DOE/PC/95214--T1

HIGH TEMPERATURE HIGH PRESSURE THERMODYNAMIC MEASUREMENTS FOR COAL MODEL COMPOUNDS

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SEMIANNUAL TECHNICAL PROGRESS REPORT

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by

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DISCLAIMER

PROJECT OBJECTIVES AND SCOPE

The overall objective of this project is to develop a better thermodynamic model for predicting properties of high-boiling coal derived liquids, especially the phase equilibria of different fractions at elevated temperatures and pressures. The development of such a model requires data on vapor-liquid equilibria (VLE), enthalpy, and heat capacity which would be experimentally determined for binary systems of coal model compounds and compiled into a database. The data will be used to refine existing models such as UNIQUAC and UNIFAC.

TECHNICAL HIGHLIGHTS AND MILESTONES

A M.S. graduate student Mr. Ahmad Al-Ghamdi has been recruited to work on this project. The flow VLE apparatus designed and built for a previous project has been upgraded and recalibrated for data measurements for this project. The modifications include better and more accurate sampling technique and addition of a digital recorder to monitor temperature, pressure and liquid level inside the VLE cell. VLE data measurements for system benzene-ethylbenzene have begun. The vapor and liquid compositions will be measured using the Perkin-Elmer Autosystem gas chromatograph. A capillary column made by Supelco has been purchased for the analysis.

For enthalpy and heat capacity measurements, SETARAM C-80 calorimeter has been purchased and installed. The instrument can be used for calorimetric property measurements at temperatures upto 300 C and pressures upto 1500 psi. Enthalpy measurements for the system benzene-ethylbenzene have begun. Simultaneously, we have undertaken the design of a calorimetric cell that will allow enthalpy measurements at pressures upto 10000 psi.

In what follows the VLE apparatus, and the preliminary work completed for the VLE measurements for the benzene-ethylbenzene system are described. A description of the calorimeter and the measured enthalpy data for the benzene-ethylbenzene system will be included in the next report.

VAPOR-LIQUID EQUILIBRIUM (VLE) MEASUREMENTS

THE APPARATUS:

From a previous project funded by Department of Energy we built an apparatus to measure VLE data for both known mixtures of aromatic compounds and heavy polynuclear coal liquids. The apparatus is shown in Figure 1 with the cross section of the equilibrium cell shown in Figure 2. The same apparatus will be used for the VLE measurements necessary for this project.

The apparatus can be divided into four sections, feed section, equilibration section, sampling section, and lastly the control-panel section. The maximum designed temperature and pressures for this system are 500°C and 2000 psi, respectively. All parts and tubing, including the ones exposed to the high temperature zones, are made of stainless steel (type 316). The tubing used in the fabrication is mostly of 1/4 inch diameter and at some places of 3/8 inch diameter. The fittings used are swagelok compression type, made of the same material SS-316.

This VLE apparatus consists of the equipment/components namely, feed tank, positive displacement metering pump, pre-heater oven, main heater oven, vapor-liquid equilibrium cell with a circular coil of tubing around it in which the liquid gets heated before entering the cell, two heat-exchangers, two control valves, one safety valve, one pulsation dampening bottle, eighteen plug valves (most of the fittings are of 1/4" diameter), and two strainers.

The purpose of designing and fabrication of this type of apparatus is to provide a steady supply of test liquid mixture, into the vapor-liquid equilibrium cell, at a very small flow rate and under controlled pressure. The liquid is heated, gradually to the equilibrium temperature in two ovens, before it is introduced into the VLE cell to achieve the equilibrium between the liquid and the vapors. Once we have reached this stage, vapor and the liquid will continuously be separated and sent to their respective coolers, through the respective openings out of the VLE cell. The vapors and the liquid streams are cooled and sent to the sample bottles through metering valves, for the collection of the samples. The amount of the sample taken can be controlled by opening of the metering (needle) valves for the desired time period. The excess amount of vapor and liquid streams are sent back to the main feed tank.

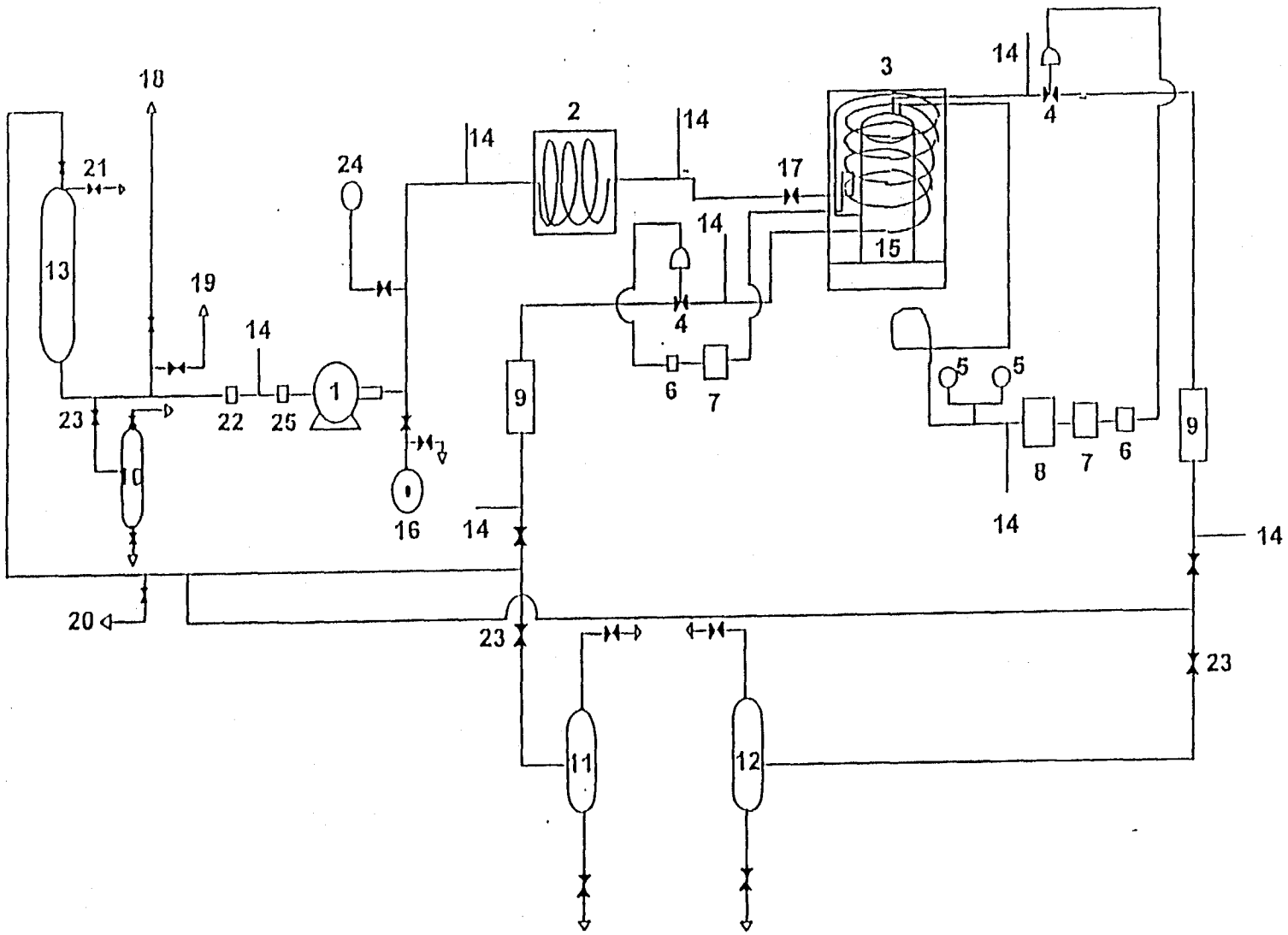


Figure 1. High temperature - High pressure flow VLE apparatus

Legend: Next Page

Legend for VLE flow apparatus

1. Positive displacement feed pump
2. Preheater oven
3. Main oven
4. Level and pressure control valves
5. Pressure gages
6. Electric to pneumatic transducer for liquid level and pressure control loops
7. Pressure and liquid level controllers
8. Pressure transmitter
9. Heat exchangers for liquid and vapor
10. Feed sample collector
11. Liquid sample collector
12. Vapor sample collector
13. Feed tank
14. Thermocouples
15. Vapor-liquid equilibrium cell
16. Pressure relief safety valve/rupture disk
17. High temperature hand control valve
18. Feed fill line
19. Pressure test gas inlet
20. Drain point
21. Vent point
22. 60 μm Strainer
23. Needle valves
24. Pump discharge pressure gage
25. 230 μm Strainer

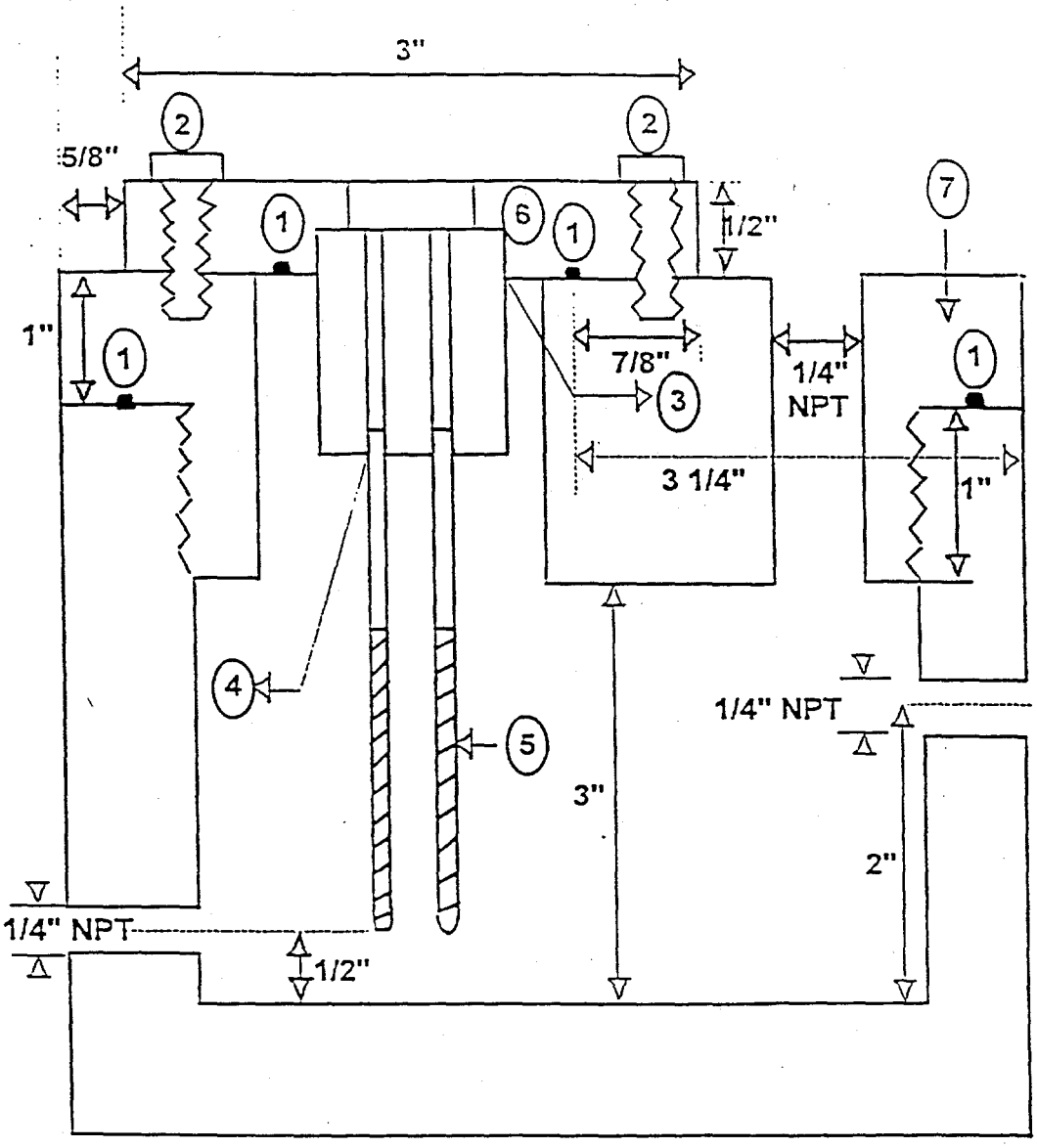


Figure 2. Equilibrium cell for the VLE apparatus

Legend:

1. O-ring
2. 3/16" x 7/8" bolts
3. Small fillet weld
4. Trepan and weld
5. 316 SS tubes with sensors for level measurement
6. Flange for liquid level sensor
7. Lid of VLE cell

Note: The cell is made of SS 316 and has a wall thickness of 1" all through.

The main advantage of this type of flow apparatus is that a steady state continuous system is established, as the amount of vapor and liquid being taken out of the system at equilibrium is continuously compensated by the fresh liquid-mixture stream coming in at the equilibrium temperature. After start-up, the system takes about an hour to come to desired temperature and pressure and it takes another two hours for the liquid and vapor in the VLE cell to equilibrate. These times although long are considerably shorter than equivalent equilibration times for a static equilibrium cell.

The control panel consists of the pre-heater controller, the main heater controller, two controllers for the pressure and level control loops, a thermocouple key, a temperature digital display and two pressure gauges. The original apparatus used a three pen chart recorder to record the pressure, liquid level and the temperature in the VLE cell. This has been replaced by a multi-signal digital chart recorder that allows saving of the signals on memory cards for further data analysis. All these components of the apparatus are very carefully placed on a frame, built from channels, fittings and wood panels.

The equilibrium cell is a cylindrical vessel made of stainless steel 316 with 1" thick walls (Figure 2). The cap of the cell is threaded and screws into the main body. Various ports are provided in the cell body for feed inlet, liquid and vapor outlet, pressure line and insertion of the thermocouple probe. A large port is provided at the top of the cell for mounting of the liquid level sensor. This sensor is welded to a flange which is bolted to the top of the cap. Stainless steel and inconel vented 'O' rings are used as seals for the cell cap as well as the flange carrying the liquid level sensor.

To achieve equilibrium in the VLE cell, temperature, pressure and liquid level in the cell need to be controlled as closely as possible. The temperature is controlled by the Honeywell UDC5000 temperature controller provided with the main oven. Two feedback control loops are used to control liquid level and the pressure in the cell. The liquid level is sensed by an electrical conductivity probe and controlled by manipulating a control valve on the liquid outlet line. The pressure in the cell is sensed by a Rosemont pressure transmitter and controlled by manipulating a control valve on the vapor outlet line. Once the cell contents reach conditions close to the desired values, the control loops are successful in maintaining them at the required values with minimal fluctuations.

The VLE apparatus uses an opaque stainless steel cell unlike the see-through glass window

cells used in various other studies in the literature. As a result , reliable level sensing is very crucial in our measurements. The electrical conductivity probe used in our apparatus was purchased from Delta M corporation who modified their existing LC-2300 conductivity probe to operate at higher temperatures (<500°C) and higher pressures (<1500 psi) according to our specifications. The Delta M LC2000 series of instruments employ thermal based sensors. Power is supplied to the sensors, and the returning sensor signal is converted to a standard 4-20 mA signal by solid state electronics.

The sensing element in the LC2000 Series level probes is a wire with a linear resistance versus temperature coefficient R(T). The temperature, and therefore the resistance, of this wire at any point along its length is determined by the amount of heater power to the probe and the thermal heat transfer from the probe surface to the surrounding media. The heat transfer properties (thermal conductivity and diffusivity), of the liquid whose level is to be measured is generally significantly greater (as much as 100 times) than the air or vapor phase above it. Therefore an increment of resistance (delta R) in the sensor wire is directly proportional to the length not submerged in the liquid. With many level sensing techniques, a change in the process temperature will alter the operation of the device, yielding false readings. The Microtuf LC2000 Series design includes a compensation feature which avoids this problem. The heated sensor has a temperature profile which is the sum of the temperature of the media with which it is in contact plus an incremental temperature determined by the amount of self heating and the thermal properties of the two media. The second (unheated) sensor, located adjacent to and parallel with the heated sensor, has a temperature profile which exactly matches the media temperature near the heated sensor. The unheated sensor signal is electronically subtracted from that of the heated sensor, leaving only the thermal based level signal which is now relatively independent of the temperature of the media. For the previous DOE project calibration curves were prepared for the level probe at various temperatures ranging from 50 C to 400 C. The probe signal was found to be pressure independent. These calibration curves will be used in the current measurements.

PROCEDURE:

A schematic flow diagram of the flow-type apparatus designed and made for this work is shown in figure 1 (numbers in brackets in what follows correspond to legend numbers of Figure 1). Feed from the feed tank (13) is filtered through two strainers (22 & 25) of 60 and 230 microns respectively and is pumped, by a positive displacement metering pump (1), to the pre-heater oven

(2). The liquid stream is heated while it passes through a coil shaped tubing in the pre-heater (2). The coiled tubing provides the maximum surface area for the heat transfer to the liquid flowing through it. Here the temperature of the liquid is raised to within 10 - 20 °C of the temperature desired in the main heater oven (3). The feed then enters the second coil placed inside the main heater where the temperature of the liquid stream is again raised so as to bring it close enough, i.e., $\pm$ 1 °C to the desired temperature within the vapor-liquid equilibrium cell (15). The vapor and liquid flow rates out of the VLE cell are controlled by two control valves (4), placed on the respective lines. Manipulation of the output of these valves to increase or decrease the flow rates of the vapors and liquid from the cell, help to control the pressure and the liquid level to desired values. The vapor and liquid from the cell are carried by two separate lines to the two respective double pipe heat exchangers (9), where they are cooled down to 35 - 50 °C. A sampling point is provided on each line (11,12). Streams from the two heat exchangers are then combined and sent back to the feed tank. A third sample point (10) is provided on the feed line. The samples of the feed, vapor, and the liquid streams can be taken once the equilibrium conditions have been established. The quantity of the samples to be taken, can be easily controlled with the help of the metering valves (23) (needle valve), placed in the sample extension lines. Once the samples are collected, they are tested and analyzed by chromatographic methods.

Both the pre-heater and the main oven are provided with independent controllers, which control the set points in the range of $\pm$ 1 °C temperature difference. The main heater controller works on the weighted average of the two inputs, one from the interior of the oven and the other from the inside of the vapor-liquid equilibrium cell. Both of these along with the other thermocouples, placed at various locations, are of J type Iron/Constantan. These thermocouples were calibrated against two reference points of water, i.e., freezing and boiling points.

The pressure and liquid levels are controlled by two feedback control loops. The pressure of the VLE cell is measured by the Rosemont pressure transmitter, which sends a 4-20 mA signal to the controller which then manipulates the flow rate of the vapor out of the VLE cell through a control valve placed in the vapor line.

The liquid level inside the VLE cell is measured by the Delta-M LC2300 level sensor. The probe, after sensing the level, sends the signal to the controller which in turn manipulates the control valve on the liquid outlet line in order to keep the level constant.

METHOD OF ANALYSIS:

The analysis of the samples (benzene, ethylbenzene mixtures) obtained from the Vapor-Liquid apparatus are carried out by the gas chromatographic method. The method specifically designed for the benzene-ethylbenzene binary system is given below:

Instrument:	Perkin-Elmer AutoSystem gas chromatograph
Injector:	Programmed split-splitless (PSS), with narrow glass liner
Column:	Supelco Beta-Dex 110, Fused silica capillary column, 30m, 0.25mm ID
Detector:	Flame Ionization detector (FID)
Carrier Gas:	Helium (inlet pressure 15psi)
Injection size:	0.1 microliter
Dilution solvent:	Methanol
Injector temperature:	200 C
Column temperature:	50 C
Detector temperature:	260 C
Data analysis:	Waters Maxima chromatographic software

The standard used for calibration was a solution of equal volumes of benzene and ethylbenzene. The solution was diluted by methanol solvent so that 0.1 microliter of the solution would contain approximately 100 nanograms of each of benzene and ethylbenzene, a limit as recommended by Supelco, the distributor of the GC column. The chromatogram for the standard and the data analysis are given in the appendix. Assuming a linear relation between the response and concentration, the concentration of brnzene in an unknown solution would then be given by

$$\text{Vol \% benzene in unknown} = R_B / (R_B + k * R_{EB})$$

where R_B and R_{EB} are responses of benzene and ethylbenzene in the unknown sample in microvolts-sec, and k is the ratio of the response factor of ethylbenzene to that of benzene corresponding to the standard solution (see the appendix)

$$k = 3.560436E\text{-}05/3.136934E\text{-}05 = 1.1350$$

DESIGN OF VLE EXPERIMENTS:

Plans are to measure VLE data for the benzene-ethylbenzene system along six isotherms, 180 C, 210 C, 250 C, 280 C, 300 C, 320 C. Altogether nine different feed compositions will be used to cover as wide a range of data as possible. The following table gives the feed compositions, the temperatures and the expected pressures for the proposed data measurements. The pressures are esimated from the vapor pressures of the pure liquids assuming an ideal mixture.

Table 1

Design of VLE Experiments

Data Point	Feed Composition Vol % Benzene	Temperature C	Estimated Pressure psi
1	95	180	152
2	95	210	213
3	95	250	440
4	95	280	650
5	90	180	138
6	90	210	215
7	90	250	380
8	90	280	616
9	85	180	132
10	85	210	246
11	85	250	364
12	85	280	585
13	70	180	117
14	70	210	222
15	70	250	350
16	70	280	528

Table 1 (continued)

Design of VLE Experiments

Data Point	Feed Composition Vol % Benzene	Temperature C	Estimated Pressure psi
17	50	180	92
18	50	210	184
19	50	250	261
20	50	280	450
21	50	300	470
22	30	180	70
23	30	210	145
24	30	250	215
25	30	280	370
26	30	300	390
27	15	180	58
28	15	210	115
29	15	250	180
30	15	280	303
31	15	300	314
32	15	320	330
33	10	180	52
34	10	210	107
35	10	250	161
36	10	280	258
37	10	300	280
38	10	320	310

Table 1 (continued)
Design of VLE Experiments

Data Point	Feed Composition Vol % Benzene	Temperature C	Estimated Pressure psi
39	5	180	47
40	5	210	99
41	5	250	150
42	5	280	260
43	5	300	275
44	5	320	290

PRELIMINARY DATA:

The VLE apparatus was upgraded by replacing the old pen chart recorder with the digital chart recorder. All the instruments in the apparatus were then tested for proper performance. Trial runs were made to practice bringing the system to desired conditions of pressure, temperature and liquid level as fast as possible and holding it to these conditions for a prolonged period of time. This required manipulating the PID control parameters for the pressure, the level and the temperature controllers. Next, some preliminary data points were measured and these are listed in Table 2. Reproducibility of these data are currently being tested.

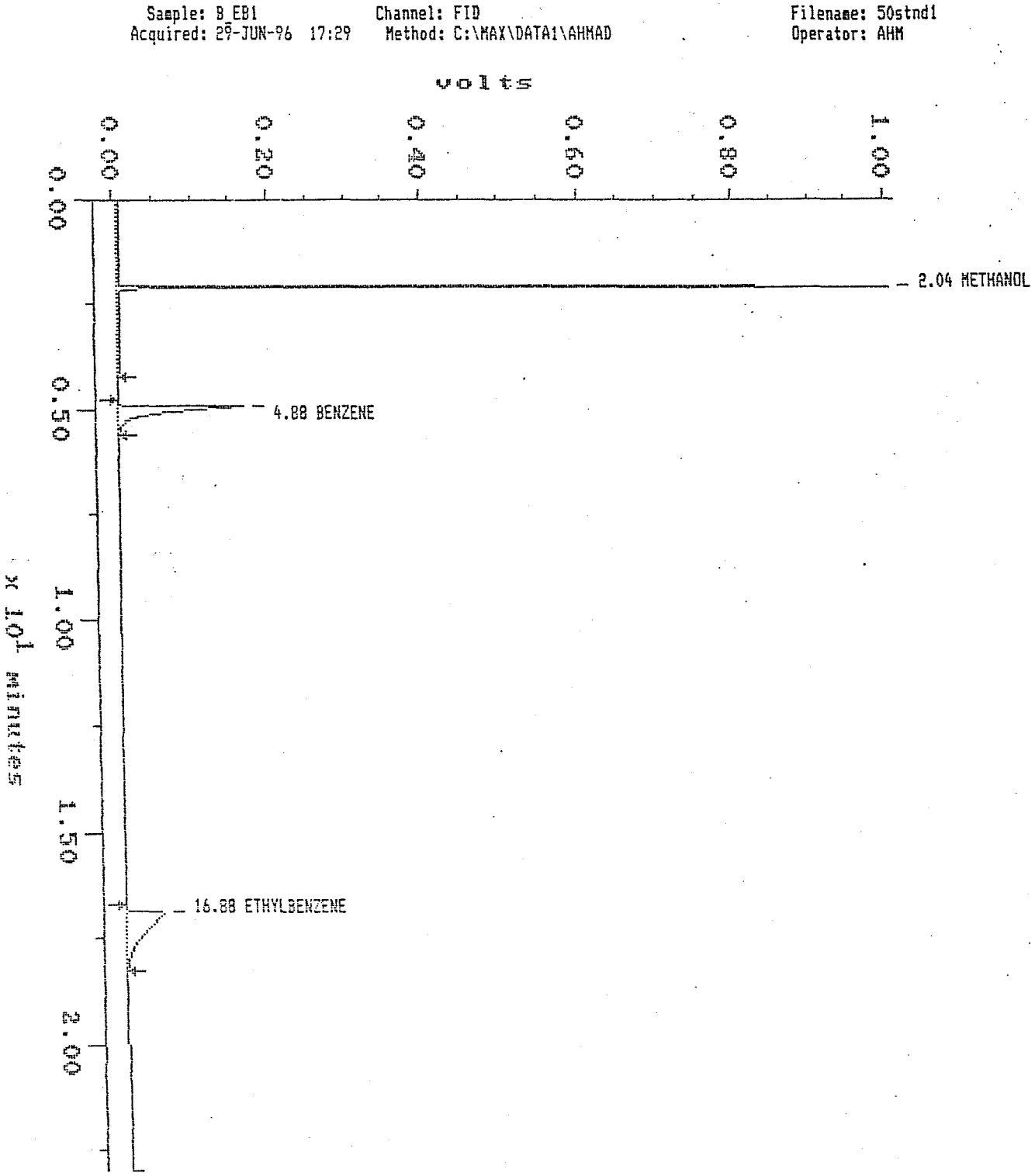
Table 2

Preliminary VLE data for benzene-ethylbenzene system

Data Point	Temperature C	Pressure psi	Phase	Vol % Benzene	Mole % Benzene
1	180	120	Liquid	92.2	94.2
			Vapor	96.8	97.7
2	180	123	Liquid	90.6	93.0
			Vapor	97.6	98.2
3	181.5	120	Liquid	91.8	93.9
			Vapor	96.4	97.4
4	199.7	175	Liquid	93.5	95.2
			Vapor	97.3	98.0

APPENDIX

GC calibration using standard solution of 50 vol% benzene concentration



BASELINE 810 PEAK INTEGRATION REPORT

Printed: 29-JUN-1996 18:29:55

SAMPLE: B_EB1 Type: STND
#1 in Method: VLE Instrument: Perkin Elmer GC
Acquired: 29-JUN-1996 17:29 Filename: 50stnd1
Rate: 2.0 points/sec Index: 1
Duration: 23.000 minutes
Operator: AHM

DETECTOR: FID

PK#	ID#	Peak Start (minutes)	Peak End (minutes)	Retention (minutes)	Type	Peak Area (microvolt-sec)	Peak Height (microvolt)	Area Percent	Hght Percent	Component Name
1	1	0.000	4.242	2.042	DB	1925060.7	998279.68	39.10	82.85	METHANOL
2	2	4.742	5.583	4.883	BB	1593913.2	161522.38	32.37	13.40	BENZENE
3	3	16.708	18.275	16.883	BB	1404322.4	45178.865	28.52	3.75	ETHYLBENZENE
TOTAL						4923296.3	1204980.9			

BENZENE Calibration Report

Printed: 29-JUN-1996 18:30:16

Quant Basis: Area
Curve Type: Linear
Y-axis Label: Concentration
Rejection Tolerance: None
Weighting: None
Internal Standard: None
Forced Through Origin: No
Corr. Coef. (r): 1.0000000
Coef. of Determination (r^2): 1.0000000

Equation: Conc = 3.136934E-05 * R

Sample	File Name	Valid	Concentration	Response	Calc'd Concentration	% Deviation	Response Factor
B_EB1	50stnd1	Y	5.000000E+01	1.5939131E+06	5.000000E+01	0	3.136934E-05

ETHYLBENZENE Calibration Report

Printed: 29-JUN-1996 18:30:21

Quant Basis: Area | Rejection Tolerance: None | Internal Standard: None
Curve Type: Linear | Weighting: None | Forced Through Origin: No
Y-axis Label: Concentration
Corr. Coef. (r): 1.0000000 | Coef. of Determination (r^2): 1.0000000

Equation: Conc = 3.560436E-05 * R

Sample	File Name	Valid	Concentration	Response	Calc'd Concentration	% Deviation	Response Factor
B_EB1	50stnd1	Y	5.000000E+01	1.4043224E+06	5.000000E+01	0	3.560436E-05