FOSSIL
ENERGY

315
2/10/81
M.E.

②

DR-2827

DOE/ET/10069-T5

MASTER

EDS COAL LIQUEFACTION PROCESS DEVELOPMENT. PHASE V

EDS Product Quality

Interim Report

Dist-217
NTIS-25

DO NOT MICROFILM
COVER

March 1981

Work Performed Under Contract No. AB01-77ET10069

Exxon Research and Engineering Company
Florham Park, New Jersey

U. S. DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

SOLVENT REFINED COAL (SRC) PROCESS

**Vapor-Liquid Equilibrium Measurements
for the SRC-II Process**

INTERIM REPORT

By
R. M. Henry

October, 1980

Work Performed Under Contract DEAC-0179-ET10104

Gulf Science & Technology Company

Chemical and Minerals Division
P. O. Drawer 2038
Pittsburgh, Pennsylvania 15230

ABSTRACT

This report summarizes vapor-liquid equilibrium studies conducted to support the Solvent Refined Coal project by The Pittsburgh & Midway Coal Mining Company under contract with the Department of Energy. Discussed herein are experimental details and results of measurements to obtain vapor-liquid equilibrium data at conditions simulating those which occur during the gas-liquid separation steps in the SRC-II coal liquefaction process. Separation and compositional analyses of liquid and gas phases permitted calculation of the equilibrium K values for the various components of the mixture. Experimental methods and apparatus used in this work were compared to a system recently described in the literature. The measured K values agreed to within an average of $\pm 5\%$ of published values and showed that the experimental system developed is satisfactory. Internal consistency of each experiment was evaluated by a material balance consistency test, and an average material balance of 99.7% was obtained over the 15 experiments. Data obtained from this work will serve as the basis for K value correlations used in process design calculations for the SRC-II Demonstration Plant.

TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES.....	1
LIST OF TABLES.....	11
I. SUMMARY.....	1
II. INTRODUCTION.....	2
III. EXPERIMENTAL.....	2
A. Basic Experimental Approach.....	2
B. Flowing VLE Unit.....	5
C. Experimental Procedure.....	7
D. Materials.....	10
1. Coal Liquids.....	10
2. Gas Mixture.....	10
E. Analytical Procedures.....	12
1. Gas Phase Analyses.....	12
2. Coal Liquid Analyses.....	12
F. Calculations.....	13
G. Material Balance Consistency Test.....	26
IV. RESULTS AND CONCLUSIONS.....	28
A. High Pressure Measurements.....	28
B. Low Pressure Measurements.....	31
V. ACKNOWLEDGEMENTS.....	38
VI. REFERENCES.....	39

LIST OF FIGURES

	<u>Page</u>
1. Sampling and Analyses Schemes.....	4
2. Flowing Vapor/Liquid Equilibrium Apparatus.....	6
3. Material Balance Consistency Test for the Experiment at 200 psig and 650°F.....	27
4. Equilibrium K Values for the System H_2/CH_4 /Coal Liquids/ Water at 2000 psig.....	30
5. Equilibrium K Values for the System H_2/CH_4 /Coal Liquids at 2000 psig.....	33
6. Equilibrium K Values for the System H_2/CH_4 /Coal Liquids at 125 psig.....	36
7. Equilibrium K Values for the System H_2/CH_4 /Coal Liquids at 200 psig.....	37

LIST OF TABLES

	<u>Page</u>
I. Experimental Conditions for the Vapor/Liquid Equilibrium Measurements for the System Hydrogen/Methane/Coal Liquids/Water.....	9
II. Coal Liquids Characterization.....	11
III. Comparison of the True Boiling Point Distillation with the GC Simulated Distillation.....	13
IV. Calculated Solubility of Water in Coal Liquids at 2000 psig....	20
V. Equilibrium K Values for the System Hydrogen/Methane/Coal Liquids/Water at 2000 psig and 400°F.....	22
VI. Mass Balance for the Individual VLE Experiments.....	25
VII. Equilibrium K Values for the System Hydrogen/Methane/Coal Liquids/Water at 2000 psig.....	29
VIII. Equilibrium K Values for the System Hydrogen/Methane Coal Liquids at 2000 psig.....	32
IX. Equilibrium K Values for the System Hydrogen/Methane Coal Liquids at Low Pressures.....	35

I. SUMMARY

This report gives the experimental details and results of measurements to obtain vapor-liquid equilibrium data at conditions which would simulate those occurring during the gas-liquid separation steps in the SRC-II coal liquefaction process. Equilibrium was established at the temperature and pressure of interest between the coal liquids, hydrogen and methane both with and without the presence of water. Separation and compositional analyses of the resulting liquid and gas phases permitted calculation of the equilibrium K values for the various components of the complex mixture. The high pressure separator conditions were simulated by making measurements at 2000 psig at temperatures from 400 to 700°F while the atmospheric flash unit conditions were simulated with pressures of 200 and 125 psig at temperatures of 500 and 650°F. Attempts to obtain higher temperatures were unsuccessful due primarily to thermal decomposition of the coal liquid feed. This was detected by slightly erratic pressure behavior and the detection of ethylene in the overhead gases. In the experiments in which water was present, measurements could not be made above 550°F because it was not possible to maintain a liquid phase in the separator. This point is termed the critical solution end point or the triple critical point and in this case lies between 550 and 600°F at 2000 psig. The water solubility in the coal liquids near this point was calculated to be about 62 mole percent.

To check the methods and apparatus used in this work measurements were first made on a known system. The system chosen was hydrogen/methane/tetralin whose VLE properties were recently described in the literature. The measured K values agreed to within an average of $\pm 5\%$ of the published values and showed that the system, procedures and methods of analyses which were developed are satisfactory, and that acceptable vapor-liquid equilibrium data for high temperatures and pressures could be obtained.

The internal consistency of each experiment was evaluated by a material balance consistency test. Material balances ranging from 94 to 107% were obtained with an average over the 15 experiments of 99.7%.

The data obtained in this work are to serve as the experimental basis for the K value correlations used in process design calculations for the SRC-II demonstration plant.

II. INTRODUCTION

The development and commercialization of the SRC-II process requires knowledge of the phase behavior of coal derived liquids for the proper design of processing equipment such as separators and distillation towers. Such fundamental data for coal derived liquids are practically non-existent. The existing correlations and predictive methods have as their experimental base measurements made on either pure components or distillate cuts from petroleum. Therefore, application of these methods for predicting the behavior of coal liquids could lead to erroneous results because of the great difference in chemical composition between coal liquids and petroleum.

Therefore, the objective of this work was to obtain the equilibrium K values for coal liquids at processing conditions of specific interest. The data obtained can then be used to confirm or modify the K value correlations now in use.

III. EXPERIMENTAL

A. Basic Experimental Approach

The approach taken to obtain the vapor-liquid equilibrium data was to establish equilibrium between the hydrogen, methane, coal liquids, and water at the desired temperature and pressure in a dynamic, flowing system. Then, once equilibrium has been established, to separate the gas and liquid phases, return each phase to ambient conditions and, by analyses of each phase, reconstruct the composition at equilibrium conditions. This can best be seen schematically in Figure 1. When the gas phase enters the low-pressure separator and cools to room temperature the water and higher boiling hydrocarbons will condense. The total gas flow over a designated period of time is

measured, and a sample is taken for gas chromatographic analysis. In the experiments in which water was used, the liquid phase is centrifuged to separate the oil and water and the volume of each phase was measured. The oil phase composition is then determined by gas chromatography and its specific gravity measured. Similarly, the liquid phase, as it cools in the low-pressure separator, releases the dissolved gases, the volume of gas is measured, and a sample taken for gas chromatographic analysis. The bottom liquid layer is then treated in the same manner as the overhead liquid layer. With these data it is possible to calculate the composition of each phase at equilibrium conditions and determine the appropriate equilibrium K value for that temperature and pressure.

Figure 1
Sampling and Analyses Scheme

B. Flowing VLE Unit

The operation of the flowing VLE unit can best be seen in the simplified schematic shown in Figure 2. The coal liquids and water (if used) are fed from the resevoirs by means of high pressure Milton-Roy metering pumps to the preheater loop and contactor. The flow rate of the gas mixture, contained in the high pressure (3500 psig) cylinder, is controlled by an Annin valve according to the differential pressure across a D/P cell which has a variable restrictor. The combined streams from the preheat loop enter the contactor, which is a stainless steel tube packed with quartz chips to provide intimate contact between phases. The equilibrated mixture enters the high pressure separator where the vapor and liquid streams separate and are drawn off.

The liquid level in the separator is maintained by a capacitance probe level controller which is located in a high pressure Jerguson guage in parallel with the separator. The signal from the capacitance probe operates an Annin valve which controls the liquid layer flow to the atmospheric separator. The vapor flow and, therefore, the system pressure is controlled by a micrometering valve. The valve is heated to prevent condensation.

Both the overhead gases and the liquid bottoms are cooled by line chillers installed ahead of the low pressure separators in order to insure condensation of the liquid phases and aid in the liquid-gas separation. Both low-pressure separators are equipped with septums so that gas samples can be withdrawn with syringes for gas chromatographic analysis. The gas streams from both separators then pass to the wet test meters and vented to the blowdown line while the liquids are retained in the separators.

Figure 2

FLOWING VAPOR/LIQUID EQUILIBRIUM APPARATUS

The performance of the apparatus was checked by determining the vapor/liquid equilibrium of the hydrogen/methane/tetralin system. This system was chosen because it closely approximates the system we wish to investigate and had recently been studied and reported in the literature.⁽¹⁾ The results of this work which were reported earlier,⁽²⁾ showed the measured K values agreed to within an average of $\pm 5\%$ of the published values indicating the methods and experimental procedures developed to be satisfactory.

C. Experimental Procedure

First the desired gas flow rate and pressure were established. The liquid feed pumps, previously adjusted to give the desired liquid flow rates were then turned on. After a steady-state flow was achieved, the oven heaters were turned on to bring the contactor and separator to equilibrium temperature. It took approximately 1-1/2 hours from start-up until equilibrium conditions were achieved. This was determined by a nearly constant vapor phase composition measured by two successive GC analyses. Once equilibrium was established, the run was continued for four hours during which time the liquid samples were gathered, the gas volumes measured, and two GC analyses of both overhead and bottom gas streams were made. Duplicate analyses were made in lieu of running duplicate experiments in hopes this would give us a measure of our reproducibility. To run duplicate experiments at shorter times would not have given sufficiently large overhead liquid samples for analysis.

If water was one of the liquid phases used, the two liquid samples were centrifuged to separate the water and coal liquid phases. The two phases were separated by decanting or placing in a separatory funnel and withdrawing the heavy layer and the volume of each measured. The density of the coal liquid layer was determined and a sample submitted for a simulated distillation by gas chromatography.

In this manner measurements were carried out at 2000 psig at temperatures of 400 to 550°F with water present in the liquid feed. Additional measurements at 2000 psig were made at 400 to 700°F without added water

and at varying liquid flow rates. Low pressure measurements were made at 200 and 125 psig at temperatures of 500 and 650°F also without water present. The experimental conditions used for each run are given in Table I. With water present, experiments were not possible beyond 550°F at 2000 psig because of the disappearance of the liquid phase. This phenomena in binary liquid systems is termed the "critical solution temperature"⁽⁴⁾ and is, in this case, between 550 and 600°F. No effort was made to pinpoint the temperature more exactly.

TABLE I

**EXPERIMENTAL CONDITIONS FOR THE VAPOR-LIQUID EQUILIBRIUM
MEASUREMENTS FOR THE SYSTEM HYDROGEN/METHANE/COAL LIQUIDS**

<u>Temperature</u> <u>°F</u>	<u>Pressure</u> <u>psig</u>	<u>Gas Flow Rate</u> <u>Standard Cu ft/hr</u>	<u>Liquid Flow Rate, cc/hr</u>	
			<u>Water</u>	<u>Coal Liquids</u>
400	2000	0.565	100	100
450	2000	0.565	100	100
500	2000	0.565	100	100
550	2000	0.565	100	100
400	2000	0.565	0	100
500	2000	0.565	0	100
600	2000	0.565	0	100
700	2000	0.565	0	100
400	2000	0.565	0	25
500	2000	0.565	0	25
600	2000	0.565	0	25
500	200	0.141	0	50
650	200	0.141	0	50
500	125	0.141	0	50
650	125	0.141	0	50

D. Materials

1. Coal Liquids

To obtain liquid feeds for the VLE experiments solid-free distillate fractions from the P-99 coal liquefaction unit were blended to approximate the composition of the feed streams of interest. For the high pressure runs the composition approximated the feed stream to the first- and second-stage separators. Its composition was:

<u>Component</u>	<u>Parts by Weight</u>
Debutanized Solvent	2
Process Solvent	1

For the low pressure studies the composition approximated the feed to the atmospheric flash unit. It had the following composition.

<u>Component</u>	<u>Parts by Weight</u>
Debutanized Solvent	1
Process Solvent	2
Heavy Distillate (650-1050°C)	1

For purpose of the vapor-liquid equilibrium calculations, the coal liquids were further characterized by obtaining their specific gravities and true boiling point distillation curves. In addition, the molecular weights of each fraction collected during the fractionation were determined. The data for each coal liquid sample are given in Table II.

2. Gas Mixture

The gas used throughout this work was obtained from Matheson Gas Products and was a high-pressure (3500 psi) mixture of 84.4% hydrogen and 15.6% methane. The analysis was checked in triplicate on a chromatograph which had been independently calibrated with the following results:

TABLE II

COAL LIQUIDS CHARACTERIZATION

<u>Distillation</u> <u>Range °F</u>	<u>High-Pressure Separator Liquids</u>			<u>Low-Pressure Separator Liquids</u>		
	<u>Yield</u> <u>Wt%</u>	<u>Specific</u> <u>Gravity</u>	<u>Mol</u> <u>Weight</u>	<u>Yield</u> <u>Wt%</u>	<u>Specific</u> <u>Gravity</u>	<u>Mol</u> <u>Weight</u>
IBP-300	17.5	0.7720	107	8.1	.7775	94
300-400	15.8	0.9036	141	10.2	.6129	122
400-500	29.8	0.9646	172	18.2	.9646	160
500-600	11.5	0.9888	192	17.0	.9888	191
600-700	9.5	1.0217	224	15.1	1.0291	221
700+	15.9	-	320	31.4	-	286

<u>Component</u>	<u>Weight Percent</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Hydrogen	84.1	84.2	84.1
Methane	15.9	15.8	15.9

Since the agreement was so close, it was decided to use the Matheson certified analysis in all calculations.

E. Analytical Procedures

1. Gas Analysis

Two chromatographs were used to obtain the composition of the gas phase samples. One chromatograph used a flame ionization detector to measure the hydrocarbon content. Since it could not detect hydrogen, a second chromatograph equipped with a thermal conductivity detector measured the hydrogen and methane content. Knowing the methane/hydrogen ratio, the hydrogen concentration in the total stream could be calculated. The column used for the hydrocarbon analyses was DC-200 on Chromasorb P and the carrier gas was He. After injection of the sample, the column was heated from 40° to 150°C at a programmed heating rate of 5°/min. Hydrocarbons up to about C₁₀ could be detected. The second chromatograph used a 5Å mole sieve-packed column and argon as the carrier gas. The column temperature was maintained at 30°C.

2. Coal Liquid Analysis

Both overhead and bottom coal liquid samples were analyzed by gas chromatography to give the weight percent eluted (distilled) as a function of temperature. This method is termed a simulated distillation. A comparison of the results of the simulated distillation with those obtained by true boiling point distillation are given in Table III.

TABLE III

COMPARISON OF THE TRUE BOILING POINT DISTILLATION
WITH THE GAS CHROMATOGRAPHY SIMULATED DISTILLATION

<u>Distillation Range °F</u>	<u>High Pressure Separator Liquids</u>		<u>Low Pressure Separator Liquids</u>	
	<u>TBP Distillation</u>	<u>GC SIM Distillation</u>	<u>TBP Distillation</u>	<u>GC SIM Distillation</u>
IBP-300	17.5	17.4	8.1	8.1
300-400	15.8	25.6	10.2	11.9
400-500	29.8	30.0	18.2	19.3
500-600	11.5	11.0	17.0	18.9
600-700	9.5	8.6	15.1	19.6
700+	15.9	7.4	31.4	22.2

It can be seen that the results are not identical and that, in particular, the heavy ends (700+ fraction) are quite different. This is because the very heavy ends are retained on the column and are, therefore, not accounted for in determining the distribution. However, because the quantity of liquids collected in each run was insufficient for a true boiling point distillation, it was necessary to use the simulated distillation results for all liquid sample analyses.

F. Calculations

To illustrate the method of calculations, the data taken during the run at 400°F and 2000 psig will be used. The following data were collected:

RUN CONDITIONS = 400°F, 2000 psig
 RUN TIME = 240 minutes
 ROOM TEMPERATURE = 23.6°C
 BAROMETRIC PRESSURE = 740.92 mm Hg

TOTAL GAS FEED = 0.565 STD cu ft/hr x 4 hr = 2.2600 cu ft
 TOTAL COAL LIQUIDS FEED = 400 cc
 TOTAL WATER FEED = 375 cc

OVERHEAD GAS VOLUME = 2.2695 cu ft
 BOTTOMS GAS VOLUME = 0.3235 cu ft

WATER RECOVERED: OVERHEAD = 6.75 cc
 BOTTOMS = 370.00 cc
 TOTAL = 376.75 cc

COAL LIQUID RECOVERED: OVERHEAD = 6.00 cc
 BOTTOMS = 380.00 cc
 TOTAL = 386.00 cc

COAL LIQUID DENSITIES: OVERHEAD = 0.8477 g/cc
 BOTTOMS = 0.9388 g/cc

DENSITY OF WATER AT R.T. = 0.9974 g/cc

GAS ANALYSES (GAS CHROMATOGRAPHY)

OVERHEAD

<u>COMPONENT</u>	<u>MOLE %</u>	
Hydrogen	85.5635	TC Detector
Methane	14.4365	
Methane	82.179	FI Detector
C ₂ +	17.821	

BOTTOM

<u>COMPONENT</u>	<u>MOLE %</u>	
Hydrogen	74.9935	TC Detector
Methane	25.0065	
Methane	85.224	FI Detector
C ₂ +	14.776	

COAL LIQUID ANALYSES (GC SIMULATED DISTILLATION)

<u>Distillation Range °F</u>	<u>Weight Fraction</u>	
	<u>Overhead</u>	<u>Bottoms</u>
IBP-300	33.0	12.32
300-400	41.4	22.36
400-500	21.7	31.88
500-600	3.9	13.92
600-700	0	10.67
700+	0	9.05

These data constituted a basic data set needed for calculation of the equilibrium K value for each component for each equilibrium temperature and pressure.

1. Vapor Calculations

The vapor volumes are corrected to standard temperature and pressure (760 mm and 273.16°K) by the following expression

$$V_c = V_a \times \frac{P_a}{760} \times \frac{273.16}{T_a}$$

where P_a = atmospheric pressure in mm Hg

T_a = ambient temperature in °K

V_a = measured volume of gas in cu ft

V_c = corrected volume of gas in cu ft

In this case for the overhead gas fraction $V_a = 2.2695$ cu ft, $P_a = 740.92$ mm Hg and $T_a = (273.16 + 23.6) = 296.76^\circ\text{K}$. Substituting into the above equation

$$V_c = 2.2695 \times \frac{740.92}{760} \times \frac{273.16}{296.76}$$

$$V_c = 2.0369 \text{ cu ft at } 0^\circ\text{C and } 760 \text{ mm Hg}$$

The number of moles of gas in this volume is

$$\text{no. moles} = 2.0369 \text{ cu ft} \times 28.317 \text{ liters/cu ft} / 22.414 \text{ moles/liter}$$

$$\text{no. moles} = 2.5733$$

From the compositional analysis of the gas, the number of moles of each component can be determined. From the H_2/CH_4 ratio the gas phase composition was determined to be

<u>Component</u>	<u>Mole Fraction</u>
Hydrogen	0.829661
Methane	0.139983
C ₂ +	0.030356

Therefore the number of moles of each component is

<u>Component</u>	<u>Moles</u>
Hydrogen	$0.829661 \times 2.5733 = 2.1350$
Methane	$0.139983 \times 2.5733 = 0.3602$
C ₂ +	$0.030356 \times 2.5733 = 0.0281$

Similar calculations are done then for the bottom or liquid gases.

2. Liquid Calculations

The measured volume of overhead coal liquids was 6.0 cc and its density determined to be 0.8477 g/cc.

Therefore, the weight of overhead coal liquids is $6.0 \times 0.8477 = 5.0862$ grams. From the simulated distillation and the molecular weights of the various distillate fractions determined on the original coal liquids sample the number of moles of each fraction were calculated. For the overhead liquids:

<u>Distillation Range, °F</u>	<u>M.W.</u>	<u>Weight Fraction</u>	<u>Grams</u>	<u>Moles</u>
IBP-300	107	0.330	1.6784	0.01568
300-400	141	0.414	2.1057	0.01493
400-500	172	0.217	1.1037	0.00642
500-600	192	0.039	0.1984	0.00103
600-700	224	0	0	0
700+	320	0	0	0
		<u>1.000</u>	<u>5.0862</u>	

Similarly the number of moles of water is $6.75 \text{ cc} \times 0.9974 \text{ g/cc} / 18.016 = 0.3736$. The number of moles of all components are totaled and the mole fraction of each calculated:

<u>Component</u>	<u>Moles</u>	<u>Mole Fraction (Y_i)</u>
Hydrogen	2.1350	0.71525
Methane	0.3602	0.12067
C ₂ ⁺	0.0781	0.02616
IPB-300°F	0.01568	0.00525
300-400°F	0.01493	0.00501
400-500°F	0.00642	0.00215
500-600°F	0.00103	0.00035
600-700°F	0.0	0.0
700+°F	0.0	0.0
Water	<u>0.3736</u>	<u>0.12516</u>
	2.98496	1.00000

This then gives the mole fraction composition of the vapor phase at the equilibrium temperature and pressure.

Identical calculations are carried out to determine the equilibrium liquid phase composition with the exception that the solubility of the water in the coal liquids, and the coal liquids solubility in the water must be

determined. Neither of these quantities were measured experimentally. A completely different system of sampling would have been necessary to obtain a measure of the solubility of water in the coal liquids or the solubility of the coal liquids in water at equilibrium conditions. Therefore, it was necessary to rely on the literature for obtaining best estimates of their mutual solubilities.

Hydrocarbon-water solubilities at elevated temperatures and pressures were measured by Griswold and Kasch⁽⁵⁾. They showed that good estimates of the solubility of water in hydrocarbon mixtures of widely varying molecular weights could be obtained from the relation

$$K_w = (P/X)_w$$

where K_w = Henry's Law constant at system temperature

P_w = pressure of water vapor over the two-phase mixture

X_w = mole fraction of water soluble in oil

From the author's graph of Henry's Law constant versus temperature and the measured concentration of water in the vapor, the mole fraction of water present in the oil phase at each of the four experiments containing water was calculated. The results are given in Table IV.

As was mentioned previously, at 600°F there was a disappearance of the liquid phase in the experiments in which water was present indicating we had exceeded the critical solution temperature. It is interesting to note that for the benzene/water system Rebert and Kay⁽⁶⁾ determined the mole fraction of water to be 86 mole percent at the critical solution end point at 528.8°F and 2300 psia. Therefore, the 62 mole percent for a coal liquid near its critical solution temperature is not unreasonable. Values for other hydrocarbons have been reported⁽⁷⁾ and range from 28 to 80 mole percent water at temperatures from 433 to 606°F depending upon the particular hydrocarbon.

The hydrocarbon solubility in water at these temperatures (400-550°F) were also measured by Griswold and Kasch⁽⁵⁾ and found to range from 0.1 to 0.5 mole percent. This was considered small enough to be neglected so no corrections were made for the solubility of the hydrocarbons in water.

Table IV

**CALCULATED SOLUBILITY OF WATER
IN COAL LIQUIDS AT 2000 PSIG**

<u>Temp., °F</u>	<u>Mole fraction Water In Vapor Phase</u>	<u>Water Partial Pressure, psia</u>	<u>Henry's Law Constant, psia</u>	<u>Mole Fraction Water In Coal Liquids</u>
400	0.125	250	1900	0.131
450	0.225	450	2050	0.219
500	0.420	840	2140	0.392
550	0.687	1374	2220	0.619

The equilibrium hydrocarbon liquid phase composition for this example then is:

<u>Component</u>	<u>Moles</u>	<u>Mole Fraction (X_i)</u>
Hydrogen	0.2636	0.0903
Methane	0.0879	0.0302
C ₂ +	0.0152	
IBP-300°F	0.4107	0.1461
300-400°F	0.5657	0.1940
400-500°F	0.6612	0.2268
500-600°F	0.2586	0.0887
600-700°F	0.1699	0.0582
700+°F	0.1009	0.0346
Water	<u>0.3854</u>	<u>0.1310</u>
	2.9191	0.9999

The C₂+ fraction was combined with the IBP-300°F fraction to include all hydrocarbons from C₂ to C₇.

The equilibrium K value for a particular component then is defined as the ratio of the mole fraction of that component in the vapor phase divided by its mole fraction in the liquid phase or

$$K = Y_i/X_i$$

The calculated K values for each component of the mixture at 2000 psig and 400°F are given in Table V.

3. Mass Balance

The total moles of feed recovered or accounted for is

Table V

**EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS/WATER
AT 2000 PSIG AND 400°F**

<u>Component</u>	<u>Vapor Phase Mole Fraction</u>	<u>Liquid Phase Mole Fraction</u>	<u>Equilibrium K Value</u>
Hydrocarbon Phase			
Hydrocarbon	0.71525	0.09037	7.914
Methane	0.12067	0.03015	4.002
C ₂ -C ₇	0.03141*	0.14608*	0.2151
Boiling Range, °F			
300-400	0.00501	0.19405	0.0258
400-500	0.00215	0.22681	0.0095
500-600	0.00035	0.08872	0.0039
600-700	0.0	0.05822	--
700+	0.0	0.03458	--
Water	0.12516	0.13100	0.955
Water Phase			
Water	0.12516	1.0000	0.125

- * The C₂+ Fraction was combined with the IPB-300°F fraction to include all hydrocarbons from C₂-C₇ in one fraction.

Water	20.4794	moles
Overhead	2.9849	moles
Bottoms	<u>2.5337</u>	moles
Total No. Moles	25.9980	

The total moles of feed is determined as follows:

Total Gas Feed = $2.2600 \text{ cu ft} \times 28.317 \text{ liters/cu ft} / 22.414 \text{ liters/mole}$

Total Gas Feed = 2.8550 moles

Total Moles Water = $375 \text{ cc} \times 0.9974 \text{ g/cc} / 18.016 \text{ g/mole}$

Total Moles Water = 20.7607

Total Weight Coal Liquids = $400 \text{ cc} \times 0.9388 = 375.52 \text{ grams}$

By simulated distillation

Moles IBP-300°F = $0.1704 \times 375.52 \div 107 = 0.5980$

Moles 300-400°F = $0.2596 \times 375.52 \div 141 = 0.6914$

Moles 400-500°F = $0.2836 \times 375.52 \div 172 = 0.6192$

Moles 500-600°F = $0.1216 \times 375.52 \div 192 = 0.2370$

Moles 600-700°F = $0.0873 \times 375.52 \div 224 = 0.1463$

Moles 700°+ = $0.0775 \times 375.52 \div 320 = \underline{0.0909}$

Total 2.3828

Therefore the total moles in the feed

Water	20.7607
Coal Liquids	2.3828
Gas Blend	<u>2.8550</u>
Total	25.9985

Mass Balance = $25.9980 / 25.9985 \times 100 = 100.00\%$

The material balances achieved for each experiment calculated in the above manner are given in Table VI. The difference between the value calculated above and that shown in Table VI is due to the difference between computer and hand calculations. In the hand calculations much rounding off occurred which, of course, does not occur in computer calculations. Table VI values are computer calculated values.

Table VI

MASS BALANCE FOR THE INDIVIDUAL VLE EXPERIMENTS

<u>Run No.</u>	<u>Temp., °F</u>	<u>Press., psig</u>	<u>Total Moles Feed</u>	<u>Total Moles Recovered</u>	<u>% Material Balance</u>
032680	400	2000	25.9996	25.9550	99.8
032780	450	2000	27.6604	27.3872	99.0
032880	500	2000	27.3539	26.9170	98.4
033180	550	2000	27.3837	27.7422	101.3
040780	400	2000	5.2389	5.0374	96.1
040880	500	2000	5.2091	5.1921	99.6
041080	600	2000	5.2091	5.0498	96.9
041680	700	2000	5.2384	5.3294	101.7
050780	400	2000	3.4525	3.5016	101.4
050880	500	2000	3.4703	3.2587	93.9
050980	600	2000	3.4525	3.6617	106.0
052080	500	200	3.9901	3.8674	96.9
052280	650	200	1.8735	1.8515	98.8
052880	500	125	1.7316	1.1754	99.1
060280	650	125	1.7577	1.8866	107.3

G. Material Balance Consistency Test

The data from each run was tested for internal consistency by a material balance consistency test suggested by Starling⁽³⁾. If F is the total number of moles of feed to the equilibrium cell and V and L the moles of vapor and liquid, respectively, at equilibrium, then

$$F = V + L \quad [1]$$

If we let $F = 1$ then

$$L = 1 - V \quad [2]$$

If Z_i , Y_i and X_i are the mole fractions of the i th component in the feed, vapor and liquid phases, respectively, then

$$Z_i F = Y_i V + X_i L \quad [3]$$

or from [2] above

$$Z_i = Y_i V + X_i (1-V) \quad [4]$$

dividing by Z_i and V and rearranging gives

$$Y_i/Z_i = \frac{1}{V} - \frac{(1-V)}{V} X_i/Z_i \quad [5]$$

Therefore, a plot of Y_i/Z_i versus X_i/Z_i for each component should yield a straight line with an intercept of $\frac{1}{V}$ and slope of $-\frac{(1-V)}{V}$. A typical plot is shown in Figure 3 for the data from the run made at 200 psig and 650°F. Only one point, the 700+°F fraction, deviated significantly from the straight line which was obtained by linear regression using the other seven data points. While showing the degree of internal consistency of the experimental data, these plots can also be used to correct scattered data points to make them consistent with the other data. In the case of the 700+°F point one

Figure 3

MATERIAL BALANCE CONSISTENCY TEST FOR
THE EXPERIMENT AT 200 PSIG AND 650°F

could move it parallel to the X_1/Z_1 axis until it intercepts the straight line and read or calculate a new value of X_1/Z_1 and from this calculate a new K value. Of course, this assumes greater confidence in the vapor phase analysis than the liquid phase analysis and shifts the entire error to an error in the liquid phase analysis. Further, to be completely consistent the mole fraction of each component in the liquid phase would have to be recalculated and this would yield somewhat different K values for all components. In any case in which graphical corrections were used in this work, this was not done. The graph was used to estimate a better value for certain points without altering the values of the other components.

IV. RESULTS AND CONCLUSIONS

A. High Pressure Measurements

1. Hydrogen/Methane/Coal Liquids/Water at 2000 psig

A summary of the K values obtained are given in Table VII and shown graphically in Figure 4. It can be seen that measurements were made only to 550°F. As mentioned earlier it was not possible to maintain a liquid phase in the separator at 600°F. This indicated that the critical solution temperature had been exceeded. From a literature correlation, the solubility of water in the coal liquid phase at 550°F was estimated to be about 62 mole percent. This is close to the critical solution concentrations reported in the literature for other hydrocarbons.

Table VII

**EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS*/WATER
AT 2000 psig**

<u>Component</u>	<u>400°F</u>	<u>450°F</u>	<u>500°F</u>	<u>550°F</u>
Hydrocarbon Phase				
Hydrogen	7.914	7.166	6.701	6.997
Methane	4.002	4.087	4.356	4.563
C ₂ -C ₇ Hydrocarbons	0.215	0.301	0.459	0.637
Boiling Range, °F				
300-400	0.0258	0.0535	0.1115	0.1813
400-500	0.0095	0.0234	0.0538	0.1127
500-600	0.0039	0.0103	0.0233	0.0551
600-700	0.0	0.0	0.0119	0.0332
700+	0.0	0.0	0.0	0.0038
Water	0.955	1.027	1.071	1.110
Water Phase				
Water	0.125	0.225	0.420	0.687

* High Pressure Separator Liquids Composition

Figure 4

EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS/WATER AT 2000 PSIG

The most likely source of error for the equilibrium values reported here is the assumption of little or no hydrocarbon solubility in the water phase. From the experimental data given previously, it can be seen that the largest material balance loss was with the coal liquids. This would indicate some water solubility at room temperature and, therefore, an even higher solubility at elevated temperatures. The assumption then of $X_{H_2O} = 1$ would be incorrect. Since we do not have analyses of the water phase at equilibrium conditions nor a good method of estimation, the magnitude of the error cannot be determined.

2. Hydrogen/Methane/Coal Liquids System at 2000 psig

A summary of the K values obtained in the water free system are given in Table VIII and shown graphically in Figure 5. The data include runs made at two different coal liquid feed rates, 100 cc/hr and 25 cc/hr. It can be seen that very little difference could be observed. It is felt the scatter observed in the liquid fractions is within experimental error due to the variability of results of the simulated distillation method of liquid analysis.

B. Low Pressure Measurements

The measured K values at conditions simulating those in the low pressure separators are given in Table IX and shown in Figures 6 and 7. It can be seen in Figure 7 that some of the K values for the experiment at 650°F were readjusted by the graphical method explained earlier.

Table VIII

EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS*
AT 2000 psig

Component	400°F		500°F		600°F		700°F	
	Coal Liq.	Feed Rate	Coal Liq.	Feed Rate	Coal Liq.	Feed Rate	Coal Liq.	Feed Rate
	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr
Hydrogen	9.338	9.9741	7.7271	8.0184	6.0714	7.3877	4.5027	--
Methane	4.279	4.385	3.9888	4.2440	3.598	3.8881	3.3152	--
C ₂ -C ₇ Hydrocarbons	0.1637	0.1101	0.2801	0.2481	0.4813	0.3356	0.7386	--
Boiling Range, °F								
300-400	0.0235	0.0219	0.0757	0.0672	0.1857	0.1433	0.3714	--
400-500	0.0090	0.0083	0.0309	0.0286	0.0845	0.0754	0.2102	--
500-600	0.0037	0.0030	0.0130	0.0071	0.0297	0.0252	0.0992	--
600-700	--	0.0002	--	0.0042	0.0152	0.0118	0.0582	--
700+	--	--	--	--	--	--	0.0073	--

* High pressure separator liquids composition

Figure 5

EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS AT 2000 PSIG

It was also in this experiment that ethylene was detected in the overhead gas analysis indicating thermal cracking was occurring and could account for the poorer internal consistency. It can also be seen in Figure 6 that at 125 psig the methane and hydrogen solubilities decrease with increasing temperature while at higher pressures the reverse is observed.

Table IX

**EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS*
AT LOW PRESSURES**

<u>Component</u>	Equilibrium K Values			
	125 psig		200 psig	
	<u>500°F</u>	<u>650°F</u>	<u>500°F</u>	<u>650°F</u>
Hydrogen	142.5	186.6	101.8	67.6
Methane	83.3	107.3	54.4	44.4
C ₂ -C ₇ Hydrocarbons	1.914	4.233**	1.006	2.024
Boiling Range, °F				
300-400	0.748	2.272**	0.539	1.418
400-500	0.255	0.960	0.145	0.627
500-600	0.063	0.389	0.042	0.227
600-700	0.027	0.056	0.012	0.057
700+	0	0.022**	0	0.027

* Low pressure separator liquids composition

** Values graphical corrected by material balance consistency test

Figure 6

EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS AT 125 PSIG

Figure 7

**EQUILIBRIUM K VALUES FOR THE SYSTEM
HYDROGEN/METHANE/COAL LIQUIDS AT 200 psig**

V. ACKNOWLEDGMENTS

Our appreciation and thanks are given to Mr. Richard Query who carried out the experimental runs and set up and calibrated the gas chromatographs for the gas phase analyses. Our thanks are also given to Dr. Richard Pannell who devised the gas chromatographic simulated distillation method for the analysis of coal derived liquids and allowed us to use the equipment. Finally we would like to acknowledge Mr. Robert Jacoby and Mr. John Swansiger for the original design of the flowing VLE apparatus.

VI. REFERENCES

1. Simnick, J. J., Sebastian, H. M., Lin, H. M., and Chao, K. C., J. Chem. Eng. Data, 25, 147 (1980).
2. Memo: R. M. Henry and R. C. Query to J. L. Stephenson, "Evaluation of the Flowing Vapor/Liquid Equilibrium Apparatus," Reference 6270FT07-50-20, May 29, 1980.
3. Starling, Kenneth E., (Private Communication).
4. Rebert, C. J. and Hayworth, K. E., A.I.C.H.E. Journal, 13, 118 (1967).
5. Griswold, R. and Kasch, J. E., Ind. Eng. Chem, 34, 804 (1942).
6. Rebert, C. J. and Kay, W. B., A.I.C.H.E. Journal, 5, 285 (1959).
7. Barton, P. and Fenske, M. R., Ind. Eng. Chem. Process Des. Develop., 9, 18 (1970).