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PHASE EQUILIBRIUM STUDIES

By
P. M. Mathias
F. P. Stein

September 1983

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International Coal Refining Company
Allentown, Pennsylvania

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for the

UNITED STATES DEPARTMENT OF ENERGY
Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

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Chemicals, Inc. (APCI).

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TABLE OF CONTENTS

ABSTRACT -----	2
EXECUTIVE SUMMARY -----	3
1. Introduction -----	5
2. Aqueous Systems -----	9
3. Correlation of Existing Coal-Fluid Phase-Equilibrium Data -----	32
4. New Phase-Equilibrium Data on SRC-I Coal Fluids -----	64
5. Comparison between Model and Phase-Equilibrium Data on SRC-I Coal Fluids -----	69
6. Conclusions and Recommendations -----	70
Nomenclature -----	72
Literature Cited -----	74

APPENDICES

I. Definition of SRC-I Components -----	78
II. Reasons for Selecting Peng-Robinson EOS as the Phase-Equilibrium Model -----	80
III. Definition of Local-Composition Peng-Robinson Equation of State -----	81
IV. Prediction of the Equation-of-State Binary Parameters -----	83
V. Excerpt from SRC-I Baseline Design Technical Data Book: 3.50 Three-Phase Equilibrium -----	89
Figures -----	99

ABSTRACT

A phase equilibrium model has been developed for the SRC-I process, as well as the other coal-liquefaction processes. It is applicable to both vapor/liquid and liquid/liquid equilibria; it also provides an approximate but adequate description of aqueous mixtures where the volatile electrolyte components dissociate to form ionic species.

This report completes the description of the model presented in an earlier report (Mathias and Stein, 1983a). Comparisons of the model to previously published data on coal-fluid mixtures are presented. Further, a preliminary analysis of new data on SRC-I coal fluids is presented. Finally, the current capabilities and deficiencies of the model are discussed.

EXECUTIVE SUMMARY

This report presents a description and evaluation of the phase equilibrium model developed for the SRC-I process (as well as the other coal-liquefaction processes) by the Engineering and Scientific Systems Department of Air Products and Chemicals, Inc. under subcontract to the International Coal Refining Company (ICRC). It also presents a preliminary analysis of new data on SRC-I coal fluids.

It is usual practice to treat the essentially continuous coal-fluid mixture as a set of pseudocomponents, each defined by a narrow range in normal boiling temperature. The current model characterizes each pseudocomponent by the normal boiling point, specific gravity, and a "polar parameter." A reliable procedure to predict the polar parameter has yet to be developed, but workable values have been determined for SRC-I pseudocomponents.

The phase equilibrium model is an enhanced form of the Peng-Robinson equation of state. Two enhancements have been made. The first is designed to represent the vapor pressures of all fluids, including those which are highly polar. The second is the incorporation of density-dependent local-composition theory in order to describe the complex behavior exhibited by mixtures containing highly polar substances (e.g., the liquid/liquid equilibria of water/coal-fluid mixtures).

The model also includes developments designed to describe aqueous mixtures containing volatile electrolytes, such as ammonia and carbon-dioxide. A simple reaction model has been proposed to account for the

strong mutual increase in solubility caused when both acids (e.g., carbon-dioxide) and bases (e.g., ammonia) are present in the aqueous phase.

The model has been evaluated by comparison with data from other coal-liquefaction processes. Since all coal-liquefaction processes are fundamentally similar, the comparison is appropriate. Further, the favorable comparisons obtained suggest that the model is generally applicable to coal-fluid mixtures.

ICRC is conducting a program to obtain phase equilibrium measurements to provide verification of current design conditions for the SRC-I Demonstration Plant and data for developing reliable correlations. Unfortunately, the data measurement has encountered severe operational problems which have caused long delays. Thus, only preliminary analysis and comparisons with the model have been completed. Detailed results will be presented in a forthcoming report.

1. INTRODUCTION

The Engineering and Scientific Systems Department (ESSD) of Air Products and Chemicals, Inc. (APCI) has developed a phase equilibrium model for the SRC-I process. The model is currently being used in the Post-Baseline review of the SRC-I process design.

Although the immediate application of the model is the SRC-I process, data from other coal-liquefaction processes were also used in the development and testing. Thus, the model may be considered to be generally applicable to coal-liquefaction processes.

This report contains only a brief description of the model since most of its features have been presented in a previous report (Mathias and Stein, 1983a). The only new development presented herein is with respect to aqueous systems. Here a simple model has been proposed to describe the dissociation of the volatile electrolytes (e.g., ammonia and carbon-dioxide) in water. Aqueous systems are described in Chapter 2.

The fraction of the coal-fluid stream that boils above n-pentane ($T_b > 100^\circ\text{F}$) contains components that are essentially unknown and also too numerous to be treated separately. It is accepted practice to treat this total mixture as a set of pseudocomponents, each defined by a range of normal boiling temperatures. In petroleum modeling the pseudocomponents are characterized only by the normal boiling point and specific gravity, but this is probably inadequate for the relatively complex coal fluids. Since practical procedures incorporating a more detailed and meaningful description of pseudocomponents have not yet been developed, we have

retained the simple petroleum characterization, but also employed a new parameter termed the "polar parameter" into which all the complex behavior has been lumped. The pseudocomponents employed in the simulation of the SRC-I process are defined in Appendix I.

The phase equilibrium model is an enhanced form of the Peng-Robinson (1976) equation of state; several reasons justifying this choice are presented in Appendix II. Two modifications to the model originally proposed by Peng and Robinson have been made. The first, which is relatively minor, is the extension of the temperature-dependent function designed to represent the vapor pressure of pure fluids. The original Peng-Robinson model is accurate for nonpolar but not for polar substances; the simple modification proposed overcame this problem.

The second modification to the Peng-Robinson model is the incorporation of a truncated version of the density-dependent local-composition theory proposed by Mathias and Copeman (1983). This modification enables the model to describe the complex behavior exhibited by mixtures containing highly polar substances. For example, the enhanced model provides a good description of the liquid/liquid equilibria of some systems representative of water/coal-fluid mixtures.

The equations defining the "local-composition" Peng-Robinson model (hereafter referred to as PRLC) are presented in Appendix III. In the application to the SRC-I process, the local-composition enhancements have only been invoked for pair interactions involving water. Thus, the unmodified Peng-Robinson model is employed for the other components and their mixtures. This means that the previously established, reliable and

accurate descriptions provided by the original Peng-Robinson equation of state for these mixtures are in effect here.

The binary interaction parameters (k_a , k_b , and t in Appendix III) are extremely important since the component fugacities - and, therefore, the vapor/liquid and liquid/liquid equilibrium ratios - are very sensitive to them. Thus the reliability and accuracy of the phase equilibrium model is strongly determined by the quality of the binary interaction parameters. In the case of interactions involving true, pure components (e.g., hydrogen and n-pentane) the binary parameters can, and usually are, determined by regressing binary phase equilibrium data. However, the binary constants for pairs involving the pseudocomponents generally have to be estimated from generalized correlations. The binary-parameter correlations that are currently employed are presented in Appendix IV. They are designed to provide an optimum description of most available data. But it should be noted that further tuning of these binary-parameter correlations will probably be the most effective way to improve the current model.

The above discussion together with the modifications for aqueous systems presented in Chapter II completes the description of the phase equilibrium model. The remaining chapters of this report present analysis of new data on SRC-I coal fluids and evaluation of the model by comparison with a variety of data representing phase equilibria in coal-conversion processes. Finally, the current capabilities and deficiencies of the model are summarized in the last chapter.

There is publicly available data from the other coal-liquefaction processes (e.g., SRC-II and EDS) and the phase equilibria of all coal-conversion processes are fundamentally similar. Thus the present model has been compared with selected data of interest in Chapter 3.

ICRC is conducting a program to obtain phase equilibria measurements to provide verification of current design conditions for the SRC-I Demonstration Plant and data for developing reliable correlations (Mehta et al., 1983). This part of the project is only in a preliminary stage. The current status is outlined in Chapters 4 and 5.

2.0 AQUEOUS SYSTEMS

There are several parts of the SRC-I Process where two liquid phases (an aqueous phase and a coal-liquid phase) form. This phase separation is caused mainly by the immiscibility of water and the relatively heavy coal liquids ($T_b > 100^\circ\text{F}$) and is predicted to reasonable accuracy by the model with the generalized binary constants presented in Table A-2. However, it is also of interest to describe the solubility of light components in the aqueous phase; in particular, it is important to correlate the aqueous solubilities of the volatile, weak electrolytes (e.g., ammonia and carbon-dioxide) since they are relatively high.

The local-composition Peng-Robinson (PRLC) equation of state is directly applicable to the aqueous solubility of "inert" components like hydrogen and methane, since it has been designed to describe high liquid-phase nonideality. However, the weak electrolytes introduce a complication beyond the capabilities of the PRLC model since they react chemically to produce ionic species. There are several models (e.g., Edwards et al., 1978a, Beutier and Renon, 1978, and Chen et al., 1982) that have been designed specifically for the weak-electrolyte/water system, but none of these are applicable to the more important coal-fluid phase equilibria. Thus, we developed a simplified extension to the PRLC model that has incorporated only the dominant features of the weak-electrolyte/water system.

Section 2.1 describes the application of the unmodified PRLC model to binary mixtures of light components (including weak electrolytes) with water. The unmodified model is applicable to binary mixtures of weak

electrolytes and water since the chemical reaction may be safely neglected except in very dilute solutions; for example, Edwards et al. (1978b) have found that in the ammonia/water binary, chemical-reaction effects are only important where the mole fraction of ammonia is less than 10^{-3} . However, the chemical-reaction effects become important in multicomponent solutions containing both acids and bases. The simplified model, which is described in Section 2.2, assumes that only the acid-base combinations of reactions need to be accounted for. Section 2.3 applies the model to a problem of interest and comments on its accuracy.

2.1 Binary Mixtures

The binary parameters of the PRLC equation of state were regressed to fit experimental data for the light-component/water mixtures of interest. In general, the model is capable of correlating the binaries to sufficient accuracy; the average error in K-values is generally within 10%. Table 2.1 presents the final values of the binary parameters for the species employed in the SRC-I simulation and Table 2.2 describes the data used in the regression.

Figure 2.1 presents an example of how well the PRLC model correlates the data. It is evident that the model provides an accurate description of the composition of all three co-existing phases over the temperature range of the data. It should also be noted that the model correctly indicates that the critical end-point (at which the propane-rich liquid merges with the vapor) is slightly above 200°F; the experimental critical end-point is 205.7°F.

As mentioned above, the unmodified PRLC model is applicable to weak-electrolyte/water binaries since the chemical-reaction effects are only important for extremely dilute solutions. Thus, it is defensible to apply the unmodified model to the aqueous binaries with NH_3 , CO_2 , and H_2S . However, HCl is a strong electrolyte and therefore is significantly dissociated even at the concentrations of interest. Surprisingly, the PRLC model with the parameters listed in Table 2.1, provides an excellent fit of the data. Figures 2.2 and 2.3 present a comparison of the calculated results to the data of Harned and Owen (1958). In light of the good fit, this mode of description of the $\text{HCl}/\text{H}_2\text{O}$ pair was retained. It should be mentioned that an accurate description of the HCl solubility is not critical since any reasonable model predicts that practically all the HCl dissolves in the aqueous phase at the conditions of interest.

2.2 Volatile-Electrolyte/Water Systems

The volatile electrolytes in the SRC-I process are HCl , NH_3 , CO_2 , and H_2S . These undergo the following reactions. First dissociations of the electrolytes:

Second dissociations of CO_2 and H_2S :

Carbamate reaction:

Dissociation of water:

The objective of the simplified model proposed here is to include only the dominant reactions. As mentioned before, the first dissociation (reactions I-IV) may be safely neglected (or effectively described by the PRLC model in the case of HCl) for binaries with water. The second dissociations of CO_2 and H_2S (reactions V and VI) have extremely low equilibrium constants and thus may also be neglected in the case of binaries. The carbamate reaction (VII) is important and should be included in any reasonable model. The dissociation of water (reaction VIII) has an extremely low dissociation constant. It is important since H^+ and OH^- will have a strong tendency to form H_2O and thus acids and bases cause a significant mutual increase in dissociation -- the acid-base effect.

The simplified model proposed herein only includes the acid-base combinations of reactions and the carbamate reaction as shown below. The acid-base reaction between HCl and NH_3 is obtained by combining reactions I, II, and VIII:

Similarly, the acid-base reaction between CO_2 and NH_3 is described by a combination of reactions II, III, and VIII:

The analysis of data for the $\text{NH}_3/\text{HS}/\text{H}_2\text{O}$ system indicated that two acid-base reactions needed to be employed: the combination between reactions II, IV, and VIII, and between II, VI, and VIII:

The carbamate reaction (VII) must also be included:

Reactions a, b, c, d, and e comprise the proposed simplified model. Reaction a is assumed to go to completion but the extent of reactions b, c, d, and e are determined by equilibrium constants. Thus, the extent of reaction b is given by,

$$K'_b = \frac{a_{\text{NH}_4^+} a_{\text{HCO}_3^-}}{a_{\text{NH}_3} a_{\text{CO}_2} a_{\text{H}_2\text{O}}} \quad (1)$$

The activities "a" in equation 1 are equal to the product of the mole fraction and the activity coefficient. We have chosen a simpler form of the chemical equilibrium expression as follows:

$$K_b = K'_b \left[\frac{\gamma_{\text{NH}_3} \gamma_{\text{CO}_2} \gamma_{\text{H}_2\text{O}}}{\gamma_{\text{NH}_4^+} \gamma_{\text{HCO}_3^-}} \right] = \frac{x_{\text{NH}_4} x_{\text{HCO}_3^-}}{x_{\text{NH}_3} x_{\text{CO}_2} x_{\text{H}_2\text{O}}} \quad (2)$$

Equation 2 assumes that the equilibrium constant may be written in terms of the mole fractions of the species involved. This is equivalent to the assumption that the product of the activity coefficients is a constant dependent only on temperature over the range of concentrations of interest.

The equilibrium constants K_b , K_c , K_d , and K_e were empirically determined as simple functions of temperature to obtain an optimum fit of experimental data of interest.

$$K_b = \exp \left[34.592 - 0.0831 T \right] \quad (3)$$

$$K_c = \exp \left[19.024 - 0.04267 T \right] \quad (4)$$

$$K_d = \exp \left[18.504 - 0.05231 T \right] \quad (5)$$

$$K_e = \exp \left[3.94 \right] \quad (6)$$

In equations 3-6, the temperature is in Kelvin.

The above model for volatile electrolytes has been combined with the PRLC model. Modifications to the PRLC model occur only for aqueous solution containing both ammonia (base) and at least one of the acidic electrolytes (CO_2 , H_2S , HCl). In this case fugacity coefficients are first calculated by the PRLC model. Then the extents of reactions are computed using the equilibrium expressions described above and the effect on component fugacity coefficients determined by using the apparent

concentration approach (Copeman and Stein, 1982). The effect of the ionic species on the liquid-phase nonideality has been neglected.

It should be noted that the proposed model for weak-electrolyte/water systems is rather simple since it ignores several secondary, but nonetheless important, effects. It is thus expected that all the inadequacies of the model are lumped into the reaction equilibrium constants.

Tables 2.3 and 2.4 present a comparison of the proposed model with experimental data for the $\text{NH}_3/\text{CO}_2/\text{H}_2\text{O}$ system. While the agreement with experimental data is not as good as for those models designed specifically for electrolyte systems (e.g., Edwards et al., 1978a, Beutier and Renon, 1978 and Chen et al., 1982) it does capture the essential features of the behavior. Figure 2.4 presents a comparison of calculated partial pressures at 100°C with the data of Pawlikowski et al. (1982). In the applications of interest, the ammonia partial pressure is not of great interest since most of it dissolves in the aqueous phase. In the case of CO_2 , the partial pressure is very small at low concentrations since essentially all of it reacts with ammonia. However, there is a sharp increase in CO_2 partial pressure as the stoichiometric amount is approached. The proposed model provides a good description of this feature.

Tables 2.5, 2.6 and 2.7 present a similar comparison of the proposed model with experimental data for the $\text{NH}_3/\text{H}_2\text{S}/\text{H}_2\text{O}$ ternary. Again, the conclusion is that the model provides a reasonable description of the observed behavior.

2.3 Application of the Aqueous System Model

The primary applications intended for this model in the SRC-I Process are the 3-phase decanters. Unfortunately, there are no experimental data at these conditions to evaluate the model. Thus it is of interest to compare the present method with the method employed in the SRC-I Baseline Design, which employed two simulators: REFINE (CHEMSHARE) and the TIDES program developed at the University of California, Berkeley (Pawlikowski, 1981).

The procedure adopted in the Baseline Design has been described in the SRC-I Baseline Design Technical Data Book (ICRC, 1984). For convenience, the relevant portion of the Data Book has been presented in this report as Appendix V.

Some important differences between the two methods should first be pointed out. The present approach distributes all components among the three phases, whereas the Data Book method was forced to assume that some components are completely insoluble in the aqueous phase. The current model permits all calculations to be done automatically within a single process simulator, whereas the old method required the manual meshing of results from two computer programs (REFINE and TIDES) -- a tedious and time-consuming task.

Tables 2.8-2.13 present the results of the calculations with the current model. These predict the composition of the streams leaving separators V-12405, V-12408, and V-12502, each at two temperatures,

135°F and 110°F, respectively. Tables 2.8-2.13 are intended to duplicate Tables 3.501-506 of the Data Book, respectively (see Appendix V).

The following comments indicate the major similarities and differences between the two methods:

- As a first approximation, the two methods are equal. Only the electrolyte components are significantly soluble in the aqueous phase; essentially all the hydrogen-chloride and most of the ammonia are dissolved in the water; the aqueous solubilities of hydrogen-sulfide and carbon-dioxide are relatively high.
- The aqueous solubilities of hydrogen-sulfide and carbon-dioxide compare reasonably well at the low pressures (16 and 80 psia), but show relatively high differences at the high pressure (1920 psia). However, it should be noted that TIDES is not intended for high-pressure applications. Further, the current method predicts that the ratio of the solubility of carbon-dioxide to hydrogen-sulfide is higher than indicated by TIDES. These differences can only be resolved by experimental measurements.
- The two methods predict similar solubilities of water in the oil phase, with the present method always slightly higher. Both models are probably low since they do not take heteroatomic effects into account.

In conclusion, the present model is of adequate accuracy to be used for the description of the 3-phase decanters. Its primary advantage is that it permits the entire simulation to be done with a single simulator, without necessitating the tedious and time-consuming task of manually meshing two computer programs. However, it should be noted that the proposed model makes several simplifying assumptions which might not be valid.

Table 2.1

Binary Parameters for Light Components(1) with Water(2)

Light Component(1)	k _{a21}	k _{b21}	t ₁₂	t ₂₁
Hydrogen	-3.0327	-0.0069	0.0413	0
Nitrogen	0.6	-0.4010	0.7222	0
Argon	0.6	-0.3719	0.5753	0
Ammonia	-0.3612	-0.1750	0.0730	0.1973
Hydrogen-chloride	0.0151	0.1641	0.6256	0
Carbon-monoxide	0.6	-0.2101	0.5506	0
Carbon-dioxide	0.2458	-0.1629	0.3727	0.6109
Hydrogen-sulfide	0.1	-0.2718	0.3568	0.6187
Methane	0.5200	-0.3830	0.7187	0
Ethane	0.6237	-0.0899	0.6655	0
Propane*	0.6069	-0.0914	0.9374	0.1331
n-Butane*	0.5682	0	0.9855	0
n-Pentane*	0.5903	0	1.2658	0

* LLE data also used in regression.

Table 2.2

Experimental Data Used to Regress Binary
Parameters for Aqueous Systems

Other Component	No. of Data	Temp. Range °F	Max. Press. psia	Reference
Hydrogen	20	32-212	14696	Deming and Shupe (1932)
Nitrogen	18	122-466	4409	Saddington and Krase (1934)
Argon	6	68-158	15	Wilhelm et al. (1977)
Ammonia	14	212-302	354	Pawlikowski et al. (1982)
Hydrogen-Chloride	14	77	10	Harned and Owen (1958)
Carbon-Monoxide	6	68-158	15	Wilhelm et al. (1977)
Carbon-Dioxide	48	32-212	2939	Munjai (1966); Wiebe and Gaddy (1939)
Hydrogen Sulfide	35	100-340	1750	Selleck et al. (1952)
Methane	16	122-600	2450	Gillespie and Wilson (1982)
Ethane	25	100-340	5322	Culberson and McKetta (1950)
Propane	12	42-200	602	Kobayashi and Katz (1953)
n-Butane	4	100-280	591	Reamer et al. (1952)
n-Pentane	3	101-302	308	Gillespie and Wilson (1982)

Table 2.3

Comparison of Calculated Partial Pressures of

NH₃ and CO₂ to Experimental Results by

Otsuka et al. (1960) for NH₃/CO/H₂O

T, °C	m NH ₃	m CO ₂	Partial Pres. NH ₃ , mmHg		Partial Pres. CO ₂ , mmHg	
			Exp.	Calc.	Exp.	Calc.
20	1.23	0.804	1.4	4.7	16.8	1.9
	4.59	0.551	48.4	62.9	0.1	0.03
	11.33	2.034	120.	150.	0.2	0.1
40	2.17	1.89	3.4	5.0	304.	236.
	9.13	1.72	208.	256.	1.2	0.9
	15.28	3.67	322.	369.	1.1	2.0
60	1.99	1.39	22.8	26.4	442.	265.
	7.51	2.48	364.	274.	14.9	29.9
	11.32	3.87	485.	371.	20.0	37.2
80	3.15	1.36	109.	172.	256.	281.
	4.82	0.70	408.	531.	17.5	12.5
	8.66	0.663	802.	1083.	19.0	3.4
100	2.90	1.450	157.	227.	1211.	2481.
	4.29	0.905	540.	687.	146.	176.
	7.37	1.099	1022.	1310.	107.	82.

Table 2.4
Comparison of Calculated Pressures to
Experimental Results by Pawlikowski et al.
(1982) for NH₃/CO₂/H₂O

T, °C	m NH 3	m CO 2	Total Pressure, bars		P NH 3, bars		P CO 2, bars	
			Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
100	9.57	5.44	16.7	16.0	0.24	0.49	15.7	14.6
	9.57	5.14	11.4	12.4	0.37	0.55	10.5	10.9
	9.57	4.64	6.5	8.1	0.56	0.68	5.17	6.53
	9.57	3.61	4.1	4.0	1.11	1.08	1.52	2.04
	3.12	2.00	17.9	11.2	0.12	0.21	16.7	10.0
	3.12	1.66	9.28	5.8	0.19	0.29	8.37	4.54
	3.12	0.978	2.90	2.15	0.42	0.54	1.22	0.65
	3.12	0.851	2.23	1.98	0.78	0.59	0.50	0.42
150	8.36	2.20	34.4	30.2	4.73	4.59	24.1	20.9
	7.38	1.49	27.3	20.1	4.12	4.54	19.4	11.0
	2.62	1.24	34.7	48.7	0.82	1.52	30.5	41.7
	5.10	1.38	32.1	27.4	1.76	3.05	28.2	19.5
	5.10	1.02	19.4	17.8	2.91	3.31	14.3	9.81
	4.82	0.560	14.7	11.0	3.03	3.59	8.41	2.85
	4.29	0.315	9.50	9.03	3.91	3.45	2.06	1.02
	2.78	1.10	33.8	37.6	1.13	1.65	29.8	30.8
	2.79	0.709	22.8	19.0	1.02	1.77	18.5	12.3
	2.74	0.413	14.5	10.7	1.35	2.02	9.08	4.00

Table 2.5

Comparison Between Calculated and Experimental (Leyko and
Piatkiewicz, 1964) Results for Pressure Over Aqueous Solutions
Containing 7.34 Moles NH_3 /Kg H_2O and 2.30 Moles H_2S /Kg H_2O

T, °C	Total Pres., mmHg		Partial Pres. NH_3 , mmHg		Partial Pres. H_2S , mmHg	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
80	1216	1133	722	560	266	267
90	1725	1673	996	768	398	449
100	2356	2415	1262	1031	570	719
110	3238	3412	1558	1355	889	1109

Table 2.6

Comparison of Calculated Partial Pressures of NH_3 And H_2S to

Experimental Results by Miles and Wilson (1975) for
 $\text{NH}_3/\text{H}_2\text{S}/\text{H}_2\text{O}$ at 80°C .

m NH 3	m H S 2	Partial Pres. NH ₃ , mmHg		Partial Pres. H S, mmHg	
		Exp.	Calc.	Exp.	Calc.
2.332	1.151	136	122	319	461
5.112	1.143	575	474	94.8	84
5.538	5.305	72.6	83	12140	6490
9.245	7.935	209	170	9506	4567
10.201	5.983	597	392	1916	1552
22.627	5.561	2285	1778	241	186

Table 2.7

Comparison of Calculated Partial Pressures of NH_3 and

H_2S to Experimental Results by Leyko (1959) for

$\text{NH}_3/\text{H}_2\text{S}/\text{H}_2\text{O}$

T, °C	m NH 3	m H S 2	Partial Pres. NH ₃ , mmHg		Partial Pres. H S, mmHg	
			Exp.	Calc.	Exp.	Calc.
20	2.25	1.07	11	5.8	7.5	16
	4.91	2.34	21	14	23	33
	9.36	4.46	44	27	38	46
	15.66	7.46	80	45	62	46
30	9.36	4.46	79	48	74	83
	15.65	7.45	129	78	124	82
40	2.25	1.07	27	19	31	54
	4.91	2.34	58	43	93	106
	9.35	4.48	119	81	137	143
	15.65	7.45	215	131	238	140
50	2.25	1.07	45	32	60	94
	4.91	2.34	89	71	130	180
	9.35	4.45	190	134	235	234
45	15.65	7.45	255	168	291	181

Table 2.8

Equilibrium Phase Distribution of Vessel V-12405
Calculated Using the PRLC Model

Pressure = 1920 psia; temperature = 135°F

Components	Vapor Phase (lbmol/hr)	Hydrocarbon Phase (lbmol/hr)	Aqueous Phase (lbmol/hr)
H2O	26.7110	0.7920	3613.1759
H2	8368.3146	13.7363	5.8619
N2	316.0107	0.5280	0.0616
AR	53.6190	0.2601	0.0209
NH3	1.0217	0.0966	95.1811
HCL	3.0493-04	1.1606-05	4.2996
CO	418.1490	0.7356	0.1159
CO2	56.6223	0.9212	35.9563
H2S	165.3897	9.6912	44.8192
CH4	917.0552	6.2611	0.2850
C2H6	227.9330	7.6141	0.0533
C3H8	101.4173	9.1705	0.0124
C4H10	41.2232	9.9730	0.0039
C5H12	15.0740	8.9257	3.9814-04
TBP125	20.7203	16.0790	0.0010
TBP175	8.6000	15.8996	6.7775-04
TBP225	4.1638	17.8362	2.9139-04
TBP275	1.3399	15.2602	1.2024-04
TBP325	0.3715	12.6287	6.0015-05
TBP375	0.0739	9.3260	2.0793-04
TBP425	0.0344	14.2654	4.3678-04
TBP475	0.0227	37.8779	1.1999-04
TBP525	0.0104	37.8904	3.0686-05
TBP575	4.0740-04	5.2997	1.7486-06
TBP625	1.6516-04	5.2999	3.3493-07
TBP675	3.4746-06	0.4000	1.6674-08
TBP725	8.9924-07	0.4000	5.7295-09
TBP775	1.5858-08	0.0300	4.2576-11
Total flow:			
lbmol/hr	1.0744+04	257.1996	3799.8509
lb/hr	8.0726+04	2.7779+04	7.0004+04
cuft/hr	3.7846+04	554.1595	1180.5914

Table 2.9

Equilibrium Phase Distribution of Vessel V-12405
Calculated Using the PRLC Model

Pressure = 1920 psia; temperature = 110°F

Components	Vapor Phase (lbmol/hr)	Hydrocarbon Phase (lbmol/hr)	Aqueous Phase (lbmol/hr)
H2O	14.6196	0.5035	3625.6006
H2	8367.2118	14.8573	5.8099
N2	315.9451	0.5931	0.0609
AR	53.5769	0.3025	0.0204
NH3	0.3074	0.0411	95.9519
HCL	8.3239-05	4.1917-06	4.2999
CO	418.0591	0.8297	0.1100
CO2	46.2948	0.9726	46.2327
H2S	166.0552	13.1843	40.6603
CH4	915.8834	7.4317	0.2825
C2H6	225.6700	9.8804	0.0490
C3H8	98.1838	12.4044	0.0115
C4H10	37.6577	13.5389	0.0033
C5H12	12.4081	11.5915	2.9605-04
TBP125	16.6472	20.1520	7.2252-04
TBP175	6.0662	18.4334	4.0164-04
TBP225	2.6172	19.3827	1.5419-04
TBP275	0.7464	15.8536	5.8733-05
TBP325	0.1854	12.8145	2.7869-05
TBP375	0.0328	9.3671	1.0641-04
TBP425	0.0140	14.2858	2.3578-04
TBP475	0.0081	37.8920	6.0062-05
TBP525	0.0037	37.8964	1.4070-05
TBP575	1.3582-04	5.2998	7.8017-07
TBP625	5.4220-05	5.2999	1.3403-07
TBP675	1.0608-06	0.4000	6.5274-09
TBP725	2.5365-07	0.4000	2.1100-09
TBP775	4.1001-09	0.0300	1.3586-11
Total flow:			
lbmol/hr	1.0698+04	283.6392	3819.0954
lb/hr	7.8635+04	2.9323+04	7.0551+04
cuft/hr	3.6137+04	587.2135	1170.5187

Table 2.10

Equilibrium Phase Distribution of Vessel V-12408
Calculated Using the PRLC Model

Pressure = 80 psia; temperature = 135°F

Components	Vapor Phase (lbmol/hr)	Hydrocarbon Phase (lbmol/hr)	Aqueous Phase (lbmol/hr)
H2O	79.3612	0.3115	755.4151
H2	1243.9457	0.1312	0.0299
N2	363.0557	0.0421	0.0041
AR	25.6904	0.0091	5.3052-04
NH3	8.2353	0.0677	12.2967
HCL	5.9798-04	1.9078-06	0.9993
CO	309.0593	0.0379	0.0044
CO2	18.9512	0.0245	2.8242
H2S	48.7440	0.2455	4.0106
CH4	158.0146	0.0832	0.0030
C2H6	80.3598	0.2392	0.0012
C3H8	36.8638	0.3359	4.1180-04
C4H10	27.0536	0.7462	2.7497-04
C5H12	17.9274	1.3725	6.7884-05
TBP125	32.6776	4.2222	2.9257-04
TBP175	23.4019	7.8977	3.5446-04
TBP225	15.9320	14.0675	2.6444-04
TBP275	5.6719	15.0278	1.4591-04
TBP325	1.2815	11.4182	7.0212-05
TBP375	0.1775	6.3221	1.8584-04
TBP425	0.0485	6.4510	2.9486-04
TBP475	0.0119	7.9879	4.6047-05
TBP525	0.0047	7.9951	1.3724-05
TBP575	4.1566-05	0.2999	2.4302-07
TBP625	1.4331-05	0.2999	5.3421-08
TBP675	1.0345-07	0.0089	1.1651-09
Total flow:			
lbmol/hr	2496.4711	85.6458	775.5919
lb/hr	4.2849+04	1.0018+04	1.4116+04
cuft/hr	1.9871+05	194.8812	236.6995

Table 2.11

Equilibrium Phase Distribution of Vessel V-12408
Calculated Using the PRLC Model

Pressure = 80 psia; temperature = 110°F

Components	Vapor Phase (lbmol/hr)	Hydrocarbon Phase (lbmol/hr)	Aqueous Phase (lbmol/hr)
H2O	38.4143	0.2212	796.4744
H2	1243.8947	0.1660	0.0332
N2	363.0378	0.0561	0.0042
AR	25.6866	0.0127	5.5190-04
NH3	3.9075	0.0538	16.6387
HCL	1.8396-04	9.2297-07	0.9998
CO	309.0432	0.0508	0.0045
CO2	16.4677	0.0325	5.2996
H2S	47.2938	0.3830	5.3230
CH4	157.9780	0.1180	0.0031
C2H6	80.2204	0.3778	0.0012
C3H8	36.6289	0.5704	4.0855-04
C4H10	26.4556	1.3439	2.5849-04
C5H12	16.7534	2.5464	5.8490-05
TBP125	29.2055	7.6941	2.3601-04
TBP175	18.0899	13.2097	2.5199-04
TBP225	9.8786	20.1213	1.5075-04
TBP275	2.6963	18.0037	6.6726-05
TBP325	0.4933	12.2067	2.7854-05
TBP375	0.0585	6.4414	7.9182-05
TBP425	0.0144	6.4855	1.2866-04
TBP475	0.0030	7.9970	1.7867-05
TBP525	0.0011	7.9988	4.7076-06
TBP575	9.4067-06	0.2999	7.9025-08
TBP625	3.1356-06	0.2999	1.5124-08
TBP675	2.0785-08	0.0090	3.1876-10
Total flow:			
lbmol/hr	2426.2238	106.7008	824.7843
lb/hr	3.9976+04	1.1925+04	1.5084+04
cuft/hr	1.8507+05	234.5737	249.4664

Table 2.12

Equilibrium Phase Distribution of Vessel V-12502
Calculated Using the PRLC Model

Pressure = 16 psia; temperature = 135°F

Components	Vapor Phase (lbmol/hr)	Hydrocarbon Phase (lbmol/hr)	Aqueous Phase (lbmol/hr)
H2O	13.0898	1.2582	245.4479
H2	15.7605	0.0387	7.5308-04
N2	9.4731	0.0266	2.1865-04
AR	0.8923	0.0076	3.7147-05
NH3	2.1289	0.4243	4.3465
HCL	1.8459-05	1.4238-06	0.0599
CO	7.5772	0.0225	2.2136-04
CO2	2.1594	0.0675	1.2729
H2S	2.4465	0.2985	0.9548
CH4	3.1598	0.0400	1.2344-04
C2H6	4.1038	0.2960	1.3119-04
C3H8	2.7820	0.6179	6.5201-05
C4H10	3.9370	2.6629	8.5155-05
C5H12	3.3232	6.2767	2.7349-05
TBP125	6.3400	20.3600	1.2464-04
TBP175	3.8513	32.4488	1.2937-04
TBP225	2.1239	47.0765	7.9367-05
TBP275	0.7851	52.5154	4.6105-05
TBP325	0.2570	58.1436	3.2551-05
TBP375	0.0680	61.7325	1.6453-04
TBP425	0.0168	57.4835	2.3930-04
TBP475	2.5926-05	0.4499	2.4095-07
TBP525	1.0189-05	0.4499	7.2759-08
Total flow:			
lbmol/hr	84.2766	342.6985	252.0848
lb/hr	2931.9309	3.8711+04	4586.6489
cuft/hr	3.3401+04	758.5930	76.9193

Table 2.13

Equilibrium Phase Distribution of Vessel V-12502
Calculated Using the PRLC Model

Pressure = 16 psia; temperature = 110°F

Components	Vapor Phase (lbmol/hr)	Hydrocarbon Phase (lbmol/hr)	Aqueous Phase (lbmol/hr)
H2O	4.9052	0.7739	254.1192
H2	15.7481	0.0512	0.0010
N2	9.4648	0.0350	2.8130-04
AR	0.8891	0.0107	4.8336-05
NH3	0.8271	0.2964	5.7763
HCL	4.6168-06	5.9012-07	0.0599
CO	7.5700	0.0298	2.7913-04
CO2	1.3215	0.0653	2.1131
H2S	1.9532	0.4055	1.3413
CH4	3.1422	0.0577	1.6084-04
C2H6	3.9348	0.4650	1.5727-04
C3H8	2.4400	0.9599	7.1252-05
C4H10	2.8799	3.7200	7.4637-05
C5H12	1.9680	7.6319	1.8524-05
TBP125	3.4186	23.2814	7.5509-05
TBP175	1.8030	34.4969	6.9362-05
TBP225	0.8970	48.3029	3.8304-05
TBP275	0.2963	53.0037	2.0784-05
TBP325	0.0865	58.3135	1.4013-05
TBP375	0.0200	61.7799	7.7802-05
TBP425	0.0044	57.4954	1.1562-04
TBP475	5.8578-06	0.4499	1.0324-07
TBP525	2.2860-06	0.4499	2.7569-08
Total flow:			
lbmol/hr	63.5704	352.0769	263.4125
lb/hr	1917.7094	3.9494+04	4817.3150
cuft/hr	2.4184+04	766.6526	79.6910

3.0 CORRELATION OF EXISTING COAL-FLUID PHASE-EQUILIBRIUM DATA

This chapter compares the PRLC model with 3 separate sets of coal-fluid phase-equilibria data:

- Flash results from the Wilsonville pilot plant
- Vapor-Liquid Equilibrium measurements for the SRC-II process.
- Volatilities of EDS coal liquids at high temperatures and pressures.

Direct coal-liquefaction processes are fundamentally similar and thus the present model should be applicable to coal-fluids from other processes.

3.1 Comparison to Flash Results with Wilsonville Data

This section compares the present phase-equilibrium model to experimental data measured for a typical run of the Gas Recovery Area of the Wilsonville pilot plant: material balance run no. 118 (Southern Company Services, Inc., 1977). In the course of the Baseline Design of the SRC-I process, the CHEMSHARE REFINER simulator was compared to the same data (SRC-I Baseline Design Technical Data Book, ICRC, 1983). Thus, this section presents a side-by-side comparison of the two methods (CHEMSHARE and present PRLC model) with the experimental data.

A block diagram of the relevant portion of the Gas Recovery Area of the Wilsonville pilot plant is presented in Figure 3.1. The components and pseudocomponents employed for the PRLC simulation together with their characterization and feed rate into the high-pressure separator V-103 are presented in Table 3.1. The specific gravities and polar parameters of the pseudocomponents were obtained from Figures A-1 and A-2, respectively.

Not all intermediate and outlet streams have been experimentally analyzed for run no. 118 MB. However, a few experimental measurements are available to assess the accuracy and reliability of some aspects of the thermodynamic properties predicted by the two simulation programs.

Table 3.2 presents a comparison of the Wilsonville vapor analyses and the REFINE and PRLC simulation results for vessels V-104, V-105, and V-110. This table also shows the comparison of the calculated and measured flow rates of the gas streams from vessels V-104 and V-105. Inspection of these results show fairly good agreement between measured qualities and the values computed by both simulators.

A comparison of the calculated and measured liquid flow rates from V-105 is shown in Table 3.3. The PRLC simulation provides better agreement with the measured flow rate of distillate oil than REFINE. The specific gravity of the distillate oil calculated by the two simulators is in close agreement with each other, but slightly different from the value measured at Wilsonville. The two calculated flow rates of water are again in good agreement, but significantly higher than the value measured at Wilsonville; it is likely that measured water flow rate is low.

A comparison of the Wilsonville GC simulated distillations for V-105 distillate oil and the V-110 liquid stream with the REFINE and PRLC predicted TBP curves for these streams are presented in Figures 3.2 and 3.3, respectively. The two predicted TBP curves are virtually coincident and show good agreement with the measured distillation curves.

The above comparisons indicate that both simulators provide a reasonably good description of several important separations in the Wilsonville Gas Recovery Area. But it should be noted that these comparisons do not provide a sensitive test of many of the important aspects of a coal-conversion model; for example, the high temperature and pressure solubility of light components in coal liquids and volatility of coal liquids.

In this regard it is useful to compare the K-values predicted by the two simulators for the high-pressure separator V-103. The comparisons are presented in Table 3.4. The PRLC K-value for water is significantly higher than that predicted by CHEMSHARE, but there is no experimental data to determine which value is more accurate. In the case of hydrogen the PRLC K-value is higher than that of CHEMSHARE by about 27%. We expect that the PRLC value is more accurate. CHEMSHARE predicts extremely low K-values for nitrogen and carbon-monoxide; the PRLC predictions are again judged to be more accurate since nitrogen and carbon-monoxide are certainly more volatile than carbon-dioxide. The predictions for the rest of the components are in reasonably good agreement.

In conclusion, the comparisons with the Wilsonville data indicate that both simulators are adequate for the aspects tested, but the tests are insensitive to other important properties required of a coal-conversion phase-equilibrium model.

3.2 Comparison to Vapor-Liquid Equilibrium Measurements for the SRC-II Process.

The Pittsburgh & Midway Coal Mining Company under contract with the Department of Energy conducted a series of vapor/liquid equilibrium studies in support of the SRC-II project. The results of measurements to obtain vapor/liquid equilibrium data at conditions simulating those which occur in the gas/liquid separation step of the SRC-II coal-liquefaction process have been reported by Henry (1980). This section compares the predictions of the present model to this data.

In the experimental measurements reported by Henry, 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 analysis of the resulting vapor and liquid phases were made in order to calculate the 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 ranging from 400 to 700°F while the atmospheric flash conditions were simulated with pressures of 200 and 125 psig and temperatures of 500 to 650°F. Attempts to obtain higher temperatures were unsuccessful mainly due to thermal decomposition of the coal-liquid feed. In the experiments in

which water was present, measurements could not be made above 550°F because the critical solution end point was approached making it difficult to maintain a liquid phase in the separator.

Two coal liquids were prepared whose composition approximated the fluids in the high-pressure and low-pressure sections of the SRC-II process. Each of the two coal liquids was characterized by dividing it into 100°F boiling fractions and determining the specific gravity and molecular weight of each fraction. The results are presented in Table 3.5.

While the distribution of the coal liquids presented in Table 3.5 was obtained by true boiling point (TBP) distillation, the analysis during the equilibrium experiment required for the K-values of the coal liquids was done by gas chromatography (termed simulated distillation). This was necessary since the quantity of coal liquids collected in each run was insufficient for a true boiling point distillation. A comparison of the results of the simulated distillation with those obtained by true boiling and distillation is given in Table 3.6. It can be seen that the results are not identical; in particular, the heavy ends are quite different. Henry (1980) explains that the difference arises because the heavy ends are retained on the gas chromatograph column and are, therefore, not accounted for in determining the distribution.

Due to this difference, two computer calculations have been made for comparison with each experiment: the first using the true boiling point distribution (Table 3.5) and the second the GC simulated distillation (Table 3.6). It will be seen that the calculated K-values are relatively

insensitive to the feed composition of the coal liquids. But it should be noted that inaccuracies in analyzing the equilibrium vapor and liquid will directly affect the K-values reported by Henry (1980). Thus, the K-values reported for the heavier fractions are likely to be relatively inaccurate.

Tables 3.7 and 3.8 present the calculated equilibrium K-values for the low-pressure experiments using the true boiling point and GC simulated distillations, respectively, to describe the coal-fluid feed distribution. Inspection of the two tables indicates that there is virtually no difference in the calculated K-values; the maximum difference is 4% (methane at 200 psig and 650°F), which is within the experimental accuracy. Thus, only the calculated results with the TBP coal-fluid distribution are presented graphically. Figures 3.4 and 3.5 show graphical comparisons of the calculated results to the data of Henry (1980) at 125 and 200 psig, respectively.

A cursory examination of Figures 3.4 and 3.5 indicates that the calculated and experimental K-values are in reasonably good agreement. Before a detailed comparison is made some comments are in order. A phase-equilibrium model, especially one that is equation-of-state based, is much better at predicting trends than absolute values. Thus, for example, the present model correctly predicts that the isobaric K-values of hydrogen and methane decrease with increasing temperature, whereas the heavier components show the opposite trend. Further, the temperature derivatives are expected to be relatively accurate. Also, the ratios of the isothermal K-values are correctly predicted to be approximately inversely proportional to the absolute pressure, which is a good approximation at low pressures. (In the present case, raising the pressure from 125 psig to

200 psig decreases the K-values by a factor of about 1.5.) On the other hand, experimental measurements are made independently and thus the correct trends are not ensured. Therefore the detailed comparison provides an opportunity to assess the internal consistency and hence the precision and accuracy of the experimental data.

Figures 3.4 and 3.5 indicate that the calculated K-values for hydrogen and methane are too low. However, the experimental data at 125 psig incorrectly shows that the K-values for these components increase with increasing temperature, and thus one or both sets of data are in error. But the fact that the calculated K-values of hydrogen and methane are consistently low suggests that the low-pressure model predictions for these components are too small, probably by about 20%.

The fraction C_2-C_7 is a rather large fraction to be considered as a single pseudocomponent. It has somewhat arbitrarily been assumed that the pseudocomponent boils at 200°F but the results are obviously sensitive to this choice. The comparisons indicate that the calculated value is too high. But note that the experimental K-values decrease by too large a factor in going from 125 psig to 200 psig.

Similar analyses may be made for the heavier fractions and further minor inconsistencies pointed out in the experimental data. Considering all this, the calculated K-values for the heavier fractions are judged to be in good agreement with the experimental data.

The calculated results for the high-pressure flashes without water are presented in Tables 3.9 and 3.10. Comparison of these two tables shows

that the calculated values are insensitive to the coal-fluid distribution at low temperatures. The sensitivity increases at the high temperature, but is still quite small (for hydrogen at 700°F and 100 cc/hr coal-fluid feed rate the difference is about 12%). Again, only the calculated results using the TBP coal-fluid distribution are compared graphically with the experimental data (in Figures 3.6 and 3.7).

The PRLC model predicts that in going from the high flow rate of coal liquids (100 cc/hr) to the low flow rate (25 cc/hr) the K-values of hydrogen and methane increase whereas the K-values of the other components decrease. This is consistent with the experimental data reported by Henry (1980).

Regarding the K-value of hydrogen, Figure 3.6 indicates that the calculated value is accurate, but Figure 3.7 suggests that the calculated value is high. We believe that the PRLC model is accurate in predicting the trend from the 100 cc/hr to the 25 cc/hr flow rate and thus the experimental data at one of the flow rates is likely to be inaccurate.

Comparison of the temperature variation in each of Figures 3.6 and 3.7 with the variation between the figures leads to the conclusion that the K-values for all the other components are in satisfactory agreement with the data.

The calculated results for the high-pressure flashes with water are presented in Tables 3.11 and 3.12. Note that K-values of all components are shown in the water phase. However, these are probably of little practical value since the total predicted concentration of the hydrocarbons and hydrogen in the aqueous phase varies from 0.12 mole % at 400°F to .58 mole % at 550°F. Again, the coal-fluid distribution causes a relatively small change in the calculated K-values but the effect increases with temperature.

The calculated results (TBP coal-distribution) are compared with experimental data for the K-values between the vapor and the hydrocarbon phase in Figure 3.8. The experimental K-values for hydrogen show a greater decrease due to the water than predicted by the model. The comparisons for hydrocarbon components are similar to the non-water case.

The calculated K-values for water are higher than the "experimental" data. However, it should be noted that the K-value for water reported by Henry (1980) was not measured but rather based on the correlation by Griswold and Kasch (1942). Thus, this important aspect of the model has yet to be evaluated experimentally.

The calculated and experimental K-values for water in the aqueous phase are compared graphically in Figure 3.9. The predicted values are in

reasonably good agreement with the data. No comparison can be made for the aqueous K-values of the other components since the data were not measured. But, as mentioned above, the solubilities are very small and therefore accurate predictions are probably of little practical importance.

The favorable comparisons between experimental data and predicted results indicate the PRLC model is of adequate accuracy for the design of the gas/liquid separation section of the SRC-II coal-liquefaction process.

3.3 Comparison of Experimentally-Measured Volatilities of EDS Coal Liquids at High Temperatures and Pressures

One of the principal areas of data uncertainty in the Exxon Donor Solvent (EDS) coal liquefaction process was the volatility of coal liquids at reactor conditions (Wilson et al., 1981). Thus the Exxon Research and Engineering Company conducted an experimental program to alleviate this problem (Wilson et al., 1981, and Hwang et al., 1983). This section compares the predictions of the present model to the data measured on EDS coal liquids.

Hwang et al. (1983) have reported that the coal source has little effect on the volatility of coal liquids, provided the liquids have a similar boiling-point distribution. Thus, we expect favorable comparisons with the EDS data will validate the application of the PRLC model to all coal-liquefaction reactors.

Data on three Illinois and two Wyoming coal liquids have been reported in the open literature. These liquids have been divided into the standard pseudocomponents using the boiling-point distributions reported by Hwang et al. (1983). The results are presented in Table 3.13; the specific gravities of the pseudocomponents are as presented in Table A-1. The boiling-point distributions of the coal liquids are presented graphically in Figure 3.10. It is evident that, with the exception of ILL-3, all the coal liquids have approximately equivalent distributions; ILL-1 has a relatively large amount of material which boils close to 400°F, but this is probably a minor difference.

24 experimental runs have been reported with temperatures ranging from 700 to 850°F and pressures from 1500 to 2407 psia. Varying amounts of hydrogen, methane (and hydrogen-sulfide for 2 runs) and coal liquids were employed. The weight fraction of material vaporized, and the K-values (weight) of the light components have been reported for each run. The experimental results are summarized in Table 3.14. Note that the run numbers in Table 3.14 will be used as identification in the following discussion.

Table 3.15 presents a comparison of the PRLC model with the experimental data for the weight fraction of the coal vaporized. Inspection of this table shows that the present model produces good agreement with the experimental data (errors are within about 10%), except for the runs with ILL-1 at 850°F (nos. 5-8) and run no. 12 with ILL-2.

Wilson et al. (1981) and Hwang et al. (1983) have compared the same experimental data to predictions by the standard models employed by Exxon: Chao-Seader (the model proposed by Chao and Seader, 1961, with the modifications of Grayson and Streed, 1963) and the variation of the Redlich-Kwong equation proposed by Zudkevitch and Joffe (1970), known as the RKJZ equation. Both models have been evaluated in their original forms (with the Maxwell-Bonnel, 1958 vapor pressure equation) and with the coal-fluid modifications proposed by Wilson et. al. (1981), known as the "New Method." All these models have been described in detail by Wilson et al. (1981). In the following, side by side evaluations of the predictions by the Exxon models and the present method are offered.

Figure 3.11 presents a graphical comparison of two of the Exxon methods (Hwang et al., 1983) and the PRLC model for the vaporization data of the Wyoming coals. The present model is equivalent to or marginally better than the two Exxon methods for this comparison.

The present model fared relatively badly for some of the runs presented in Table 3.15 (Run nos. 5-8, 10, 12). We have attempted to use an internal-consistency approach to determine whether this is due to model inadequacy, erratic data or a combination of the two; the method is similar to the one presented by Hwang et al.(1983). All runs at a pressure of 1950 psia and for all coal liquids except ILL-3 (the boiling-point distribution is significantly different) were gathered, and recalculated by assuming that the coal liquid is WA-5. We made the reasonable assumption that at fixed temperature, the weight fraction vaporized correlates with the number of moles of gas per unit mass of feed. The assumption is only made in order to collapse the data into a visually discernible order.

The results are presented in Table 3.16 and Figure 3.12. It is evident that the above assumption is approximately valid since an obvious pattern has emerged. It is also evident that some of the runs which exhibit the largest errors are also those which depart from the common trends of Figure 3.12.

It should be noted that the calculated volatility of the coal liquid is sensitive to the assumed boiling-point distribution, particularly at high temperatures. The boiling-point distributions reported by Hwang et al. (1983) were determined by Gas-Chromatograph simulated distillation

which have not yet been standardized for coal liquids. This is potentially an additional source of error.

We conclude that the PRLC model provides a reasonably good description of the high temperature and pressure volatility of coal fluids (about 10%). The larger errors in Table 3.15 are possibly due to inaccurate data.

The comparisons of the calculated K-values (weight) of hydrogen to the experimental data are presented in Table 3.17. The agreement is not very good and the calculated values are apparently biased low. This appears to be inconsistent with the comparisons to SRC-II data presented in the previous section, but it is not necessarily so since there is little or no overlap in temperature range between the two sets of measurements. A graphical comparison of two of the Exxon methods and the present method to the data for the Wyoming coals is presented in Figure 3.13. This Figure shows that there is considerable scatter in the experimental measurements and that both the "RKJZ with New Method" and PRLC provide a good description of the data.

The results for the weight K-value of methane presented in Table 3.18 and Figure 3.14 lead to similar conclusions.

Table 3.1

Components and Pseudocomponents Employed for the PRLC Simulation
of the Gas Recovery Area of the Wilsonville Pilot Plant.

Component	Specific Gravity	Polar Parameter	Flow Rate into V-103* lbs/day
Water	-	-	977.1
Hydrogen	-	-	812.0
Nitrogen	-	-	46.3
Carbon-monoxide	-	-	232.1
Carbon-dioxide	-	-	371.9
Hydrogen-sulfide	-	-	71.9
Methane	-	-	950.8
Ethane	-	-	429.7
Propane	-	-	297.4
i-Butane	-	-	45.6
n-Butane	-	-	105.2
ABP 115°F	0.649	0	73.0
ABP 209°F	0.748	-0.049	168.5
ABP 300°F	0.868	-0.178	296.6
ABP 410°F	0.955	-0.300	8784.3
ABP 488°F	0.986	-0.311	17277.0
ABP 607°F	1.036	-0.161	8291.7
ABP 692°F	1.116	-0.128	4433.3
ABP 879°F	1.204	-0.094	2051.2
ABP 1374°F	1.310	0	6072.0

*Total Flow rate is 51788 lbs/day

Table 3.2
Comparison of Wilsonville Pilot Plant Datasm
with ChemShare REFINE and PRLC Calculations

Component	V-104 overhead			V-105 overhead ^a			V-110 overhead ^b		
	Wilsonville Analysis (mol %)	ChemShare REFINE (mol %)	PRLC (mol %)	Wilsonville Analysis (mol %)	ChemShare REFINE (mol %)	PRLC (mol %)	Wilsonville Analysis (mol %)	ChemShare REFINE (mol %)	PRLC (mol %)
H2	81.4	81.1	81.7	69.0	71.4	65.7	74.7	73.9	69.8
N2	0.3	0.3	0.3	-	-	-	-	-	-
CO	1.5	1.4	1.7	1.2	3.0	1.3	1.3	3.1	1.4
CO2	1.1	1.6	1.5	1.4	2.3	2.8	1.2	2.2	2.5
H2S	0.1	0.3	0.3	0.1	0.8	1.2	0.5	0.6	0.9
C1	11.8	11.6	11.2	15.1	12.5	15.5	15.8	12.1	15.4
C2	2.5	2.4	2.2	5.8	5.2	6.6	4.2	4.7	5.4
C3	0.9	1.0	0.8	4.2	2.8	4.3	1.8	2.3	3.2
IC4	0.1	0.1	0.07	0.6	0.4	0.6	0.1	0.3	0.6
NC4	0.2	0.2	0.14	1.3	1.0	1.3	0.2	0.8	1.0
C5+	0.07	0.05	0.06	1.3	0.58	0.7	0.2	-	-
	-----	-----	-----	-----	-----	-----	-----	-----	-----
	100.0	100.0	100.	100.0	100.0	100.	100.0	100.0	100.
Meter no.	FE424			FE520			-		
Meter reading	4.767			6.417			-		
Meter factor	1,500			173			-		
SCFH	7,150	6,793	7,018	1,110	1,186	985	-		
Temp. (°F)	119	119	119	100	100	100	608	608	608
Press. (psig)	2,355	2,355	2,355	15	15	15	127	127	127

^a Nitrogen - free basis.

^b C5+ and nitrogen-free basis

Table 3.3

Comparison of Wilsonville Data With ChemShare®

REFINEsm and PRLC Models

<u>V-105 distillate oil</u>	<u>Wilsonville</u>	<u>ChemShare[®]</u>	<u>PRLC</u>
Meter	FE-257		
Meter reading	9.05		
Meter factor	0.10		
gpm	0.905	0.98	0.89
Specific gravity	0.987	0.971	0.974
<u>V-105 water</u>			
Meter	FE-528		
Meter reading	1.2		
Meter factor	21.3		
lb/hr	32	37.9	37.7

Table 3.4

Comparison of REFINE and PRLC K-Values for Vessel V-103
(T = 652°F; P = 2392 psia)

Component	K-values	
	^a REFINE	PRLC
Water	1.19	1.74
Hydrogen	4.30	5.48
Nitrogen	1.43	5.67
Carbon-monoxide	1.72	5.59
Carbon-dioxide	2.83	2.92
Hydrogen-sulfide	2.49	1.76
Methane	3.61	3.39
Ethane	2.00	2.06
Propane	1.96	1.49
i-Butane	1.38	1.19
n-Butane	1.31	1.08
ABP 115°F	0.83	0.74
ABP 209°F	0.48	0.44
ABP 300°F	0.29	0.25
ABP 410°F	0.14	0.13
ABP 488°F	0.077	0.071
ABP 607°F	0.026	0.028
ABP 692°F	0.011	0.014
ABP 879°F	0.0012	0.0025
ABP 1374°F	0	0.000024

^a

See SRC-I Baseline Design Technical Data Book (ICRC, 1984) for documentation on REFINE version used.

Table 3.5

Characterization of SRC-II Coal Liquids

(Yield Obtained by TBP Distillation)

Distillation Range, °F	Boiling Point °F	High Pressure Separator Liquids			Low-Pressure Separator Liquids		
		Yield Wt %	Specific Gravity	Mol Weight	Yield Wt %	Specific Gravity	Mol Weight
IBP-300	200	17.5	0.7720	107	8.1	0.7775	94
300-400	350	15.8	0.9036	141	10.2	0.9129	122
400-500	450	29.8	0.9646	172	18.2	0.9646	160
500-600	550	11.5	0.9888	192	17.0	0.9888	191
600-700	650	9.5	1.0217	224	15.1	1.0291	231
700+	800	15.9	1.1280*	320	31.4	1.1280*	286

*Value not reported by Henry (1980), but read from Figure A-1.

Table 3.6

Comparison of the True Boiling Point Distillation with the
Gas Chromatograph Simulated Distillation for SRC-II Coal Liquids

Distilla- tion Range, °F	High-Pressure Separator Liquids		Low-Pressure Separator Liquids	
	TBP Distillation	GC SIM Distillation	TBP Distillation	GC SIM Distillation
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

Table 3.7

Calculated Equilibrium K-values for the System²

Hydrogen/Methane/Coal-Liquids¹

at Low Pressures

Component	125 psig		200 psig	
	500°F	650°F	500°F	650°F
Hydrogen	116.1	92.49	76.1	59.8
Methane	56.8	52.90	36.9	33.8
C ₂ -C ₇	2.46	5.03	1.64	3.34
300-400°F	0.611	1.76	0.410	1.19
400-500°F	0.211	0.819	0.143	0.562
500-600°F	0.0643	0.338	0.0438	0.235
600-700°F	0.0175	0.127	0.0121	0.0899
700+	0.0022	0.026	0.0015	0.0186

¹Coal-liquid distribution from TBP distillation (Table 3.5)

²Flow rate of hydrogen:methane:coal-liquid is 0.902:0.133:100 (lbs)

Table 3.8

Calculated Equilibrium K-values for the System²

Hydrogen/Methane/Coal-Liquids¹

at Low Pressures

Component	125 psig		200 psig	
	500°F	650°F	500°F	650°F
Hydrogen	116.0	90.8	75.9	58.4
Methane	55.5	51.2	36.1	32.62
C ₂ -C ₇	2.44	4.96	1.62	3.30
300-400°F	0.610	1.76	0.410	1.19
400-500°F	0.212	0.821	0.144	0.565
500-600°F	0.0646	0.340	0.0441	0.237
600-700°F	0.0177	0.129	0.0122	0.0917
700+	0.0022	0.026	0.0015	0.0193

¹Coal-liquid distribution from GC simulated distillation (Table 3.6)

²Flow rate of hydrogen:methane:coal-liquid is 0.702:0.133:100 (lbs)

Table 3.9
Calculated Equilibrium K-values for the System¹
Hydrogen/Methane/Coal Liquids
at 2000 psig

Component	400 °F		500 °F		600 °F		700 °F	
	Coal Liquid Feed Rate		Coal Liquid Feed Rate		Coal Liquid Feed Rate		Coal Liquid Feed Rate	
	100 cc/hr ²	25 cc/hr ³	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr
Hydrogen	10.39	10.50	8.82	9.11	7.21	7.78	5.56	6.55
Methane	4.20	4.28	4.10	4.25	3.83	4.10	3.40	3.89
C ₂ - C ₇	0.119	0.117	0.238	0.230	0.411	0.385	0.629	0.574
300-400 °F	0.0237	0.0230	0.0668	0.0622	0.151	0.133	0.292	0.241
400-500 °F	0.0068	0.0065	0.0254	0.0231	0.0727	0.0612	0.170	0.130
500-600 °F	0.0017	0.0016	0.0086	0.0075	0.0309	0.0248	0.0894	0.0632
600-700 °F	0.00040	0.00037	0.0026	0.0022	0.0124	0.0092	0.0443	0.0286
700+ °F	0.00004	0.00004	0.0004	0.0003	0.0027	0.0019	0.0139	0.0077

¹ Coal-liquid distribution from TBP distillation (Table 3.4)

² Flow rate of hydrogen:methane:coal-liquid is 1.479:0.280:100 (lbs)

³ Flow rate of hydrogen:methane:coal-liquid is 5.916:1.120:100 (lbs)

Table 3.10
Calculated Equilibrium K-values for the System¹
Hydrogen/Methane/Coal Liquids¹
at 2000 psig

Component	400 °F		500 °F		600 °F		700 °F	
	Coal Liquid Feed Rate		Coal Liquid Feed Rate		Coal Liquid Feed Rate		Coal Liquid Feed Rate	
	100 cc/hr ²	25 cc/hr ³	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr	100 cc/hr	25 cc/hr
Hydrogen	10.29	10.42	8.54	8.86	6.76	7.39	4.94	6.10
Methane	4.01	4.14	3.93	4.07	3.61	3.87	3.10	3.64
C ₂ - C ₇	0.118	0.116	0.238	0.230	0.415	0.389	0.644	0.583
300-400 °F	0.0238	0.0231	0.0679	0.0635	0.158	0.139	0.317	0.255
400-500 °F	0.0068	0.0066	0.0263	0.0240	0.0778	0.0654	0.192	0.142
500-600 °F	0.0018	0.0017	0.0089	0.0079	0.0338	0.0270	0.105	0.0706
600-700 °F	0.00040	0.00038	0.0027	0.0024	0.0136	0.0103	0.0546	0.0330
700+ °F	0.00004	0.00004	0.0004	0.0004	0.0032	0.0022	0.0186	0.0094

¹ Coal-liquid distribution from GC simulated distillation (Table 3.5)

² Flow rate of hydrogen:methane:coal-liquid is 1.479:0.280:100 (lbs)

³ Flow rate of hydrogen:methane:coal-liquid is 5.916:1.120:100 (lbs)

Table 3.11
Calculated Equilibrium K-values for the System²
Hydrogen/Methane/Coal-Liquids¹/Water
at 2000 psig

COMPONENT	400°F	450°F	500°F	550°F
Hydrocarbon phase				
Hydrogen	10.20	9.01	7.53	5.75
Methane	4.22	4.13	3.89	3.38
C2 - C7	0.142	0.224	0.344	0.507
300-400°F	0.0305	0.0604	0.117	0.218
400-500°F	0.0092	0.0220	0.0512	0.116
500-600°F	0.0025	0.0073	0.0207	0.0576
600-700°F	0.00063	0.0022	0.0077	0.0269
700+°F	0.00007	0.0003	0.0015	0.0075
H2O	1.30	1.46	1.58	1.60
Water phase				
Hydrogen	1010.	545.	282.0	130.
Methane	171.	112.	70.7	40.8
C2 - C7	162.	113.	75.8	46.2
300-400°F	74.1	56.4	41.3	27.8
400-500°F	22.8	21.1	18.5	14.9
500-600°F	34.0	29.9	25.1	19.4
600-700°F	55.3	45.0	35.3	25.8
700+°F	23.3	19.2	15.9	12.8
H2O	0.145	0.254	0.417	0.635

¹Coal-liquid distribution from TBP distillation (Table 3.4)

²Flow rate of hydrogen:methane:coal-liquid:water is 1.479:0.280:100:105.2 (lbs)

Table 3.12

Calculated Equilibrium K-values for the System²

Hydrogen/Methane/Coal-Liquids¹/Water

at 2000 psig

COMPONENT	400°F	450°F	500°F	550°F
Hydrocarbon phase				
Hydrogen	10.00	8.74	7.10	5.14
Methane	4.08	3.96	3.65	3.07
C2 - C7	0.142	0.224	0.349	0.525
300-400°F	0.0307	0.0615	0.122	0.238
400-500°F	0.0093	0.0227	0.0548	0.132
500-600°F	0.0026	0.0076	0.0226	0.0685
600-700°F	0.00064	0.0023	0.0086	0.0335
700+°F	0.00007	0.0003	0.0018	0.0102
H2O	1.29	1.45	1.54	1.50
Water phase				
Hydrogen	1000.	543.	279.	124.
Methane	171.	111.	70.4	39.5
C2 - C7	163.	114.	77.6	47.6
300-400°F	74.7	57.4	42.8	29.4
400-500°F	23.0	21.6	19.4	16.1
500-600°F	34.3	30.7	26.6	21.5
600-700°F	56.1	46.4	37.8	29.2
700+°F	23.0	20.0	17.3	15.0
H2O	0.145	0.255	0.420	0.635

¹Coal-liquid distribution from GC simulation distillation (Table 3.5)

²Flow rate of hydrogen:methane:coal-liquid:water is 1.479:0.280:100:105.2 (lbs)

Table 3.13

Pseudocomponent Distribution of EDS Coal Liquids

T _b , °F	SG	Weight %				
		ILL-1	ILL-2	ILL-3	WA-5	WA-6
325	0.8620	--	--	--	1.0	1.0
375	0.9328	6.5	13.3	8.0	12.4	12.3
425	0.9680	39.5	25.8	14.3	23.9	22.4
475	0.9698	14.5	19.3	11.8	18.4	16.4
525	0.9881	11.4	16.5	8.2	13.8	13.2
575	1.0122	9.4	10.2	7.8	9.1	12.3
625	1.0328	6.8	6.1	7.3	5.9	10.4
675	1.0679	3.6	3.9	6.8	4.6	5.2
725	1.0966	1.5	4.9	6.5	3.2	6.8
775	1.1168	3.7	--	6.2	6.5	--
825	1.1375	3.1	--	5.6	0.9	--
875	1.1570	--	--	4.8	--	--
925	1.1752	--	--	3.3	--	--
975	1.1960	--	--	3.1	--	--
1080	1.2177	--	--	6.3	--	--

Table 3.14

VLE Measurements on H_2 - CH_4 - H_2S - Coal Liquid Mixtures

Expt. No.	T, °F	P, Psia	Coal Liquid	Feed Composition, Wt% *			Measured Data		
				H ₂	CH ₄	H ₂ S	Wt % Vaporized	K _{H₂}	K _{CH₄}
1	700	1500	ILL-1	1.02	1.60	----	13.9	50.4	31.8
2	700	1500		0.91	3.44	0.75	17.7	39.4	27.5
3	700	1950		1.04	1.46	----	10.75	46.8	30.0
4	700	2400		1.02	1.42	----	9.06	43.4	27.7
5	850	1500	ILL-1	0.94	1.38	----	33.7	15.1	10.9
6	850	1950		1.13	1.64	----	30.8	13.0	9.31
7	850	1950		0.76	2.97	0.62	25.5	11.1	9.35
8	850	2407		0.78	1.11	----	11.2	15.5	11.80
9	700	1950	ILL-2	0.99	1.40	----	12.4	48.0	29.4
10	775	1950		1.40	1.95	----	21.9	32.0	21.7
11	850	1950		1.15	1.49	----	40.0	11.9	7.87
12	850	1950		0.855	1.21	----	43.3	9.56	6.90
13	700	1950	ILL-3	1.03	1.36	----	8.0	91.1	60.6
14	775	1950		1.26	1.54	----	13.0	64.7	38.0
15	850	1950		1.31	1.97	----	23.6	40.4	28.5
16	880	1950		1.27	1.90	----	26.8	53.6	40.7
17	700	1950	WA-5	1.154	1.421	----	12.43	44.85	28.58
18	775	1950		0.949	1.169	----	16.55	22.58	15.02
19	850	1950		1.119	1.377	----	34.19	12.05	8.68
20	700	1950	WA-6	0.725	0.893	----	6.66	46.05	34.78
21	775	1950		0.548	0.674	----	6.53	34.24	26.33
22	850	1950		0.852	1.049	----	22.80	11.91	8.71
23	775	1950	ILL-2	1.13	1.60	----	21.30	30.0	21.9
24	775	1950		1.72	2.45	----	30.2	34.2	20.5

*Balance is Coal Liquid

Table 3.15

Volatility of EDS Coal Liquids
Comparison of Modified Peng-Robinson to Experimental Data

Expt. No.	Coal Liquid	Weight % Vaporized		
		Data	Calculated	% Error
1	ILL-1	13.9	14.8	6.5
2		17.7	19.7	11.3
3		10.75	11.4	6.0
4		9.06	9.0	- 0.7
5	ILL-1	33.7	44.2	31.2
6		30.8	39.5	28.2
7		25.5	38.2	49.8
8		11.2	16.9	50.9
9	ILL-2	12.4	10.8	-12.9
10		21.9	27.8	26.9
11		40.0	41.4	3.5
12		43.3	28.8	-33.5
13	ILL-3	8.0	7.8	- 2.5
14		13.0	14.3	10.0
15		23.6	23.5	- 0.4
16		26.8	26.8	0.0
17	WA-5	12.43	12.1	- 2.7
18		16.55	16.1	- 2.7
19		34.19	35.0	2.4
20	WA-6	6.66	6.6	- 0.9
21		6.53	7.1	8.7
22		22.80	24.2	6.1
23	ILL-2	21.3	21.9	2.8
24		30.2	34.9	15.6

Table 3.16

Calculation of Vaporization Assuming All Coal Liquid(s) are WA-5
(P = 1950 psia)

Expt. No.	T, °F	Moles Gas per 100 lbs. Feed	Weight % Vaporized	
			Experimental	Calculated
3	700	0.61	10.75	11.1
6	850	0.66	30.8	36.8
9	700	0.58	12.4	10.5
10	775	0.82	21.9	26.0
11	850	0.66	40.0	36.5
12	850	0.50	43.3	26.1
17	700	0.66	12.43	12.1
18	775	0.54	16.55	16.1
19	850	0.63	34.19	35.0
20	700	0.42	6.66	6.8
21	775	0.31	6.53	7.4
22	850	0.49	22.80	25.0
23	775	0.66	21.30	20.6
24	775	1.01	30.2	32.3

Table 3.17

K-value (Weight) of Hydrogen
Comparison of Modified Peng-Robinson to Experimental Data

Expt. No.	Coal Liquid	K-value of Hydrogen		
		Data	Calculated	% Error
1	ILL-1	50.4	48.2	- 4.4
2		39.4	39.4	0.0
3		46.8	45.1	- 3.6
4		43.4	42.2	- 2.8
5	ILL-1	15.1	9.9	=34.4
6		13.0	9.2	-29.2
7		11.1	7.0	-36.9
8		15.5	7.7	-50.3
9	ILL-2	48.0	42.9	-10.6
10		32.0	20.4	-36.3
11		11.9	8.0	-32.8
12		9.56	7.4	-22.6
13	ILL-3	91.1	86.2	- 5.4
14		64.7	51.3	-20.7
15		40.6	29.4	-27.2
16		53.6	23.5	-56.2
17	WA-5	44.85	48.6	8.4
18		22.58	22.9	1.4
19		12.05	10.4	=13.7
20	WA-6	46.05	48.9	6.2
21		34.24	22.4	-34.6
22		11.91	9.6	-19.4
23	ILL-2	30.0	19.8	-34.0
24		34.2	21.0	-38.6

Table 3.18

K-value (Weight) of Methane
Comparison of Modified Peng-Robinson to Experimental Data

Expt. No.	Coal Liquid	K-value of Methane		
		Data	Calculated	% Error
1	ILL-1	31.8	28.4	-10.7
2		27.5	23.7	-13.8
3		30.0	26.7	-11.0
4		27.7	25.0	- 9.7
5	ILL-1	10.9	7.4	-32.1
6		9.31	6.9	-25.9
7		9.35	5.4	-42.2
8		11.80	5.9	-50.0
9	ILL-2	29.4	25.4	-13.6
10		21.7	13.6	-37.3
11		7.87	6.1	-22.5
12		6.90	5.7	-17.4
13	ILL-3	60.6	52.1	-14.0
14		38.0	33.7	-11.3
15		28.5	21.0	-26.3
16		40.7	17.3	-56.8
17	WA-5	28.58	28.7	0.4
18		15.02	15.1	0.3
19		8.68	7.7	-11.3
20	WA-6	34.78	28.8	-17.2
21		26.33	14.8	-43.8
22		8.71	7.2	-17.3
23	ILL-2	18.7	13.2	-29.4
24		20.5	14.0	-31.7

4.0 NEW PHASE-EQUILIBRIUM DATA ON SRC-I COAL FLUIDS

ICRC is conducting a program to obtain phase-equilibria measurements on SRC-I coal fluids in order to provide verification of current design conditions of the SRC-I Demonstration Plant and to provide data for the development of reliable correlations. The contract for the phase-equilibria measurements has been placed with Chromaspec Corporation in Houston. The aims, design, and schedule of the program have been presented elsewhere (Mehta et al., 1983).

Unfortunately, Chromaspec has encountered severe operating problems which have caused significant slippage in the schedule. Thus, only a small fraction of these data have been received, for which analysis is in progress. No results are presented here; a complete analysis will be provided in a final report when the project is completed.

4.1 Description of Criteria Used to Assess Quality of the Data

We established the following four criteria which will be used to assess the internal consistency and reasonableness of the trends of the phase equilibria data:

- Qualitative comparisons of GC Distillation Data simulated for C_5+ among feed, vapor samples, and liquid samples.

- Component material balances.
- Trends of weight fraction K-values with experimental temperature
- Trends of weight fraction K-values at fixed conditions with mid-cut normal boiling temperatures.

These tests will reveal certain inconsistencies in data, but they are not to be confused with thermodynamic consistency tests which are a rigorous part of the science of thermodynamics.

The simulated GC Distillation curves for the C_5+ material must follow certain qualitative relationships among the feed, equilibrium vapor and equilibrium liquid. Figure 4.1 is a qualitative picture of the expected behavior.

The feed curve was put on Figure 4.1 arbitrarily as a reference; it does not represent any quantitative data. Clearly the equilibrium vapor samples are lighter and to the left of the feed; the liquid equilibrium samples are to the right.

If the experimental flash temperatures are very high, all of the feed would vaporize and the vapor sample would coincide with the feed. Thus, on Figure 4.1, the curve labeled VETH (Vapor, Experimental Temperature High) lies nearer to the feed than the curve labeled VERL (Vapor, Experimental Temperature Low).

On the liquid side a low experimental flash temperature would not vaporize anything making the liquid sample coincident with the feed. Thus, on Figure 4.1 the liquid curve labeled LETL (Liquid, Experimental

Temperature Low) lies nearer to the feed than the curve labeled LETH (Liquid, Experimental Temperature High), which would contain only the heaviest of the heavy material as a liquid.

A component material balance can be used to check certain internal consistencies in VLE data:

$$z_i = Lx_i + Vy_i \quad (4.1)$$

where z_i , x_i , y_i are the mass fractions of species i in the feed, liquid, and vapor, respectively, and L and V are the mass fractions of equilibrium liquid and vapor, respectively. Simple rearrangement leads to

$$\frac{y_i}{z_i} = -\frac{L}{V} \frac{x_i}{z_i} + \frac{1}{V} \quad (4.2)$$

which shows that a plot of y_i/z_i against x_i/z_i for several species should yield a straight line with slope of $-L/V$ for the run under consideration.

In accordance with theory and experience on boiling-point cuts in the petroleum industry, it is expected that, at a fixed pressure removed from the critical region of the mixture, the log of the K-value of a given cut will vary approximately linearly with the reciprocal of the absolute temperature. The K-value should increase with increasing temperature.

In addition, at a given temperature and a given pressure the K-value

of a given species can be expected to be approximately proportional to its vapor pressure. Now, at a given temperature a monotonic function exists between log vapor pressure and reciprocal absolute normal boiling temperature of a component i . Therefore, a monotonic function should exist between $\log K_i$ (weight fraction) and reciprocal absolute mid-cut boiling temperature of species i .

4.2 Data for Medium-Pressure Separator

VLE data for Task 2.1.4 (Third Stage Medium-Pressure Separator) were reported by Chromaspec for the quarter November-January 1983. These data are experimental measurements for three temperatures of 320°F, 290°F, and 260°F at a fixed pressure of 80 psia made using a static cell.

Application of the four criteria defined above revealed that the data were qualitatively wrong. The main problem was diagnosed to be vapor entrainment.

A similar problem was discovered by Chromaspec and revised data were received on July 8, 1983. Initial analysis of the new data indicates that it meets the quality criteria. The analysis is still in progress and, therefore, final results are not available.

4.3 Future work

All data received from Chromaspec will be analyzed for quality and internal consistency. The results will be presented in a forthcoming report.

5.0 COMPARISON BETWEEN MODEL AND PHASE-EQUILIBRIUM DATA ON SRC-I COAL

FLUIDS

Due to slippage in the experimental program, work on this task has not progressed to an extent warranting any discussion. Results will be presented in a forthcoming report.

6.0 CONCLUSIONS AND RECOMMENDATIONS

A phase equilibrium model has been developed for the SRC-I process, as well as the other coal-liquefaction processes. It is applicable to both vapor/liquid and liquid/liquid equilibria. An additional unique feature is that it provides an approximate but adequate description of aqueous mixtures where the volatile electrolyte components dissociate to form ionic species.

The program to obtain phase equilibrium measurements for design verification and correlation development has been delayed due to experimental problems. A complete report will be prepared when this part of the project is completed.

The evaluations presented in this report indicate that the model may be employed for all coal-liquefaction processes. It provides good prediction of the gas/liquid separations in the SRC-II process, and the high-temperature and pressure volatilities of EDS coal liquids.

The present model is unique since it also describes the behavior of weak electrolytes in water. Therefore, the same model is applicable to the entire SRC-I process. The main advantage of this is that it considerably simplifies and speeds-up the development of computer simulations. It should be mentioned that the aqueous/weak-electrolyte model presented is rather simple. However, the success of the simple model will hopefully motivate more sophisticated, but practical, developments.

The PRLC model has proved to be powerful in describing complex behavior, including liquid/liquid equilibria. But accurately correlated behavior only results by employing tuned binary parameters, regressed from experimental data. Further, application to pseudocomponents requires the development of generalized correlations for the binary parameters; these can only be deduced from a large range of experimental data. Lastly, coal-fluid pseudocomponents are complicated mainly because their heteroatomic groups cause complex behavior.

Fortunately, light-component/coal-fluid or coal-fluid/coal-fluid phase equilibria not involving water are apparently insensitive to heteroatomic content and thus relatively easily generalized. But tight designs may dictate that ever smaller effects be accurately accounted for.

Phase equilibria involving water, especially liquid/liquid equilibria, are certainly strongly influenced by heteroatoms in the coal fluids. Here there are virtually no reliable data.

Accurate and reliable data will be extremely important for further model development.

NOMENCLATURE

- a - constant in Peng-Robinson equation, equation III-1
- a^{NC} - local composition parameter, equation III-17
- b - constant in Peng-Robinson equation, equation III-1
- c_i - constants to represent vapor pressure, equation III-6
- k_a - binary parameter for constant a, equation III-15
- k_b - binary parameter for constant b, equation III-16
- K_w - Watson K-factor ($=T_b^{1/3}/SG$)
- K - chemical equilibrium constant
- P - pressure
- P_c - critical pressure
- R - gas constant
- SG - specific gravity
- t - local composition binary parameter, equation III-18
- T - temperature
- T_b - normal boiling point
- T_c - critical temperature
- v - molar volume
- x_i - mole fraction of component i
- Z - compressibility factor ($=Pv/RT$)
- α - dimensionless temperature-dependent function, equation III-5
- ω - acentric factor
- n - polar parameter, equation III-7
- ϕ_i - fugacity coefficient of component i

NOMENCLATURE (Continued)

Subscripts

b - value at normal boiling point

c - value at critical point

r - reduced quantity

ji - refers to ji binary pair

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APPENDIX I

Definition of SRC-I Components

The components chosen for the Post-Baseline simulation of the SRC-I process are similar to those previously employed for the Baseline Design. These are divided into pure components and pseudocomponents. The pure components are: water, hydrogen, nitrogen, argon, ammonia, hydrogen-chloride, carbon-monoxide, carbon-dioxide, hydrogen-sulfide, methane, ethane, propane, n-butane, and n-pentane. All of these are common components whose properties are well established.

It is accepted practice to treat the essentially continuous coal-fluid slate as a set of pseudocomponents, each determined by a range in normal boiling temperature. As in the Baseline Design, the pseudocomponents have been defined to be 50°F cuts starting from 100°F and up to 950°F. All of the heavy material (950+°F) has been lumped into a cut assumed to boil at 1050°F. The SRC-I pseudocomponents are presented in Table A-1.

In addition to the boiling point, other characterizing variables must be specified for each component. The specific gravities shown in Table A-1 are those chosen by Gulf for the SRC-II process (Gray and Holder, 1982). Limited comparisons have indicated that these specific gravities are also appropriate for SRC-I fluids. Most of the pure-component parameters are determined in terms of the normal boiling point and

specific gravity by employing correlations presented previously (Mathias and Monks, 1982, and Mathias and Stein, 1983a). The parameters for which correlations are available are the critical temperature, critical pressure, molecular weight, and the constants in the polynomial for the ideal gas heat capacity. We have chosen to override the correlation for the molecular weight and instead use the values employed in the SRC-I Baseline Design.

The only required pseudocomponent parameter for which a correlation has yet to be developed is the polar parameter. We have chosen the values presented in Table A-1. These were mainly determined to provide a good fit of enthalpy data (Mathias and Stein, 1983b) but also reflect the fact that the heteroatom-containing substances are concentrated in the boiling range, 300-600°F.

In the event that coal-fluid pseudocomponents are defined differently from those presented in Table A-1, Figures A-1 and A-2 provide a means of estimating the specific gravity and polar parameters, respectively.

Table A-1

Characteristic Parameters Assumed for SRC-I Pseudocomponents

Boiling Range °F	Normal Boiling Point, °F	Specific Gravity	Molecular Weight	Polar Parameter, η
100 - 150	125	0.6800	78.43	0
150 - 200	175	0.7360	88.40	0
200 - 250	225	0.7720	97.58	-0.074
250 - 300	275	0.8142	107.49	-0.145
300 - 350	325	0.8620	118.08	-0.212
350 - 400	375	0.9328	130.62	-0.266
400 - 450	425	0.9680	143.29	-0.310
450 - 500	475	0.9698	155.18	-0.320
500 - 550	525	0.9881	170.01	-0.275
550 - 600	575	1.0122	188.02	-0.200
600 - 650	625	1.0328	201.61	-0.150
650 - 700	675	1.0679	218.29	-0.132
700 - 750	725	1.0966	237.04	-0.122
750 - 800	775	1.1168	256.05	-0.114
800 - 850	825	1.1375	277.98	-0.105
850 - 900	875	1.1570	297.00	-0.095
900 - 950	925	1.1752	321.50	-0.085
950+	1050	1.2177	450.00	-0.056

APPENDIX II

Reasons for Selecting Peng-Robinson EOS as the Phase-Equilibrium Model

An extended form of the Peng-Robinson (1976) equation of state has been adopted as the phase equilibrium model. Several reasons justifying the selection are given below:

- The accuracy and reliability of the Peng-Robinson equation in determining vapor/liquid equilibrium of non-polar mixtures has already been established (Oellrich et al., 1981).
- The Peng-Robinson equation is slightly superior to the similar Soave (1972) equation; vapor/liquid K-values are marginally better and liquid densities are significantly more accurate.
- Computational characteristics are favorable for computer simulation; the computational time is reasonable and problems with computation robustness will be minimal.
- Because the Peng-Robinson model is used in other APCI business areas, parallel development and expertise can, and was, drawn upon.
- The model can be readily modified to describe complex systems.

APPENDIX III

Definition of the Local-Composition Peng-Robinson Equation of State

According to the modified Peng-Robinson equation proposed for mixtures, the pressure is given as a function of temperature and molar volume as follows:

$$P = \frac{RT}{v-b} - \frac{1}{v(v+b) + b(v-b)} \left\{ a + \frac{a^{NC}}{2RT} F_v \right\} \quad (III-1)$$

The quantity F_v has been introduced to simplify the notation

$$F_v = \frac{1}{2\sqrt{2}b} \ln \left[\frac{v + (1+\sqrt{2})b}{v + (1-\sqrt{2})b} \right] \quad (III-2)$$

a , a^{NC} , and b are mole fraction averaged quantities as defined below:

$$a = \sum_i \sum_j x_i x_j (1 - k_{aji}) \sqrt{a_i a_j} \quad (III-3)$$

$$a^{NC} = \sum_i x_i^2 a_{ci}^2 \sum_j x_j t_{ji} \quad (III-4)$$

$$b = \sum_i \sum_j x_i x_j (1 - k_{bji}) (b_i + b_j)/2 \quad (III-5)$$

The pure component quantities in equation III-3, III-4, and III-5 are defined in terms of the critical temperature (T_c), the critical pressure (P_c), and parameters (c_1 , c_2 , and c_3) designed to describe the vapor pressure.

$$a_i = a_{ci} \alpha_i \quad (\text{III-6})$$

$$a_{ci} = 0.45724 R^2 T_{ci}^2 / P_{ci} \quad (\text{III-7})$$

$$\alpha_i = \left[1 + c_{1i} (1 - \sqrt{T_{ri}}) + c_{2i} (1 - \sqrt{T_{ri}})^2 + c_{3i} (1 - \sqrt{T_{ri}})^3 \right]^2 \quad (\text{III-8})$$

$$b_i = 0.07780 RT_{ci} / P_{ci} \quad (\text{III-9})$$

All configurational properties can be derived from the equation of state defined above using standard thermodynamic relationships.

The Helmholtz energy of a mixture is given by

$$A = -RT \ln (v-b) - a F_v - \frac{a^{NC}}{2RT} F_v^2 \quad (\text{III-10})$$

The fugacity coefficient of component i in an n-component mixture is given by

$$\begin{aligned} \ln (\phi_i) = & \ln \left[\frac{RT}{P(v-b)} \right] + (1-Z) - \left\{ a + a^{NC} \frac{F_v}{RT} \right\} \frac{F_v}{RT} \\ & + 2 \sum_j x_j b_{ji} / h \left[Z-1 + \left\{ a + a^{NC} \frac{F_v}{RT} \right\} \frac{F_v}{RT} \right] - 2 \frac{F_v}{RT} \sum_j x_j a_{ji} \\ & - \frac{1}{2} \left\{ \frac{F_v}{RT} \right\}^2 \left\{ \sum_j x_j^2 a_{cj}^2 t_{ij} + 2 x_i a_{ci}^2 \sum_j x_j t_{ji} \right\} \end{aligned} \quad (\text{III-11})$$

APPENDIX IV

Prediction of the Equation-of-State Binary Parameters

The binary parameters (k_a , k_b , t in Appendix II) are an extremely important part of the phase equilibrium model since the component fugacities - and ultimately the vapor/liquid and liquid/liquid equilibrium ratios - are usually very sensitive to them. In fact, the accuracy of the model is largely determined by the quality of the binary interaction parameters. In the case of pairs where both components are not pseudocomponents, the binary parameters can - and usually are - determined by regressing phase equilibrium data. For example, Chapter 2 presents a case where the interaction parameters obtained from regressing binary and ternary phase equilibria data provide a good description of multicomponent aqueous systems. However, in the case where at least one component of the pair is a pseudocomponent, the binary parameters must be predicted in terms of some measurable variable of the pseudocomponent(s).

The preliminary phase equilibrium report (Mathias and Stein, 1983a) presented correlations of the binary parameter for the important pure component/pseudocomponent pairs. These have been used unchanged except for cases where the pure components are hydrogen and methane. The final correlations for the binary parameters are summarized in Table A-2.

The correlation for the hydrogen/pseudocomponent binary parameter was modified since the predicted K-values for hydrogen in coal liquids was found to be high when compared to experimental data (mainly SRC-II data from Henry, 1980). An evaluation of the modified correlation to data with

model compounds is presented in Table A-3. A comparison of the average errors in Table A-3 to those in the previous report (Mathias and Stein, 1983a) indicates that the two correlations are approximately equivalent.

A similar situation occurred for methane. The evaluation of the modified correlation to data with model compounds is presented in Table A-4. In this case the modified correlation has caused a small deterioration in the fit of the model-compound data. However the new correlation has been retained since it enables good comparison with data for actual coal fluids (for example, Henry, 1980).

In the case of pure-component/pseudocomponent pairs not covered by Table A-2 and for all pseudocomponent/pseudocomponent pairs, the default value of 0.0 has been assumed for all binary parameters. It should be noted that the accuracy of the model can be systematically improved with enhanced binary-parameter correlations obtained through new experimental data.

Table A-2

Summary of Equation-of-State Binary Parameters
for Pairs Containing Coal-Fluid Pseudocomponents (2)

Other Component(1)	k a ₂₁	k b ₂₁	t 12	t 21
Hydrogen	-1.0	0.196SG - 0.1604	0	0
Nitrogen	0.10	-0.03	0	0
Carbon-monoxide	0.10	-0.03		
Methane	0.03	0	0	0
Carbon Dioxide	0.13	0	0	0
Hydrogen Sulfide	0.03	0	0	0
Water	-0.115 + 0.0457 K _w	0	0	- 15.336 + 0.01171 T _b /SG + 5470.4 SG/T _b

- See Appendix III for definition of binary parameters.
- SG, K_w, and T_b refer to properties of the coal-fluid pseudocomponent

Table A-3
Prediction of Hydrogen/Coal Fluid VLE^a

^b Solvent	$T_b(^{\circ}\text{F})$	SG	No. of Data	Temp range ($^{\circ}\text{F}$)	Max. Pressure (psia)	^c Error (K_{H_2})	^c Error (K_{solv})	^d Data Source
Benzene	176.3	0.879	49	320-500	2,582	2.8	1.6	2
Bicyclohexyl	460.4	0.896	28	372-803	3,674	7.4	6.3	1
Diphenylmethane	491.1	1.006	27	373-803	3,674	8.2	9.6	1
m-Cresol	306.1	1.034	41	372-732	3,674	8.1	4.7	1
1-Methyl- naphthalene	471.9	1.020	27	372-803	3,674	7.1	7.3	1
m-Xylene	282.5	0.864	27	373-588	3,674	3.4	4.3	1
n-Butane	31.1	0.579	44	130-250	2,448	11.5	2.1	3
n-Decane	345.4	0.730	26	373-951	3,702	3.3	5.0	1
n-Hexane	155.7	0.659	47	40-400	9,999	3.7	22.0	4
n-Octane	258.2	0.703	49	374-518	2,182	6.2	1.2	2
Quinoline	458.8	1.094	27	373-804	3,674	8.4	4.9	1
Tetralin	405.6	0.970	24	373-732	3,674	3.1	6.9	1
Toluene	231.1	0.867	25	372-576	3,680	3.8	4.9	1
n-Hexadecane	548.3	0.773	29	371-736	3,681	6.1	5.5	1
Thianaphthene	427.8	1.165	27	370-805	3,674	11.2	5.5	1

^a $k_a = -1.0$; $k_b = 0.196$ SG_{solv} -0.1604.

^bAll solvent properties calculated from T_b , SG.

^cAverage absolute error in K-value.

^dData sources are listed after Table A-4.

Table A-4
Prediction of Methane/Coal-Fluid VLE^a

^b Solvent	$T_b(^{\circ}\text{F})$	SG	No. of Data	Temp range ($^{\circ}\text{F}$)	Max. Pressure (psia)	^c Error (K_{CH_4})	^c Error (K_{solv})	^d Data Source
Benzene	176.3	0.879	18	298-442	3,519	5.4	4.9	1
Diphenylmethane	491.1	1.006	25	373-805	3,670	1.6	4.3	1
m-Cresol	396.1	1.034	25	372-740	3,674	14.5	6.1	1
1-Methyl- naphthalene	471.9	1.020	27	376-807	3,645	9.5	8.0	1
m-Xylene	282.5	0.864	22	370-589	2,929	5.3	2.6	1
n-Decane	345.5	0.730	64	100-590	4,000	4.8	9.0	1,5
n-Hexadecane	548.3	0.773	24	373-807	3,664	6.8	18.2	4
Quinoline	458.8	1.094	28	373-805	3,670	8.9	4.3	1
Tetralin	405.6	0.970	24	372-737	3,647	7.5	9.6	1
Toluene	231.1	0.867	26	301-518	3,665	8.0	4.0	1

^a $k_a = 0.03$ $k_b = 0$

^bAll solvent properties calculated from T_b , SG.

^cAverage absolute error in K-value.

^dData sources are on following page.

DATA SOURCES FOR TABLES A-3 AND A-4

1. Chao, K. C., Purdue University, EPRI Project RP367, 1975-present.
2. Connolly, J. F. 1962. J. Chem. Phys. 36:2897.
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4. Nichols, W. B., H. H. Reamer, and B. H. Sage. 1957. AIChEJ 3:262.
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3.50 THREE-PHASE EQUILIBRIA

3.51 Method Used to Estimate the Equilibrium Compositions of Streams Leaving Three-Phase Separators

Within the reaction system of the SRC-I process block, volatile weak electrolyte type compounds such as ammonia, carbon dioxide, and hydrogen sulfide, as well as water and hydrogen chloride, are produced by chemical reaction. Following the primary separation of the reactor effluent in the Coal Dissolver Effluent Separator, additional water is introduced into the high-pressure vapor stream to facilitate removal of ammonium chloride salts, formed by reaction of ammonia and hydrogen chloride, as water-soluble salts. In general, the molar concentration of ammonia exceeds that of hydrogen chloride, and therefore, it has been assumed that all of the hydrogen chloride present has been stoichiometrically converted to ammonium chloride salts. These weak electrolyte compounds are then removed from the process by two principal means: (1) by decantation of an aqueous phase containing dissolved quantities of these weak electrolyte compounds from three-phase hydrocarbon/water separators, and (2) by conventional gas scrubbing with DEA solution. Within the SRC-I block, three multiphase separators, namely V-12405, V-12408 and V-12502, have been provided for partial removal of water-soluble weak electrolyte compounds, for removal of dissolved ammonium chloride salts, and for removal of excess water.

The ChemShare[®] REFINESM simulator contains a three-phase flash algorithm suitable for prediction of the equilibrium phase compositions of three-phase separator vessels with the following limitations (3):

- 1) It assumes that hydrocarbons are completely immiscible in water and that a pure liquid water phase will form when the vapor and hydrocarbon liquid phase are saturated.
- 2) It assumes that the solubility of water in the hydrocarbon liquid is described by the curve for kerosene in Figure 9A1.4 of the API Technical Data Book⁽¹⁸⁾.

Since the REFINESM simulator assumes that a pure aqueous phase is formed during three-phase equilibria, it obviously does not take into account the dissolution of weak electrolyte compounds described previously, which are also removed with the aqueous phase. To overcome this particular limitation, a second computer program named SURF was utilized to estimate the composition of the aqueous phase leaving each three-phase separator.

During the latter stages of the SRC-I process design, a new phase equilibria program called TIDES became available which had computational capabilities superior to those of the SURF program. The two programs do predict somewhat different distributions of acid gas components, but the total vapor and liquid stream flow rates they predict are not significantly different, and hence do not affect the process design. While the results reported in the Baseline design were developed with the SURF program, the superior TIDES program was used for the phase equilibria predictions in this data book.

The TIDES computer program, developed by E. M. Pawlikowski at the University of California⁽¹⁹⁾, calculates vapor/liquid equilibria of aqueous solutions containing one or more volatile weak electrolytes, such as ammonia, carbon dioxide, and hydrogen sulfide, together with other gases such as hydrogen, nitrogen, carbon monoxide, and the light hydrocarbons methane through propane. The Tides program calculates vapor/liquid equilibria for multisolute systems by simultaneous solution of the equations reflecting mass balances, dissociation equilibria, charge balances, and phase equilibria. This computer program is available on the APCI computer system and was used by Catalytic, Inc. in their engineering analysis of three-phase separators.

The following three-step procedure was utilized by Catalytic, Inc. to estimate the composition of the equilibrium streams leaving separators V-12405, V-12408, and V-12502. The procedure will be described using Vessel V-12405 as an example.

First, the stream composition and pressure data for the feed stream to vessel V-12405, namely stream number 4416, were obtained from the Baseline Design Material Balance Summary. These data were used as the input for a REFINESM equilibrium flash calculation at a specified temperature. The results of this calculation gave an initial estimate of the amount of pure water condensed and decanted. The same feed stream composition, pressure, and temperature data were then used as input to a Tides equilibrium flash run. However, in this case all hydrocarbon components boiling higher than propane

were lumped together with the propane and treated as a single component. The results of the Tides flash calculation showed the amount of condensed water produced and the quantity of each weak electrolyte compound dissolved in the aqueous phase. It is important to note that the amount of water condensed, predicted by both the REFINEsm and Tides programs, were in close agreement. Since the component flow rates of the weak electrolytes and water leaving in the aqueous phase were now fully known from the Tides program results, it was then only necessary to calculate the equilibrium distributions for the remaining components present in the hydrocarbon vapor and liquid phases. To do this, the amounts of ammonia, carbon dioxide, and hydrogen sulfide found dissolved in the aqueous phase by the Tides program were subtracted from the corresponding quantities of each of these components present in the original V-12405 feed stream (i.e., stream 4416), to produce a modified feed stream. The modified feed stream composition data, together with the temperature and pressure data, were used as input for a second REFINEsm equilibrium flash run. The results from this second REFINEsm run produced the component flow rates for each component leaving vessel V-12405 in the equilibrium hydrocarbon-rich vapor and liquid phases. Finally, this same procedure was also utilized to estimate the composition of the equilibrium streams leaving Vessels V-12408 and V-12502.

3.52 The Effect of Temperature on Three-Phase Equilibria

Since three-phase equilibria calculations are dependent on the knowledge of at least four separate equilibrium constants for each component present in the system, it was decided that the most effective way to present the results for three-phase equilibria would be to illustrate the sensitivity of the equilibrium phase compositions to changes in operating temperature. Therefore, three-phase equilibria calculations were performed, using the method described in Section 3.51, for separators V-12405, V-12408, and V-12502. Phase equilibrium results were obtained at two temperatures, 135°F (Baseline design value), and 110°F (an off-design condition). System pressure was held constant throughout the calculations at their design values of 1,920, 80, and 16 psia, respectively.

Tables 3.501 and 3.502 present the phase equilibrium results for separator V-12405 at 135 and 110°F, respectively. Specifically, these tables show the molar flow rates for each component leaving this separator in the equilibrium hydrocarbon vapor, hydrocarbon liquid, and the aqueous phases. The impact of a change in separator temperature on the phase equilibrium results will be illustrated by direct comparison of the values in these tables.

Comparison of the first columns of Tables 3.501 and 3.502 for the equilibrium vapor stream shows that the molar flow rates of almost all components decrease as the separator temperature declines from 135 to 110°F, as would be expected. However, the components hydrogen, nitrogen, and argon deviate from this trend in that their molar component flow rates remain constant despite the change in temperature. Comparison of the third columns of Tables 3.501 and 3.502 for the aqueous phase shows that the molar flow rates of water, ammonia, carbon dioxide, and hydrogen sulfide all increase as the separator temperature declines from 135 to 110°F. Comparison of the second columns of Tables 3.501 and 3.502 for the liquid hydrocarbon phase shows that the molar flow rate for all components, with the exception of water, increase as the separator temperature is lowered from 135 to 110°F. However, owing to the solubility characteristics of water in hydrocarbons, the molar flow rate of water in the hydrocarbon phase decreases as the separator temperature declines from 135 to 110°F.

Tables 3.503, 3.504, 3.505, and 3.506 present analogous equilibrium phase results for separators V-12408 and V-12502, respectively. The trends of the equilibrium phase compositions with temperature for both of these separators are exactly the same as the trends described above for separator V-12405.

Table 3.501
Equilibrium Phase Distribution
Data for Vessel V-12405^a

Pressure = 1,920 psia; temperature = 135°F

Components	Vapor phase (mol/hr)	Hydrocarbon phase (mol/hr)	Aqueous phase (mol/hr)
H ₂ O	14.0	0.6547	3,626.0
H ₂	8,376.0	11.9	-
N ₂	316.0	0.575	-
A	53.4	0.458	-
NH ₃	0.681	0.0493	95.6
HCl	-	-	4.28
CO	418.0	1.06	-
CO ₂	71.4	0.752	21.3
H ₂ S	152.0	5.66	62.2
Methane	918.0	5.57	-
Ethane	231.0	4.63	-
Propane	106.0	4.62	-
Butane	44.3	6.86	-
Pentane	16.8	7.16	-
100-150°F TBP	20.8	16.0	-
150-200°F TBP	7.93	16.6	-
200-250°F TBP	3.55	18.4	-
250-300°F TBP	1.14	15.5	-
300-350°F TBP	0.381	12.6	-
350-400°F TBP	0.114	9.26	-
400-450°F TBP	0.0718	14.2	-
450-550°F TBP	0.120	75.7	-
550-650°F TBP	0.00279	10.6	-
650-750°F TBP	-	0.760	-
750-850°F TBP	-	0.030	-
850-950°F TBP	-	-	-

^aDistribution data satisfy conditions of simultaneous chemical and physical equilibria.

The assumption is made that NH₃ and HCl react stoichiometrically to form NH₄Cl salts in the aqueous phase. NH₄Cl salts in the aqueous phase = 229 lb/hr.

Solubility calculation is based on Air Products' "Tides" program (ClA054).

Table 3.502
Equilibrium Phase Distribution
Data for Vessel V-12405^a

Pressure = 1,920 psia; temperature = 110°F

Components	Vapor phase (mol/hr)	Hydrocarbon phase (mol/hr)	Aqueous phase (mol/hr)
H ₂ O	6.94	0.444	3,633.0
H ₂	8,375.0	12.4	-
N ₂	316.0	0.607	-
A	53.4	0.526	-
NH ₃	0.235	-	96.1
HCl	-	-	4.28
CO	417.0	1.14	-
CO ₂	65.7	0.841	27.0
H ₂ S	150.0	7.57	62.9
Methane	917.0	6.55	-
Ethane	230.0	5.82	-
Propane	104.0	6.28	-
Butane	41.6	9.62	-
Pentane	14.3	9.65	-
100-150°F TBP	16.4	20.5	-
150-200°F TBP	5.42	19.1	-
200-250°F TBP	2.18	19.9	-
250-300°F TBP	0.661	16.0	-
300-350°F TBP	0.212	12.7	-
350-400°F TBP	0.061	9.31	-
400-450°F TBP	0.035	14.3	-
450-550°F TBP	0.063	75.8	-
550-650°F TBP	-	10.6	-
650-750°F TBP	-	0.766	-
750-850°F TBP	-	0.031	-
850-950°F TBP	-	0.003	-

^aDistribution data satisfy conditions of simultaneous chemical and physical equilibria.

The assumption is made that NH₃ and HCl react stoichiometrically to form NH₄Cl salts in the aqueous phase. NH₄Cl salts in the aqueous phase = 229 lb/hr.

Solubility calculation is based on Air Products' "Tides" program (C1A054).

Table 3.503
Equilibrium Phase Distribution
Data for Vessel V-12408^a

Pressure = 80 psia; temperature = 135°F

Components	Vapor phase (mol/hr)	Hydrocarbon phase (mol/hr)	Aqueous phase (mol/hr)
H ₂ O	77.9	0.224	757.0
H ₂	1,244.0	0.116	-
N ₂	363.0	0.0526	-
A	25.7	0.0182	-
NH ₃	8.31	0.0529	12.2
HCl	-	-	1.04
CO	309.0	0.0647	-
CO ₂	19.6	0.0196	2.08
H ₂ S	48.2	0.163	4.59
Methane	158.0	0.0859	-
Ethane	80.4	0.164	-
Propane	37.5	0.186	-
Butane	27.3	0.535	-
Pentane	18.2	1.08	-
100-150°F TBP	33.2	3.70	-
150-200°F TBP	23.8	7.48	-
200-250°F TBP	16.4	13.6	-
250-300°F TBP	6.46	14.2	-
300-350°F TBP	1.92	10.8	-
350-400°F TBP	0.419	6.10	-
400-450°F TBP	0.168	6.33	-
450-550°F TBP	0.136	15.9	-
550-650°F TBP	-	0.636	-
650-750°F TBP	-	0.00920	-
750-850°F TBP	-	-	-
850-950°F TBP	-	-	-

^aDistribution data satisfy conditions of simultaneous chemical and physical equilibria.

The assumption is made that NH₃ and HCl react stoichiometrically to form NH₄Cl salts in the aqueous phase. NH₄Cl salts in the aqueous phase = 56 lb/hr.

Solubility calculation based on Air Products' "Tides" program (C1A054).

Table 3.504
Equilibrium Phase Distribution
Data for Vessel V-12408^a

Pressure = 80 psia; temperature = 110°F

Components	Vapor phase (mol/hr)	Hydrocarbon phase (mol/hr)	Aqueous phase (mol/hr)
H ₂ O	37.7	0.166	797.0
H ₂	1,242.0	-	-
N ₂	363.0	0.071	-
A	25.7	0.0250	-
NH ₃	3.82	0.059	16.7
HCl	-	-	1.04
CO	309.0	0.071	-
CO ₂	17.6	0.023	4.09
H ₂ S	46.2	0.264	6.48
Methane	158.0	0.125	-
Ethane	80.3	0.266	-
Propane	37.4	0.318	-
Butane	26.8	0.998	-
Pentane	17.2	2.05	-
100-150°F TBP	30.0	6.90	-
150-200°F TBP	18.7	12.6	-
200-250°F TBP	10.5	19.5	-
250-300°F TBP	3.45	17.2	-
300-350°F TBP	0.898	11.8	-
350-400°F TBP	0.184	6.34	-
400-450°F TBP	0.070	6.43	-
450-550°F TBP	0.0510	16.0	-
550-650°F TBP	-	0.637	-
650-750°F TBP	-	0.009	-
750-850°F TBP	-	-	-
850-950°F TBP	-	-	-

^aDistribution data satisfy conditions of simultaneous chemical and physical equilibria.

The assumption is made that NH₃ and HCl react stoichiometrically to form NH₄Cl salts in the aqueous phase. NH₄Cl salts in the aqueous phase = 56 lb/hr.

Solubility calculation based on Air Products' "Tides" program (C1A054).

Table 3.505
Equilibrium Phase Distribution
Data for Vessel V-12502^a

Pressure = 16 psia; temperature = 135°F

Components	Vapor phase (mol/hr)	Hydrocarbon phase (mol/hr)	Aqueous phase (mol/hr)
H ₂ O	13.9	0.943	245.0
H ₂	15.8	-	-
N ₂	9.53	0.036	-
A	0.851	0.0250	-
NH ₃	2.06	0.294	4.52
HCl	-	-	0.055
CO	7.57	0.036	-
CO ₂	2.45	0.068	1.02
H ₂ S	3.40	0.293	1.09
Methane	3.18	0.062	-
Ethane	4.19	0.200	-
Propane	3.06	0.386	-
Butane	4.40	2.15	-
Pentane	3.89	5.75	-
100-150°F TBP	7.05	19.6	-
150-200°F TBP	4.14	32.2	-
200-250°F TBP	2.30	46.9	-
250-300°F TBP	0.968	52.3	-
300-350°F TBP	0.423	58.0	-
350-400°F TBP	0.176	61.6	-
400-450°F TBP	0.063	57.4	-
450-550°F TBP	-	0.937	-
550-650°F TBP	-	-	-
650-750°F TBP	-	-	-
750-850°F TBP	-	-	-
850-950°F TBP	-	-	-

^aDistribution data satisfy conditions of simultaneous chemical and physical equilibria.

The assumption is made that NH₃ and HCl react stoichiometrically to form NH₄Cl salts in the aqueous phase. NH₄Cl salts in the aqueous phase = 3.0 lb/hr.

Solubility calculation based on Air Products' "Tides" program (C1A054).

Table 3.506
Equilibrium Phase Distribution
Data for Vessel V-12502^a

Pressure = 16 psia; temperature = 110°F

Components	Vapor phase (mol/hr)	Hydrocarbon phase (mol/hr)	Aqueous phase (mol/hr)
H ₂ O	5.25	0.561	254.0
H ₂	15.8	0.0440	-
N ₂	9.52	0.0447	-
A	0.855	0.0209	-
NH ₃	0.655	0.190	6.03
HCl	-	-	0.0549
CO	7.55	0.0523	-
CO ₂	1.69	0.0624	1.79
H ₂ S	2.80	0.392	1.59
Methane	3.18	0.0612	-
Ethane	4.07	0.321	-
Propane	2.84	0.605	-
Butane	3.41	3.14	-
Pentane	2.42	7.23	-
100-150°F TBP	3.91	22.7	-
150-200°F TBP	2.00	34.3	-
200-250°F TBP	1.01	48.2	-
250-300°F TBP	0.405	52.8	-
300-350°F TBP	0.168	58.3	-
350-400°F TBP	0.0661	61.7	-
400-450°F TBP	0.0230	57.4	-
450°F-550°F TBP	-	0.937	-
550-650°F TBP	-	-	-
650-750°F TBP	-	-	-
750-850°F TBP	-	-	-
850-950°F TBP	-	-	-

^aDistribution data satisfy conditions of simultaneous chemical and physical equilibria.

The assumption is made that NH₃ and HCl react stoichiometrically to form NH₄Cl salts in the aqueous phase. NH₄Cl salts in the aqueous phase = 3.0 lb/hr.

Solubility calculation based on Air Products' "Tides" program (C1A054).

Figure 2-1
Propane-Water 3-Phase Equilibrium
Comparison with data of Kobayashi and Katz (1953)

Figure 2-2
HCl/H₂O Binary at 25°C
Calculated Vs. Data of Harned and Owen (1958)

Figure 2-4
 $\text{NH}_3\text{-CO}_2\text{-NH}_3$ at 100°C

Figure 3-1
Block Diagram of Wilsonville Plant -
Gas Recovery Area

Figure 3-2
Wilsonville Emery Coal Run 118 MB (April 3-4, 1977)
V-105 Distillate Oil

Figure 3-3
Wilsonville Emery Coal Run 118 MB (April 3-4, 1977)
V-110 Flash Tank Dist. & SRC (Solids-Free)

Figure 3-4
Equilibrium K-Values for the System
Hydrogen/Methane/Coal-Liquids at 125 psig

Figure 3-5
Equilibrium K-Values for the System
Hydrogen/Methane/Coal-Liquids at 200 psig

Figure 3-6
Equilibrium K-Values for the System
Hydrogen/Methane/Coal-Liquids at 2000 psig
(Coal-Liquids Flow Rate 25 cc/hr)

Figure 3-7
Equilibrium K-Values for the System
Hydrogen/Methane/Coal-Liquids at 2000 psig
(Coal-Liquids Flow Rate 100 cc/hr)

Figure 3-8
Equilibrium K-Values for the System
Hydrogen/Methane/Coal-Liquids/Water at 2000 psig
(Hydrocarbon Phase)

Figure 3-9
Equilibrium K-Values for the System
Hydrogen/Methane/Coal-Liquids/Water at 2000 psig
(Water in the Aqueous Phase)

Figure 3-10
Boiling-Point Distribution
of EDS Coal Liquids

Figure 3-11*

Analysis of Vaporization Data ($P = 1950$ psia)
for Wyoming Coal Liquids with Various Correlations

Figure 3-12*
 Effect of Gas on Vaporization of Coal Liquids
 (P = 1950 psia). Full Line is Calculation if All
 Coal Liquids are Assumed to be WA-5

* Patterned after Hwang et al, 1983

Figure 3-13*

K-values of Hydrogen in Wyoming Coal
Liquids at 1950 psia

Figure 3-14*

K-values of Methane in Wyoming Coal
Liquids at 1950 psia

Figure 4-1
Qualitative GC Simulated Distillations for
Feed and Equilibrium Vapor and Liquid Phases

Figure A-1
Specific Gravity Assumed for SRC-I Pseudocomponents

Figure A-2
Correlation of Polar Parameter η for SRC-I Pseudocomponents