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ENTHALPY STUDIES
Final Report

By
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F. P. Stein

May 1984

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Air Products and Chemicals, Inc.
Allentown, Pennsylvania

and

Lehigh University
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ENTHALPY STUDIES - FINAL REPORT

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for the

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

MASTER

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ENTHALPY STUDIES

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ABSTRACT

The previously developed coal-fluid enthalpy model has been evaluated and enhanced using data on SRC-I fluids and model-compound mixtures measured by researchers at the Colorado School of Mines. In general, good agreement has been obtained with data for SRC-I coal fluids. Surprisingly, the description of the enthalpy of model-compound mixtures is not as good, indicating that the inevitable lumping of the components in coal-fluid mixtures is advantageous.

The model developed herein will provide the capability for improved designs of several key heat exchangers in the SRC-I process. Further, this work has identified deficiencies in existing models, which suggest the focus of future research.

EXECUTIVE SUMMARY

This report describes the evaluation and enhancement of the enthalpy model developed for the SRC-I process (as well as the other coal-liquefaction processes). Both the initial development and the present analysis have been done by the Engineering and Scientific Systems Department of Air Products and Chemicals, Inc. (APCI) under subcontract to the International Coal Refining Company (ICRC). A preliminary version of the model was used in the Post-Baseline review of the SRC-I process design (Duffy et al., 1983), and the final version will be employed by APCI in the "ASPEN PLUS Modeling of the SRC-I Demonstration Plant" (APCI, 1984).

ICRC, recognizing the need for thermophysical data on coal liquids and coal-fluid model compounds, embarked upon a 2-year experimental program. Specifically, the overall program objectives were to obtain vapor/liquid equilibrium (VLE) and enthalpy data to develop correlations and verify the designs of several important pieces of process equipment in the SRC-I demonstration plant. The experimental program has been described in detail by Mehta and Chu (1984). The enthalpy portion of the overall program was subcontracted to the Colorado School of Mines; the data are presented in Vol. 3 of the report by Mehta and Chu (1984) and the final report from the Colorado School of Mines (Mehta, Kidnay and Yesavage, 1984).

The Engineering and Scientific Systems Department of APCI has had a subcontract from ICRC to develop thermophysical property correlations (in particular, phase equilibrium and enthalpy) for use in the design of

the SRC-I and other coal-liquefaction processes. Past development work has been described in several publications (Enthalpy: Mathias and Monks, 1982, Mathias and Stein, 1983a; and Mathias and Miller, 1983. Phase equilibrium: Mathias and Stein, 1983b & c).

The enthalpy model uses a modification of the Peng-Robinson (1976) equation of state proposed by Mathias and Copeman (1983). It was developed mainly from publicly available data on coal fluids and related model compounds (Mathias and Monks, 1982). Analysis of a portion of the data from the ICRC program (Mehta and Chu, 1984) has been presented by Mathias and Stein (1983a). This report presents an analysis of the remaining data from the Colorado School of Mines and the conclusions of the coal-fluid enthalpy model development effort.

The generalized (predictive) model has provided good agreement with experimental data on coal fluids. Surprisingly, the agreement with the data on model-compound mixtures is not as good. The practical conclusion is that, within the framework of the present model, it is better to lump various types of components within the same pseudocomponent.

The enthalpy model has achieved the main objective of an improved model for the design of several key heat exchangers in the SRC-I process. Further, the work has identified deficiencies in existing models, which suggest the focus of future research.

1. INTRODUCTION

The Engineering and Scientific Systems Department of Air Products and Chemicals, Inc. (APCI) has completed a project to develop a model to predict the enthalpies of coal-fluid mixtures, in particular the enthalpies of mixtures present in the coal liquefaction section of the SRC-I process. A preliminary version of the model was used in the Post-Baseline review of the SRC-I process design (Duffy et al., 1983), and the final version will be employed by APCI in the "ASPEN PLUS Modeling of the SRC-I Demonstration Plant" (APCI, 1984).

The enthalpy model has been described in previous reports (Mathias and Monks, 1982, Mathias and Stein, 1983a); only details relevant to the present analysis are repeated here. A key feature of the model is the proposed "extended corresponding-states framework." The most successful petroleum models (e.g., Kesler and Lee, 1976) have been based on the three-parameter corresponding-states framework (Pitzer, 1955). Pitzer's theory postulates that the compressibility factor (and thus other derived thermodynamic functions) can be represented at constant temperature and pressure by a linear function of the acentric factor, ω . However, the Pitzer framework is inadequate to describe the polar and associative behavior of coal fluids. Thus Mathias and Monks proposed an extended theory by allowing the acentric factor to vary linearly with reduced temperature; the temperature derivative is determined by a new parameter, termed the polar parameter η . It should be noted that the "polar parameter" is an empirical, lumped quantity; it is a polar parameter since its value is zero for nonpolar substances.

The extended corresponding-states framework has been implemented using the "local-composition" Peng-Robinson equation of state (Peng and Robinson, 1976; Mathias and Copeman, 1983). This equation of state is defined in Appendix II. We have already shown that this approach provides a good description of the enthalpy of pure components, even those which are polar (e.g., m-cresol). The description of mixtures is considerably more complex since the binary interaction parameters (see Equations II-3, 4, 5) must be determined; this issue is addressed in Chapter 3.

It is current practice to treat the fraction of the coal-fluid stream that boils above n-pentane ($T_b > 100^\circ\text{F}$) as a set of pseudo components, each defined by a range in normal boiling temperature. Thus, the model parameters for each pseudocomponent must be predicted in terms of its measurable properties, termed characterization variables. Correlations for all the model parameters have been developed in terms of the usual characterization variables, normal boiling point and specific gravity (Mathias and Monks, 1982; Mathias and Stein, 1983a & b). It should be noted that the "correlation" for the polar parameter is only in terms of the boiling point and based on few data for SRC-I fluids (Mathias and Stein, 1983a); its applicability is thus limited to SRC-I fluids - and perhaps to the coal type (Illinois #6 from the Colonial Mine; see Mehta and Chu, 1984). The components employed in the simulation of the SRC-I are presented in Appendix I.

ICRC has conducted a program to obtain measurements of thermophysical properties in order to provide verification of the current design conditions for the SRC-I demonstration plant and data for developing reliable correlations (Mehta and Chu, 1984). Task 3 of the

overall program concerns enthalpy measurements and was placed with Professors Kidnay and Yesavage of the Colorado School of Mines. A portion of this enthalpy data has already been used to evaluate and enhance the enthalpy model (Mathias and Stein, 1983a). The analysis of the remaining data is reported here. Table 1.1 presents a summary of the enthalpy data program; the '*' marks indicate data sets that are analyzed in this report.

Chapter 2 evaluates the model with respect to the enthalpy of t-decalin. Chapter 3 analyses the capability of the model for mixtures containing different types (acid/base/aromatic/saturate, ABAS) of coal-fluid model compounds. Chapter 4 compares the predictions of the model to the heat capacity data on the heavy coal fluids obtained by the differential scanning calorimetry (DSC) method. Finally, Chapter 5 provides an overall assessment of the model and suggests areas for future research.

Table 1.1

Summary of Task 3: Enthalpy Program

Task 3.1: Process Check Points

- 3.1.1 Bottoms from HP Flash Drum
- 3.1.2 Overhead from HP Flash Drum
- 3.1.3 Second Stage MP Flash Drum Overhead - Liquid 1.3H
- 3.1.4 Wilsonville Process Solvent

Task 3.2: Correlation Check Points

Measurements on four 50°F boiling range cuts:

- 700-750°F
- 600-650°F
- 500-550°F
- 400-450°F

Task 3.3: Mixtures of Heteroatom Compounds

Quinoline

- Decalin
- m-Cresol/Quinoline
- m-Cresol/1-Methylnaphthalene/Decalin
- Quinoline/1-Methylnaphthalene/Decalin
- m-Cresol/Quinoline/1-Methylnaphthalene/Decalin

2. ENTHALPY OF t-DECALIN

t-Decalin is representative of the saturated naphthenes found in coal fluids. The enthalpy measurements were made in the reference fluid boil-off flow calorimeter (for details see Mehta and Chu, 1984, Vol. 3) at the isobars 20, 50, 100, 150, 200, 250, 456, and 1500 psia and temperatures up to about 720°F.

The model compound was first treated as a pseudocomponent described only by its normal boiling point and specific gravity (369.1°F and 0.870, respectively). The results are presented in Figure 2.1. The calculated enthalpies are in reasonably good agreement with the data, but the saturation temperatures calculated by the model are clearly too low. This is mainly due to inaccurate prediction of the critical temperature and pressure; the model predicts values of 739.7°F and 431.1 psia, whereas the values reported by Reid et al. (1977) are 782.3°F and 455.6 psia, respectively. In particular, the predicted critical temperature is too low.

Figure 2.2 compares the vapor pressures of t-decalin from several sources. The dashed line is the model prediction using only the boiling point and specific gravity as input; the open circles are the values estimated from the enthalpy data; the solid circles are the smoothed data recommended by the Coal Conversion Systems Technical Data Book (1979); and finally, the full line is the model prediction if the critical constants from Reid et al. (1977) are used. It is evident that (1) the enthalpy data provides good estimates of the vapor pressure, (2) the characterization correlations for the critical constants are seriously in

error for this model compound, and (3) the model provides a good description of the vapor pressure of t-decalin if accurate values of the critical constants are used.

It is thus of interest to compare the model calculations with the experimental data if better estimates of the parameters are used. Figure 2.3 presents this comparison; the critical constants and ideal gas heat capacity of t-decalin were obtained from the listing in Reid et al. (1977). As expected, a good fit of both the enthalpy and the vapor pressure is obtained.

Close examination of Figures 2.1 and 2.3 indicates that the calculated vapor heat capacities are low at temperatures above about 500°F. Now, at these conditions the vapor heat capacity is essentially equal to the ideal gas term. (Our calculations indicate that the nonideality contribution to the vapor heat capacity at 500°F and 30 psia is approximately 0.01 Btu/lb°F, which is relatively small.) Thus there is a significant difference between calculated and experimental ideal heat capacities.

Table 2.1 presents the ideal gas heat capacity of t-decalin from several sources. The predictions of the pseudocomponent correlation are in reasonably good agreement with those of the correlation in Reid et al. (1977). Further, the values from Reid et al. (1977) agree almost exactly with those reported by Stull et al. (1969), which is a very reliable compilation. Therefore there is significant disagreement between previously accepted values and the present data for the ideal gas heat capacity of t-decalin.

The researchers at the Colorado School of Mines have recognized this problem. After completion of their DOE Contract, the enthalpy data were further screened and additional data were measured. The updated data, which have been presented by Robinson (1984), include a new isobar (30 psia) and an extended temperature range (up to 787°F). Figure 2.4 presents a comparison between the enthalpy model and the updated data. There is still a significant discrepancy between experimental and calculated ideal gas heat capacities.

It is not clear whether the accepted values or the experimental data are incorrect. The values reported in Stull (1969) are based on estimation techniques, whereas the experimental values have been produced from a reliable apparatus. Thus, we expect that the experimental data are correct. It should also be noted that the impact of these differences upon the process design is very small.

Figure 2.4 also shows that the Peng-Robinson equation predicts inaccurate enthalpies in the critical region. This aspect is beyond the capabilities of a simple model like Peng-Robinson. However, this deficiency will not have any impact upon the process design.

The analysis presented in this chapter leads to the following important conclusions:

1. The vapor pressures derived from the enthalpy data are good. This is evidence of the reliability of the experimental data.

2. The characteristic correlations are inaccurate in predicting the critical properties of the saturated naphthene t-decalin.

However, past experience indicates that the results for full range coal liquids are in good agreement with experimental data.

3. If accurate values of the parameters are employed, the enthalpy model produces good agreement with the data.

4. There is disagreement between previously accepted values and the experimental data for the ideal gas heat capacity of t-decalin.

Our feeling is that the experimental data are correct.

Table 2.1

Ideal Gas Heat Capacity of t-Decalin

Ideal Gas Heat Capacity (Btu/lb°F)				
T(K)	T(°F)	Correlation	Reid (1977)	Stull (1969)
300	80.3	0.311	0.292	0.292
400	260.3	0.411	0.412	0.411
500	440.3	0.500	0.516	0.515
600	620.3	0.577	0.607	0.609
700	800.3	0.641	0.684	0.685
800	980.3	0.694	0.750	0.748

3. ENTHALPY OF TERNARY AND QUATERNARY MIXTURES

Experimental data on mixtures of model compounds are very important since specific interactions can be studied. This is especially important in the present case since the interactions between the various pairs of components present in coal fluids can be quite different. There are no known measurements on mixtures of model compounds representing coal fluids. Task 3.3 of the ICRC data program (see Table 1.1) has been designed to provide this important information.

It is convenient to divide coal-fluid components into groups according to their functional groups. The important functional groups include: acids, bases, aromatics, and saturates (ABAS). The mixtures of Task 3.3 have been chosen to provide information on the interactions between components representative of each of these four functional groups:

acid	-	m-cresol
base	-	quinoline
aromatic	-	1-methylnaphthalene
saturate	-	t-decalin

The present correlation treats the coal-fluid mixture as a single distribution of components. In effect, several types (functional groups) of components are lumped into each pseudocomponent. The mixture data provide an opportunity to evaluate the inaccuracies of such an assumption.

Future correlation approaches will probably treat the coal-fluid slate as a mixture of several sub-mixtures, each containing a continuous distribution (either boiling-point or molecular-weight) of a particular type of component (e.g., ABAS). For example, Cotterman, Dimitretis and Prausnitz (1984) report success in treating a petroleum fluid as composed of two sub-mixtures: paraffin and aromatic. Use of this approach with petroleum fluids is relatively simple since the interaction between the paraffin and aromatic types can be assumed to be "ideal." However, a realistic description of coal fluids must also employ acid and base types - with the concomitant nonideal interaction between the sub-mixtures. The analysis of this chapter should provide results useful for such future efforts.

Table 3.1 defines the six ternary and four quaternary mixtures whose enthalpies were determined by the Colorado School of Mines researchers. The results, again measured in the reference fluid boil-off flow calorimeter, have been presented in the final report by Mehta, Kidnay and Yesavage (1984). In general, two isobars (30 and 1500 psia) have been reported for each mixture.

The pure-component parameters used for the four model compounds are presented in Table 3.2. m-Cresol, quinoline and 1-methylnaphthalene have been treated as pseudocomponents since previous work (Mathias and Stein, 1983a) has indicated that this produces good results. For t-decalin, the parameters from Reid et al. (1977) have been used, as described in the previous chapter.

Model calculations were first made with all the binary interaction parameters (see equations II-3, 4, and 5) set equal to zero. This may be considered as prediction of the experimental data. The comparisons are presented in Figures 3.1 through 3.9. Examination of these nine figures reveals the following features:

1. The predicted values of the vaporization temperature at a pressure of 30 psia are always high.
2. The predicted enthalpies of vaporization are always low.
3. The predicted liquid heat capacities are slightly low.
4. The differences between predicted and experimental results increase as the concentration of m-cresol and quinoline increases, although m-cresol tends to produce greater "nonideality."

The local-composition Peng-Robinson equation of state defined in Appendix II contains 4 interaction parameters for each pair of components. Therefore it is likely that an optimum set of values for the 24 binary parameters can be found which will simultaneously produce a good fit for all nine mixtures of this quaternary system. However that would defeat the purpose of this analysis, which is to study the nature of the interaction between the functional groups. Therefore we decided to employ only the standard Peng-Robinson binary parameter (k_a in Equation II-3). A further advantage of using only one binary parameter is that generalization to the case of undefined mixtures is less difficult.

Attempts to find optimum values of the six k_a binary parameters were made. We quickly discovered that an improvement in the enthalpy fit resulted in a deterioration of the vapor/liquid equilibrium (VLE) fit, and vice versa. Thus use of only this parameter cannot produce a simultaneous fit of both properties.

Table 3.3 presents the optimum set of parameters that produce a "best" fit of the enthalpy data. It should be noted that a rigorous optimization was not done and, therefore, better results may be obtained by fine-tuning the parameters. The m-cresol/quinoline parameter has been set at -0.20, as determined previously for the binary mixture (Mathias and Stein, 1983a). Interactions between 1-methylnaphthalene and t-decalin have been set to the default value (0.0) since a specific interaction between these functional groups is not expected to occur. The data indicate that the interactions of the nonpolar components with m-Cresol are slightly stronger than those with quinoline. For the sake of brevity, only the results for Ternary 1 (high m-cresol concentration), Ternary 2 (high quinoline concentration), and Quaternary 3 (high concentration of m-cresol and quinoline) are presented in Figures 3.10, 3.11 and 3.12, respectively. These figures indicate that a significantly improved fit of the enthalpy has been obtained, but at the expense of a serious deterioration of the description of phase equilibrium.

Table 3.3 also presents the optimum set of parameters in order to produce a good fit of the VLE. The results for Ternary 1, Ternary 2 and Quaternary 3 are presented in Figures 3.13, 3.14 and 3.15, respectively. In this case, VLE is much improved, but the enthalpy predictions are poor.

As mentioned above, use of additional parameters may produce a good description of both VLE and enthalpy with the same set of parameters, but generalization to the case of undefined mixtures will become very difficult. Thus, it appears that the approach of treating the coal-fluid as composed of several sub-mixtures, each containing a single type of component, may be undermined by the necessity of complicated interaction parameters between the sub-mixtures.

On the other hand, the relatively simple approach used currently lumps many types of components into the same pseudocomponent. However, good results were obtained for both the enthalpy and VLE of three full range coal liquids (Mathias and Stein, 1983a) with the assumption that all binary interaction parameters between all pairs of pseudocomponents are equal to the default value of 0.0. Further, Mathias and Stein also found that an equimolar mixture of m-cresol and quinoline is reasonably well described as a single pseudocomponent. Thus, experimental evidence indicates that the simple approach is effective in practice.

It is not clear why the simple approach produces good results. A reasonable explanation is that each pseudocomponent is a mixture of the four important functional groups (ABAS). Therefore, the nonideal interactions have essentially been accounted for by the polar parameter for each pseudocomponent (Table 4-1). That is, the mixture of pseudocomponents is relatively ideal.

While the sophisticated approach will probably be superior in the long run, these problems will have to be overcome first. Additional analysis of the valuable data on this quaternary system may provide the clues to an effective solution.

Table 3.1

Mixture Identification

Ternary 1:	m-Cresol/1-Methylnaphthalene/t-Decalin 60.33/29.33/10.34 (Mole percent)
Ternary 2:	Quinoline/1-Methylnaphthalene/t-Decalin 60/30/10 (Mole percent)
Ternary 3:	m-Cresol/1-Methylnaphthalene/t-Decalin 20/40/40 (Mole percent)
Ternary 4:	m-Cresol/1-Methylnaphthalene/t-Decalin 40/10/50 (Mole percent)
Ternary 5:	Quinoline/1-Methylnaphthalene/t-Decalin 10/40/40 (Mole percent)
Ternary 6:	Quinoline/1-Methylnaphthalene/t-Decalin 40/10/50 (Mole percent)
Quaternary 1:	m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin 30/15/40/15 (Mole percent)
Quaternary 2:	m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin 15/30/40/15 (Mole percent)
Quaternary 3:	m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin 20/20/40/20 (Mole percent)

Table 3.2
Pure-Component Parameters of Model Compounds

	$T_b(^{\circ}\text{F})$	SG	MW	$T_c(^{\circ}\text{F})$	$P_c(\text{psia})$	Polar Parameter
m-Cresol	396.1	1.038	113.6 ¹	811.7 ¹	653.7 ¹	-0.28
1-Methylnaph- thalene	472.3	1.020	144.0 ¹	927.0 ¹	528.3 ¹	0.0
Quinoline	458.8	1.094	130.7 ¹	962.6 ¹	658.5 ¹	0.08
t-Decalin	369.1	0.870	138.3 ²	782.3 ²	455.6 ²	0.0

¹ Calculated from pseudocomponent correlations

² From Reid et al. (1977)

Table 3.3

Interaction Parameters (k_a) for Coal-Fluid Model Compounds

Pair		Interaction Parameter Set		
		Default	Enthalpy	VLE
m-Cresol	- Quinoline	0.0	- 0.20	0.0
m-Cresol	- 1-Methnaph.	0.0	- 0.12	0.08
m-Cresol	- t-Decalin	0.0	- 0.12	0.08
Quinoline	- 1-Methnaph.	0.0	- 0.08	0.04
Quinoline	- t-Decalin	0.0	- 0.08	0.04
1-Methnaph.	- t-Decalin	0.0	0.0	0.0

4. DIFFERENTIAL SCANNING CALORIMETRY DATA

It was necessary to obtain the experimental data on the heavy samples (700-750°F fraction and V-110 Bottoms, see Table 1.1) using the differential scanning calorimetry (DSC) method. The Colorado School of Mines researchers have stated (Mehta and Chu, 1984, Vol. 3) that the reason is that the samples are solid at room temperature and, therefore, it was not feasible to run them in the flow calorimeter without drastic equipment modifications.

The DSC method is well suited to measuring the heat capacities of solid and liquid samples. However, the apparatus and instrumentation of DSC prohibit scanning at temperatures where vaporization occurs; the samples are encapsulated, but not sealed, at approximately atmospheric pressure. Any significant vaporization loss not only results in poor heat capacity measurements, but also damages the calorimeter. For these reasons, an upper limit of 512°F was set for both samples. The CSM researchers have stated that this upper limit was satisfactory for the V-110 Bottoms, but apparently not for the 700-750°F distillation fraction since a total weight loss of about 10% occurred during the scanning process.

Only smoothed values of the heat capacity have been presented in the report by CSM. However, we preferred to have the actual measurement. At our request, Professor Kidnay of CSM supplied us with the "raw" data.

DSC measurements were first made on the 600-650°F fraction. These data intentionally overlap previous measurements made with the flow

calorimeter. The reliability of the latter method has been established and thus can be used as a check on the DSC apparatus and procedure. Kidnay and Yesavage (Vol. 3 of Mehta and Chu, 1984) have reported that the DSC data are about 4-7% greater than the "true" (flow calorimeter) values for this material. Figure 4.1 presents a comparison between the DSC data and the present enthalpy model. The calculated results with the polar parameter optimized from the flow cell measurements ($\eta = -0.15$, Mathias and Stein, 1983a; also see Figure A-2) also indicate that the DSC data are high, by about the same amount.

Figure 4.2 presents a comparison between the DSC data and calculated results for the 700-750°F distillation cut. The gap in the experimental data between 10 and 142°F is due to a phase transition in the coal liquid. The two calculated curves shown are with the predicted value of the polar parameter ($\eta = -0.12$, Figure A-2) and the default value of zero. Both curves generally underpredict the data. However, it should be noted that comparisons with the 600-650°F cut indicate that the DSC measurements are biased high and, therefore, the predictions (full line) may be close to the "true" value. At 300°F, the predicted value (0.466 Btu/lb°F) is 5% lower than the measured liquid heat capacity (0.49 Btu/lb°F).

The DSC data indicate that the liquid heat capacity levels off sharply at the higher temperatures ($T > 400^\circ\text{F}$); this is inconsistent both with the predicted behavior and past results from the flow cell. One possible explanation is that the reported 10% sample loss occurs at about 400°F.

Simulated gas chromatographic analyses performed at both APCI and CSM (Vols. 1 and 3 of Mehta and Chu, 1984) indicate that about 35-40% of the 700-750°F fraction boils below 700°F. Therefore, an additional calculation was made assuming this fraction is a 40/60 (by weight) mixture of two fractions, 650-700°F and 700-750°F. However, this only results in a small increase in the predicted liquid heat capacity. For example, at 300°F, the value increases from 0.466 to 0.472 Btu/lb°F.

It is of interest to compare the present data to the data measured by Gulf on similar SRC-II boiling fractions and also using the DSC procedure (Gray, 1981). The results, presented in Figure 4.3, indicate that the temperature dependence of the heat capacity of SRC-II liquids is markedly higher than that of SRC-I liquids. This is highly unlikely and therefore the difference must be due to an error in the DSC method, which has an unproven record of reliability. Since the predicted curve, which is based on the flow calorimeter data, shows better agreement with the DSC data from the Colorado School of Mines, it appears that Gulf's data may be in error.

Table 4.1 and Figure 4.4 show the boiling-point distribution of V-110 Bottoms in comparison to the three liquids already analyzed (Mathias and Stein, 1983a). It is clear that V-110 is the heaviest of the four coal liquids. Figure 4.5 presents a comparison between the data and calculated results. As opposed to the comparisons for the 600-650°F and 700-750°F, the predicted results are higher than the DSC data. Again, the data show an unexpected levelling off at the higher temperatures; this time, however, the sample loss during the scanning process was negligible.

One anomalous point is that the data do not show the expected solid/liquid phase transition.

We are not sure whether the differences are caused by errors on the part of the model or the data. This issue cannot be resolved until the reliability and accuracy of the DSC method are established. In any event, the differences between predicted values and the data are reasonably small (5-15%) and, therefore, the impact upon the design may be correspondingly small.

Table 4.1

Component Distribution of SRC-I Coal Liquids

Component	V-105	1.3H	Process Solvent	V-110
100-150°F	0.7	-	-	-
150-200°F	1.4	-	-	-
200-250°F	1.1	-	-	-
250-300°F	1.4	-	-	-
300-350°F	1.7	-	-	0.1
350-400°F	2.7	2.0	-	0.2
400-450°F	16.1	4.0	8.5	2.5
450-500°F	26.7	19.0	17.4	9.7
500-550°F	20.6	32.0	16.1	14.3
550-600°F	10.7	18.0	16.2	14.3
600-650°F	7.9	10.0	13.8	16.4
650-700°F	4.1	8.0	10.6	11.8
700-750°F	1.3	5.0	7.4	11.6
750-800°F	2.9	2.0	3.8	8.2
800-850°F	-	-	2.2	3.1
850-900°F	-	-	1.5	2.5
900-950°F	-	-	1.5	2.2
950+°F	-	-	1.0	3.1
Water	0.7	-	-	-

5. CONCLUSIONS

The enthalpy model developed in this project has produced good agreement with the data on coal fluids measured by the flow calorimeter. Comparison with the data on three full-range coal liquids (V-105, 1.3H Blend and Process Solvent) indicates that the enthalpy as well as the VLE can be adequately described. Thus the model should enable improved designs of several key heat exchangers in the coal liquefaction section of the SRC-I process.

Comparison with the experimental data on the heavier coal liquids for which the DSC method was used did not lead to any definite conclusions, mainly due to the unproven reliability of the DSC technique. However, the differences between the predicted results and the data are not large.

The present correlation approach divides the coal-fluid mixture into a single distribution - in effect, lumping several types of functional groups into each pseudocomponent. This simple approach appears to have the unexpected advantage that a good description of the properties of full-range coal liquids (i.e., mixtures of pseudocomponents) can be obtained without the complication of non-zero interaction parameters between pseudocomponents in the equation of state.

However, long term development of thermophysical models will surely benefit from the sophisticated approach of assuming that the coal-fluid is made up of several continuous distributions, each containing only a particular type of component. The model-compound mixture data analysed in this work are very important in this regard since they provide an

indication of the interaction effects between types of components. The analysis presented herein indicates that these interaction effects are significant -- and are not amenable to description by simple means. This is an important problem that requires research attention.

Finally, this work has not addressed the development of models for the heavy (950+°F) fraction. This is another problem which requires future research.

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APPENDIX I

Definition of SRC-I Components

The components being used currently in the simulation of the SRC-I process are similar to those previously employed for the SRC-I Baseline Design (International Coal Refining Company, 1984) and the Post-Baseline review of the SRC-I process design (Duffy et al., 1983). These are divided into pure components and pseudocomponents. The pure components are hydrogen, nitrogen, argon, ammonia, hydrogen chloride, carbon monoxide, carbon dioxide, oxygen, hydrogen sulfide, carbonyl sulfide, sulfur dioxide, methane, ethane, propane, n-butane, n-pentane and water. All of these are common components whose properties are well established.

It is current 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 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.

The practice of treating the coal-fluid mixture as a set of pseudocomponents is somewhat arbitrary and may also cause excessive computational loads. Recent research (for example, Cotterman and Prausnitz, 1984) suggests that it is advantageous to treat this mixture as a continuous distribution - continuous thermodynamics. Although extremely promising, continuous thermodynamics is not yet ready for industrial application.

A further problem arises from the assumption that all the heavy material (950°F) can be lumped into a single pseudocomponent, since a few streams in the SRC-I process contain up to 50% material boiling above 950°F . One possible solution is to divide the 1050°F cut into several high-boiling components. For example, Brule et al. (1982) have used 14 hypothetical components, with normal boiling points of 975 to 1625°F in 50°F increments, to describe this portion of the mixture in their simulation of the critical-solvent-deashing (CSD) section of the SRC-I demonstration plant. This assumption could easily be adopted here, but we have no experimental evidence to select a particular set and relative composition of the high-boiling pseudocomponents. Further, all the experimental data analyzed in this report is on 950°F material. As has been noted by many investigators, the area of characterization of heavy fractions requires much more experimental and theoretical research.

In addition to the boiling point, other characterizing variables must be specified for each pseudocomponent. The specific gravities shown in Table A-1 are those employed by Gulf for the SRC-II process (Gray and Holder, 1982). Limited comparisons with experimental data (Vol. I of Mehta and Chu, 1984) 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, 1983b). 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 differences introduced are small (<5%).

The only required parameter for which a correlation has yet to be developed is the polar parameter. We have chosen the values presented in Table A-1. As noted by Mathias and Stein (1983a), the "polar parameter" lumps all effects not accounted for by the boiling point and specific gravity. It is thus an empirical quantity for which a generalized correlation may not be possible. However, it is reasonable to expect that polarity - and hence heteroatomicity - will strongly affect its value. The values presented in Table A-1 are only an educated guess which reflects 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
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

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:

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

The quantity F_v has been introduced to simplify the notation

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

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

$$a = \sum_i \sum_j x_i x_j (1 - k_{aji}) (a_i a_j)^{1/2} \quad (II-3)$$

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

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

The pure component quantities in equations II-3, II-4, and II-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:

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

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

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

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

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

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

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

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

Figure 2.1
 Enthalpy of t-Decalin: Peng-Robinson Vs. Experimental Data
 (Treated as Pseudocomponent, TB=369.1 °F SG=.870)

Figure 2.2
Vapor Pressure of t-Decalin

Figure 2.3
 Enthalpy of t-Decalin: Peng-Robinson Vs. Experimental Data
 (Decalin properties from Reid et al., 1977)

Figure 2.4
 Enthalpy h -Decalin: Peng-Robinson Vs. Data of Robinson (1984)
 (Decalin properties from Reid et al., 1977)

Figure 3.1
Enthalpy of m-Cresol/1-Methylnaphthalene/t-Decalin
Composition: 60.33/29.33/10.34
Interaction Parameters: Default (Table 3.3)

Figure 3.2
Enthalpy of Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 60/30/10
Interaction Parameters: Default (Table 3.3)

Figure 3.3
Enthalpy of m-Cresol/1-Methylnaphthalene/t-Decalin
Composition: 20/40/40
Interaction Parameters: Default (Table 3.3)

Figure 3.4
Enthalpy of m-Cresol/1-Methylnaphthalene/t-Decalin
Composition: 40/10/50
Interaction Parameters: Default (Table 3.3)

Figure 3.5
Enthalpy of Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 20/40/40
Interaction Parameters: Default (Table 3.3)

Figure 3.6
Enthalpy of Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 40/10/50
Interaction Parameters: Default (Table 3.3)

Figure 3.7
Enthalpy of m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 30/15/40/15
Interaction Parameters: Default (Table 3.3)

Figure 3.8
Enthalpy of m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 15/30/40/15
Interaction Parameters: Default (Table 3.3)

Figure 3.9
Enthalpy of m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 20/20/40/20
Interaction Parameters: Default (Table 3.3)

Figure 3.10
Enthalpy of m-Cresol/1-Methylnaphthalene/t-Decalin
Composition: 60.33/29.33/10.34
Interaction Parameters: Enthalpy (Table 3.3)

Figure 3.11
Enthalpy of Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 60/30/10
Interaction Parameters: Enthalpy (Table 3.3)

Figure 3.12
Enthalpy of m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 20/20/40/20
Interaction Parameters: Enthalpy (Table 3.3)

Figure 3.13
Enthalpy of m-Cresol/1-Methylnaphthalene/t-Decalin
Composition: 60.33/29.33/10.34
Interaction Parameters: VLE (Table 3.3)

Figure 3.14
Enthalpy of Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 60/30/10
Interaction Parameters: VLE (Table 3.3)

Figure 3.15
Enthalpy of m-Cresol/Quinoline/1-Methylnaphthalene/t-Decalin
Composition: 20/20/40/20
Interaction Parameters: VLE (Table 3.3)

Figure 4.1
Liquid Heat Capacity of Cut 600–650°F at 15 psia
Peng–Robinson Vs. Experimental Data

Figure 4.2
Liquid Heat Capacity of Cut 700--750°F at 15 psia
Peng--Robinson Vs. Experimental Data

Figure 4.3
 Liquid Heat Capacity of Cut 700–750°F at 15 psia
 Peng–Robinson Vs. Experimental Data (CSM and Gulf)

Figure 4.4
Boiling-Point Distribution of SRC-I Coal Liquids

Figure 4.5
Liquid Heat Capacity of V-110 Bottoms at 15 psia
Peng-Robinson Vs. Experimental Data

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

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

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