

VAPOR-LIQUID EQUILIBRIUM OF H-COAL LIQUIDS, WATER, AND A NINE-COMPONENT LIGHT GAS MIXTURE

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INTRODUCTION

The need for and utility of "K" value data (K = mole fraction vapor/mole fraction liquid) for the efficient design and operation of coal liquefaction plants is well established. In recent computer simulations in the H-Coal process, these factors had to be estimated from meager data for similar petroleum-derived materials, a procedure that may be unsatisfactory due to the difference in the nature of coal-derived and petroleum-derived materials. The "K" values are the key to the design of vessel size and strength, throughput, and in the final analysis of the entire process.

The present project was undertaken to support the H-Coal pilot plant operated by Ashland Petroleum Co. Three mixtures were run consisting of differing amounts of atmospheric-still overhead and bottoms, and vacuum-still overhead and bottoms from products of the Process Development Unit (PDU) Run #5 at Hydrocarbons Research, Inc. (HRI) which processed Illinois #6 coal in the syncrude mode of operation. The mixtures were intended to match true boiling point (TBP) fractions predicted for flash drums in which material from the reactor is depressurized and cooled.

This project was complicated by the diversity of the properties of the components of the samples, the large number of components, and the variety of the operating conditions of the experiments. Thus, new techniques were developed for the collection of the samples, for the partitioning of the samples, and for the analysis of each part of the samples.

APPARATUS

Vapor-liquid-equilibrium (VLE) measurements were made in a 2-liter autoclave, Figure 1, which was described previously (1) and was suited for measurements on complex systems. Sufficient liquid was placed in the vessel so that at operating conditions the liquid volume would be about 1300 cc. Mixing and contact between the gas and liquid phases were effected by the hollow shaft mixer which drew gas down the tube and dispensed it in the cavitation produced by the impeller. The vapor sampling procedure consisted of opening the valve at the autoclave into an evacuated manifold, closing it again, pumping manifold to vacuum, closing vacuum valve, opening autoclave and bomb valves, closing both valves, pumping the manifold to vacuum, and removing bomb. In a similar manner, the liquid was sampled through a dip tube into the evacuated liquid sample bomb. The tubing is 0.040-in. ID, and the lengths were kept to a minimum to reduce holdup.

The autoclave body was heated with a standard furnace, and the head was heated with two 500-watt heaters. The sample bombs were fitted with custom-made Glas-Col heating jackets, and all tubing and valves were heated. The entire system was essentially isothermal. Temperatures were measured with thermocouples at many points of the system with the autoclave controlled to about 0.5° C. Pressures were measured with a bourdon tube gauge and a pressure transducer, both of which were calibrated against a deadweight gauge. Liquid phase samples of 5 to 15 g were weighed to an accuracy of 1 or 2 mg in their bombs on a large, double-pan analytical balance. Gas phase samples weighed 50 to 300 mg.

SAMPLE PARTITION

A variety of techniques was used to divide the liquid phase and gas phase samples into their respective liquid and dissolved gas, and gas and condensate parts. Each bomb was cooled with solid CO₂ to try to effect a separation between butane and pentane. The gas from each bomb was expanded through a 0.040-in. ID metal tube and a glass trap into a 100-cc glass burette. The gas was then transferred into a bulb for collection. Between 5 and 30 expansions were needed to remove dissolved gases from the bombs down to the vapor pressure of the liquid. The bombs were warmed and cooled several times to allow more gases to escape from the liquid. The collection bulbs varied from a 10-cc syringe for total gas volumes of 2 cc at 1 atm up to glass bulbs with 500-cc capacity for samples as were taken during the VLE runs at 3000 psi. The gases in the collection bulbs were thoroughly mixed by drawing them down into the burette and returning them to the bulb several times. Gas was then transferred to a 30-cc cell for measurement of NH₃ by infrared analysis and to a syringe for charging to a gas chromatograph.

After all dissolved gases were removed, the bombs were mounted on a low-volume metal manifold in such a way that their contents could drain into a glass bulb. The manifold and glass bulb were evacuated, the manifold and sample bomb were heated to 100° C, the bulb was immersed in liquid N₂ and the bomb valve was opened. Since the pressure in the bomb was atmospheric due to the water vapor pressure, the bomb emptied quickly. The remaining liquid adhering to the inner surfaces of the bomb was vapor transferred to the bulb by slowly raising the bomb and manifold temperature up to about 300° C over a period of 6 to 8 hours. The glass bulb was warmed to room temperature, removed, capped, weighed, and was ready for analysis of its water and coal liquid content.

ANALYSIS

Ammonia in the gas samples was determined by absorption at 3330 cm⁻¹ in the infrared. The spectra of ammonia in this region shows a number of sharp and strong bands, and there was no significant interference from other compounds in the gas sample. The gas cell (Precision cells, type 34, 10 cm, IR transmitting)¹ was filled directly from the vacuum system described above. Calibration for ammonia determination was accomplished by IR response following injection of measured aliquots of ammonia solution into the evacuated cell.

Determination of gaseous components other than ammonia was carried out by gas chromatography. The dual-column system consisted of a 120-cm 5A molecular sieve column and a 140-cm Porapak R column connected in line through a Valco 10-port valve. Operation of the valve introduced the gas sample to the Porapak column. After the earliest eluting components (hydrogen, oxygen, nitrogen, and methane) eluted from the Porapak to the molecular sieve column, the valve was reversed to interchange the position of the columns. In this way, chromatograms from the two columns were obtained overlaying each other in a single pattern. Proper selection of column lengths, starting temperature and program rate permitted all components to be resolved in the combined chromatogram. The early eluting components (hydrogen, oxygen, nitrogen, carbon dioxide, ethane, methane, hydrogen sulfide) were monitored by a thermal conductivity detector. Hydrocarbons including and beyond propane were monitored by a flame ionization detector. Gas samples from high temperature runs were sometimes found to contain carbon monoxide. This was a well resolved but late eluting component due to its passage through the molecular sieve column. It was monitored by the thermal conductivity detector.

¹ Reference to specific equipment or trade names does not imply endorsement by the Department of Energy.

This analysis was carried out in a Hewlett-Packard 5830A gas chromatograph. The carrier gas was 8.5 percent hydrogen in helium because this provides a roughly linear response by the thermal conductivity detector for hydrogen and a good response for the other components. The response curve for hydrogen was determined for a suitable range of hydrogen-air blends prepared by syringe mixing. An analyzed gas blend was used for calibration for other components.

The liquid phase samples contained water and the oil components excluding the most volatile hydrocarbons. The oil analysis was carried out by gas chromatographic simulated distillation by the ASTM D2886 procedure. Treatment of data of this procedure was expanded to present boiling point versus sample weight on the basis of both paraffin and aromatic hydrocarbon boiling-point scales. This was then converted to paraffinic or aromatic molecular-weight scales versus sample-weight distribution.

The water-oil sample was prepared for water analysis by dissolving it in sufficient ethanol or methanol-spiked ethanol to form a homogeneous solution. This was analyzed by gas chromatography on Porapak-T in a nickel column. Water and alcohols were monitored by a thermal conductivity detector. All other materials were backflushed from the column at elevated temperature. Calibration and analysis were based on alcohol-water blends and the response to ethanol or methanol as internal standards.

SAMPLE MATERIALS

Table 1 lists the blends of atmospheric-still and vacuum-still overheads and bottoms from PDU run #5 that were measured in this project. The blends were placed in the autoclave and an eight-component gas mixture of 69.47% H₂, 3.12% N₂, 0.41% CO₂, 2.02% H₂S, 17.87% C₁, 4.11% C₂, 2.00% C₃, and 1.00% C₄ was used to pressure the system as indicated in table 1. The composition of each of the mixtures at equilibrium is given in tables 2,3,4, and 5.

Table 1. Coal Liquids and Water Charged to Autoclave

PDU Material	Blend #1 350° F/142, 220 psig	Blend #2 500° F/3000 psig	Blend #3 750° F/700 psig
ASO ¹	33.00%	44.89%	7.95%
ASB ²	65.81	35.18	35.39
VSO ³	0.	6.59	31.61
VSB ⁴	0.	0.	24.46
H ₂ O	1.19	12.01	0.56
NH ₃	0.	1.33	0.03
	<u>100.00%</u>	<u>100.00%</u>	<u>100.00%</u>

¹ Atmospheric-still overheads.

² Atmospheric-still bottoms.

³ Vacuum-still overheads.

⁴ Vacuum-still bottoms.

RESULTS

The experimental results for the coal liquid blends are given in Tables 2-5. Each blend and its operating conditions presented unique challenges of operation or analysis. A material balance on the eight components of the light gas mixture and water was made for each run and used in selecting the best set of K values reported in Tables 2-4. Average or individual K values for other samples taken at the same operating conditions are also given in Tables 2-4 for comparison purposes, but they

obviously reflect some variation from the compositions given for the selected values. The material balance on NH_3 and H_2S was always less than was charged due to reactions. Some runs were discarded due to apparent plugging of the sample draw-off tubing. The concentrations of C_3 , C_4 , and C_5 at -100°F and resultant K factors are subject to a little more uncertainty in all runs because they are in the vapor-pressure range where solid CO_2 was used to try to partition the samples for analysis as gases or liquids. Condensation of gases on the walls of the burette was a problem.

During the high temperature run on blend #3, there was a significant increase in the concentration of C_1 , C_2 , C_3 , and C_4 with time and a corresponding decrease in the concentration of H_2 . Vapor and liquid samples were taken close together in time, however, so the results should be of interest. The measurements on blend #2 at high pressure were notable for large volumes (400 ml) of gas dissolved in the liquid phase; whereas, the measurements on blend #1 yielded only about 2 ml of gas from the liquid phase.

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REFERENCES

- (1) Harrison, R. H., "Hydrogen Solubility in Coal Liquids," presentation at the Second Chemical Congress of the North American Continent, Las Vegas, Nevada, August 24-29, 1980.

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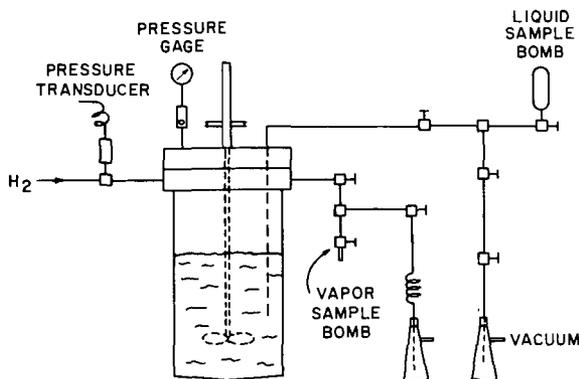


FIGURE 1. Vapor-Liquid-Equilibrium Apparatus.

Table 2. Vapor-Liquid Equilibrium at 350° F and 142 psig of Blend #1 of H-Coal Liquids from PDU Run #5

Compound	Vapor #2		Liquid #2			Sample #2		Sample #1		
	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Paraffin K*	Aromatic K*	Paraffin K*	Aromatic K*
H2	1.7696	2.016		0.002023			81.42	100.71	77.17	94.69
N2	1.3001	28.014		0.001740			69.54	86.01	61.76	75.79
CO2	0.0168	44.011		0.000338			4.61	5.70	4.48	5.49
H2S	0	34.076		0.000709			-	-	3.35	4.11
H2O	78.4861	18.016		0.837646			8.72	10.79	8.96	10.99
C1	3.1595	16.043		0.007411			39.67	49.07	35.00	42.95
C2	1.0906	30.070		0.002482			40.89	50.59	28.19	34.59
C3	1.0099	44.097		0.001993			51.33	63.50	28.95	35.51
C4	1.1623	58.124		0.002943			36.75	45.46	40.89	50.17
C5-100°F	0.9462	72.151		0.2698			0.326	0.404	1.30	1.60
100-200° F	4.4672	91.40	86.96	2.3223	94.17	88.72	0.184	0.226	0.188	0.232
200-300° F	4.1034	106.44	96.56	5.4140	111.18	99.58	0.0737	0.0900	0.122	0.147
300-400° F	1.4321	142.57	119.61	8.3473	147.66	122.86	0.0165	0.0203	0.0146	0.0177
400-500° F	0.7510	177.30	141.78	20.3826	183.82	145.94	0.0036	0.0044	0.0042	0.0051
500-600° F	0.2157	219.60	168.78	28.0558	228.27	174.31	0.0007	0.0009	0.0009	0.0011
600-700° F	-	-	-	20.8386	277.34	205.63	-	-	-	-
700-800° F	-	-	-	9.3982	337.63	244.16	-	-	-	-
800-900° F	-	-	-	3.2616	420.05	296.70	-	-	-	-
900° F+	-	-	-	0.8526	498.78	346.95	-	-	-	-

*K = mole fraction vapor/mole fraction liquid.

Table 3. Vapor-Liquid Equilibrium at 350° F and 220 psig of Blend #1 of H-Coal Liquids from PDU Run #5

Compound	Vapor #4		Liquid #4			Sample #4		Sample #3		
	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Paraffin K*	Aromatic K*	Paraffin K*	Aromatic K*
H2	3.9849	2.016		0.005449			73.51	90.77	67.08	83.12
N2	2.1413	28.014		0.004166			51.67	63.80	52.30	64.81
CO2	0.1401	44.011		0.001052			13.38	16.53	12.09	14.97
H2S	0.7597	34.076		0.003610			21.15	26.12	16.71	20.70
H2O	38.7786	18.016		0.779015			5.00	6.18	6.50	8.06
C1	6.8653	16.043		0.022457			30.73	37.94	33.63	41.67
C2	2.2462	30.070		0.014199			15.90	19.63	17.47	21.65
C3	1.7108	44.097		0.014612			11.77	14.53	12.26	15.19
C4	3.0821	58.124		0.019486			15.90	19.63	13.76	17.05
C5-100°F	3.4623	72.151		0.1129			3.08	3.80	1.77	2.19
100-200° F	12.5676	93.48	88.29	1.8901	93.84	88.51	0.671	0.827	0.192	0.242
200-300° F	13.3838	107.71	97.37	4.8647	111.51	99.80	0.286	0.350	0.0888	0.109
300-400° F	6.4491	143.60	120.27	8.2857	148.19	123.20	0.0807	0.0990	0.0218	0.0268
400-500° F	3.4361	187.67	148.40	20.5571	184.09	146.09	0.0165	0.0204	0.0046	0.0056
500-600° F	0.8046	222.42	170.57	29.7044	227.95	174.11	0.0028	0.0034	0.0008	0.0010
600-700° F	0.1878	265.86	198.30	21.2130	278.27	206.22	0.0009	0.0011	0.0002	0.0002
700-800° F	-	-	-	8.6342	337.24	243.85	-	-	-	-
800-900° F	-	-	-	2.8087	419.91	296.61	-	-	-	-
900° F+	-	-	-	1.0651	508.08	352.87	-	-	-	-

*K = mole fraction vapor/mole fraction liquid.

Table 4. Vapor-Liquid Equilibrium at 500° F and 3,000 psig of Blend #2 of H-Coal Liquids from PDU Run #5

Compound	Vapor #3			Liquid #3			Sample #3		Average of Four Samples †	
	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Paraffin K*	Aromatic K*	Paraffin K*	Aromatic K*
H ₂	5.803	2.016		0.19242			5.19	5.73	5.72	6.28
N ₂	3.803	28.014		0.17834			3.67	4.05	3.92	4.30
CO ₂	0.175	44.011		0.00719			4.17	4.62	4.17	4.57
NH ₃	1.247	17.031		0.07124			3.01	3.32	2.77	3.04
H ₂ O	32.815	18.016		7.30120			0.77	0.85	0.77	0.84
C ₁	10.147	16.043		0.58191			3.00	3.31	3.11	3.41
C ₂	3.506	30.070		0.31577			1.91	2.11	1.97	2.17
C ₃	2.131	44.097		0.20602			1.78	1.96	1.76	1.93
C ₄	1.564	58.124		0.08673			3.10	3.42	1.24	1.37
C ₅ -100° F	1.223	72.151		0.0301			7.01	7.71	2.47	2.72
100-200° F	9.658	90.53	86.40	3.8394	87.85	84.69	0.42	0.46	0.31	0.34
200-300° F	11.148	108.63	97.95	6.1111	110.93	99.42	0.32	0.35	0.26	0.28
300-400° F	8.171	142.96	119.86	10.5052	147.55	122.79	0.138	0.151	0.169	0.184
400-500° F	6.803	178.18	142.34	22.0021	182.91	145.36	0.055	0.060	0.084	0.099
500-600° F	1.807	215.16	165.94	24.2466	228.09	174.20	0.014	0.015	0.024	0.026
600-700° F	-	-	-	16.2584	276.73	205.24	-	-	-	-
700-800° F	-	-	-	6.8157	337.01	243.70	-	-	-	-
800° F	-	-	-	1.2503	404.55	286.81	-	-	-	-

*K = mole fraction vapor/mole fraction liquid.

† Includes sample #3.

Table 5. Vapor-Liquid Equilibrium at 750° F and 700 psig of Blend #3 of H-Coal Liquids from PDU Run #5 †

Compound	Vapor			Liquid			Paraffin K*	Aromatic K*
	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt	Wt Pct	Paraffin Mol Wt	Aromatic Mol Wt		
H ₂	2.161	2.016		0.02043			15.21	18.88
N ₂	1.419	28.014		0.01140			17.92	22.25
CO ₂	0.460	44.011		0.00731			9.10	11.16
H ₂ S	0.121	24.076		0			-	-
C ₁	0.099	28.011		0.00135			10.44	12.92
NH ₃	0.056	17.031		0.00095			8.48	10.90
H ₂ O	15.571	18.016		0.7270			3.08	3.82
C ₁	6.665	16.043		0.13036			7.35	9.13
C ₂	3.622	30.070		0.08747			5.96	7.40
C ₃	3.234	44.097		0.07379			6.30	7.83
C ₄	1.019	58.124		0.02505			5.84	7.29
C ₅	0.128	72.151		0.00521			3.59	4.54
C ₆	0	86.178		0.00207			-	-
C ₇	0	100.205		0.00241			-	-
< 300° F	1.271	109.6	99.3	1.105	111.4	100.7	0.17	0.21
300-400° F	5.095	150.5	124.7	1.525	148.7	123.5	0.48	0.59
400-500° F	18.995	184.1	146.1	10.569	184.6	146.5	0.26	0.32
500-600° F	25.894	227.2	173.6	23.776	229.4	175.0	0.16	0.20
600-700° F	11.896	272.9	202.8	25.084	282.7	209.1	0.07	0.09
700-765° F	2.295	330.0	239.2	-	-	-	-	-
700-800° F	-	-	-	17.507	340.3	245.8	0.02	0.02
800-900° F	-	-	-	9.064	424.3	299.4	-	-
900-975° F	-	-	-	4.350	514.0	356.6	-	-
975° F+	-	-	-	5.924	673.6	458.5	-	-

*K = mole fraction vapor/mole fraction liquid.

† Other samples were taken at these conditions but analytical data are incomplete.