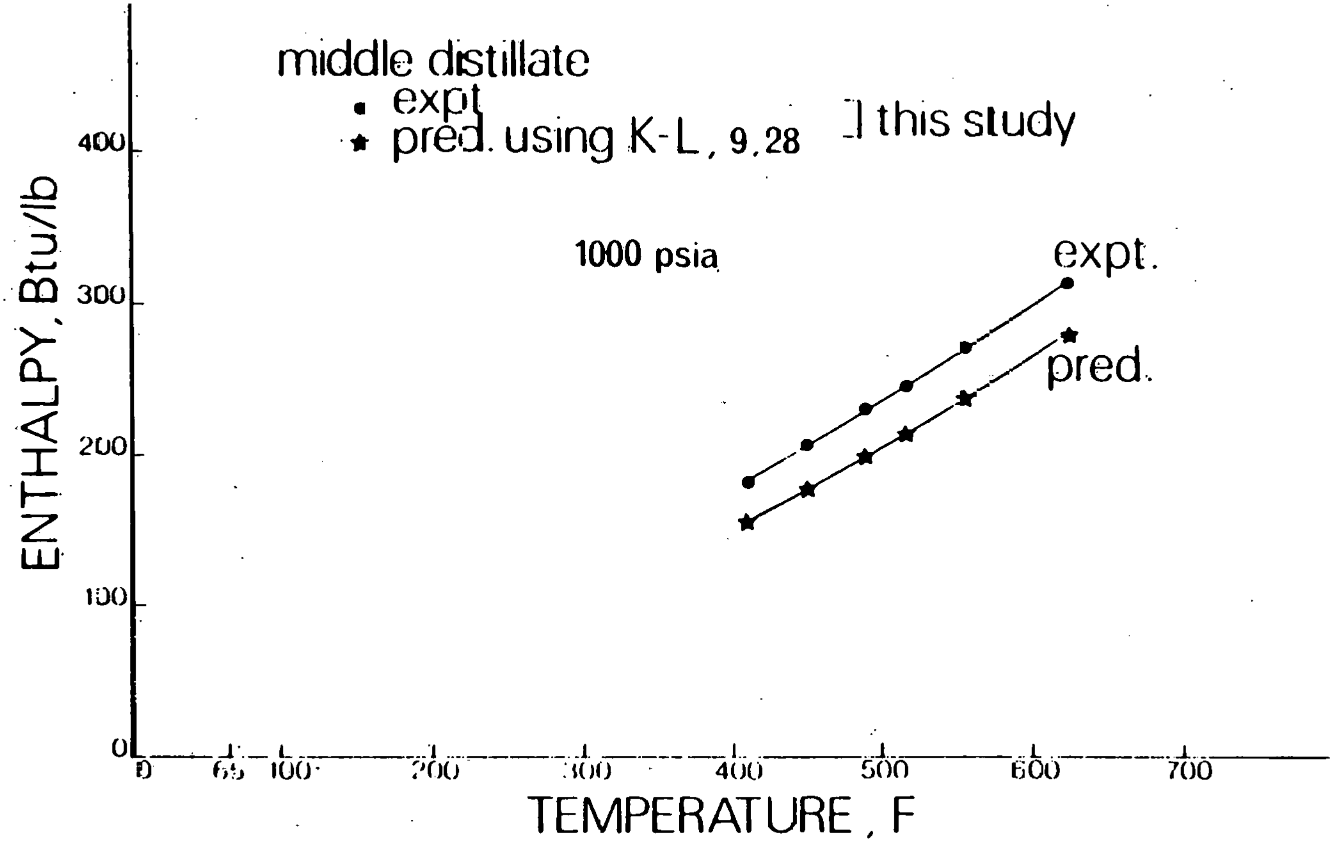

Figure 8. A Comparison Between the Experimental and Predicted Enthalpy Values for the Middle Distillate at the 1000 Isobar.

calculated using ideal gas heat capacities and corresponding states;and the liquid enthalpy curves in both Johnson-Grayson and Kesler-Lee correlations are, at least in theory, redundant.

### Pure Model Compounds

The Kesler-Lee (9, 28) correlation was used to predict the enthalpy values of bezene, 1-methyl naphthalene, m-xylene, n-pentanol, n-hexanol, and m-cresol. The calcuations were performed in both the liquid and vapor phases and the detailed results are tabulated in Appendix II. Some of the results are presented graphically in Figures 9 to 14. It should be noted that the critical properties and the acentric factors of these pure compounds used for predicting the enthalpy values, were also estimated by the Kesler-Lee's correlations in order to be consistent with the earlier comparisons for coal liquids.

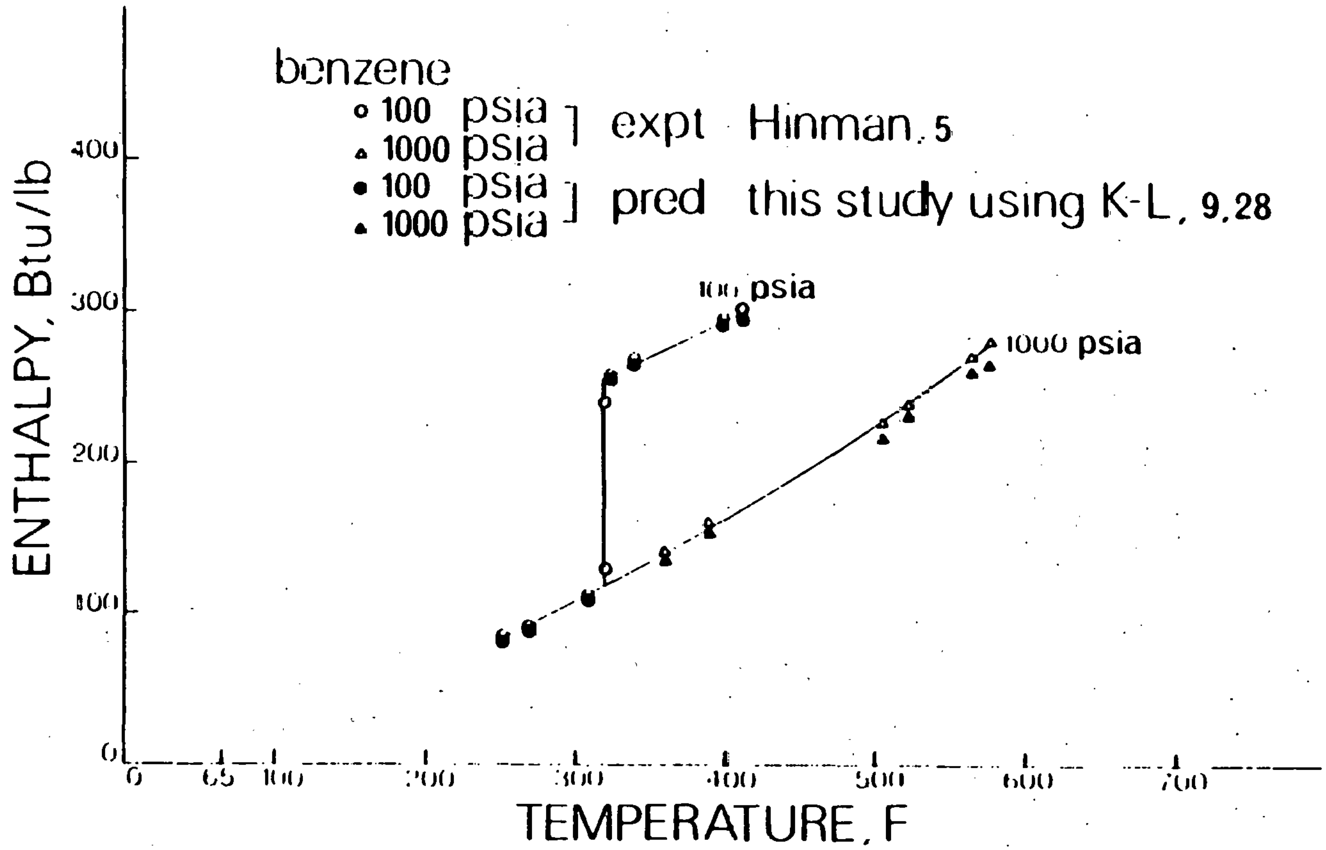

Figure 9. A Comparison Between the Experimental and Predicted Enthalpy Values for Benzene

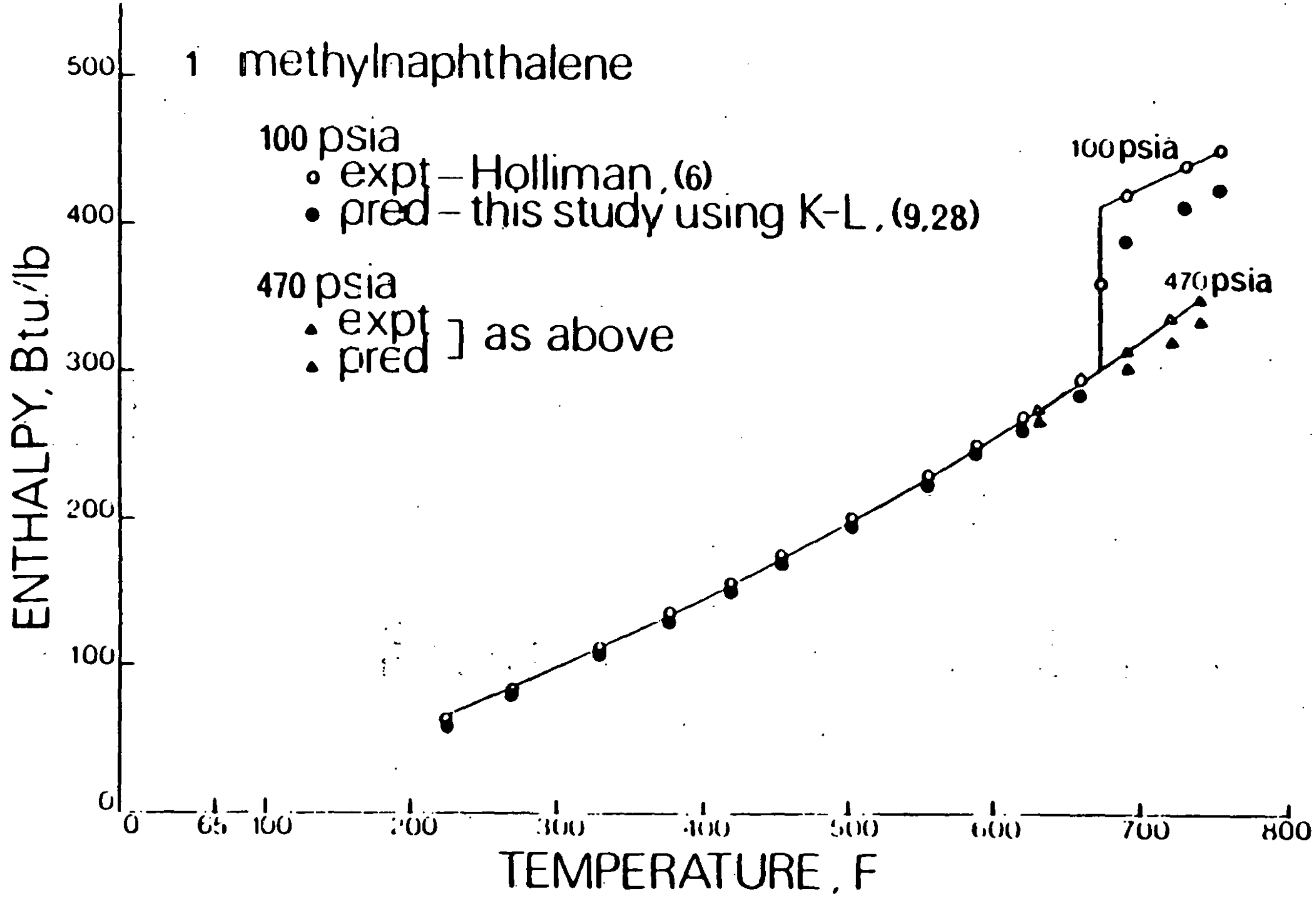

Figure 10. A Comparison Between the Experimental and Predicted Enthalpy Values for 1-Methylnaphthalene

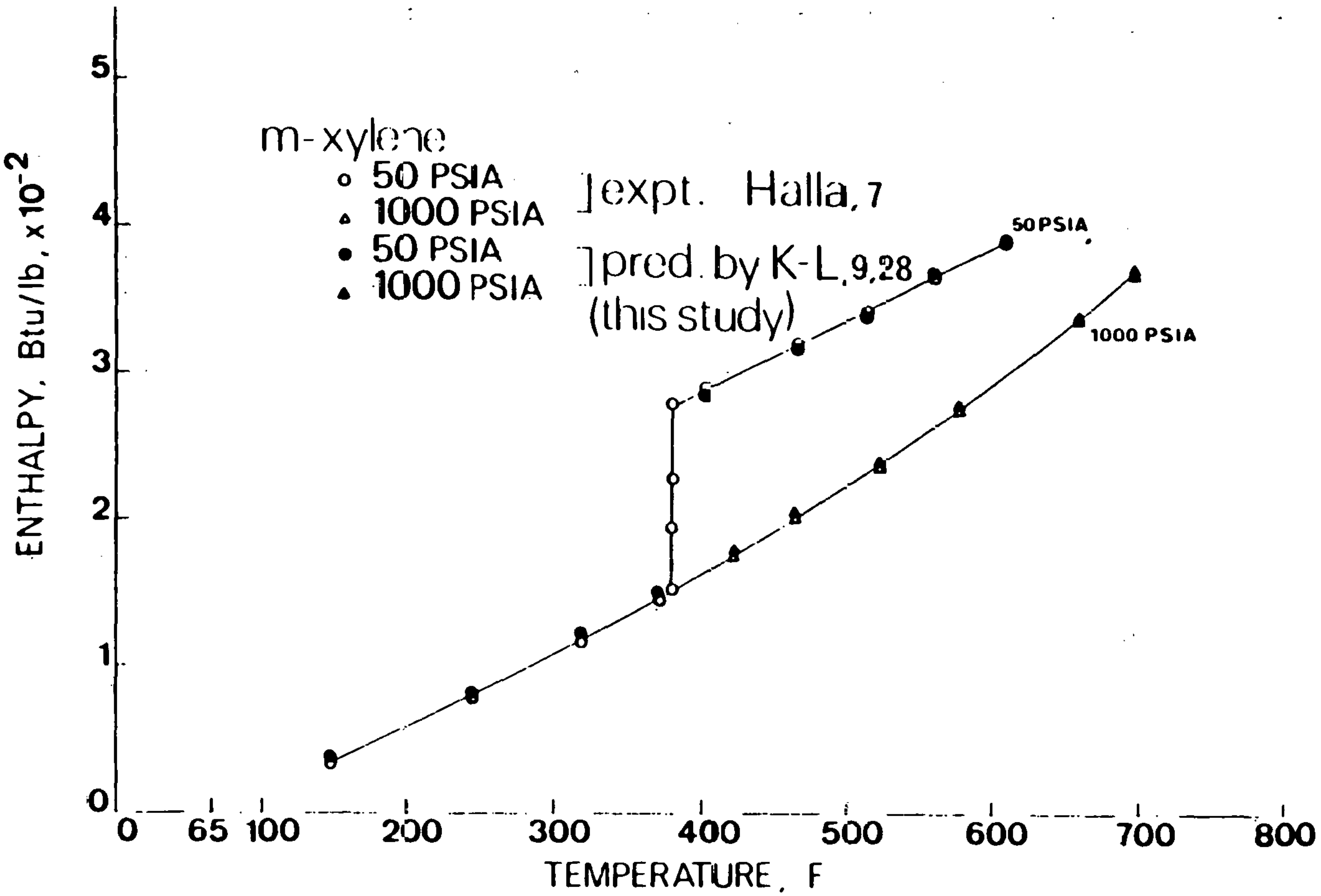

Figure 11. A Comparison Between the Experimental and Predicted Enthalpy Values for m-Xylene

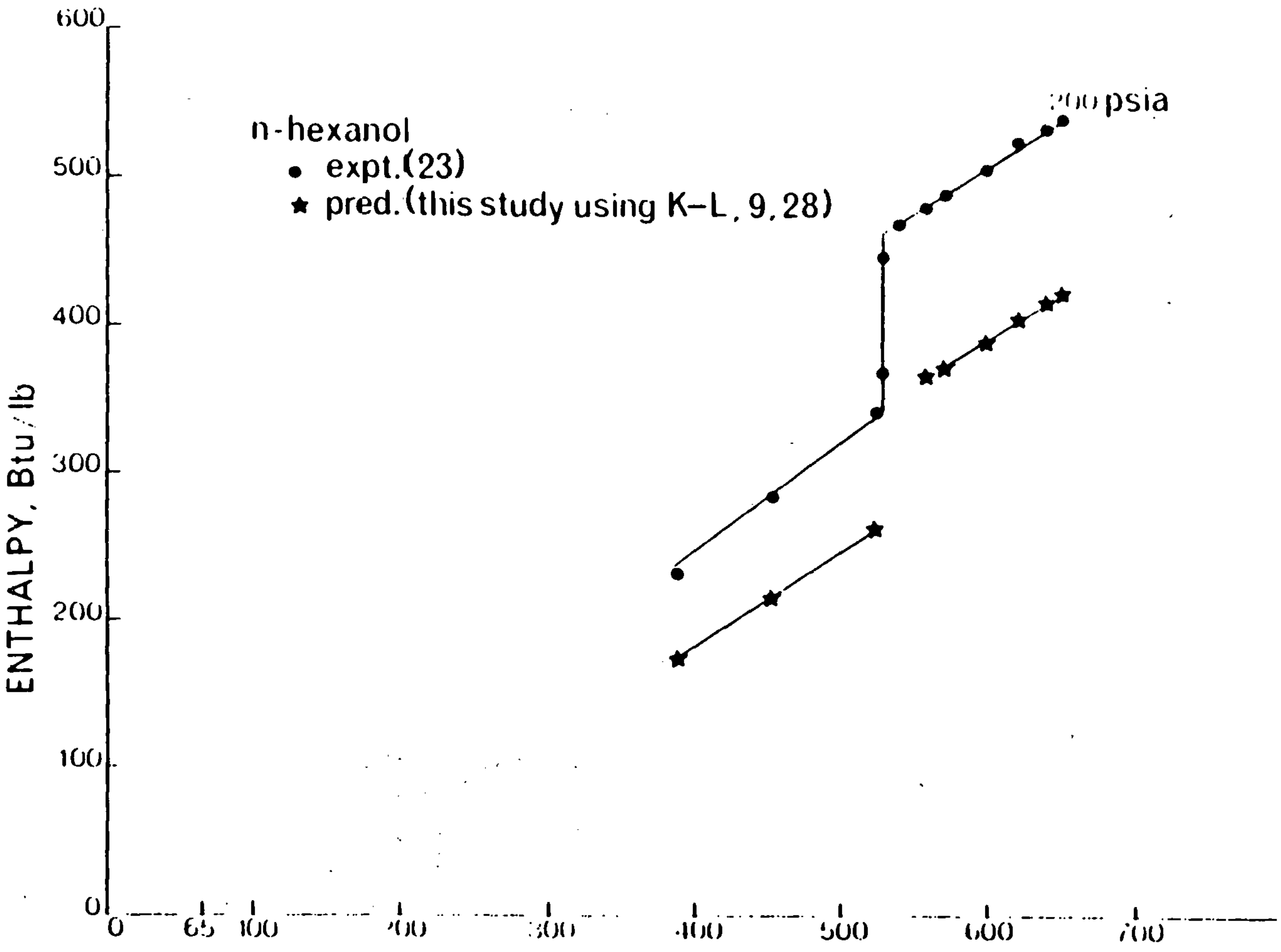

Figure 12. A Comparison Between the Experimental and Predicted Enthalpy Values for n-Hexanol

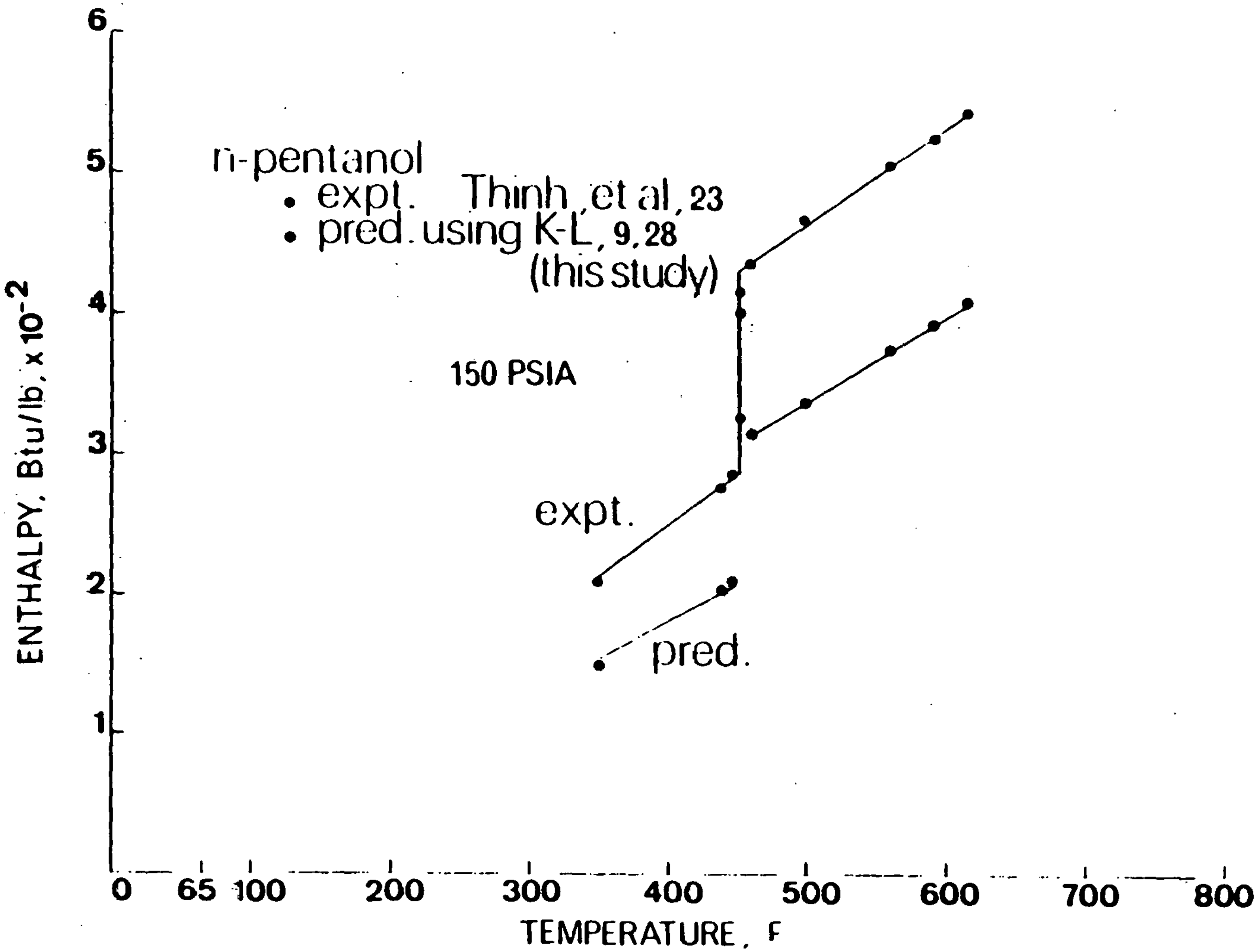

Figure 13. A Comparison Between the Experimental and Predicted Enthalpy Values for n-Pentanol

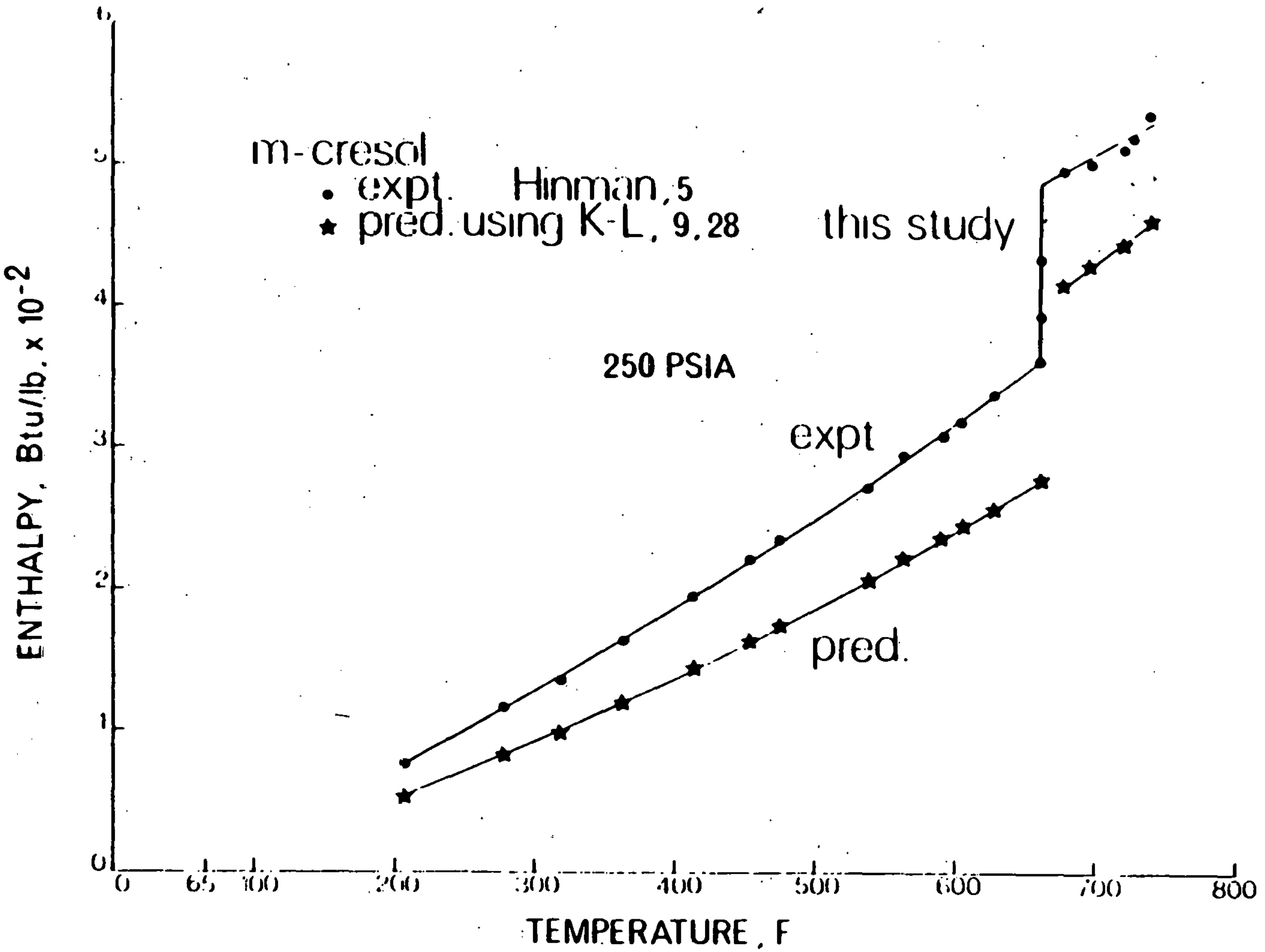

Figure 14. A Comparison Between the Experimental and Predicted Enthalpy Values for m-Cresol

## PREVIOUS RESULTS

The Johnson-Grayson (8) and Lee-Kesler (9, 28) correlations were also used by Omid (2), Sharma (3) and Andrew (4) to predict the enthalpy values of several coal liquids studied earlier, along with the petroleum oils of Lenoir and Hipkin (27), and the results compared with the experimental values. Table 5 summarizes the results of these comparisons along with the appropriate references. The signs are presented for those systems where there was a distinct bias in the results, the negative sign indicating that the calculated enthalpies were lower than the experimental ones.

## Table 5

### Average Differences Between Experimental Enthalpy Data and the Correlations of Johnson-Grayson (8) and Kesler-Lee (9, 28)

| | | | Average Error, Btu/$lb_m$ | |
|---|---|---|---|---|
| **Coal-Derived Liquids** | **Reference** | **Number of Data Points** | **Johnson-Grayson** | **Kesler-Lee** |
| West. Kent. | Omid (2) | 13 | -2.3 | -1.6 |
| West. Kent Dist. | Omid (2) | 42 | -3.9 | -3.6 |
| Utah Dist. | Sharma (3) | 33 | -11.8 | -12.1 |
| Synthoil Dist. | Andrew (4) | 19 | -36.4 | -35.7 |
| **Petroleum Liquids** | | | | |
| Alaskan Naphtha | Lenoir-Hipkin(26)Expt.<br>Omid (2), Corr | 20 | 5.2 | 2.7 |
| Kerosene Cut | " | 23 | 2.9 | 1.7 |
| Fuel Oil (#2) | " | 11 | 1.7 | 0.5 |
| Gas Oil | " | 36 | 1.7 | 1.5 |
| Aromatic Naphtha | " | 20 | 2.9 | 4.0 |

## DISCUSSION OF THE RESULTS OF COMPARISON

In Table 6 are presented the average absolute errors using each of the two predictive techniques, outlined earlier, for all the three oils under study.

Average differences for all the coal-derived liquids studied so far and the petroleum oils of Lenoir and Hipkin are presented in Table 7. Also presented in this table are the API gravity and the Watson characterization factor, K. For almost all of the coal liquids, and for both the correlations considered, the predicted values were biased low relative to the experimental ones. However, in some cases, as is apparent from the table, the comparisons were excellent, while in others the deviations were too large for the petroleum correlations to be used as predictive techniques for enthalpies of coal liquids. Moreover, there appears to be a considerable variation in these differences, depending largely upon the coal liquid that is considered. A comparison of the average absolute error of the petroleum liquids with the results for coal-derived liquids, shows that while the correlations do an excellent job of predicting enthalpies of petroleum fractions, their success is mixed for coal derived liquids.

Table 8 presents the average error as a function of the elemental analysis, as well as the amount of paraffins,

## Table 6

## Average Error Comparison for Coal-Liquids

| Coal-Derived Liquid | Number of Points | Average Error Btu/$lb_m$ | |
|---|---|---|---|
| | | Johnson-Grayson | Kesler-Lee |
| SRC-I Naphtha | 51 | 2.9 | 4.1 |
| 1046 | 29 | 8.1 | 11.1 |
| Middle Distillate | 36 | 24.9 | 26.7 |

## Table 7

### Average Differences Between Experimental Enthalpy Data and the Correlations of Johnson-Grayson (8) and Kesler-Lee (9, 28)

| Coal-Derived Liquids | Reference | Number of Points | Average Error, Btu/lb$_m$ Johnson-Grayson | Average Error, Btu/lb$_m$ Kesler-Lee | °API | Watson K |
|---|---|---|---|---|---|---|
| West. Kent | Omid (2) | 13 | -2.3 | -1.6 | 21.8 | 10.9 |
| West. Kent. Dist. | Omid (2) | 42 | -3.9 | -3.6 | 28.5 | 10.7 |
| Utah Dist. | Sharma (3) | 33 | -11.8 | -12.1 | 29.4 | 10.8 |
| Synthoil Dist. | Andrew (4) | 19 | -36.4 | -35.7 | 13.2 | 10.0 |
| SRC-1 Naphtha | Andrew (4)(Expt.)<br>This Study (corr.) | 51 | 2.9 | 4.1 | 49.7 | 11.2 |
| 1046 Naphtha | This Study | 29 | - 8.1 | -11.1 | 41.0 | 10.9 |
| Middle Dist. | This Study | 36 | -24.9 | -26.7 | 13.5 | 9.9 |
| Petroleum Liquids | | | | | | |
| Alaskan Naphtha | Lenoir-Hipkin (26), Expt.<br>Omid (2), (corr.) | 20 | 5.2 | 2.7 | 50.5 | 11.6 |
| Kerosene Cut | " | 23 | 2.9 | 1.7 | 43.5 | 11.8 |
| Fuel Oil (#2) | " | 11 | 1.7 | 0.5 | 33.0 | 11.7 |
| Gas Oil | " | 36 | 1.7 | 1.5 | 35.3 | 11.8 |
| Aromatic Naphtha | " | 20 | 4.9 | 4.0 | 34.5 | 10.5 |

### Table 8

Average Error as a Function of the Elemental Analysis and the P-O-N-A Content

| Coal Liquid | Average Error, Btu/lb | | Elemental Analysis, wt% | | | | | P-O-N-A Analysts, wt% | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | J-G | K-L | C | H | N | S | O | Paraffin | Olefins | Naphthenes | Aromatics |
| West. Kent (2) | 2.3 | 1.6 | 88.04 | 10.98 | 0.92 | - | - | 50.0 | 1.5 | 12.5 | 35.5 |
| West. Kent. Dist. (2) | 3.9 | 3.6 | 88.08 | 11.04 | 1.00 | - | - | 55.0 | 2.0 | 9.9 | 33.1 |
| Utah Dist(3) | 11.8 | 12.1 | 73.82 | 9.68 | 1.08 | - | - | 65.0 | 4.0 | 6.6 | 26.4 |
| Synthoil Dist (4) | 36.4 | 35.7 | 84.06 | 9.28 | 1.40 | 0.13 | 5.26 | 26.0 | 2.0 | 33.8 | 38.2 |
| SRC-I Naphtha (4+This Study) | 2.9 | 4.1 | 84.37 | 12.98 | 0.14 | 0.34 | 2.17 | 25.2 | 1.0 | 36.0 | 37.8 |
| 1046 Naphtha (This Study) | 8.1 | 11.1 | 85.24 | 12.36 | 0.66 | 0.34 | 1.4 | 69.0 | 6.0 | <1.0 | 24.0 |
| Middle Dist. (This study) | 24.9 | 26.7 | 85.33 | 9.05 | 1.32 | 0.15 | 3.95 | 38.0 | 1.0 | 26.2 | 34.8 |

*Oxygen determined by difference (100% - (C + H + N + S)) olefins, naphthenes and aromatics in each of the coal liquids. As is evident, there does not seem to be any trend in the values of the absolute errors as a function of the above quantities. This is better apparent in Figures 15 & 16, where plots of the average error vs. nitrogen and aromatic contents, respectively, have been presented for illustration purposes.

It was originally believed that the high level of aromatics in coal-derived liquids would result in major property differences between coal liquids and petroleum liquids. However, it appears that the presence of aromatics causes only a minor difference between the predicted values and the experimental data. This is best illustrated by comparing the results for the aromatic naphtha petroleum liquid with the other results (Table 7). Also of note is a comparison between the Western Kentucky distillate (average error 3.6 Btu/lb$_m$) with the Utah Distillate (average error = 12.1 Btu/lb$_m$). These two oils have virtually identical characterization properties ($^{o}$API and K) and yet, the correlation works well for the Western Kentucky distillate but is marginal for the Utah distillate.

The other major difference between coal liquids and petroleum liquids is the higher level of organic oxygen and nitrogen compounds in coal liquids. Since the experimental enthalpy data for the coal liquids, are higher than the

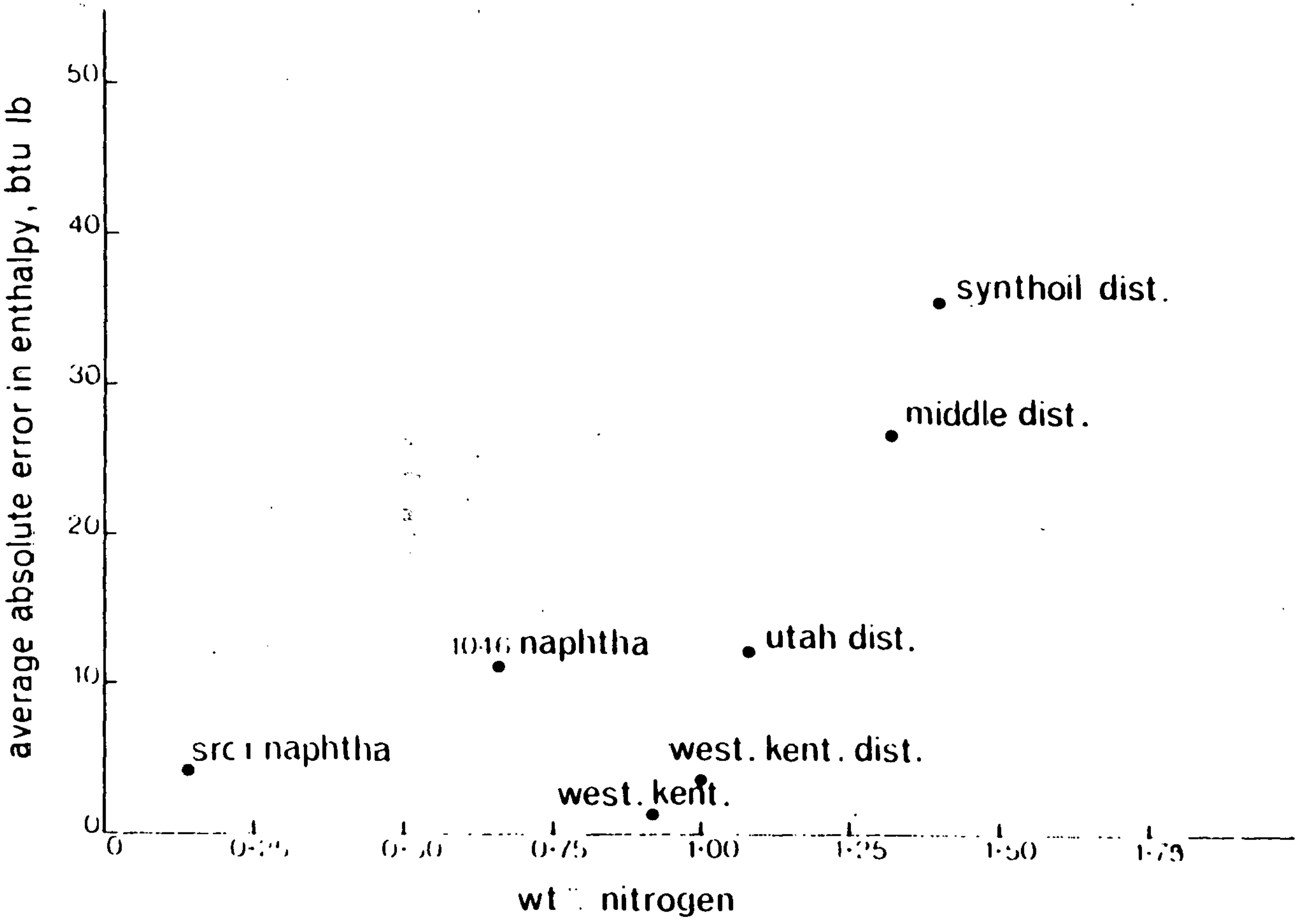

Figure 15. Average Absolute Error in Enthalpy as a Function of the Nitrogen Content for Coal-Derived Liquids

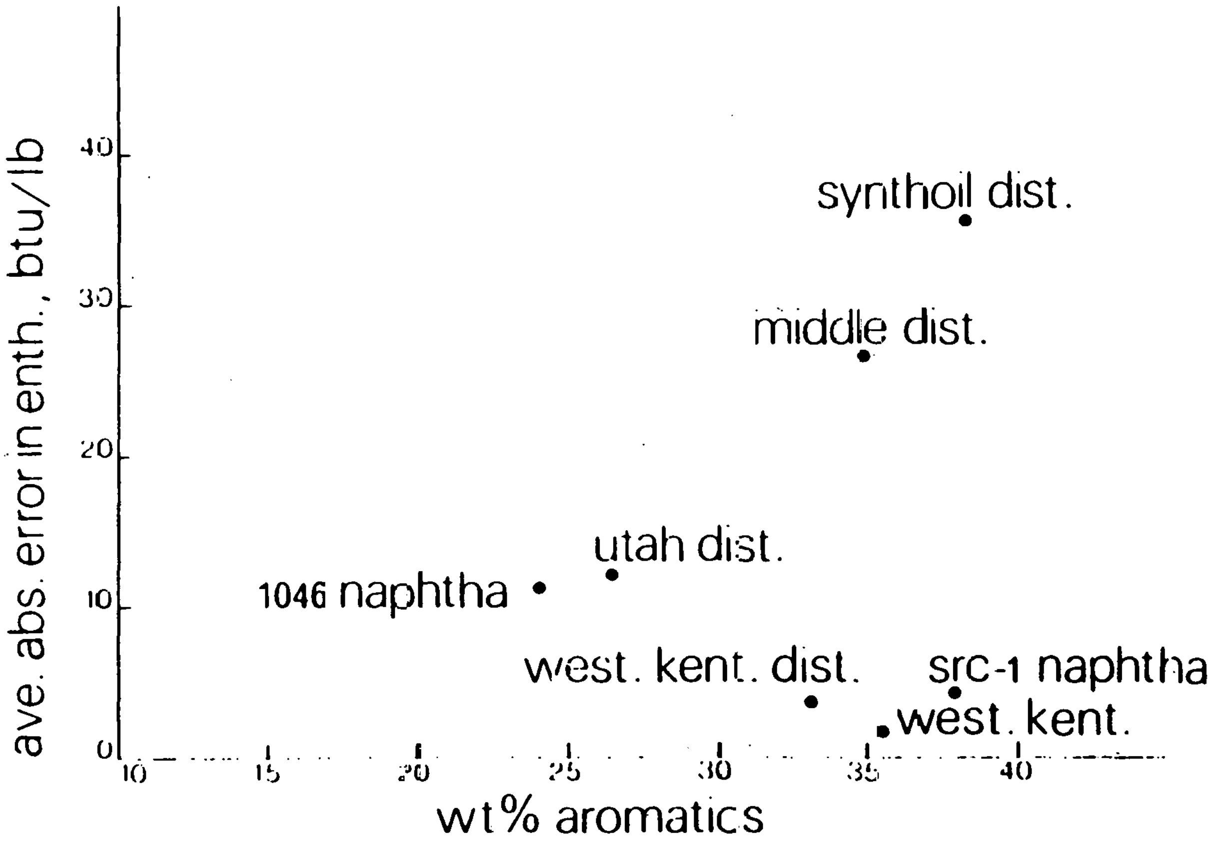

Figure 16. Average Absolute Error in Enthalpy as a Function of the Aromatic Content for Coal-Derived Liquids

calculated enthalpies, this would be consistent with an association effect and an energy of association. Organic oxygen and nitrogen compounds are highly polar, and association such as hydrogen bonding is quite likely in such fluids. Ordinarily, one would expect the effect of hydrogen bonding to increase with an increase in the amount of heteroatoms present in coal liquids. But, this in not true in its own right, since, for example, the hydrogen bonding effects will depend on whether the oxygen present in coal liquids is tied up in an ether linkage or a phenolic linkage. Moreover, the coal-liquids are a highly complex mixture of very many different compounds and other interactions, apart from hydrogen bonding, also may very well be present. Furthermore, the composition of the coal liquids, in terms of the heteroatomic content and aromaticity, depends primarily on the processing conditions used (29, 30). Thus, it is clear that the problem of quantifying the effect of hydrogen bonding in coal liquids is not a trivial one.

To further illustrate the effect of association, comparisons were made between the Kesler-Lee correlation and the experimental data for several model compounds. Detailed comparisons are presented in Appendix II for benzene, 1-methylnaphthalene, m-xylene, n-pentanol, n-hexanol and m-cresol. Some of the results of these comparisions have been presented graphically in Figures 9-14. As with coal-derived liquids, the calculated results are consistently lower than the experimental values. Average errors for each compound are presented in Table 9. As can be seen, the error increases in going from monoaromatic to diaromatic, with the difference for benzene and m-xylene being somewhat greater than the results for the petroleum liquids. However, the most significant differences are obtained for the alcohols and the phenol derivative, m-cresol, where significant amounts of association are known to occur. The gas chromatograph-mass spectrometer (GCMS) analyses, performed by Dr. C. V. Philip of the Chemical Engineering Department, Texas A & M University, on the coal-derived liquids indicate that they are relatively high in these phenol derivatives. To illustrate the effect that the presence of these heteroatomic compounds have on the enthalpy results, GCMS data for heteroatomics of each oil together with the average error, between correlation and data, are presented in Table 10 and Figure 17. The GCMS results reported are the normalized total heteroatomic percentage. It is important to note, however, that the GCMS results may not be extremely quantitative since, for most of the oils, there was a considerable percentage of non-identifiable

# Table 9

## Average Differences Between Experimental Enthalpy Data and the Correlation of Kesler-Lee for Pure Compounds

| Compound | Number of Data Points | Average Error Btu/$lb_m$ |
|---|---|---|
| Benzene | 28 | 4.9 |
| m-Xylene | 60 | 4.5 |
| 1-Methylnaphthalene | 31 | 14.2 |
| n-Pentanol | 14 | 75.5 |
| n-Hexanol | 14 | 92.5 |
| m-Cresol | 52 | 71.5 |

## Table 10

## Average Error vs Heteroatomic Content for Coal-Liquids

| Coal Derived Liquids | Average Error Btu/$lb_m$ | GCMS Results $\frac{\%\ \text{Heteroatomics}}{\%\ \text{Identifiable}} \times 100\%$ |
|---|---|---|
| West. Kent. | 1.6 | 2.56 |
| West. Kent. Dist. | 3.6 | 3.75 |
| SRC-1 Naphtha | 4.1 | 14.27 |
| 1046 Naphtha | 11.1 | 10.56 |
| Utah Dist. | 12.1 | 21.34 |
| Middle Dist. | 26.7 | 19.14 |
| Synthoil Dist. | 35.7 | 24.05 |

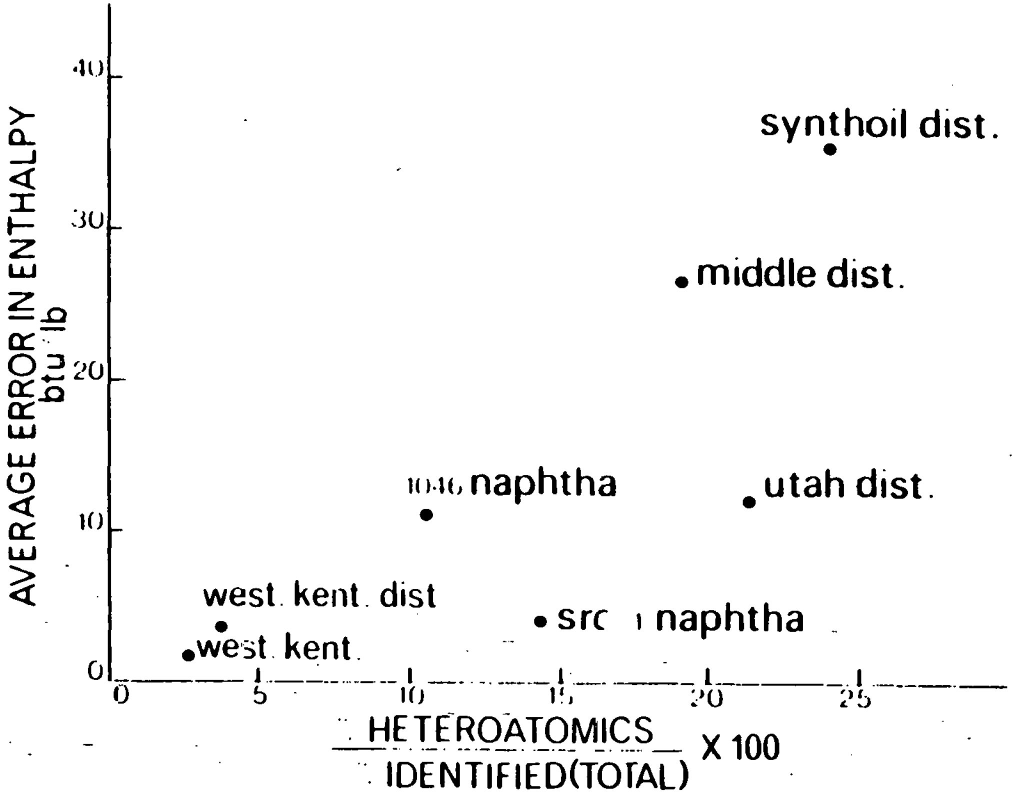

Figure 17. Average Absolute Error in Enthalpy as a Function of the Heteroatomic Content From GCMS Results for Coal-Derived Liquids

compounds persent. In addition, if errors in the correlation are a result of the energy of association, this energy would be a strong function of the heteroatomic type and distribution in an oil, as well as the total percentage. In any case, there does appear to be a distinct dependence of the amount of heteroatoms present on the ability of the correlation to predict the measured enthalpy. By noting the good agreement obtained for the Western Kentucky and its distillate, it can at least be said that the correlations work well for those coal-derived liquids that have a small percentage of heteroatoms. Tewari, et al. (29, 30) conducted viscosity and calorimetric studies on the interaction of quinoline with heavy oils and asphaltenes derived from the same coal, but at varying process conditions. Based on their measurements, they have suggested that the increase in both the viscosity and the molar enthalpies of interaction of coal-liquids are, in part, owing to the effect of hydrogen bonding involving largely the aromatic, phenolic group, OH. Moreover, they have also shown that, in general, the molar enthalpy of interaction increased with an increased in oxygen content and decreased aromaticity. This is consistent with the high enthalpy values of the coal liquids. Hence, it is clear that the enthalpy change is a strong function of the strength of molecular interactions in these systems which are, primarily, attributed to the hydrogen-bonding affects.

In summary, at this stage, it appears that association of heteroatomic compounds in coal-derived liquids may cause the experimental enthalpy differences to be considerably higher than the results calculated from correlations developed for non-polar, petroleum derived, fluids. The presence of high concentrations of aromatic compounds in coal-derived liquids seems to cause a minor discrepancy between calculated and experimental enthalpies. Thus, to develop an accurate method of calculating the enthalpy of coal-derived liquids, some method of easily characterizing this degree of association in coal-derived liquids is necessary. This task is compounded by the fact that the major compound type responsible for the association is organic oxygen; yet, in a standard elemental analysis, organic oxygen is usually obtained by difference and often represents the overall error in the analysis. Other possible methods of characterizing association include viscosity measurements and molecular weight determinations. These are discussed in the following chapters. Finally, once a means of characterizing association is available, the effect it has on enthalpy must eventually be incorporated into the petroleum correlations to make them suitable for application to coal-derived liquids.

# APPENDIX I

# COMPARISON OF EXPERIMENTAL AND PREDICTED ENTHALPIES FOR COAL-DERIVED LIQUIDS

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## TABLE 1

### Comparison of Experimental and Predicted Enthalpies for SRC-I Naphtha

| Pressure, Psia | Temp., $^{o}F$ | $\Delta H_{J-G}$, $Btu/lb_m$ | $\Delta H_{K-L}$ $Btu/lb_m$ | $\Delta H_{Expt.}$ $Btu/lb_m$ |
|---|---|---|---|---|
| 30 | 337.2 (v) | 279.1 | 278.0 | 268.8 |
| 30 | 362.6 (v) | 291.6 | 284.9 | 281.8 |
| 30 | 420.4 (v) | 321.4 | 318.3 | 312.5 |
| 50 | 159.0 (l) | 45.7 | 45.2 | 47.2 |
| 50 | 184.9 (l) | 59.3 | 57.2 | 60.1 |
| 50 | 256.5 (l) | 99.3 | 98.3 | 100.5 |
| 50 | 381.0 (v) | 299.4 | 296.2 | 293.0 |
| 50 | 412.2 (v) | 315.1 | 313.3 | 310.7 |
| 50 | 460.0 (v) | 340.1 | 338.6 | 336.4 |
| 50 | 514.0 (v) | 369.4 | 366.2 | 368.7 |
| 50 | 571.1 (v) | 401.7 | 401.9 | 400.7 |
| 100 | 218.4 (l) | 78.0 | 78.3 | 75.2 |
| 100 | 266.5 (l) | 105.6 | 104.9 | 108.3 |
| 100 | 318.5 (l) | 136.7 | 136.3 | 137.7 |
| 100 | 429.7 (v) | 320.8 | 310.1 | 311.6 |
| 100 | 464.4 (v) | 338.1 | 334.2 | 331.1 |
| 100 | 497.1 (v) | 358.8 | 350.1 | 353.0 |
| 100 | 526.5 (v) | 373.7 | 365.1 | 372.6 |
| 200 | 235.3 (l) | 87.7 | 88.3 | 88.1 |
| 200 | 327.0 (l) | 141.9 | 143.3 | 141.9 |
| 200 | 401.4 (l) | 191.6 | 191.5 | 190.0 |
| 200 | 522.4 (v) | 363.8 | 357.3 | 361.2 |
| 200 | 559.4 (v) | 386.8 | 382.3 | 384.6 |

## TABLE 1 (cont.)

## Comparison of Experimental and Predicted Enthalpies for SRC-I Naphtha

| Pressure, Psia | Temp., °F | $\Delta H_{J-G}$, Btu/lb$_m$ | $\Delta H_{K-L}$, Btu/lb$_m$ | $\Delta H_{Expt.}$, Btu/lb$_m$ |
|---|---|---|---|---|
| 300 | 259.0 (l) | 101.9 | 100.4 | 102.1 |
| 300 | 307.0 (l) | 131.2 | 129.7 | 130.6 |
| 300 | 385.1 (l) | 180.6 | 179.7 | 180.5 |
| 300 | 464.4 (l) | 239.4 | 233.4 | 234.5 |
| 300 | 538.7 (v) | 367.7 | 353.6 | 359.8 |
| 300 | 551.6 (v) | 371.7 | 365.5 | 370.0 |
| 300 | 575.6 (v) | 390.1 | 383.7 | 393.1 |
| | | | | |
| 500 | 415.2 (l) | 202.6 | 201.2 | 199.7 |
| 500 | 475.3 (l) | 247.3 | 241.0 | 240.3 |
| 500 | 632.7 (v) | 413.4 | 406.7 | 415.4 |
| 500 | 650.6 (v) | 426.2 | 416.7 | 429.2 |
| | | | | |
| 900 | 501.5 (f) | 262.6 | 256.3 | 261.9 |
| 900 | 533.8 (f) | 285.2 | 279.4 | 285.4 |
| 900 | 599.2 (f) | 337.2 | 333.0 | 340.2 |
| | | | | |
| 1000 | 463.7 (f) | 239.0 | 231.2 | 233.3 |
| 1000 | 528.9 (f) | 282.1 | 274.0 | 282.6 |
| 1000 | 603.5 (f) | 337.8 | 333.3 | 339.6 |
| 1000 | 627.0 (f) | 358.0 | 355.5 | 358.0 |
| 1000 | 655.3 (f) | 381.8 | 381.4 | 385.1 |
| 1000 | 683.4 (f) | 409.5 | 408.6 | 412.7 |
| 1000 | 719.0 (f) | 439.7 | 439.6 | 446.3 |

## TABLE 1 (cont.)

## Comparison of Experimental and Predicted Enthalpies for SRC-1 Naphtha

| Pressure, Psia | Temp., $^oF$ | $\Delta H_{J-G}$, Btu/lb$_m$ | $\Delta H_{K-L}$, Btu/lb$_m$ | $\Delta H_{Expt.}$ Btu/lb$_m$ |
|---|---|---|---|---|
| 1500 | 529.2 (f) | 280.8 | 273.6 | 280.2 |
| 1500 | 555.2 (f) | 299.3 | 292.5 | 300.3 |
| 1500 | 578.4 (f) | 313.3 | 309.7 | 314.9 |
| 1500 | 625.9 (f) | 351.3 | 345.3 | 352.6 |
| 1500 | 663.3 (f) | 380.3 | 376.0 | 380.4 |
| 1500 | 689.1 (f) | 400.8 | 397.9 | 400.9 |
| 1500 | 719.0 (f) | 424.2 | 421.6 | 423.1 |

## TABLE 2

### Comparison of Experimental and Predicted Enthalpies for 1046 Naphtha

100 Psia

| Temp., °F | $\Delta H_{J\text{-}G}$, Btu/$lb_m$ | $\Delta H_{K\text{-}L}$, Btu/$lb_m$ | $\Delta H_{Expt.}$ Btu/$lb_m$ |
|---|---|---|---|
| 208.1 (1) | 70.8 | 68.7 | 75.0 |
| 234.4 (1) | 84.7 | 82.5 | 90.1 |
| 256.6 (1) | 97.6 | 94.4 | 103.1 |
| 279.2 (1) | 109.7 | 106.9 | 115.4 |
| 295.1 (1) | 117.5 | 115.8 | 126.4 |
| 310.6 (1) | 128.3 | 124.6 | 137.5 |
| 324.3 (1) | 136.5 | 132.5 | 146.1 |
| 334.7 (1) | 142.6 | 138.6 | 151.1 |
| 348.3 (1) | 150.6 | 146.6 | 161.9 |

200 Psia

| Temp., °F | $\Delta H_{J\text{-}G}$, Btu/$lb_m$ | $\Delta H_{K\text{-}L}$, Btu/$lb_m$ | $\Delta H_{Expt.}$ Btu/$lb_m$ |
|---|---|---|---|
| 255.9 (1) | 96.6 | 94.1 | 101.8 |
| 272.9 (1) | 106.7 | 103.4 | 111.6 |

300 Psia

| Temp., °F | $\Delta H_{J\text{-}G}$, Btu/$lb_m$ | $\Delta H_{K\text{-}L}$, Btu/$lb_m$ | $\Delta H_{Expt.}$ Btu/$lb_m$ |
|---|---|---|---|
| 148.2 (1) | 37.8 | 38.6 | 41.7 |
| 171.5 (1) | 49.3 | 50.1 | 54.7 |
| 185.0 (1) | 56.6 | 56.8 | 62.3 |
| 200.8 (1) | 67.6 | 64.9 | 69.9 |
| 213.8 (1) | 74.7 | 71.6 | 80.2 |
| 242.1 (1) | 89.7 | 86.6 | 96.3 |
| 264.8 (1) | 100.8 | 98.9 | 109.8 |
| 289.0 (1) | 115.6 | 112.4 | 124.7 |

## TABLE 2 (cont.)

## Comparison of Experimental and Predicted Enthalpies for 1046 Naphtha

300 Psia

| Temp., °F | $\Delta H_{J-G}$, Btu/lb$_m$ | $\Delta H_{K-L}$, Btu/lb$_m$ | $\Delta H_{Expt.}$ Btu/lb$_m$ |
|---|---|---|---|
| 296.6 (1) | 120.6 | 116.6 | 129.4 |
| 329.3 (1) | 138.6 | 135.4 | 149.0 |
| 340.5 (1) | 145.6 | 142.0 | 155.3 |
| 369.1 (1) | 162.8 | 159.1 | 173.9 |
| 385.6 (1) | 173.8 | 169.1 | 182.1 |
| 393.7 (1) | 178.8 | 174.1 | 189.0 |
| 408.9 (1) | 187.9 | 183.5 | 201.6 |
| 424.5 (1) | 197.9 | 193.4 | 210.0 |
| 444.7 (1) | 209.9 | 206.3 | 224.2 |
| 458.9 (f) | 219.9 | 215.5 | 232.1 |

## TABLE 3

## Comparison of Experimental and Predicted Enthalpies for 878 Middle Distillate

| Temp., °F | $\Delta H_{J-G}$, Btu/lb$_m$ | $\Delta H_{K-L}$, Btu/lb$_m$ | $\Delta H_{Expt.}$ Btu/lb$_m$ |
|---|---|---|---|
| **130 Psia** | | | |
| 436.0 (l) | 171.0 | 169.0 | 199.5 |
| 524.1 (l) | 221.0 | 218.4 | 250.7 |
| **150 Psia** | | | |
| 157.1 (l) | 36.0 | 36.0 | 42.4 |
| 185.6 (l) | 48.0 | 48.0 | 57.2 |
| 217.9 (l) | 65.0 | 62.0 | 71.4 |
| 255.7 (l) | 81.0 | 78.9 | 93.3 |
| 280.2 (l) | 93.0 | 90.3 | 105.9 |
| 315.7 (l) | 110.0 | 107.2 | 126.3 |
| 326.8 (l) | 115.0 | 112.7 | 132.9 |
| 372.9 (l) | 138.0 | 135.8 | 158.6 |
| 399.7 (l) | 152.0 | 149.6 | 175.3 |
| 424.9 (l) | 165.0 | 163.0 | 190.2 |
| 444.3 (l) | 175.0 | 173.5 | 200.1 |
| 486.1 (l) | 198.0 | 196.7 | 228.1 |
| 511.8 (l) | 213.0 | 211.3 | 243.6 |
| 535.4 (l) | 226.0 | 225.0 | 258.5 |
| 565.5 (l) | 244.0 | 242.9 | 279.8 |
| 582.1 (l) | 254.0 | 253.0 | 287.1 |
| 609.6 (l) | 271.0 | 269.9 | 308.3 |

## TABLE 3 (cont.)

## Comparison of Experimental and Predicted Enthalpies for 8/8 Middle Distillate

300 Psia

| Temp., °F | $\Delta H_{J-G}$, Btu/lb$_m$ | $\Delta H_{K-L}$, Btu/lb$_m$ | $\Delta H_{Expt.}$ Btu/lb$_m$ |
|---|---|---|---|
| 279.1 (1) | 91.0 | 89.8 | 106.9 |
| 318.9 (1) | 111.0 | 108.8 | 129.1 |
| 346.9 (1) | 125.0 | 122.6 | 144.6 |
| 372.6 (1( | 138.0 | 135.6 | 159.5 |
| 403.0 (1) | 155.0 | 151.4 | 176.1 |
| 424.7 (1) | 165.0 | 162.9 | 190.2 |
| 456.0 (1) | 181.0 | 179.9 | 207.8 |
| 485.2 (1) | 198.0 | 196.2 | 226.1 |
| 515.9 (1) | 215.0 | 213.7 | 246.8 |
| 545.7 (1) | 233.0 | 231.1 | 265.6 |
| 588.1 (1) | 258.0 | 256.6 | 291.8 |

1000 Psia

| Temp., °F | $\Delta H_{J-G}$, Btu/lb$_m$ | $\Delta H_{K-L}$, Btu/lb$_m$ | $\Delta H_{Expt.}$ Btu/lb$_m$ |
|---|---|---|---|
| 408.5 (1) | 156.0 | 154.3 | 183.7 |
| 450.3 (1) | 178.0 | 176.8 | 207.5 |
| 488.6 (1) | 200.0 | 198.1 | 230.8 |
| 516.7 (1) | 215.0 | 214.2 | 247.1 |
| 555.8 (1) | 238.0 | 237.1 | 272.0 |
| 623.5 (1) | 280.0 | 278.5 | 316.0 |

# APPENDIX II

# COMPARISON OF EXPERIMENTAL AND PREDICTED ENTHALPIES FOR MODEL COMPOUNDS

# TABLE 1

## Benzene

| Temperature, °F | $\Delta H$ expt. $\text{Btu/lb}_m$ | $\Delta H$ K-L $\text{Btu/lb}_m$ |
|---|---|---|
| **100 psia** | | |
| 250.6 (l) | 83.2 | 81.8 |
| 268.2 (l) | 92.1 | 90.5 |
| 276.2 (l) | 94.4 | 94.4 |
| 306.9 (l) | 111.2 | 109.9 |
| 323.6 (v) | 262.3 | 258.4 |
| 339.5 (v) | 270.6 | 264.9 |
| 397.9 (v) | 296.3 | 289.7 |
| 413.1 (v) | 301.9 | 293.3 |
| **400 psia** | | |
| 241.9 (l) | 79.1 | 77.6 |
| 286.9 (l) | 102.8 | 99.8 |
| 304.3 (l) | 110.8 | 108.6 |
| 335.3 (l) | 127.4 | 124.7 |
| 377.6 (l) | 151.0 | 147.4 |
| 385.2 (l) | 155.7 | 151.6 |
| 432.9 (l) | 181.9 | 178.5 |
| 445.2 (l) | 190.8 | 185.6 |
| 451.0 (l) | 194.3 | 188.9 |
| 475.8 (v) | 302.9 | 301.4 |
| 486.8 (v) | 309.2 | 307.9 |
| 498.1 (v) | 316.9 | 314.4 |
| 552.4 (v) | 354.5 | 344.3 |

TABLE 1 (cont.)

Benzene

| Temperature, $^{o}F$ | $\Delta H$ expt. Btu/$lb_m$ | $\Delta H$ K-L Btu/$lb_m$ |
|---|---|---|
| 1000 psia | | |
| 359.0 (1) | 141.0 | 137.3 |
| 388.9 (1) | 161.9 | 153.7 |
| 407.9 (1) | 168.5 | 164.2 |
| 504.7 (1) | 227.6 | 220.9 |
| 520.9 (1) | 239.3 | 230.9 |
| 563.8 (1) | 271.8 | 257.8 |
| 575.6 (1) | 283.8 | 265.3 |

## TABLE 2

m-Xylene

| Temperature, °F | ΔH expt. Btu/lb$_m$ | ΔH K-L Btu/lb$_m$ |
|---|---|---|
| 50 psia | | |
| 147.5 (1) | 34.3 | 36.2 |
| 173.9 (1) | 46.9 | 48.5 |
| 196.9 (1) | 56.8 | 59.5 |
| 244.9 (1) | 79.6 | 83.4 |
| 291.8 (1) | 103.5 | 107.8 |
| 318.5 (1) | 117.6 | 122.2 |
| 346.4 (1) | 132.7 | 137.7 |
| 372.1 (1) | 145.6 | 152.3 |
| 402.2 (v) | 291.1 | 286.5 |
| 420.9 (v) | 297.1 | 295.4 |
| 439.5 (v) | 305.3 | 304.4 |
| 465.9 (v) | 323.0 | 317.5 |
| 514.7 (v) | 344.6 | 342.2 |
| 561.3 (v) | 366.3 | 366.6 |
| 610.8 (v) | 394.1 | 393.5 |
| 250 psia | | |
| 320.1 (1) | 117.0 | 123.1 |
| 391.0 (1) | 156.5 | 163.5 |
| 406.1 (1) | 164.5 | 172.1 |
| 432.9 (1) | 181.5 | 188.1 |
| 446.9 (1) | 188.8 | 196.6 |
| 480.9 (1) | 212.2 | 217.8 |
| 486.2 (1) | 215.0 | 221.1 |

## Table 2 (cont.)

m-Xylene

| Temperature, °F | ΔH expt. Btu/$lb_m$ | ΔH K-L Btu/$lb_m$ |
|---|---|---|
| 250 psia | | |
| 508.1 (l) | 230.8 | 235.1 |
| 528.6 (l) | 240.2 | 248.4 |
| 530.5 (l) | 241.8 | 249.6 |
| 544.0 (l) | 252.1 | 258.5 |
| 546.7 (l) | 253.4 | 260.3 |
| 553.7 (v) | 348.4 | 345.9 |
| 560.7 (v) | 357.3 | 350.1 |
| 581.0 (v) | 362.1 | 362.4 |
| 603.2 (v) | 374.9 | 375.7 |
| 614.7 (v) | 384.9 | 382.6 |
| 631.7 (v) | 393.4 | 392.8 |
| 680.3 (v) | 422.8 | 422.1 |
| 500 psia | | |
| 388.8 (l) | 156.4 | 161.9 |
| 450.6 (l) | 191.9 | 198.9 |
| 475.2 (l) | 207.1 | 214.2 |
| 528.6 (l) | 241.9 | 248.4 |
| 549.7 (l) | 260.4 | 262.3 |
| 568.1 (l) | 277.6 | 274.6 |
| 589.5 (l) | 294.0 | 289.1 |
| 655.9 (v) | 377.8 | 379.4 |
| 661.7 (v) | 385.2 | 385.3 |
| 684.1 (v) | 413.7 | 403.9 |
| 693.9 (v) | 419.1 | 411.2 |

## Table 2 (cont.)

m-Xylene

| Temperature, °F | ΔH expt. Btu/lb$_m$ | ΔH K-L Btu/lb$_m$ |
|---|---|---|
| 1000 psia | | |
| 421.2 (1) | 176.1 | 181.1 |
| 464.0 (1) | 201.0 | 207.2 |
| 521.9 (1) | 235.1 | 244.0 |
| 560.8 (1) | 266.9 | 269.7 |
| 575.6 (1) | 274.3 | 279.7 |
| 624.2 (1) | 311.8 | 313.2 |
| 659.7 (1) | 338.5 | 338.5 |
| 697.6 (1) | 373.8 | 366.2 |
| 1500 psia | | |
| 555.3 (1) | 267.0 | 266.0 |
| 603.0 (1) | 297.8 | 298.4 |
| 627.3 (1) | 319.5 | 315.4 |
| 636.0 (1) | 324.1 | 321.5 |
| 669.5 (1) | 355.3 | 345.6 |
| 690.5 (1) | 368.6 | 360.9 |

## Table 3

1-Methyl-Naphthalene

| Temperature, °F<br>Inlet | $\Delta H_{expt}$<br>Btu/lb | $\Delta H_{K-L}$<br>Btu/lb |
|---|---|---|
| 75 psia | | |
| 449.8 (L) | 174.0 | 167.4 |
| 559.1 (L) | 234.1 | 226.9 |
| 566.8 (L) | 237.1 | 231.3 |
| 575.5 (L) | 250.5 | 236.3 |
| 616.1 (L) | 268.0 | 260.0 |
| 651.1 (v) | 411.2 | 374.8 |
| 679.7 (v) | 422.4 | 389.4 |
| 686.5 (v) | 423.9 | 392.9 |
| 728.9 (v) | 443.1 | 415.0 |
| 739.0 (v) | 449.1 | 420.3 |
| 100 psia | | |
| 223.9 (L) | 63.5 | 61.2 |
| 269.0 (L) | 84.3 | 80.6 |
| 328.3 (L) | 112.5 | 107.5 |
| 376.0 (L) | 135.0 | 130.3 |
| 417.9 (L) | 156.7 | 151.1 |
| 452.4 (L) | 176.0 | 168.8 |
| 501.9 (L) | 201.5 | 195.1 |
| 554.7 (L) | 231.5 | 224.4 |
| 588.1 (L) | 252.4 | 243.6 |
| 619.7 (L) | 270.5 | 262.1 |
| 659.2 (L) | 296.9 | 286.0 |
| 689.8 (v) | 422.3 | 392.4 |
| 730.9 (v) | 442.4 | 414.1 |
| 754.2 (v) | 453.9 | 426.5 |

Table 3 (cont.)

1-Methyl-Naphthalene

470 psia

| Temperature, °F<br>Inlet | $\Delta H_{expt}$<br>Btu/lb | $\Delta H_{K-L}$<br>Btu/lb |
|---|---|---|
| 584.1 (L) | 250.7 | 241.2 |
| 628.3 (L) | 276.9 | 267.3 |
| 659.9 (L) | 298.9 | 286.4 |
| 688.0 (L) | 312.9 | 303.8 |
| 690.0 (L) | 317.0 | 305.0 |
| 720.1 (L) | 340.0 | 324.1 |
| 739.9 (L) | 351.0 | 336.8 |

## Table 4

m-Cresol

| Temperature, °F | $\Delta H_{expt}$ Btu/lb$_m$ | $\Delta H_{K-L}$ Btu/lb$_m$ |
|---|---|---|
| 200 psia | | |
| 532.2 (l) | 275.1 | 204.4 |
| 564.3 (l) | 299.0 | 221.9 |
| 585.9 (l) | 306.4 | 233.9 |
| 597.6 (l) | 314.6 | 240.5 |
| 604.7 (l) | 317.8 | 244.5 |
| 615.6 (l) | 332.6 | 250.7 |
| 642.8 (v) | 480.6 | 403.4 |
| 674.6 (v) | 494.3 | 420.5 |
| 688.1 (v) | 504.6 | 429.4 |
| 702.1 (v) | 512.8 | 438.8 |
| 716.7 (v) | 525.0 | 448.5 |
| 724.0 (v) | 521.2 | 453.5 |
| 748.1 (v) | 528.2 | 469.8 |
| 749.5 (v) | 529.4 | 470.8 |
| 250 psia | | |
| 206.6 (l) | 76.1 | 52.1 |
| 277.8 (l) | 117.0 | 81.6 |
| 304.6 (l) | 130.0 | 93.2 |
| 318.8 (l) | 136.3 | 99.5 |
| 362.1 (l) | 163.6 | 119.2 |
| 370.9 (l) | 166.9 | 123.3 |
| 413.5 (l) | 195.3 | 143.7 |
| 454.3 (l) | 221.4 | 163.9 |
| 474.9 (l) | 235.6 | 174.4 |
| 537.9 (l) | 274.3 | 207.5 |
| 548.8 (l) | 283.6 | 213.4 |
| 563.7 (l) | 296.8 | 221.6 |

Table 4 (cont.)

| m-Cresol<br>Temperature, $^oF$ | $\Delta H_{expt.}$ Btu/$lb_m$ | $\Delta H_{K-L}$ Btu/$lb_m$ |
|---|---|---|
| 250 psia | | |
| 591.0 (1) | 309.2 | 236.8 |
| 600.3 (1) | 314.6 | 242.0 |
| 605.4 (1) | 318.9 | 244.9 |
| 612.2 (1) | 326.7 | 248.8 |
| 629.3 (1) | 340.7 | 258.6 |
| 661.6 (1) | 363.4 | 277.5 |
| 678.7 (v) | 498.4 | 417.6 |
| 698.4 (v) | 503.9 | 431.4 |
| 720.8 (v) | 514.8 | 447.0 |
| 727.0 (v) | 522.7 | 451.3 |
| 744.6 (v) | 539.6 | 463.6 |
| 1000 psia | | |
| 499.9 (1) | 254.2 | 187.3 |
| 549.1 (1) | 289.3 | 213.6 |
| 605.1 (1) | 322.6 | 244.7 |
| 621.6 (1) | 332.8 | 254.2 |
| 642.3 (1) | 347.0 | 266.2 |
| 661.6 (1) | 362.4 | 277.5 |
| 739.1 (1) | 424.3 | 324.7 |
| 1500 psia | | |
| 478.7 (1) | 237.3 | 176.3 |
| 525.8 (1) | 271.4 | 201.0 |
| 575.7 (1) | 308.6 | 228.2 |
| 628.3 (1) | 346.4 | 258.0 |
| 687.4 (1) | 388.1 | 292.9 |

Table 4 (cont.)

m-Cresol

| Temperature, °F | $\Delta H_{exp}$ Btu/lb$_m$ | $\Delta H_{K-L}$ Btu/lb$_m$ |
|---|---|---|
| 705.9 (1) | 403.4 | 304.2 |
| 717.2 (1) | 411.4 | 311.1 |
| 727.6 (1) | 426.3 | 317.5 |

## Table 5

n-Pentanol

| Temperature °F | $\Delta H_{expt}$(23) Btu/lb$_m$ | $\Delta H_{K-L}$ Btu/lb$_m$ |
|---|---|---|
| 150 psia | | |
| 349.9 (L) | 209.5 | 149.8 |
| 438.5 (L) | 277.7 | 205.4 |
| 445.7 (L) | 287.0 | 210.1 |
| 459.8 (v) | 442.4 | 316.1 |
| 499.2 (v) | 469.6 | 339.7 |
| 559.5 (v) | 507.4 | 376.3 |
| 590.6 (v) | 527.0 | 395.4 |
| 615.2 (v) | 545.1 | 410.8 |
| 400 psia | | |
| 354.1 (L) | 210.8 | 152.3 |
| 357.5 (L) | 211.9 | 154.4 |
| 409.6 (L) | 254.4 | 186.8 |
| 489.2 (L) | 321.6 | 239.1 |
| 510.7 (L) | 338.8 | 253.8 |
| 549.6 (L) | 368.9 | 281.1 |

## Table 6

n-Hexanol

| Temperature °F | $\Delta H_{expt}$(23) Btu/$lb_m$ | $\Delta H_{K-L}$ Btu/$lb_m$ |
|---|---|---|
| 200 psia | | |
| 389.3 (L) | 232.6 | 174.6 |
| 454.1 (L) | 285.2 | 216.4 |
| 525.0 (L) | 343.0 | 264.7 |
| 558.4 (v) | 481.6 | 366.3 |
| 570.2 (v) | 491.3 | 374.1 |
| 597.8 (v) | 509.0 | 392.2 |
| 620.1 (v) | 527.2 | 406.8 |
| 638.2 (v) | 536.6 | 418.6 |
| 648.7 (v) | 546.3 | 425.5 |
| 400 psia | | |
| 389.6 (L) | 234.9 | 174.8 |
| 494.9 (L) | 318.0 | 243.9 |
| 550.0 (L) | 362.9 | 282.4 |
| 574.3 (L) | 381.7 | 299.9 |
| 600.2 (L) | 408.4 | 319.0 |

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