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ENTHALPY MEASUREMENTS OF A COAL LIQUID

PRODUCED BY THE SYNTHOIL PROCESS

By

James Robert Andrew

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

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DEDICATION

To My Wife, Cindy

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ABSTRACT

An operating procedure for the long term operation of the calorimeter for the collection of accurate enthalpy data is presented. Enthalpy data were taken using a Freon 11 boil-off flow calorimeter on a distillate prepared from a coal liquid produced by the Synthoil process. The data were taken over a temperature range of 155° to 742°F and at pressures of 150, 200, 500, 1,000, and 1,500 psia. Some vaporization occurred at high temperatures and low pressures.

Experimental enthalpies measured in this work and those measured by Lenoir and Hipkin¹⁰ were compared to ones predicted by the methods of Johnson-Grayson and Kesler-Lee.^{9,3,8} Average percent error ranged from -14.50% to -16.10%. The average error for the Utah and Western Kentucky Syncrudes and the Synthoil distillate were found to correlate well with the amount of aromatics in the sample. The greater the aromatic content the greater the deviation between the experimental enthalpies and those predicted by the previously mentioned correlations. All of the values predicted are lower than the experimental values. In addition, the experimental enthalpy measurements for a SRC-1 naphtha are presented in Appendix I.

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INTRODUCTION

With petroleum production expected to reach a peak in the next five to ten years and the demand for petroleum products constantly increasing year by year without a peak in the foreseeable future, the search for replacement hydrocarbon sources has begun. Among the many alternatives coal and coal liquids seem near the top of the list as viable alternatives.

When coal liquids are utilized within the next ten years, extensive knowledge of their physical and thermodynamic properties will be required to effectively process them and to optimize the products derived. Some of the important design parameters for the process and design engineers are pressure-volume-temperature measurements, phase equilibria measurements, heat capacity and enthalpy data. Enthalpy measurements are very useful because they can be used directly in the calculation of process heat loads for fractionators, heat exchangers, and many other types of process equipment.

One method for obtaining enthalpy data is by flow calorimetry. This was the method used for this research program. The flow calorimeter system was found to have an accuracy of $\pm 0.50\%$ by calibration with water and n-heptane.^{4,7} After calibration four coal liquids were run previous to the one in this study.^{4,7}

The purposes of this thesis are: 1) to give a detailed procedure for operating the calorimeter, 2) to present the enthalpy data for a distillate from a coal liquid produced by the Synthoil process, and 3) to compare predicted enthalpies with those obtained from experiment. Explanations for the observed discrepancies are discussed.

The goal of the program for coal liquids is to gather sufficient enthalpy data so that a method can be developed to accurately predict enthalpy data knowing only a few of the physical properties of the fluid of interest. Because of the success of this approach with petroleum liquids⁷, there seems reasonable probability of success in the case of coal liquids. Time will be the judge of this.

THEORY

Calorimetric methods for enthalpy measurements of fluid mixtures can be classified into two general types: batch and flow. Flow calorimetry is better for enthalpy data because it does not require volumetric data as does batch calorimetry. Volumetric data are necessary to calculate enthalpy from the experimental internal energy measured by batch calorimetry. There are also two methods of flow calorimetry by which enthalpies can be determined. The first involves adding a known amount of energy to the fluid and recording the temperature change that occurs, while the second uses a knowledge of the specific or latent heat of a reference fluid to quantify the energy input. For this research a reference fluid boil-off calorimeter was selected. There are three basic reasons for this. First, boil-off calorimeters are better suited to measurement of enthalpy differences, while direct measurement calorimeters are more suited to heat capacity studies. Secondly boil-off calorimeters are simpler in design, cheaper to construct, and have fewer mechanical problems. Thirdly, although boil-off calorimeters are less accurate than the direct ones, they can be designed to within the accuracy of design calculations. Thus, a boil-off calorimeter similar to the design of Nelson and Holcomb (1) utilizing Freon 11 (trichlorofluoromethane) as the reference fluid was selected for this study. Freon 11 is utilized

because its boiling point is close to room temperature (65°F) and its well-known thermodynamic properties. Further details of the design of the Freon 11 boil-off calorimeter are dealt with by J.R. McConnell (2).

If the First Law of Thermodynamics for an open system is applied to the flow calorimeter, it can be simplified to the following (assuming negligible potential and kinetic energy changes and no work):

$$(H_{T_2, P_2} - H_{T_1, P_1})_x = Q/M$$

where

H_{T_2, P_2} = enthalpy per unit mass of the fluid at the outlet conditions

H_{T_1, P_1} = enthalpy per unit mass of fluid at the inlet conditions

Q = net rate of heat input

M = mass flow rate of sample fluid.

x = at constant composition

With a knowledge of the latent heat of vaporization and the mass flow rates of the sample and reference fluids, this general form can be altered for a reference fluid boil-off calorimeter in which the Q term is:

$$Q = M_r \lambda_r + q$$

where

M_r = mass flow rate of the reference fluid

λ_r = latent heat of vaporization of reference fluid
($\lambda_r = 79.20$ BTU/lb_m for Freon at 65°F and 620 mm Hg)

q = heat leak term.

The heat leak term can either be a leak in which heat is transferred from the ambient conditions ($\sim 75^{\circ}\text{F}$) into the calorimeter or a heat loss from the Freon 11 system. This heat leak term is a limiting factor on the accuracy of the calorimeter. Because the heat leak term is inversely proportional to the mass flow rate, it can be seen that by increasing the mass flow rate the heat leak term can be reduced, thus increasing the accuracy of the calorimeter. However, an upper limit is imposed on this flow rate due to the size of the Freon system necessary to handle the boil-off from the calorimeter. Therefore, most flow calorimeters of this type are designed for flow rates of approximately one cubic centimeter per second. Because of possible sample size limitations, this calorimeter was designed for a half a cubic centimeter per second.

The enthalpy data that are collected are then the enthalpy change between some inlet temperature and pressure and the outlet pressure and reference temperature of 65°F . The data is collected over a temperature range of 150° - 750°F and a pressure range of 30 - 1500 psia. From the data an enthalpy versus temperature diagram at different isobars is constructed. In the two-phase region only the total enthalpy of the overall mixture is measured. To divide this measurement into liquid and vapor components a knowledge of the equilibrium ratio is

necessary. However, the enthalpy measurements can be applied directly to heat transfer calculations which is one of their major utilities.

EXPERIMENTAL EQUIPMENT AND PROCEDUREProcess Flow Sheet

The process flow sheet for the sample process and the Freon 11 systems is shown in Figure 1. The sample system is on the left of the diagram. From the surge tank the sample is pumped by a Milton-Roy dual diaphragm pump to the bladder accumulator. The dual diaphragm pump was selected because of its flow rate characteristics and pressure rating. It can operate from about 0.1 cc/sec to 5 cc/sec flow rates and to a pressure of about 1800 psig. The bladder accumulator acts as a shock absorber against the pump strokes to even out the flow. Even flow is important in avoiding hot spots in the sample which acts to reduce the chance of thermal cracking, and is also important for pressure measurement. The bladder accumulator also helps set the system pressure in combination with the back pressure regulator located after the outlet of the calorimeter.

After the bladder accumulator the sample passes through the fluidized-bed preheater. The preheater allows gradual heating of the sample in a 25 foot coil which avoids the possibility of severe temperature profiles and hot spots which might cause thermal cracking. The fluidized bed bath also is very versatile in that it allows a wide temperature range (25° - 600°C) and rapid heat up time. The positioning of the preheater bath was dictated by the necessity to have

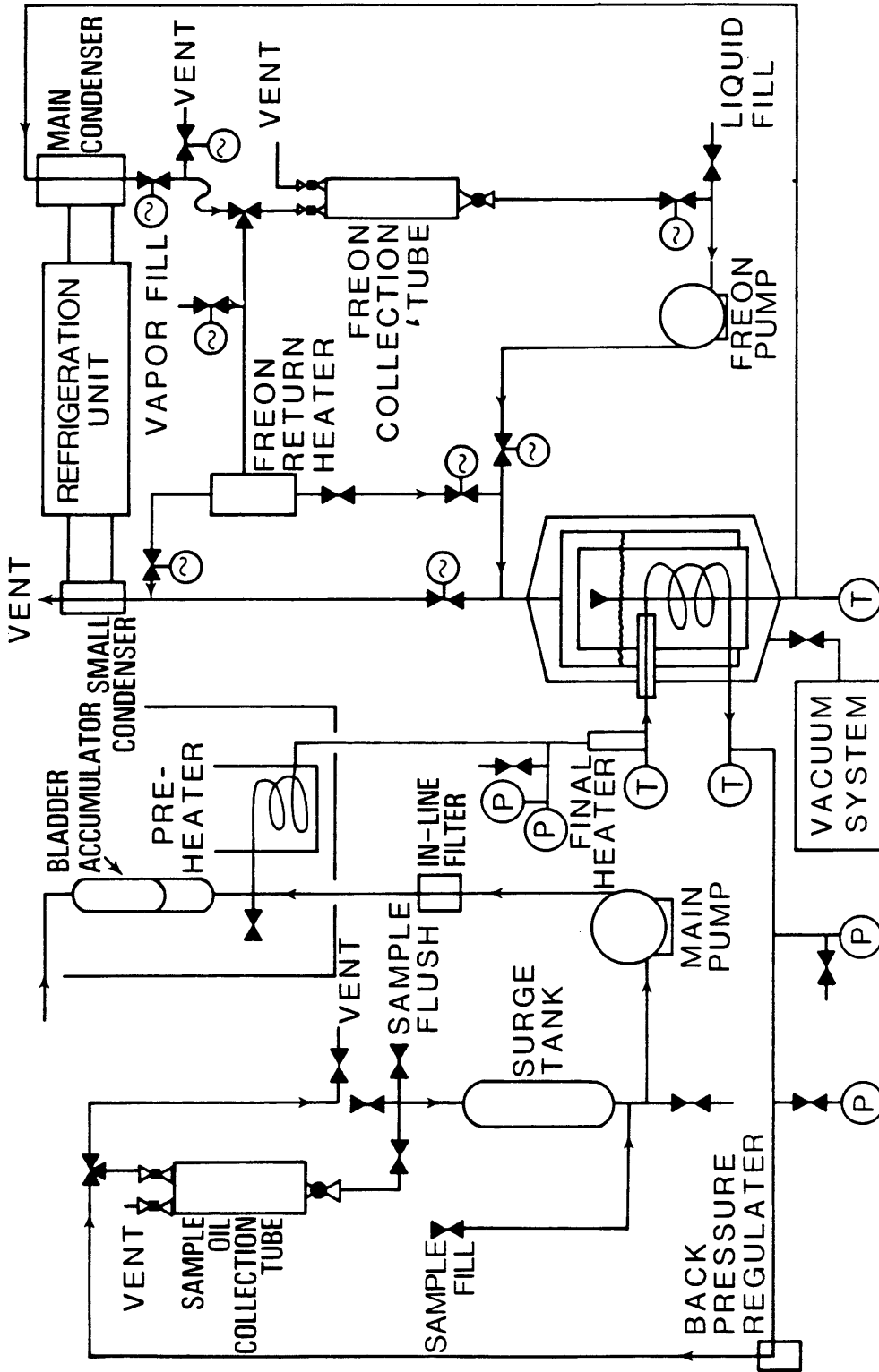


FIGURE 1

Flow Diagram of Experimental Apparatus for Enthalpy Measurements

downward flow after heating to prevent trapping of the liquid in low spots which would cause compositional changes during two phase flow. After the preheater, the sample flows past a custom-made tubular heating element that is concentric to the tube through which the oil flows. This final heater is controlled by a Honeywell SCR controller (PID Controller). At the calorimeter inlet the pressure is measured by a Heise "c" Bourdon tube pressure gauge and the temperature is measured by a 100 ohm platinum-resistance thermometer. After this the sample flows into the calorimeter where the fluid gives up its heat to the boiling Freon bath in a 35 foot coil. It exits the calorimeter at $65^{\circ}\text{F} \pm 1^{\circ}\text{F}$. At the calorimeter exit the pressure is again measured by a Heise gauge and the temperature by another platinum resistance thermometer. The sample then passes through the back pressure regulator, which controls the system pressure, into a three-way ball valve which directs the flow either to the sample collection tube (only during an experimental run) or back to the surge tank.

There are two 60 micron in-line filters in the sample system. One is located after the pump; the other just after the final heater. These filters are used to remove particulates from the fluid which might plug the line. Thus far the filter after the final heater has demanded the most frequent replacement. This is caused by the large amount of coke formation in the pre- and final heaters.

All of the piping in the sample system is 316 stainless steel to reduce to a minimum the problem of corrosion by the coal liquids. Also the diameter of the tubing used was kept as small as possible so that the volume of sample necessary for continuous running was kept to a minimum.

The required sample size is approximately two liters for a limited set of enthalpy runs. If more extensive data is required a larger amount is needed due to loss, spillage and compositional changes due to extensive temperature cycling. Five gallons is probably about the optimal size.

The Freon 11 System is shown on the right of Figure 1. The freon is stored in the calorimeter itself, which in turn is filled from a 55 gallon drum. The Freon is saturated, and thus all the heat transferred goes into vaporization of the liquid. The Freon vapor passes out of the calorimeter through the demister and into a 3/4" heated copper line. Just before entering the heated line the vapor temperature is measured. If all conditions in the calorimeter are normal this temperature is usually $65^{\circ}\text{F} \pm 1^{\circ}\text{F}$. An upset in the Freon system, such as a pressure change, can be detected by an odd Freon outlet vapor temperature. The Freon vapor line is heated to around $80^{\circ} - 90^{\circ}\text{F}$ to prevent Freon condensation. The upper line carries the Freon vapor to the main condenser where it is cooled to sub-ambient ($\sim 40^{\circ}\text{F}$) temperatures by an ethylene glycol-water mixture. The condenser is vented to the atmosphere to regulate the pressure in the calorimeter. After leaving the condenser the Freon passes through a glass U-tube

which acts as a liquid leg and also gives a good indication of the pressure stability of the Freon system. If the pressure in the Freon system is unstable due to the Freon flow rate being too high or the Freon return heater being too full, the two sides of the leg will be at unequal height, but if the system is normal the levels will be approximately the same.

After the liquid leg the Freon passes into a three-way ball valve where it is sent to a cooled collection tube if a data point is being taken or to the Freon return heater if the system is recycling. The Freon return heater raises the temperature of the return Freon to the calorimeter to its boiling point so that sub-cooled liquid is not returned to the calorimeter. If the Freon were sub-cooled it would create error in the measurements because the heat from the sample would be providing not only the heat of vaporization but enough sensible heat to raise the Freon to its boiling point. This would result in an enthalpy value that was too low. After the return heater the Freon passes through a drier which removes the water and then is returned to the outer chamber of the calorimeter. The Freon vaporized in the return heater and in the outer chamber of the calorimeter is condensed by the small condenser and returned to the calorimeter very near the saturation temperature of Freon.

The orientation of the Freon lines was dictated by many factors. The most important was the need for gravity flow

from the main condenser to the sample collection tube and the calorimeter.

Secondly the exposure time of the sub-cooled Freon to ambient temperature had to be minimized to avoid vaporization prior to measurement. Thus far very little difficulty has been experienced with vaporization.

Thirdly, the height of the room limited the space between the main condenser and sample collection tube. The piping in the Freon system is made from either copper, 316 stainless steel, or glass. No corrosion problems are anticipated with this system.

Calorimeter

The main part to any calorimetric facility is the calorimeter. The calorimeter designed and used in these enthalpy studies is shown in Figure 2. The calorimeter is constructed of both 304 and 316 stainless steel. The calorimeter consists of three chambers with Freon in the inner two and a vacuum on the outermost. The vacuum chamber acts as an insulation chamber to eliminate primarily conductive and convective heat transfer from the ambient conditions to the Freon bath. A vacuum pumping system pulls a vacuum on this chamber of around 5×10^{-4} mm Hg. The pressure should be less than 7×10^{-4} mm Hg to effectively eliminate these two modes of heat transfer. The next chamber is the outer Freon chamber. It is connected by a $\frac{1}{4}$ " tube with the inner Freon

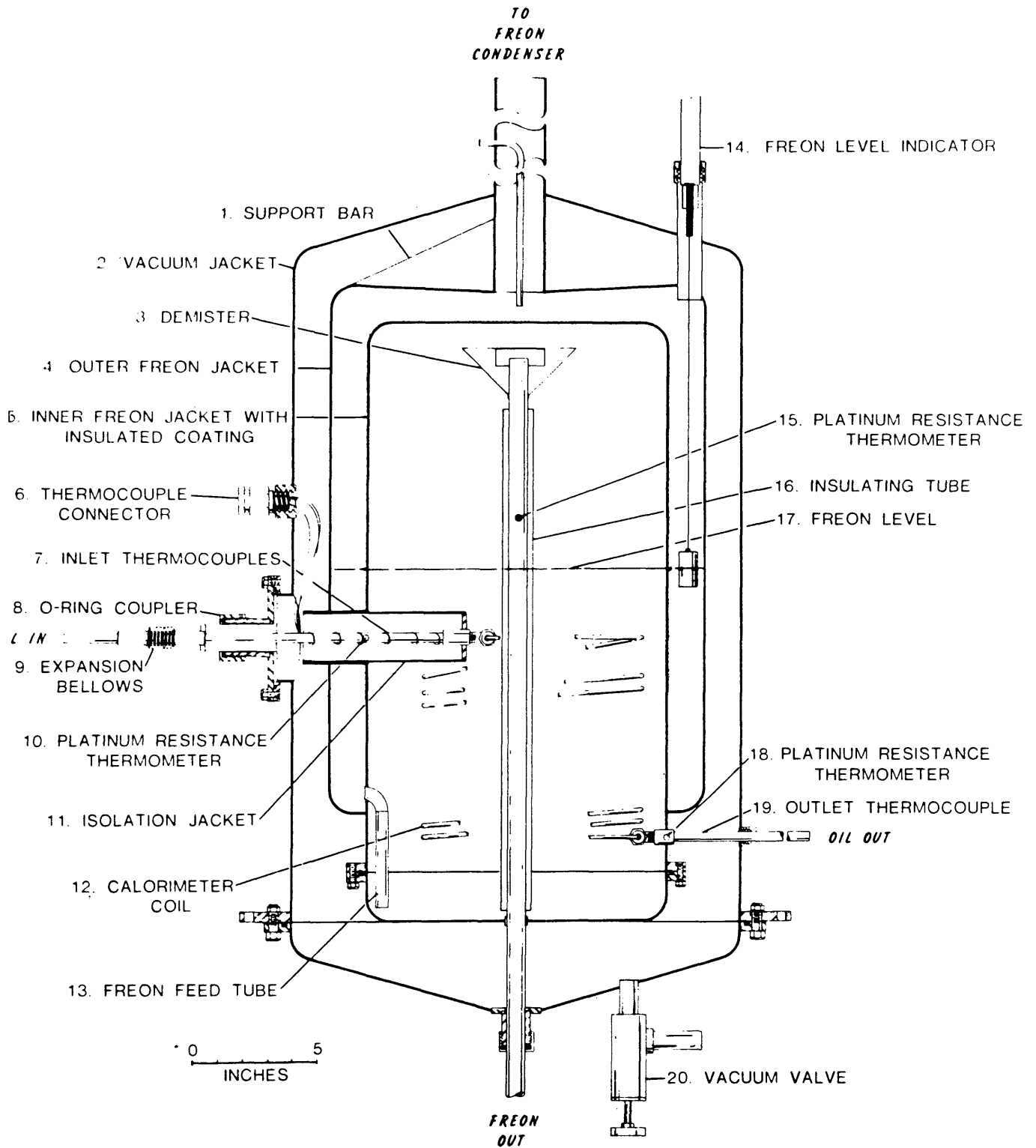


FIGURE 2

Flow Calorimeter

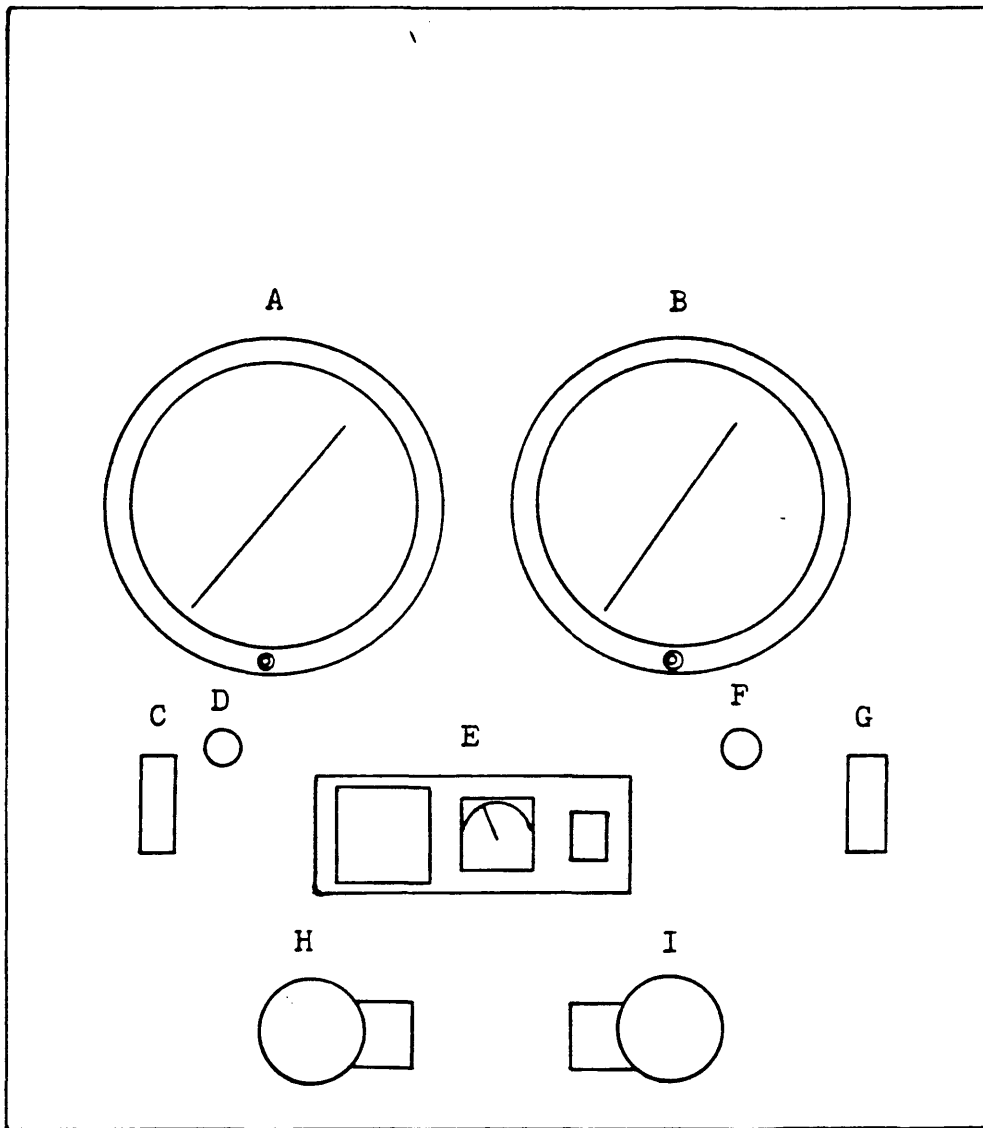
chamber. The outer chamber serves two purposes. First it acts as further insulation to eliminate any temperature differences between the inner chamber and the surroundings. Secondly, it creates more storage space for the Freon, thus eliminating excessive filling requirements. This chamber also acts as a sink for returning Freon, to prevent disturbance of the inner chamber during an experimental run. The inner Freon chamber is the one in which heat is transferred from the sample fluid to the Freon in the thirty-five foot coil. After the Freon vaporizes, it passes out of the inner chamber through a demister into the heated 3/4" line. The demister provides a tortuous path for the vapor which removes any entrained liquid in the vapor. Entrained liquid could be a problem at high inlet temperatures and if the inner chamber of the calorimeter is near full capacity. The level of the Freon in the two chambers is monitored by a glass float whose level is read on a calibrated sight glass on the top of the calorimeter. Access to the inner chamber of the calorimeter in case of trouble is through the bottom, by removing two sets of bolts which maintain the seal on the vacuum and inner chambers. There is no access to the outer Freon chamber.

The calorimeter just described was one of two possible designs. Boil-off calorimeters can be designed to measure enthalpy differences isobarically by use of a large diameter coil with virtually no pressure drop or they can measure

enthalpy differences between a high temperature and pressure and atmospheric pressure and a reference temperature by means of a capillary coil designed to produce a large pressure drop. This calorimeter employs a long coil (1/8" O.D.) to measure essentially isobaric temperature differences. However in reality there is a slight pressure drop across the calorimeter which depends on the viscosity of the sample being tested. It has been as low as 10 psia for heptane and as high as 150 psia for the Synthoil distillate. Thus the outlet pressure is corrected to a reference pressure of one atmosphere. The pressure correction of Kesler and Lee (3) is employed for this purpose. However, since the effect of pressure on liquids is very small the pressure correction is almost negligible; the largest value has been on the order of 3-4 BTU/lb. The data is corrected to 1 atm. pressure because it was decided to tie all of the data to a common reference point. Further details on the design of the calorimeter and equipment can be found in J.R. McConnell's thesis (2) and Quarterly Progress Reports for DOE contract E(49-18) - 2035.

Instrumentation and Controls

The instrument and control diagrams as drawn by Raj Sharma (4) are presented in Figures 3 and 4. The symbols are explained in the legends following the figures. The control panels are fairly self-explanatory. They contain three basic

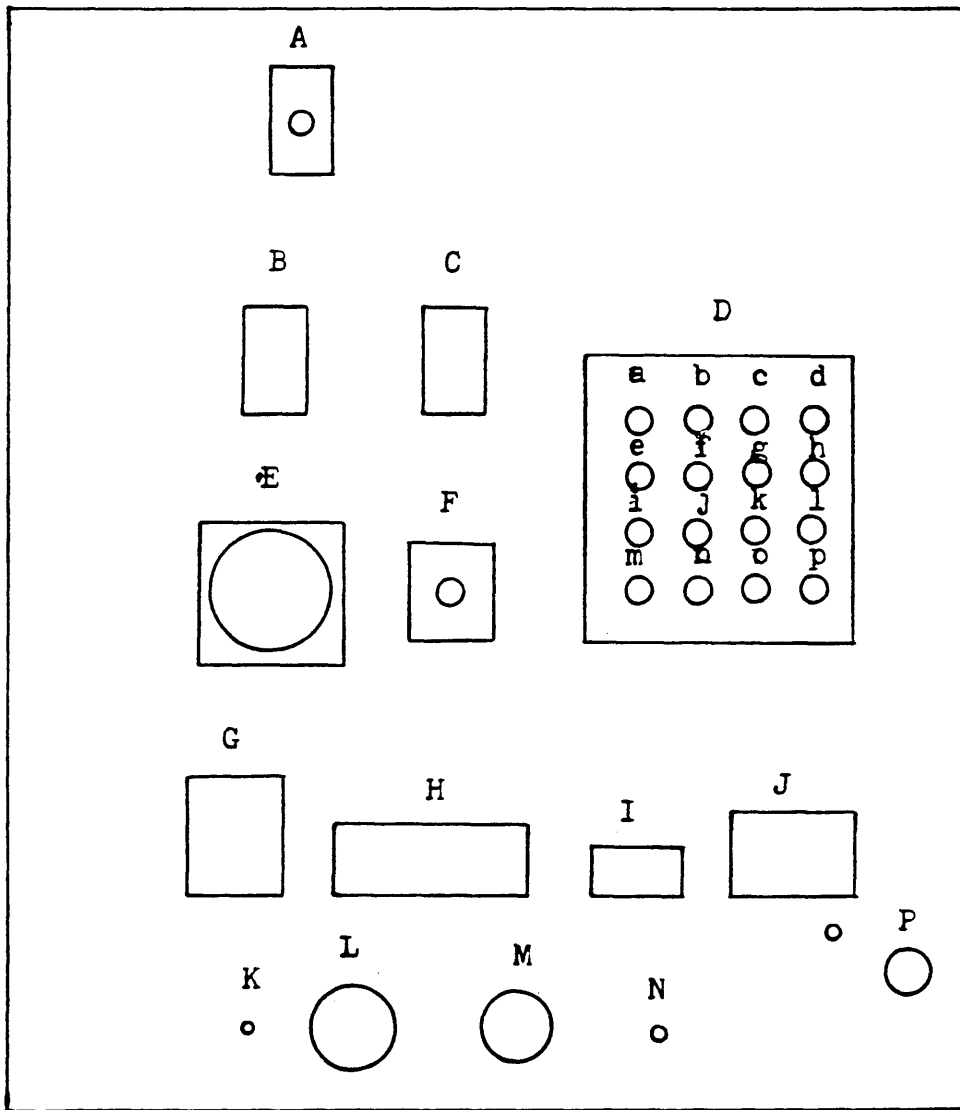


Scale: $1\frac{1}{2}'' = 1'$

FIGURE 3 LEFT MAIN CONTROL PANEL

Symbol index for Figure 3.

- A. Heise gauge for measuring the sample pressure at the calorimeter outlet (new addition)
- B. Heise gauge for measuring the sample pressure at the calorimeter inlet
- C. Air flow meter for the preheater bath
- D. Heise gauge shut off valve for (A)
- E. Preheater temperature controller
- F. Heise gauge shut off valve for (B)
- G. Water rotometer for inlet pressure transducer (not in use at present)
- H. Variac for the return heater
- I. Variac for the Freon line heater



Scale: $1\frac{1}{2}'' = 1'$

FIGURE 4. RIGHT MAIN CONTROL PANEL

Symbol index for Figure 4.

- A. SCR unit power indicating light
- B. Vacuum pump-ON/OFF switch
- C. Main pump-ON/OFF switch
- D. Main Control switches
 - a. Blank
 - b. Blank
 - c. Blank
 - d. Blank
 - e. Solenoid valve A
 - f. Solenoid valve B
 - g. Solenoid valve C
 - h. Solenoid valve D
 - i. Freon pump
 - j. Blank
 - k. Blank
 - l. Blank
 - m. Fluke meter
 - n. Temperature indicator
 - o. D.C. power supply
 - p. Temperature controller for the final heater
- E. Final heater temperature controller
- F. Run button
- G. Timer
- H. Fluke meter
- I. Omega temperature indicator

- J. D.C. power supply
- K. Voltage control switch for the inlet and outlet pressure transducers (not in use at present)
- L. Fluke meter input switch
- M. Selector switch for the thermocouples (Fluke meter) (not in use at present)
- N. Selector switch for the thermocouples (Temperature indicator)
- P. Selector switch for platinum resistance thermometers (Fluke meter)

types of instrumentation: pressure measurements, temperature measurements, heater controllers, and controls for other peripheral equipment. A brief description of each panel follows.

The left panel, shown in Figure 3, contains two Heise Bourdon tube gauges to measure the inlet and outlet of calorimeter pressures. Connections to the back of these gauges are with 1/8" O.D. 316 stainless steel tubing run to their respective locations. Also shown are two 1/8 inch regulating valves used to isolate the Heise gauges during times of large pressure surges. This prevents damage to the mechanical connections between the Bourdon tube and the gauge needle. Two rotameters are also shown; one controls the air flow to the fluidized bed bath and the other is no longer used. The PID controller shown in the lower center controls the temperature of the preheater bath. The two rheostats control the heating tapes which provide heat to the Freon line from the calorimeter to the main condenser and to the Freon return heater.

Figure 4 shows the right control panel. At the top is the indicator light for the SCR power unit, which provides power to the final heater. The demand on this heater can be gauged by the frequency of the lighting of this unit. Constant lighting is an indicator that too much of a heating load is being put on the final heater. Just below this are the power switches to the vacuum system and the main pump. The units just below these switches are the Honeywell SCR

three-mode controller for the final heater and the run switch which starts the timer to measure the length of the data runs. The bank of pushbutton switches to the right of the timer switch control solenoid valves which control the Freon system, the Freon fill system pump, and the power switches to the Fluke meter, the Omega temperature indicator, the power supply to the pressure transducer and the Honeywell controller. Below the switches are the timer, the Fluke meter, the Omega temperature indicator, and the power source for the pressure transducer. The Fluke meter is a multi-function, digital-readout instrument for the measurement of AC or DC volts and ohms of resistance. This meter is used to register the output of the pressure transducer. A second Fluke meter, which is not shown, is used to measure the output of the three platinum resistance thermometers. With the output from the Fluke meter, the different temperatures can be obtained from a prepared calibration chart. The Omega temperature indicator is used to monitor the iron-constantan thermocouple temperatures at different places in the equipment. Monitoring of these temperatures allows an appraisal of the stability of the system and a determination of any unusual conditions. On the bottom of the control panel are a series of switches. They are switches which select between the transducer voltage input or the transducer reading to be input to the first Fluke meter, an unused thermocouple switch, the switch which selects the temperatures to be read on the Omega temp-

erature indicator and the switch which selects the platinum resistance thermometer to be read.

Additional instrumentation not shown on these two figures is a third Heise gauge, used for calibration of the first two, flow meters controlling the flow rate of coolant to the condensers, and a series of valves which control the flow of nitrogen pressure to the bladder accumulator, back pressure regulator and sample system flush line.

Experimental Procedures

What follows is an abbreviated and slightly modified description of the procedures set forth in J.R. McConnell's thesis² and a discussion of the common trouble spots in the calorimeter system.

Daily Startup

The first step is the startup of the vacuum and refrigeration systems. The power switch to the vacuum system is switched on and then the fore pump is turned on and the roughing valve and the valve on the bottom of the calorimeter are opened. To turn on the refrigeration system when started the switch on the top of the main unit is switched on. After these systems are activated the air to the preheater bath is turned on and the bed fluidized. The temperature controller is then set to the desired value and switched on. The temperature is usually set to approximately 50^o-80^oF

higher than the desired inlet temperature for the first enthalpy measurement. The vacuum system is checked again, and if the pressure gauge reads below 25 mm Hg, the roughing valve is closed, the diffusion pump is switched on, and the valve connecting it to the fore pump opened. After two minutes warmup the main diffusion pump valve is opened. The vacuum system is now fully operational. At this time the Fluke meters, temperature indicator and power source are switched on. After 1 to 2 hours, depending on the ambient temperature, the refrigeration system will have lowered the temperature of the coolant inlet below 30°F and the solenoid system A can be energized to open the Freon system. The valve below the Freon return heater is closed and the rheostats controlling the heating tapes on the Freon return heater and line between the calorimeter and main condenser are turned on. The main pump is now turned on. The system pressure is then set with the back pressure regulator and bladder accumulator. The system is allowed to come to steady state under these conditions and then the first experimental point for the day can be taken. Care must be taken to adjust the valve below the Freon return heater so that the level of Freon remains constant and below the line entering from the main condenser. If Freon return heater is overfull the pressure in the inner chamber will increase and cause a pressure instability in the Freon System. If it is too low, sub-cooled Freon is being added to the calorimeter causing

experimental error.

Data Collection

For the first run of each day, the final heater does not need to be used. The inlet temperature is stable enough using only the preheater. When the inlet temperature becomes stable (less than 1^oF change per 3-4 minute period) the first run can be taken.

To take a run the following steps are taken: one operator weighs the empty sample and Freon collection tubes with their appropriate clamps and quick-disconnects. The tubes are then mounted in their holding brackets. The operator then changes the three way valve on the Freon system to the collection position and allows a little Freon to run out to cool the flex tubing and collection bottle. Now the sample and Freon collection tubes are attached to the proper lines and are ready to start the run. During these procedures, the second operator records all information pertinent to the run, such as various thermocouple temperatures, the transducer readings, atmospheric pressure, Freon outlet and sample outlet platinum resistance thermometer temperatures, and the weights of the different collection tubes.

While the first operator pushes the run button to start the timer and records the initial inlet temperature, the second operator simultaneously switches the sample and Freon system three-way valves from the return to the collection position. The calorimeter inlet and outlet pressures and

the Freon leg and calorimeter sight glass levels are recorded. The inlet temperature reading is recorded every thirty seconds during the run. Also the Freon leg and calorimeter levels are checked periodically.

The three-way valves are switched back to the return position and the timer stopped. Care must be taken to insure that all the Freon and samples are out of the connections to the collection tubes. The collection tubes are weighed and the calculations made to determine the inlet and outlet temperature and pressures of the calorimeter and the experimental enthalpy change for that set of conditions. The sample is then drained into the surge tank and the Freon is drained into the calorimeter by opening the manual valve and energizing solenoid valve D.

The final heater is used to increase the inlet temperature and the procedure is repeated at a different temperature. After an increase of approximately 125°F in the inlet temperature, the preheater bath temperature must be increased. Runs can be taken every 20 to 50 minutes depending on the sample and temperature change between runs. One-half hour should be allotted for shutdown of the equipment.

Daily Shutdown

The shutdown procedure is essentially the reverse of the startup procedure. The final heater and preheater are shutoff. The main valve on the diffusion pump is closed and the diffusion pump is shut off and allowed to cool. When

the diffusion pump is cool to the touch, the valve connecting it to the fore pump is closed, and the fore pump and the main power switch turned off. Approximately ten minutes after the preheater and final heater are turned off, the sample pump is switched off and the valve below the Freon return heater is opened fully. Ten to fifteen minutes after the main pump is shut down the solenoid group A is de-energized and the variacs shut off. The refrigeration system is then switched off and the air supply to the preheater closed. Then all instruments are turned off and the system is completely shut down.

Common Troubles

The problems with the calorimeter generally fall into two categories: operational problems and problems caused by coking at high temperatures. The latter is really a sub-category of the former but will be treated separately.

The operational problems that can occur are associated with the sample and Freon systems. No problems with the vacuum or refrigeration systems or the instrumentation has developed thus far.

The three main problems associated with the sample system other than coking are pressure instability, temperature instability and pump malfunction. Often times the cause of one is the other. For example an unstable inlet temperature can be caused by fluctuations in the flow rate or large

pressure surges while the sample is in the two phase region.

Pressure instability usually is an indication that something is wrong with the bladder accumulator. Either the nitrogen is not getting into the bladder to pressurize it or the bladder is ruptured. The first problem can be tested by removing the nitrogen line to the bladder just before it attaches and purging the line. The second problem can be tested for by opening the bladder vent while the pump is running to see if liquid is coming out. In the first case, either the valve on top of the bladder accumulator or the line leading to it should be replaced. In the second case, the accumulator must be removed and the bladder replaced.

Temperature instability is usually caused by cycling of the final heater, pressure fluctuations, or flow rate stability problems. If instability is due to the final heater it can be checked by turning off the final heater. If it is due to pressure fluctuations, the Heise gauge will show it. Temperature instability due to an unsteady flow rate can only be deduced by making several measurements of the flow rate for the same length of time. If these tests show an unsteady flow rate it is probably caused by one of two sources; either a partial plug due to coking or worn check valves on the pump. If it is a plug, the plug must be located and removed and if it is worn check valves, they must be replaced.

The Freon system really has very few problems. The most common problem is forgetting to open the valve below

the Freon return heater which causes the liquid to back up into the main condenser and sometimes even into the line between the calorimeter and main condenser. If this occurs while the pump is running, a pressure buildup in the calorimeter results and the level in the outer chamber rises, while the temperature in the Freon line goes down. This problem can be prevented by conscientious monitoring of the level in Freon return heater. However, if the problem does occur it can be easily remedied by opening the valve. The recovery time to a stable system will be directly proportional to length of time the mistake goes undiscovered. Another problem that might occur would be a low Freon level (below the top of the calorimeter coil), causing the vapor to become superheated and thus resulting in an error in the experimental measurement. This difficulty may be avoided by filling the calorimeter before it reaches the 1" mark on the sight glass. The Freon level should not exceed 6". The only other problem that occurred with the Freon system was a break in the seal between the sample and Freon systems at the calorimeter inlet causing the sample to mix with the Freon. This was corrected by draining the calorimeter and replacing the seal and the Freon.

The major problems with the calorimeter are caused by coking in the sample system lines. The problem manifests itself in several different ways. The flow rate can be unstable, a large pressure drop can occur across the calorimeter, or there can be a decrease in the flow rate at a constant

pump setting. The first two conditions are easily seen on the Heise gauges but the last condition is very difficult to determine and usually occurs because of a plug or partial plug in the preheater coil. If a large pressure drop is noted across the calorimeter coil it usually means the inline filter before the calorimeter is plugged with coke or the tubing around the final heater is plugged with coke or both. This situation is remedied by replacing the inline filter element or fittings and tubing around the final heater.

A plug or partial plug in the preheater coil is much harder to detect because no pressure measurement devices are used between the outlet of the pump and inlet of the calorimeter. As already stated this problem usually manifests itself by a decrease in the flow rate at a constant pump setting. However, the decrease is usually so slow and over such a long period of time that it goes unnoticed. This problem has occurred twice since the start of enthalpy measurements on coal liquids. Its most severe consequence is excessive wear on the pump but it can cause flow rate problems. The problem is remedied by removing the fluidization sand from the preheater and replacing the coil. This is a simple but time-consuming procedure. Aside from these few problems, the calorimeter usually runs fairly maintenance-free.

PREVIOUS RESULTS

The calorimeter was evaluated with two different test fluids. The first fluid used was water. Water was selected because of the availability of accurate enthalpy data (5). The water data consisted of thirty-three experimental measurements in the compressed liquid region, with pressures ranging from 179 to 1529 psia and temperatures from 196 to 551°F. For the water data, enthalpy values varied from 130 to 510 BTU/lbm. These operating conditions cover the range of most of the enthalpy measurements that have been taken so far on coal liquids and of any anticipated future measurements. The water results show a $\pm 0.5\%$ accuracy for the calorimeter. This accuracy is comparable or better than that of other workers in the field, notably Lenoir and Hipkin (6) who estimated their error as ± 2 BTU/lbm. Because of the high heat of vaporization of water no data could be taken in the two phase or vapor regions. Further information is given by H. Omid (7).

N-heptane was selected as the second test fluid to determine if any operational difficulties would be encountered with a two-phase or vapor state at the inlet of the calorimeter. The results show excellent agreement with literature values. Further details are given by R. Sharma (4).

Once the calorimeter had been checked for accuracy, enthalpy data on coal liquids could be taken. Enthalpy

measurements were made on four coal liquids before the Synthoil distillate. Two whole oils, one from a Utah coal and the other from a western Kentucky coal, both produced by the COED process, were charged to the system and data was taken from 100° to 750°F and from 50 to 1500 psia. After these two atmospheric distillates were prepared from the whole oils with end points of approximately 520°F and enthalpy data was taken over the same temperature and pressure range as for the whole oil. After each coal derived liquid sample, n-heptane was measured to check the reproducibility and accuracy of the calorimeter. Also at about six month intervals the platinum resistance thermometers are calibrated separately using a Leads and Northrup 8167-25-B series glass calibrated platinum resistance thermometer. The Heise gauges are also checked for accuracy using the third Heise gauge as previously mentioned.

RESULTS

Enthalpy Measurements

Following an n-heptane run, the system was purged with nitrogen to ready it for the Synthoil sample. The Synthoil was obtained from Dr. Paul M. Yavorsky at the Pittsburgh Energy Research Center. The sample analysis received with the sample is shown in Table 1. The Synthoil sample was a tar-like substance which was so viscous at room temperature that no attempt was made to take enthalpy data on the whole oil. Instead an atmospheric distillate was prepared in a laboratory batch distillation apparatus. One liter of the sample was charged to the distillation system and heated until the cut point temperature (520°F) was reached by the vapor which was condensed by air-cooling. The condensate was passed to a receiving flask. The cut point of the Synthoil sample was approximately 610°F at 760 mm Hg. An overall material balance for the batch distillation is presented in Table 2. The losses associated with the distillation were negligible (<0.36 wt %). The atmospheric cut was a light, transparent golden-brown liquid which darkened with the passage of time, probably due to oxidation of the nitrogen compounds. The residue from the distillation was a black viscous substance that was solid at room temperature.

The Synthoil distillate was characterized by a D-86 ASTM distillation and an API gravity measurement. These results are presented in Table 3. It is interesting to note

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:

	<u>Kentucky Coal</u>
<u>Proximate Analysis, wt pct</u>	
Moisture	6.1
Ash	15.5
Volatile matter	36.3
Fixed carbon	42.1
<u>Ultimate Analysis, wt pct</u>	
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

(Continued)

TABLE 1
(Continued)

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 ½ ton/day unit with a 28-ft-long fixed-fed reactor.

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

S in product, wt pct	0.4
Ash in product, wt pct7
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)	

TABLE 2Overall Material Balance (Synthoil)

Total "Crude" charged	= 15,865.17 gm
Products:	
Atmospheric Distillation (620 mm Hg) (cut point 610 ^o F @ 760 mm Hg)	= 4,034.91 gm
Residue (610 ^o 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., °F @ 0.81 ATM. *	Temp., °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 °API of Synthoil Distillate = 13.2° API.

the extremely low API gravity.

The Synthoil distillate was charged to the calorimeter system and data were taken over a temperature range of 155^o to 742^oF and at 150, 200, 500, 1,000, and 1,500 psia. The data are presented in Table 4 and Figures 5 and 6. The outlet conditions of the calorimeter were corrected to a reference state of 65^oF and 1 atm. The outlet temperatures were corrected using a heat capacity of 0.492 BTU/lb_m^oF, as found from the enthalpy versus temperature plot; however, the correction never amounted to more than 0.35 BTU/lb_m. The outlet pressure was corrected to 1 atm. using the Kesler and Lee correlation (3,8). The pressure corrections are shown in the data table. The calculation of the experimental enthalpies, the Watson K factor, the pseudocritical temperature and pressure, the acentric factor, and the pressure corrections are exactly the same in method as those presented by Raj Sharma (4).

Figures 5 and 6 show the effect of pressure on enthalpy. The low pressure (150 and 200 psia), high temperature data (greater than 600^oF) show the transition from the liquid to the two phase region.

Experiment enthalpy measurements that were made on a SRC-I Naphtha are presented in Table 1 and Figure 1 in Appendix 1. The naphtha was obtained from J.P. Naylor of the Pittsburgh and Midway Coal Mining Company. The naphtha, produced at the SRC-I pilot plant in Dupont, Washington, was a light, amber-colored liquid and was charged to the calorimeter

TABLE 4

Synthoil Distillate

Enthalpy Data 1

150 psia Run No.	Temperature Inlet °F	Pressure, psia Inlet Outlet	ΔH , exp., BTU/lb _m	Pressure Correction BTU/lb _m	ΔH Corrected BTU/lb _m
32(1)	471.6	150 18	222.9	0.32	223.2
33(1)	513.4	152 18	250.2	0.32	250.5
54(1)	526.1	148 18	260.0	0.32	260.3
34(1)	535.8	148 18	263.0	0.32	263.3
35(1)	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

1 The reference temperature and pressure are 1 atm and 65°F.

(1) Liquid Phase

(*) Two phase region (liquid and vapor)

TABLE 4
Synthoill Distillate
Enthalpy Data

200 psia Run No.	Temperature °F Inlet	Pressure, psia Inlet	Pressure, psia Outlet	ΔH , exp., BTU/lb _m	Pressure Correction BTU/lb _m	ΔH Corrected BTU/lb _m
16(1)	155.5	203	23	44.4	.43	44.8
15(1)	185.6	202	24	58.7	.43	59.1
13(1)	189.4	199	22	60.6	.43	61.0
14(1)	219.4	201	24	75.9	.43	76.3
12(1)	237.8	202	23	86.3	.43	86.7
11(1)	276.7	201	23	107.7	.43	108.1
1(1)	321.6	200	24	132.9	.43	133.3
10(1)	323.4	196	23	134.5	.43	134.9
9(1)	324.8	199	24	134.7	.43	135.1
3(1)	358.5	199	23	154.0	.43	154.4
2(1)	359.7	200	24	153.9	.43	154.3
4(1)	405.7	188	24	182.4	.43	182.8
5(1)	439.7	200	24	203.2	.43	203.6
6(1)	485.8	200	24	232.1	.43	232.5
7(1)	523.7	200	24	256.0	.43	256.4
8(1)	565.9	199	24	283.5	.43	283.9
41(1)	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

Synthoail Distillate

Enthalpy Data

500 psia Run No.	Temperature Inlet °F	Pressure, psia Inlet Outlet	ΔH , exp., BTU/lb _m	Pressure Correction BTU/lb _m	ΔH Corrected BTU/lb _m
17(1)	358.3	498 331	154.0	1.13	155.1
18(1)	415.9	499 331	188.2	1.13	189.3
19(1)	469.5	500 330	220.7	1.13	221.8
21(1)	493.0	501 350	236.7	1.13	237.8
20(1)	495.5	498 334	239.0	1.13	240.1
24(1)	524.3	501 352	256.4	1.13	257.5
25(1)	550.0	498 352	272.5	1.13	273.6
26(1)	575.2	500 350	288.7	1.13	289.8
27(1)	602.2	500 350	306.6	1.13	307.7
45(1)	612.8	500 363	315.2	1.13	316.3
23(1)	619.9	497 352	318.5	1.13	319.6
46(1)	658.7	501 370	347.7	1.13	348.8
47(1)	700.7	500 371	375.6	1.13	376.7
48(1)	729.4	495 372	397.6	1.13	398.7

TABLE 4

Synthoil Distillate

Enthalpy Data

1000 psia Run No.	Temperature Inlet °F	Pressure, psia Inlet Outlet	ΔH , exp., BTU/lb _m	Pressure Correction BTU/lb _m	ΔH Corrected BTU/lb _m
28(1)	510.5	1000 862	248.9	2.28	251.2
29(1)	558.2	1000 860	277.6	2.28	279.9
30(1)	602.1	1000 857	307.6	2.28	309.9
49(1)	627.6	1000 878	326.9	2.28	329.2
50(1)	634.1	1009 877	329.4	2.28	331.7
31(1)	636.7	1002 856	329.5	2.28	331.8
51(1)	683.3	1006 878	364.1	2.28	366.4

TABLE 4

Synthoii 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 (1)	512.5	1503 1328	247.1	3.43	250.5
57 (1)	567.8	1496 1327	283.0	3.43	286.4
58 (1)	619.0	1502 1344	316.8	3.43	320.2
59 (1)	673.2	1495 1346	356.3	3.43	359.7
60 (1)	732.5	1500 1357	396.0	3.43	399.4

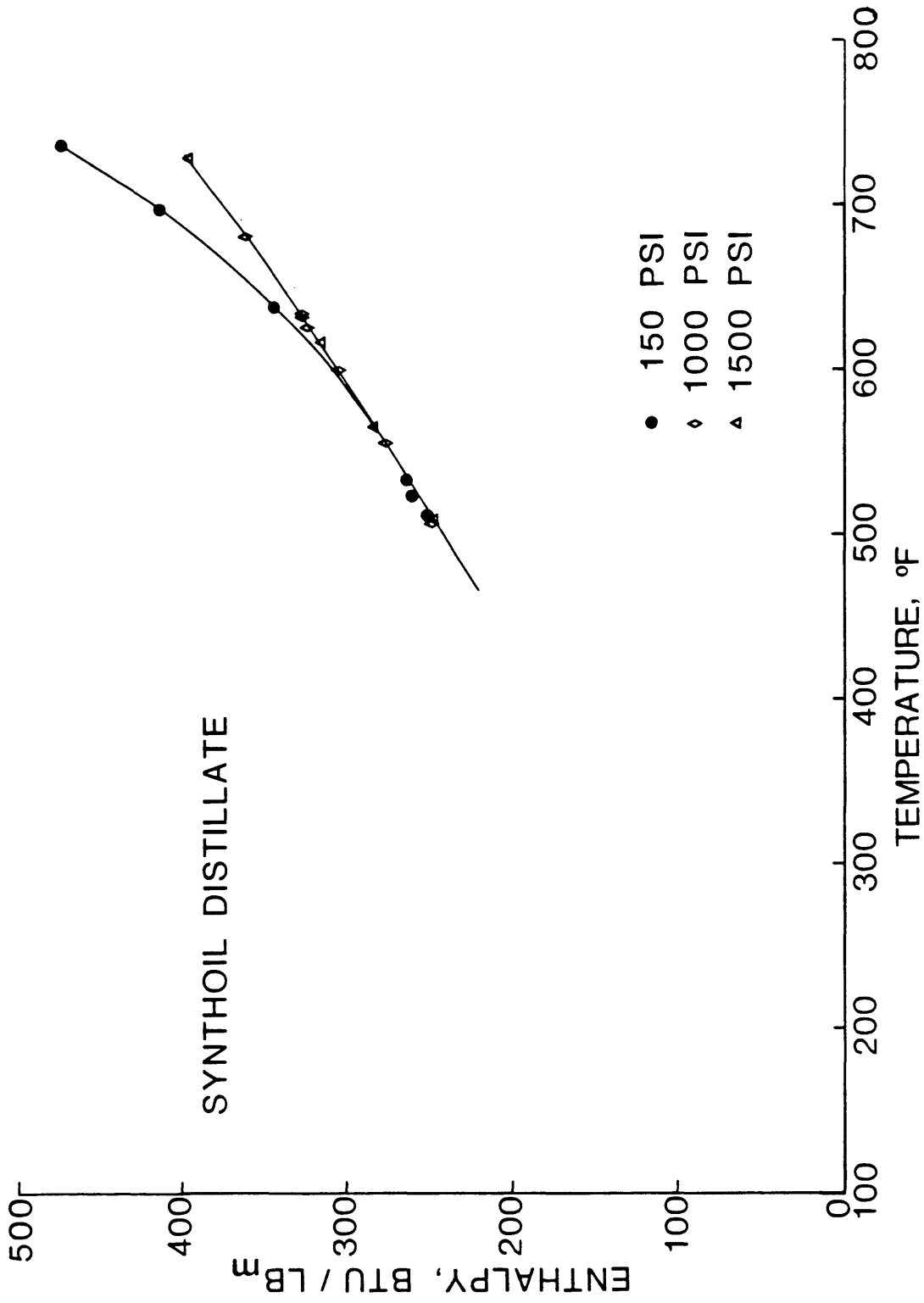


FIGURE 5

Enthalpy Difference Versus Temperature for the Synthoil
Distillate (150, 1000, 1500 psia Isobars)

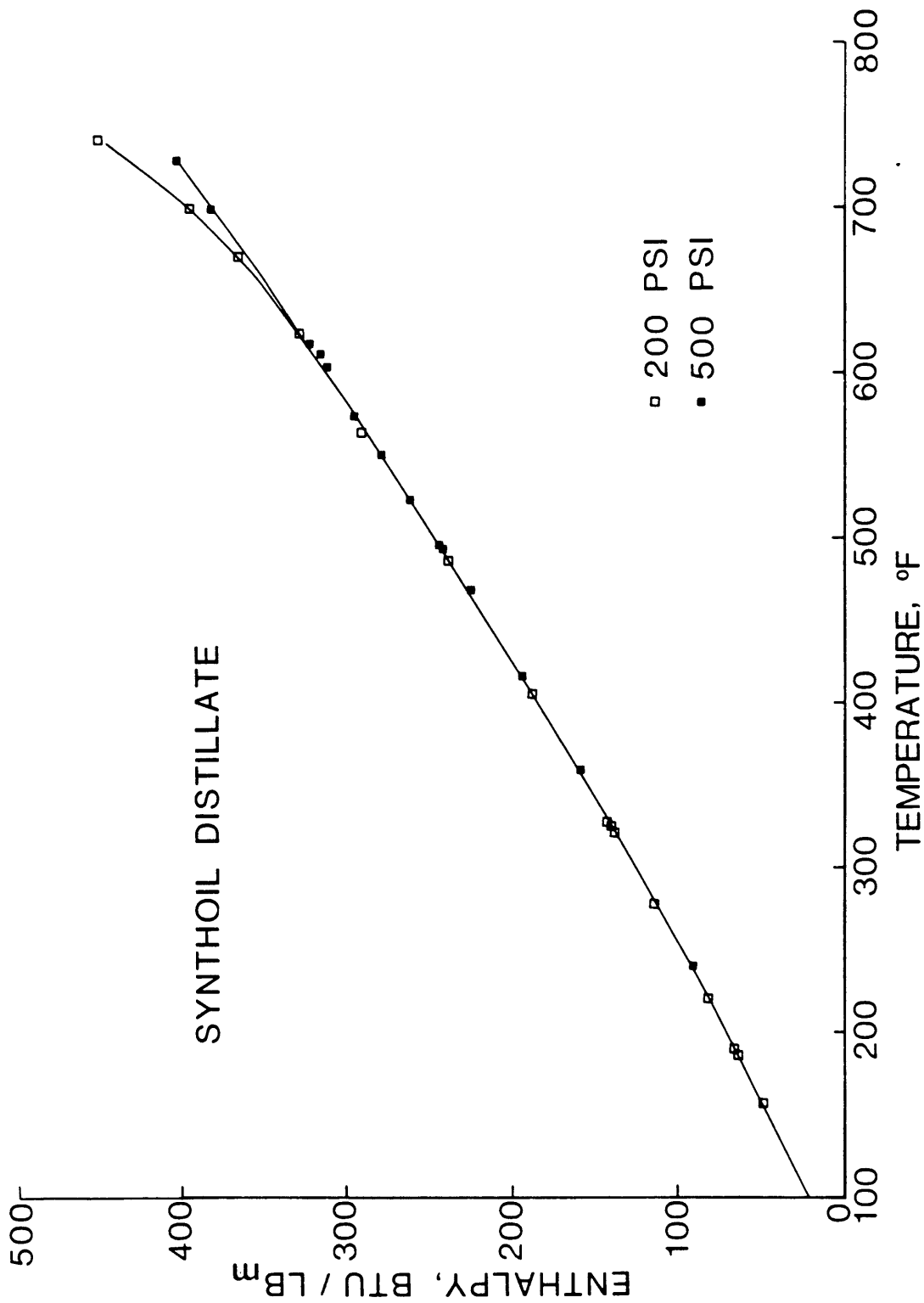


FIGURE 6

Enthalpy Difference Versus Temperature for the Synthoil Distillate (200, 500 psia Isobars)

as received. A specific gravity measurement and results of a D-86 ASTM distillation are also presented in Appendix I. These were furnished by Pittsburgh and Midway Coal Mining Company. Enthalpy data were taken at 30, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 900, 1000 and 1500 psia over a temperature range of 160 to 720°F. Figure 1 only presents part of the data but the phase envelope is fairly well defined.

Comparison of Petroleum Enthalpy Correlation Predictions with Synthoil Experimental Measurements

One of the major objectives of the program of which this research is part is to establish a means of correlating the enthalpy data in a manner in which it would become useful in design calculations. As a starting point it was decided to apply some of the enthalpy correlations developed for petroleum liquids. If they were able to predict the data then one of the objectives would be met. However, all the comparisons made with the Western Kentucky Syncrude (7) and the Utah Syncrude (4) show significant error.

The petroleum correlations chosen for comparison were the Johnson-Grayson correlation (9) as presented in the API data book, the Kesler-Lee graphical correlation (3), and the Lee-Kesler correlation in the form of analytical equations suitable for computer usage (8). As discussed by Mr. Sharma (4) all these correlations basically involve "empirical

equations at the reference state pressure for estimating the liquid and vapor phase heat capacities as well as the heat of vaporization as functions of temperature". The enthalpy change is then obtained by integration of the liquid heat capacity equation between the reference temperature and the bubble point of the mixture. Then the heat of vaporization is added, and the vapor phase heat capacity equation is integrated between the dew point and actual temperature desired. Finally a pressure correction term for deviation from the reference pressure is added.

A comparison of the three correlations mentioned above is shown in Table 5 for several different temperatures and pressures. The average error (error = $\Delta H_{\text{corr}} - \Delta H_{\text{exp}}$) for the Johnson-Grayson method is -36.44 BTU/lb_m or -14.54% (% error = $\frac{\Delta H_{\text{corr}} - \Delta H_{\text{exp}}}{\Delta H_{\text{exp}}}$). The average percent error for the Kesler-Lee graphical method is -14.50% or -35.72 BTU/lb_m. The average error for the Lee-Kesler computer method is -40.59 BTU/lb_m or -16.10%. As can be seen, the Kesler-Lee graphical method gives the best fit or least amount of error. It is interesting to note that as in all the cases this far the enthalpy values predicted by the petroleum correlations are biased low relative to the experimental values. The error in the Synthoil values is the largest to date of any of the comparisons made. As before the sample calculations for the correlation enthalpy values are the same in method as those found in Appendix IV of Sharma (4).

TABLE 5

Comparison of Experimental and Predicted
Enthalpies for a Synthoil Distillate
(Assumed Liquid Phase)

Temperature <u>Inlet</u>	°F	<u>ΔH exp.,</u> BTU/lb _m	<u>ΔH J-G</u> BTU/lb _m	<u>ΔH K-L</u> BTU/lb _m	<u>ΔH L-K</u> BTU/lb _m
<u>150 psia</u>					
	471.6	222.9	191.5	190.5	186.4
	526.1	260.0	218.5	221.5	216.5
	588.9	298.9	258.5	257.5	252.5
<u>200 psia</u>					
	155.5	44.4	35.0	34.5	34.8
	276.7	107.7	90.5	87.5	87.9
	358.5	154.0	130.5	129.5	127.5
	439.7	203.2	172.5	172.5	169.3
	523.7	256.0	219.5	220.5	215.2
<u>500 psia</u>					
	415.9	188.2	159.5	158.5	157.3
	524.3	256.4	218.5	219.5	215.9
	602.2	306.6	266.5	267.5	260.6
	658.7	347.7	301.5	302.5	294.3
	729.4	397.6	347.5	349.5	338.0
<u>1000 psia</u>					
	510.5	248.9	211.2	212.2	208.8
	627.6	326.9	281.0	283.0	275.9
	683.3	364.1	316.1	317.1	309.3
<u>1500 psia</u>					
	512.5	247.1	213.7	215.7	210.6
	619.0	316.8	278.1	278.1	271.3
	732.5	396.0	341.0	347.0	339.8

Tc = pseudocritical temperature = 1370°R

Pc = pseudocritical pressure = 416.5 psia

W = acentric factor = 0.4665

M.W. = molecular weight = 186.1

Discussion

All the comparisons made thus far between the experimental enthalpies and those predicted by the petroleum correlations are in disagreement. This error is probably due to the large amount of aromatic compounds present in coal liquids. Table 6 presents a summary of the average error $^{\circ}\text{API}$, and Watson K factor for the coal liquids that have been compared so far and also a series of petroleum liquids whose data is presented by H. Omid (7). From the table it is evident that as expected the petroleum liquids show a much better match between experimental and predicted values. The experimental values of the petroleum liquid were smoothed values from the data of Lenoir and Hipkin (10). Also noticeable is that the coal liquids have much lower K factors than the petroleum liquids. The Watson K factor is a measure of the paraffinicity of a sample; the higher the K factor the more paraffinic a sample is. As is indicated by the low Watson K factors of the coal liquids they are much less paraffinic than the petroleum liquids.

In an attempt to quantify this trend, the results from the analyses of these coal liquids and some petroleum liquids, obtained from the Bartlesville Energy Research Center, will be presented.

The method they used at BERC was basically the one developed by the USBM and API for separating and characterizing high-boiling petroleum distillates (11). The method involves first distillation of the sample to get reproducible cuts.

TABLE 6

Comparison of Kesler-Lee Graphical Correlation
for Enthalpy for Different Hydrocarbons

<u>Coal-Derived Liquids</u>	<u>Average Error (BTU/lb_m)</u>	<u>API^o</u>	<u>K_{UOP}</u>
Western Kentucky Syncrude	-2.8	21.8	10.9
Western Kentucky Syncrude Distillate	-6.3	28.5	10.7
Utah Syncrude Distillate	-13.5	29.4	10.8
Synthoil Distillate	-35.7	13.2	10.0
 <u>Petroleum Liquids</u>			
Alaskan Naphtha	+2.8	50.5	11.6
Kerosene	+1.7	43.5	11.8
#2 Fuel Oil	-0.5	33.0	11.7
Gas Oil	-1.5	35.3	11.8

The cut points are generally about 200°C, 370°C, 535°C, 675°C and finally a residue of greater than 675°C. After distillation the different cuts are separated into seven different fractions. These are the acid, base, neutral nitrogen, saturate, monoaromatics, diaromatics, and polyaromatic-polar fractions. The acid fraction is removed by anion exchange resin or a NaOH wash. The base fraction is then taken by cation exchange or acid wash. The neutral nitrogen fraction is then separated by complex formation with iron (III) trichloride supported on a clay. The other four fractions are then obtained by absorption chromatography on silica-alumina gel. Each fraction is then treated with some type of chromatography such as gel permeation or high pressure liquid chromatography to further separate the fractions into sub-fractions. Each subfraction is then further analyzed by more sophisticated analytical tools such as infrared and ultraviolet spectroscopy, excitation and emission fluorescence spectrometry, nuclear magnetic resonance spectroscopy, high resolution or low resolution-high-ionizing voltage mass spectrometry, or gas or liquid chromatography to arrive at a semiquantitative analysis of the liquids.

Here, these analyses can quantify the reason for the error in the predicted and experimental enthalpy values. Table 7 presents the general analytical results of the Western Kentucky and Utah Syncrudes, the Synthoil and a heavy petroleum crude from the Bartlett oil field in LaBette County,

Kansas. The analysis of the Bartlett crude can be considered typical for a petroleum crude.

Several interesting facts are worthy of note in Table 7. First as the Watson characterization factors indicate, the Synthoil is the least paraffinic and the most aromatic throughout the boiling range of the sample. Also the Western Kentucky and Utah Syncrudes are very similar in their composition. In all cases, the coal liquids are between 1.5 and 2.5 times more aromatic (total aromatics) than the heavy petroleum crude. These results then seem to confirm the hypothesis that the more aromatic the coal liquid is, the greater the error between the experimental and predicted enthalpy values. It would indicate that perhaps a parameter that better accommodates the aromaticity of the coal liquids than the Watson K factor is needed to effectively correlate the enthalpy data. As yet, not enough enthalpy data and analyses of coal liquid exists to create this aromaticity factor. Perhaps by the culmination of the research program and after the measurement of many more liquids, it will be possible to achieve this correlation.

TABLE 7

Comparison of Analysis Results for Similar Boiling Ranges
From Three Syncrudes and One Petroleum Crude 12, 13, 14

	Synthoil <207°C	Western Kentucky <205°C	Utah <204°C	Synthoil 207° to 363°C	Western Kentucky 205° to 380°C	Utah 204° to 381°C	Bartlett 225° to 360°C
Acids	35.3 (Phenols)	3.84	-	-	-	-	0.82
Bases	0.7	1.01	-	-	-	-	0.21
Saturates	27.1	68.3	62.2	16.0	25.0	27.8	62.9
Olefins	3.2	2.3	10.0	-	-	-	-
Monoaromatics	27.6	-	-	27.3	42.0	25.1	18.2
Diaromatics	3.2	-	-	21.6	13.0	17.5	6.5
Polyaromatics	-	-	-	7.9	5.4	7.1	5.7
Heteroatomics (Aromatic)	-	-	-	22.2	4.4	15.2	-
Total Aromatics (66.1)	30.8	22.6	21.0	79.0	64.8	64.5	30.4
Distillate Weight-Percent of Sample	4.4	21.0	13.0	42.6	54.2	45.4	17.6

TABLE 7 (Cont.)

	<u>Synthoill 363° to 531° C</u>	<u>Western* Kentucky >380° C</u>	<u>Utah* >381° C</u>	<u>Bartlett 360° to 540° C</u>
Acids	-	-	-	0.13
Bases	-	-	-	0.23
Saturates	9.7	23.8	25.8	53.7
Olefin	-	-	-	-
Monoaromatics	4.7	25.1	14.4	18.2
Diaromatics	22.6	24.3	18.4	9.2
Polyaromatics	41.1	20.0	25.1	16.7
Heteroatomics (Aromatic)	15.6	4.5	7.4	-
Total Aromatics	84.0	73.9	65.3	44.1
Distillate Weight- Percent of Sample	27.3	24.2	40.3	28.9

* Neither the Western Kentucky or Utah syncrudes contain appreciable material boiling above 530°C.

CONCLUSIONS

Although the whole Synthoil sample was too viscous for use in the calorimeter, an atmospheric distillate was prepared by batch distillation with an endpoint of about 610^oF at 760 mm Hg. Enthalpy data were taken over a temperature range of 155^o to 742^oF at isobars of 150, 200, 500, 1000 and 1500 psia. The data showed that the distillate was partially vaporized at temperatures greater than 600^oF and pressures of 150 and 200 psia.

Comparison of the experimental enthalpies to those predicted by the graphical methods of Johnson-Grayson and Kesler-Lee and the computer method of Lee-Kesler showed serious error. The error was shown to correlate well with amount of aromatics in the sample. The highly aromatic Synthoil distillate showed the largest average error of any of the coal liquids compared. In the future quantification of this trend into the Watson K factor or incorporation into some other parameter to correctly correlate the enthalpy of coal liquids will prove to be quite useful. However, a good deal more data is required before this can be accomplished.

RECOMMENDATIONS

Equipment

1. A checklist of replacement items should be maintained so that valuable time is not lost while waiting for replacement parts. Suitable time should be allotted for ordering so that the replacement parts arrive in time.

2. To obtain a better idea of the condition of the pre-heater coil, a pressure gauge or transducer should be mounted at the outlet of the pump. This will allow a determination of the pressure drop between the outlet of the pump and the inlet of the calorimeter. Excessively high outlet pressures cause a good deal more wear on the pump. When the pressure drop is too high the coil should be replaced.

3. If problems are encountered with long term storage stability of the samples perhaps a more inert container than metal should be used.

Correlations

1. Further investigation of aromaticity of a sample versus its error in predicted enthalpies might lead to a corrective parameter for the petroleum correlations to accurately predict the coal liquid enthalpies.

2. An investigation of a pseudocompound type approach might lead to more accurate enthalpy predictions. This would

involve further analytical characterization of each boiling fraction of the sample into probable compounds or compound types. Then, model compounds or groups of compounds with well-known thermodynamic properties are selected to represent the fraction. Enthalpy values are calculated by assuming a mixing rule for the fractions and set the conditions at which the enthalpy is to be calculated. Although this method is considerably more work, it would probably be more accurate.

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APPENDIX I

Characterization of the SRC-I Naphtha

ASTM Distillation

Percent Recovered (by Volume)	Temperature, °F @ 1.0 atm.
IBP	138
5	167
10	180
20	194
30	205
40	216
50	229
60	246
70	266
80	287
90	325
95	350
EP	373

(2.0 cm³ were left in the bottom of the flask). Specific Gravity 60/60 °F = 0.781.

TABLE 1

SRC-I Naphtha

Enthalpy Data 1

30 Psia Run No.	Temperature °F	Pressure psia		ΔH , exp Btu/lb _m	Pressure Correction Btu/lb _m	ΔH Cor- rected Btu/lb _m
	Inlet	Inlet	Outlet			
54(*)	254.3	30	13	109.3	+0.00	109.3
56(*)	258.0	30	13	112.4	+0.00	112.4
55(*)	268.5	30	13	137.1	+0.00	137.1
57(*)	291.2	30	21	204.5	+0.02	204.5
121(*)	321.1	31	13	257.4	+0.00	257.4
58(v)	337.2	30	13	274.6	+0.00	274.6
59(v)	362.6	30	12	288.5	+0.00	288.5
164(v)	378.9	30	13	294.6	+0.00	294.6
165(v)	420.4	30	13	316.9	+0.00	316.9

1 The reference temperature and pressure are 1 atm. and 65°F.

(l) = liquid phase

(*) = two phase region

(v) = vapor phase

TABLE 1

SRC-I Naphtha
Enthalpy Data

50 Psia Run No.	Temperature °F Inlet	Pressure psia		ΔH , exp Btu/lb _m	Pressure Correction Btu/lb _m	ΔH Cor- rected BTU/lb _m
		Inlet	Outlet			
15(l)	159.0	51	19	47.2	+0.02	47.2
14(l)	184.9	51	19	60.1	+0.02	60.1
10(l)	249.9	51	35	96.9	+0.05	97.0
31(l)	256.5	53	12	100.5	+0.00	100.5
11(*)	284.2	51	34	120.5	+0.05	120.6
24(*)	312.0	51	13	167.0	+0.00	167.0
26(*)	314.9	51	13	178.7	+0.00	178.7
1(*)	320.1	51	36	194.5	+0.05	194.6
27(*)	324.1	51	13	199.0	+0.00	199.0
25(*)	332.3	51	13	217.1	+0.00	217.1
2(*)	346.6	51	36	250.9	+0.05	251.0
28(*)	349.7	51	13	257.0	+0.00	257.0
9(*)	357.8	51	33	274.0	+0.05	274.1
8(v)	369.2	51	34	286.7	+0.05	286.8
3(v)	381.0	51	35	292.9	+0.05	293.0
29(v)	382.5	51	13	293.3	+0.00	293.3
30(v)	398.9	51	13	301.4	+0.00	301.4
4(v)	401.6	51	36	303.1	+0.05	303.2
22(v)	412.2	54	12	310.7	+0.00	310.7
5(v)	431.7	51	34	319.8	+0.05	319.9
6(v)	460.0	51	35	336.3	+0.05	336.4
7(v)	490.5	51	34	354.3	+0.05	354.4
166(v)	514.0	50	13	368.7	+0.00	368.7
167(v)	571.1	50	13	400.7	+0.00	400.7

TABLE 1

SRC-I Naphtha
Enthalpy Data

100 psia Run No.	Temperature °F Inlet	Pressure, psia		ΔH , exp Btu/lb _m	Pressure Correction Btu/lb _m	ΔH cor- rected Btu/lb _i
		Inlet	Outlet			
45(l)	218.4	100	84	75.0	+0.16	75.2
46(l)	266.5	100	84	106.1	+0.16	106.3
147(l)	309.1	100	84	130.7	+0.16	130.9
79(l)	310.8	100	80	133.2	+0.16	133.5
47(l)	318.5	99	81	137.5	+0.16	137.7
80(*)	355.1	100	80	173.3	+0.16	173.5
48(*)	363.8	99	80	180.8	+0.16	181.0
49(*)	389.6	100	80	241.1	+0.16	241.3
81(*)	397.3	103	81	265.9	+0.16	266.1
50(*)	418.4	100	80	299.6	+0.16	299.8
51(v)	429.7	100	80	313.2	+0.16	313.4
52(v)	429.0	100	80	311.4	+0.16	311.6
53(v)	464.4	99	80	332.9	+0.16	331.1
44(v)	497.1	100	78	352.8	+0.16	353.0
43(v)	526.5	100	78	372.4	+0.16	372.6

TABLE 1SRC-I Naphtha
Enthalpy Data

150 psia	Temperature °F	Pressure psia		ΔH, exp	Pressure Correction	ΔH Cor- rected
Run No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
33(1)	350.4	150	111	156.5	+0.23	156.7
34(1)	380.3	150	111	175.3	+0.23	175.5
39(*)	402.6	150	131	197.0	+0.27	197.3
36(*)	403.0	150	119	198.0	+0.25	198.3
35(*)	409.3	149	117	212.1	+0.25	212.4
38(*)	426.3	150	125	248.7	+0.26	249.0
37(*)	441.9	150	125	290.8	+0.26	291.0
40(*)	459.7	151	131	318.7	+0.27	319.0
41(V)	503.1	151	131	352.7	+0.27	253.0
42(V)	525.1	150	130	367.2	+0.27	367.5

TABLE 1SRC-I Naphtha
Enthalpy Data

200 psia	Temperature °F	Pressure, psia		ΔH, exp	Pressure Correction	ΔH Cor- rected
Run No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
60(1)	235.3	199	170	87.7	+0.38	88.1
61(1)	327.0	200	174	141.5	+0.38	141.9
62(1)	401.4	200	173	189.6	+0.38	190.0
63(1)	431.8	200	174	212.8	+0.38	213.2
64(*)	455.3	201	176	258.3	+0.38	258.7
65(*)	484.7	200	176	324.4	+0.38	324.8
66(*)	504.2	199	176	347.2	+0.38	347.6
67(v)	522.4	200	177	360.8	+0.38	361.2
68(v)	559.4	200	177	384.2	+0.38	384.6

TABLE 1SRC-I Naphtha
Enthalpy Data

250 psia	Temperature °F	Pressure, psia		ΔH, exp	Pressure Correction	ΔH Cor- rected
Run No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
71(1)	408.3	250	226	194.6	+0.50	195.1
72(1)	450.4	249	226	223.9	+0.50	224.4
73(*)	475.7	251	227	267.9	+0.50	268.4
74(*)	497.7	250	227	320.0	+0.50	320.6
70(v)	524.4	250	233	356.0	+0.51	356.5
69(v)	559.8	250	232	381.3	+0.51	381.8

TABLE 1SRC-I Naphtha
Enthalpy Data

300 psia Run No.	Temperature	Pressure, psia		ΔH , exp	Pressure	ΔH Cor-
	$^{\circ}F$ Inlet	Inlet	Outlet	Btu/lb _m	Correction Btu/lb _m	rected Btu/lb _m
77(l)	259.0	300	237	101.5	+0.57	102.1
82(l)	307.0	299	272	130.0	+0.60	130.6
78(l)	318.0	300	262	137.2	+0.57	137.8
83(l)	385.1	300	276	179.9	+0.61	180.5
84(l)	415.6	300	275	201.0	+0.61	201.6
91(l)	464.4	300	282	233.9	+0.62	234.5
85(l)	466.4	299	284	235.7	+0.63	236.3
86(*)	485.7	299	290	259.4	+0.65	260.0
87(*)	490.0	300	290	269.8	+0.65	270.4
146(*)	505.6	300	286	298.8	+0.64	299.4
92(*)	512.1	300	282	308.6	+0.62	309.2
75(*)	525.2	300	281	338.9	+0.62	339.5
93(*)	526.3	300	273	341.2	+0.62	341.8
86(v)	530.3	300	284	351.0	+0.63	351.6
76(v)	538.7	300	281	359.2	+0.62	359.8
145(v)	551.6	300	286	369.4	+0.64	370.0
94(v)	575.6	300	278	392.5	+0.62	393.1

TABLE 1SRC-I Naphtha
Enthalpy Data

400 psia Run. No.	Temperature	Pressure, psia		ΔH , exp	Pressure	ΔH Cor-
	$^{\circ}F$ Inlet	Inlet	Outlet	Btu/lb _m	Correction Btu/lb _m	rected Btu/lb _m
106(l)	324.8	401	370	140.0	+0.80	140.8
96(l)	346.1	399	379	152.2	+0.85	153.1
97(l)	387.8	399	379	180.4	+0.85	181.3
98(l)	433.0	399	380	211.2	+0.85	212.1
101(l)	478.9	400	378	244.8	+0.85	245.7
102(l)	503.5	400	378	262.4	+0.85	263.3
99(l)	524.3	400	372	279.8	+0.85	280.6
105(*)	531.7	400	363	299.3	+0.76	300.0
104(*)	540.8	400	369	328.1	+0.80	328.9
103(*)	561.1	400	371	357.9	+0.80	358.7
100(v)	584.3	400	365	390.8	+0.77	391.6

TABLE 1SRC-I Naphtha
Enthalpy Data

500 psia	Temperature OF	Pressure, psia		ΔH , exp	Pressure Correction	ΔH Cor- rected
Run No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
107(1)	415.2	500	420	198.7	+0.94	199.7
108(1)	475.3	500	454	239.3	+1.02	240.3
109(1)	519.3	501	456	272.0	+1.02	273.0
114(1)	525.8	499	476	283.3	+1.04	284.3
116(*)	558.6	500	484	314.3	+1.08	315.4
117(*)	563.9	500	486	323.3	+1.10	324.4
118(*)	569.6	500	488	334.2	+1.10	335.3
119(*)	579.4	500	488	356.3	+1.10	357.4
120(*)	583.1	498	486	365.3	+1.10	366.4
121(v)	596.6	499	485	380.9	+1.09	382.0
124(v)	611.2	500	490	395.0	+1.10	396.1
123(v)	632.7	500	489	414.3	+1.10	415.4
122(v)	650.6	498	486	428.1	+1.10	429.2

TABLE 1SRC-I Naphtha
Enthalpy Data

600 psia	Temperature OF	Pressure, psia		ΔH , exp	Pressure Correction	ΔH Cor- rected
Run No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
159(*)	568.7	600	578	313.3	+1.30	314.6
156(*)	582.4	596	586	330.5	+1.33	331.8
160(*)	589.5	600	583	334.6	+1.31	335.9
161(*)	602.2	600	584	352.5	+1.32	353.8
158(*)	609.9	600	587	366.2	+1.33	367.5
162(*)	621.9	600	584	381.3	+1.32	382.6
157(*)	624.2	600	585	386.4	+1.32	387.7

TABLE 1SRC-I Naphtha
Enthalpy Data

700 psia	Temperature OF	Pressure, psia		ΔH , exp	Pressure Correction	ΔH Cor- rected
Run. No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
125(1)	494.5	700	684	255.0	+1.54	256.5
126(1)	530.4	700	685	282.2	+1.54	283.7
127(*)	562.1	700	686	306.5	+1.55	308.1
128(*)	586.1	700	686	328.8	+1.55	330.4
129(*)	604.3	700	687	347.6	+1.55	349.2
131(*)	635.5	700	688	385.6	+1.55	387.2
132(*)	667.9	700	688	423.0	+1.55	424.6

TABLE 1SRC-I Naphtha
Enthalpy Data

900 psia		Temperature OF	Pressure, psia		ΔH , exp	Pressure Correction	ΔH Cor- rected
Run	No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
133	(1)	501.5	901	889	259.9	+2.02	261.9
134	(1)	533.8	901	890	283.4	+2.02	285.4
136	(1)	599.2	900	888	338.2	+2.02	340.2

TABLE 1SRC-I Naphtha
Enthalpy Data

1000 psia		Temperature OF	Pressure, psia		ΔH , exp	Pressure Correction	ΔH Cor- rected
Run	No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
178	(1)	463.7	1002	990	231.0	+2.25	233.3
179	(1)	528.9	1002	990	280.3	+2.25	282.6
168	(1)	603.5	1001	986	337.3	+2.23	339.6
169	(*)	627.0	1000	987	355.7	+2.23	358.0
170	(*)	655.3	1000	988	382.8	+2.24	385.1
171	(*)	683.4	1000	988	410.4	+2.24	412.7
172	(*)	719.0	1000	990	444.0	+2.25	446.3

TABLE 1SRC-I Naphtha
Enthalpy Data

1500 psia		↑ Temperature OF	Pressure, psia		ΔH , exp	Pressure Correction	ΔH Cor- rected
Run	No.	Inlet	Inlet	Outlet	Btu/lb _m	Btu/lb _m	Btu/lb _m
181	(1)	529.2	1502	1490	276.8	+3.42	280.2
182	(1)	555.2	1502	1492	297.4	+3.43	300.3
177	(1)	578.4	1500	1485	311.5	+3.40	314.9
176	(1)	625.9	1500	1484	349.2	+3.40	352.6
175	(1)	663.3	1500	1484	377.0	+3.40	380.4
174	(1)	689.1	1500	1470	397.6	+3.34	400.9
173	(1)	719.0	1500	1482	419.7	+3.39	423.1

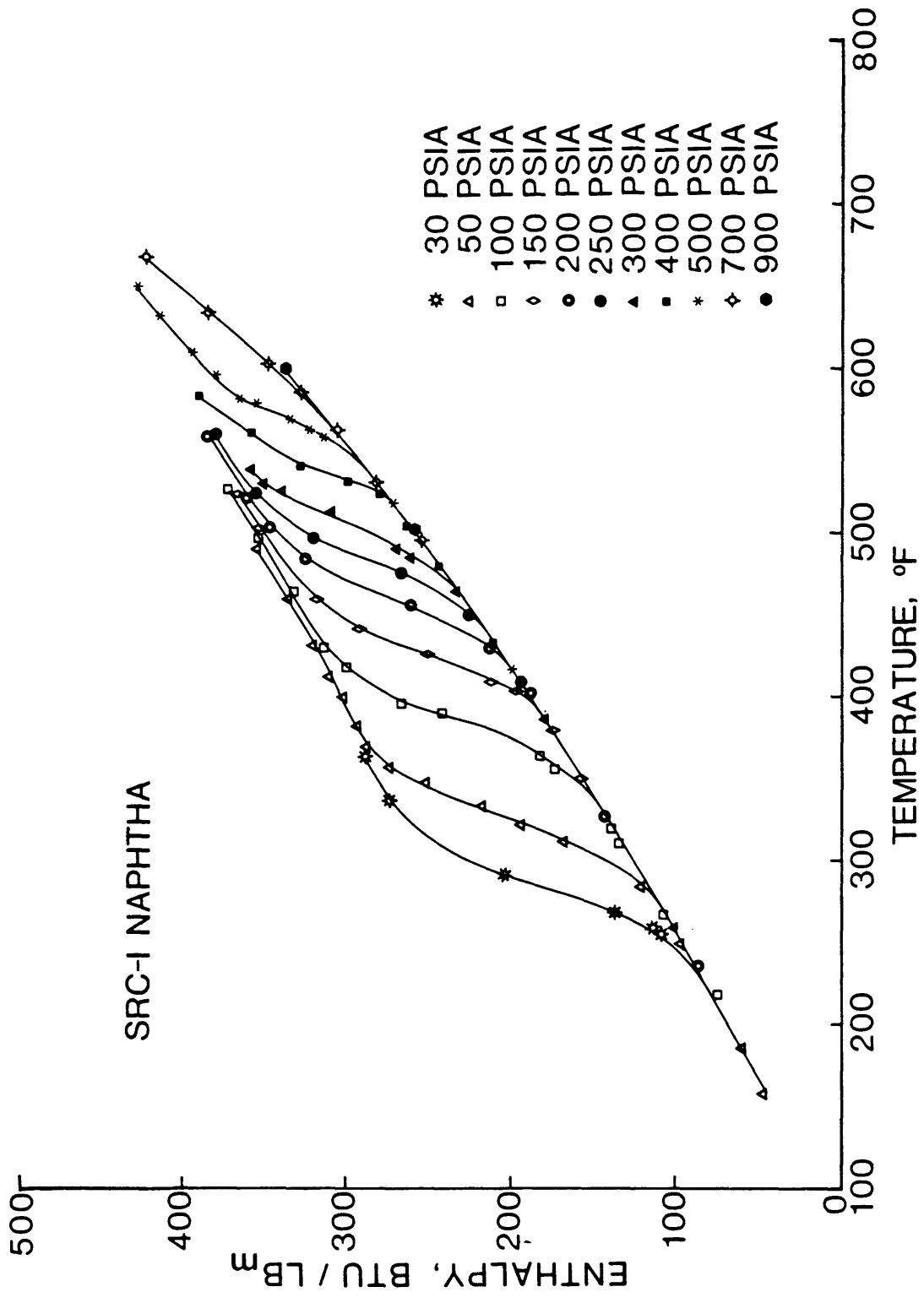


FIGURE 1

Enthalpy Difference Versus Temperature for the SRC-I Naphtha