$S_{ci}$ = centrifugal source term in $i$ momentum equation, $i = r, \theta$
$S_{vi}$ = viscous source term in $i$ momentum equation, $i = r, \theta$
$T$ = temperature of the fluid
$T_b$ = bulk temperature of the fluid
$T_w$ = wall temperature
$\tilde{T}$ = dimensionless temperature, Eq. 24
$\tilde{T}_b$ = dimensionless form of $T_b$
$u_i$ = velocity in i direction, $i = r, \theta, \phi$
$\bar{u}_\phi$ = average velocity in $\phi$ direction
$U_\phi$ = dimensionless form of $\bar{u}_\phi$

**Greek Letters**

$\eta$ = dimensionless radial coordinate, $r/d$
$\theta$ = angular coordinate, Figure 1
$\mu$ = apparent viscosity, Eq. 13
$\mu_{\text{ref}}$ = reference viscosity, Eq. 15
$\rho$ = density of the fluid
$\phi$ = axial coordinate, Figure 1

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# Multiparameter Corresponding-States Correlation of Coal-Fluid Thermodynamic Properties

**A multiparameter corresponding-states correlation has been developed to describe fossil-fluid thermodynamic properties needed to design fluid-flow, heat-exchange, and other unit operations in coal-liquefaction plants. Three equation-of-state parameters, a molecular-size/separation parameter, a molecular-energy parameter, and a molecular-orientation parameter are used to characterize nonpolar and slightly polar aromatic hydrocarbons. A conformal-solution model is developed for predicting thermodynamic properties of coal-derived mixtures.**

**M. R. BRULE, C. T. LIN,**
**L. L. LEE, and K. E. STARLING**
**University of Oklahoma, Norman, OK**

## SCOPE

The objective of this work was to develop first-generation methodologies for predicting thermodynamic properties of coal-derived fluids using current equation-of-state technology. Previously, most equations of state could not be applied directly to coal fluids. A corresponding-states framework has been modified to rapidly develop practical properties-prediction capability for the coal pilot- and demonstration-plant programs.

The three-parameter corresponding-states correlation presented here is shown to accurately describe the thermodynamic behavior of many pure coal chemicals and the bulk thermodynamic properties of undefined distillable coal fractions. The vapor/liquid equilibrium of both defined and complex distillable mixtures can be predicted using a conformal-solution model (Watanasiri et al., 1981).

Characterization techniques are outlined for converting analyses of undefined mixtures (with composition available in terms of broad fractions) into representative pseudocomponents. Empirical correlations have been developed to estimate pseudocomponent characterization parameters and ideal-gas thermodynamic properties for use with the equation of state.

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Correspondence concerning this paper should be addressed to M. R. Brulé who is presently with Kerr-McGee Corp., Oklahoma City, OK.

C. T. Lin is presently with Bechtel National, Inc., Houston, TX.

K. E. Starling is the principal investigator.

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## CONCLUSIONS AND SIGNIFICANCE

**Multiparameter corresponding-states (MPCS) correlation of coal-fluid thermodynamic properties has been demonstrated. A three-parameter corresponding-states correlation, based on perturbation theory (Pople, 1954; Pitzer et al., 1955; Starling et al., 1978) can be applied to predict the thermodynamic properties of pure coal chemicals (Brulé et al., 1979). Less accurate estimates are obtained for polar compounds. In most cases, results are sufficiently accurate to carry out constructive process design.**

**This MPCS correlation is able to reliably predict the density, enthalpy, and other thermodynamic properties of undefined distillable coal fluids. Bulk thermodynamic properties, such as density and enthalpy, for both defined and complex mixtures, are generally not very dependent on the binary-interaction parameters used in the conformal-solution model. Pseudocomponent-fraction characterization parameters can be estimated using empirical correlations that are functions of fraction average measurable properties such as normal boiling point and specific gravity. The degree of accuracy is apparently related to the amount of characterization data available.**

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## MPCS METHODOLOGY

The corresponding-states method used in this work is based on the concept of conformality. A reduced property is said to be conformal with the same reduced property of a second fluid if the reduced-property values for the two fluids are nearly equal at equivalent reduced temperature and density (Pitzer et al., 1955; Rowlinson and Watson, 1969). The classical example of conformality is provided by the thermodynamic behavior of monatomic fluids. For example, the compressibility factor of argon is almost the same as that of krypton at equal values of reduced temperature, $T^*$, and reduced density, $\rho^*$;

$$Z(T^*,\rho^*)_{Ar} \cong Z(T^*,\rho^*)_{Kr} \qquad (1)$$

Polyatomic-fluid compressibility factors are generally not conformal. However, the compressibility factors (and other reduced properties) of many nonpolar, polyatomic fluids can be correlated using the expression,

$$Z(T^*,\rho^*) = Z_o(T^*,\rho^*) + \omega Z_\omega(T^*,\rho^*) \qquad (2)$$

where $\omega$ is Pitzer's acentric factor (Pitzer et al., 1955; Pitzer, 1977). In Eq. 2, $Z_o$ and $Z_\omega$ are universal functions of $T^*$ and $\rho^*$; i.e., $Z_o$ and $Z_\omega$ are conformal for many nonpolar, polyatomic fluids.

For polar, polyatomic fluids, compressibility factors can be correlated using the relation:

$$Z(T^*,\rho^*) = Z_o(T^*,\rho^*) + \omega Z_\omega(T^*,\rho^*) + \mu^{*4}Z_\mu(T^*,\rho^*) \quad (3)$$

where $\mu^*$ is the reduced dipole moment. Other polarity parameters, such as Stiel's polarity factor (Halm and Stiel, 1971), can also be used. In Eq. 3, $Z_o$, $Z_\omega$, and $Z_\mu$ are universal functions of $(T^*,\rho^*)$ and therefore are conformal. Expansion of Eq. 3 with the use of higher-order terms in $\omega$ and $\mu^*$, as well as other corresponding-states characterization parameters, allows the correlation of thermodynamic properties for fluids with vitually any intermolecular effects (e.g., London dispersion forces, dipoles, quadrupoles, octupoles, etc. . . .). For fluids with mild dipole moments (~2 debye), and other effects in addition to those due to molecular shape and size, a convenient three-parameter approximation is possible:

$$Z(T^*,\rho^*) = Z_o(T^*,\rho^*) + \gamma Z_\omega(T^*,\rho^*) \qquad (4)$$

where $\gamma$ is an orientation parameter, similar to acentric factor but including other nonideal intermolecular effects such as weak steric and multipole anisotropies (Lee et al., 1977; Starling et al., 1978). Although relations of the type presented in Eqs. 2 and 3 can be derived from theoretical arguments (e.g., Gubbins et al., 1977), herein theory is used merely to provide a framework and starting point for the MPCS correlation of fluid thermodynamic behavior. In fact, an alternate, more empirical and usually simpler approach to MPCS correlation is to consider that reduced thermodynamic properties can be expressed by a generalized equation of state:

$$Z = Z(T^*,\rho^*,\{R\},\{E\}) \qquad (5)$$

where $\{E\}$ is a set of parameters, $E_1,E_2,\ldots$, which are dependent on corresponding-states characterization parameters. The set $\{R\}$ comprises those characterization parameters used to reduce (and sometimes to further modify, e.g., Fisher and Leland, 1970) $T$ and $\rho$ (or $P$),

$$\{R\} = (\epsilon,\sigma,\ldots; \quad \text{or} \quad T_c,P_c,\rho_c,\ldots) \qquad (6)$$

The set of equation-of-state parameters $\{E\}$ are generalized with respect to different fluids:

$$\{E\} = E_i(\{K\},\{C\}) \qquad (7)$$

One method to accomplish the generalization is to use a set of universal constants, $\{C\} = (a_i,b_i,c_i,\ldots)$, to calculate equation-of-state parameters $\{E\}$ as generalized functions of fluid characteristic properties $\{K\} = (\gamma,\mu^*,Q^*,\ldots)$. For example, $E_i$ could be of the form corresponding to Eq. 3,

$$E_i = a_i + \omega b_i + \mu^{*4}c_i \qquad (8)$$

The selection of characterization parameters is usually made with some basis in theory. The intermolecular potential energy is considered herein to involve a molecular-energy parameter, $\epsilon$, a molecular-size parameter, $\sigma$, and an orientation parameter, $\gamma$. Fluid conditions, $T$ and $\rho$, can be reduced by isotropic-reference-fluid force constants, $\epsilon$ and $\sigma$, in the following manner:

$$T^* = kT/\epsilon \qquad (9)$$

$$\rho^* = \rho\sigma^3 \qquad (10)$$

The values of $\epsilon$ and $\sigma$ can be estimated from critical properties when available,

$$\epsilon = kT_c/1.2593 \qquad (11)$$

$$\sigma^3 = 0.3189/\rho_c \qquad (12)$$

These approximations are based on the values of $\epsilon$ and $\sigma$ for monatomic fluids when the Lennard-Jones (12-6) intermolecular-potential function is assumed to be the intermolecular potential. The parameters $\epsilon$ and $\sigma$ are used to establish the isotropic contribution, $Z_o$, to the real-fluid compressibility, $Z$. The orientation parameter accounts for the anisotropic contribution, $\gamma Z_\omega$, to $Z$.

Casting the MPCS correlation in terms of molecular parameters, rather than the customary engineering parameters (e.g., $T_c,\rho_c,P_c$, etc. . . .) has unique advantages. Both thermodynamic and transport properties can be simultaneously and self-consistently correlated using the same characterization parameters, since all properties are interrelated on the molecular level (Starling et al., 1978). Molecular parameters also prove useful for characterizing high-molecular-weight hydrocarbons when critical properties used in conventional equations of state have not been or cannot be measured (Brulé et al., 1979).

## Equation of State for Thermodynamic Properties

The equation of state used in this study is a modified Benedict-Webb-Rubin (MBWR) equation (Starling, 1973) cast with a conformal-solution model for mixture-properties prediction (Starling et al., 1978). Actually, any equation of state can be cast into the MPCS framework presented here. Likewise, the CSM can be applied for prediction of the properties of mixtures using any equation of state that has been cast in the MPCS framework. The MBWR was selected because of its proven capability in accurately predicting both liquid- and vapor-phase thermodynamic properties at relative reduced temperatures as low as $T_r = 0.3$ and relative reduced densities as high as $\rho_r = 3$ (Starling, 1973). The CSM was implemented to improve the accuracy and speed of VLE predictions over most previous BWR formulations (e.g., Han and Starling, 1972). Thus, one correlation can be used to predict not only VLE for separation-equipment design, but also the enthalpies for heat-exchanger rating and densities for equipment sizing. Multiparameter corresponding states and conformal-solution model-*MPCS and CSM*—are generic methods used to build the framework. *MBWR* is a specific equation of state to which these general methods have been applied. The combined methodology is thus indicated as *CSM-MPCS-MBWR* to illustrate the different levels on which the correlation is formulated. Further, the terms 3PCS, 4PCS, etc. . . . (three-parameter, four-parameter) can be used to specifically indicate how many MPCS parameters have been used to formulate the equation of state.

The *MBWR* equation is:

$$\begin{aligned} Z = 1 &+ \rho^*(E_1 - E_2T^{*-1} - E_3T^{*-3} + E_9T^{*-4} - E_{11}T^{*-5}) \\ &+ \rho^{*2}(E_5 - E_6T^{*-1} - E_{10}T^{*-2}) \\ &+ \rho^{*5}(E_7T^{*-1} + E_{12}T^{*-2}) \\ &+ E_8\rho^{*2}T^{*-3}(1 + E_4\rho^{*2})\exp(-E_4\rho^{*2}) \end{aligned} \tag{13}$$

The use of the following relation for the coefficients $E_i$ in Eq. 13 corresponds to Eq. 7 for nonpolar fluids and casts Eq. 13 into the 3PCS form of Eq. 4:

$$E_i = a_i + \gamma b_i \tag{14}$$

The values of the universal constants, $a_i$ and $b_i$, are listed in Table 1. The orientation parameter $\gamma$, was forced to be equal to the acentric factor $\omega$ when determining the values of $a_i$ and $b_i$ from multiproperty regression analysis of experimental density, vapor pressure, and enthalpy data (using techniques given by Lin et al., 1972) for the normal paraffins methane through decane (Starling et al., 1978).

Use of Eq. 13 allows the calculation of thermodynamic properties of a single-phase nonpolar or slightly polar fluid given the three characterization parameters, $\epsilon$ (or $T_c$), $\sigma$(or $\rho_c$), and $\gamma$ for the fluid. This correlation has also been extended using a 4PCS formulation (Eq. 3) to describe the thermodynamic behavior of a number of pure halocarbons, with dipole moments up to 2.3 debye (Milani, 1978).

TABLE 1. UNIVERSAL CONSTANTS $a_i$ AND $b_i$ FOR OBTAINING PARAMETERS $E_i$ FOR THE CSM-3PCS-MBWR

$E_i = a_i + \gamma b_i$

| $i$ | $a_i$ | $b_i$ |
|---|---|---|
| 1 | 1.45907 | 0.32872 |
| 2 | 4.98813 | −2.64399 |
| 3 | 2.20704 | 11.3293 |
| 4 | 4.86121 | 0 |
| 5 | 4.59311 | 2.79979 |
| 6 | 5.06707 | 10.3901 |
| 7 | 11.4871 | 10.3730 |
| 8 | 9.22469 | 20.5388 |
| 9 | 0.094624 | 2.76010 |
| 10 | 1.48858 | −3.11349 |
| 11 | 0.015273 | 0.18915 |
| 12 | 3.51486 | 0.94260 |

## Conformal-Solution Model

For mixtures, the conformal-solution formalism assumes that the mixture properties are the same as those of a hypothetical pure fluid characterized by parameters $\sigma_x$, $\epsilon_x$, and $\gamma_x$. The following semiempirical mixing rules are used to obtain these three mixture characterization parameters as functions of composition (Lee et al., 1979; Watanasiri et al., 1982):

$$\sigma_x{}^{4.5} = \sum_i\sum_j x_ix_j\sigma_{ij}{}^{4.5} \tag{15}$$

$$\epsilon_x\sigma_x{}^{4.5} = \sum_i\sum_j x_ix_j\epsilon_{ij}\sigma_{ij}{}^{4.5} \tag{16}$$

$$\gamma_x\sigma_x{}^{3.5} = \sum_i\sum_j x_ix_j\gamma_{ij}\sigma_{ij}{}^{3.5} \tag{17}$$

The pair characterization parameters, $\sigma_{ij}$, $\epsilon_{ij}$, and $\gamma_{ij}$, are functions of the pure-fluid characterization parameters $\sigma$, $\epsilon$, and $\gamma$ of components $i$ and $j$, and are calculated using the following combining rules:

$$\sigma_{ij} = \xi_{ij}(\sigma_i\sigma_j)^{1/2} \tag{18}$$

$$\epsilon_{ij} = \zeta_{ij}(\epsilon_i\epsilon_j)^{1/2} \tag{19}$$

$$\gamma_{ij} = \tfrac{1}{2}(\gamma_i + \gamma_j) \tag{20}$$

The binary-interaction parameters (BIPs), $\xi_{ij}$ and $\zeta_{ij}$, are indicative of deviations from ideal-solution behavior. BIPs are normally determined from regression analysis of binary-mixture thermodynamic data.

The density is calculated implicitly by solving Eq. 13. Other thermodynamic properties can be derived by the classical thermodynamic relations (e.g., Reid et al., 1977). The following is the expression, derived from Eq. 13, for the enthalpy departure, $H - H^o$,

$$\begin{aligned} \frac{(H - H^o)}{R(\epsilon_x/k)} &= \rho^*[E_1T^* - 2E_2 - 4E_3T^{*-2} + 5E_9T^{*-3} \\ &- 6E_{11}T^{*-4}] + \rho^{*2}[E_5T^* - 1.5E_6 - 2E_{10}T^{*-1}] \\ &+ 0.2\rho^{*5}[6E_7 + 7E_{12}T^{*-1}] + E_8[3 - (3 + 0.5E_4\rho^{*2} - E_4^2\rho^{*4}) \\ &\exp(-E_4\rho^{*2})]E_4{}^{-1}T^{*-2} \end{aligned} \tag{21}$$

where $H$ is the enthalpy of the fluid and $H^o$ is the ideal-gas-state enthalpy of the fluid at the system temperature. The ideal-gas enthalpy must be calculated to obtain the enthalpy. The expression for the entropy departure, $S - S^o$, is

$$\begin{aligned} \frac{(S - S^o)}{R} &= -ln\,[\rho^*RT^*\epsilon_x/k\sigma_x{}^3] \\ &- \rho^*[E_1 + 2E_3T^{*-3} - 3E_9T^{*-4} + 4E_{11}T^{*-5}] \\ &- 0.5\rho^{*2}[E_5 + E_{10}T^{*-2}] + 0.2E_{12}\rho^{*5}T^{*-2} \\ &+ 2E_8[1 - (1 + 0.5E_4\rho^{*2})\exp(-E_4\rho^{*2})]E_4^{-1}T^{*-3} \end{aligned} \tag{22}$$

where $S$ is the entropy of the fluid and $S^o$ is the ideal-gas entropy of the fluid at system temperature and unit pressure (1 atm, 1 kPa, etc. . . .).

The fugacity, $\hat{f}_i$, of the ith component in a mixture is:

$$\begin{aligned} ln\left(\frac{\hat{f}_i}{x_if_i^o}\right) &= (1 + \overline{V}_i)\frac{H - H^o}{RT} - \frac{S - S^o}{R} + (\overline{R}_i - \overline{V}_i)(Z - 1) \\ &+ \rho^*[\overline{E}_{1,i} - \overline{E}_{2,i}T^{*-1} - \overline{E}_{3,i}T^{*-3} + \overline{E}_{9,i}T^{*-4} - \overline{E}_{11,i}T^{*-5}] \\ &+ \frac{\rho^{*2}}{2}[\overline{E}_{5,i} - \overline{E}_{6,i}T^{*-1} - \overline{E}_{10,i}T^{*-2}] \\ &+ \frac{\rho^{*5}}{5}(\overline{E}_{7,i}T^{*-1} + \overline{E}_{12,i}T^{*-2}) \\ &+ \overline{E}_{8,i}T^{*-3}[1 - e^{-E_4\rho^{*2}} - \frac{1}{2}E_4\rho^{*2}e^{-E_4\rho^{*2}}]/E_4 \end{aligned} \tag{23}$$

where $f_i^o$ is the standard-state reference fugacity, taken to be unity.

The derivatives in Eq. 23 are:

$$\overline{E}_{j,i} \equiv \left.\frac{\partial E_j}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= b_j \gamma_x \left[ 2 \left( \frac{\sum\limits_m x_m \gamma_{mi} \sigma_{mi}^{3.5}}{\gamma_x\ \sigma_x^{3.5}} - 1 \right) - \frac{3.5}{3} \overline{R}_i \right] \quad (24)$$

$$\overline{R}_i \equiv \left.\frac{1}{\sigma^3} \frac{\partial \sigma^3}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= \frac{6}{4.5} \left[ \frac{\sum\limits_m x_m \sigma_{mi}^{4.5}}{{\sigma_x}^{4.5}} - 1 \right] \quad (25)$$

$$\overline{V}_i \equiv - \left.\frac{1}{T^*} \frac{\partial T^*}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= 2 \left[ \frac{\sum\limits_m x_m \epsilon_{mi} \sigma_{mi}^{4.5}}{\epsilon_x {\sigma_x}^{4.5}} - 1 \right] - \frac{4.5}{3} \overline{R}_i \quad (26)$$

## ESTIMATION OF THERMOPHYSICAL PROPERTIES OF DEFINED PURE ORGANIC FLUIDS

Application of any property correlation to pure coal chemicals and defined hydrocarbon mixtures is of limited practical use in coal-liquefaction-process design *per se*. However, properties calculations for known-component systems are necessary to develop and test correlations before applying them to complex undefined fluids.

For applying MPCS correlations to undefined fluids, average properties of pseudocomponent fractions making up the complex mixture are often used to estimate correlation parameters. Characterization correlations must be developed to relate these measurable properties to MPCS characterization parameters. One strategy for developing characterization correlations is to first develop a data set consisting of MPCS parameters (e.g., critical temperature or pressure) vs. measurable properties (e.g., ASTM inspection data such as average boiling point, specific gravity, etc. . . .) for selected pure and defined-mixture systems representative of those in coal liquefaction. Using this known-component-data base, generalized correlations can be developed for estimating MPCS characterization parameters from undefined-fraction inspection data. The development of the characterization-data base begins with establishing the capability of the correlation to predict pure-compound properties.

### Pure Coal Chemicals

To calculate the thermophysical properties of pure coal chemicals using the CSM-3PCS-MBWR correlation, critical temperature, critical molar density (or inversely, volume), and the orientation parameter are required. A list of characterization parameters for selected coal-related chemicals is given in Table 2. The light gases listed in Table 2 are some of those usually included in a material balance for a coal-liquefaction plant. Table 2 also includes polycyclic aromatic hydrocarbons (PCAHs) for which values of $\gamma$ were determined using multiproperty analysis. For the PCAHs and other coal chemicals shown, the cumulative average absolute deviation (%AARD as defined in Table 2) is 1.8% for vapor pressure, 1.6% for density, and 2.3% for enthalpy departure. A more detailed compendium including other coal chemicals is also available (Brulé et al., 1979). The CSM-3PCS-MBWR correlation has also been successfully applied to describe the VLE of defined coal mixtures (Watanasiri et al., 1982).

In Table 2, critical temperature and density for the light gases are experimental values. For heavier compounds with no critical data, $T_c$ and $\rho_c$ are estimated empirically, e.g., Lydersen's method (Reid et al., 1977). The orientation parameter can be determined via multiproperty analysis. A good estimate of $\gamma$ can also be obtained using only one vapor-pressure datum, which can conveniently be the normal boiling point, the boiling point at 1333 Pa (10 mm Hg), or another reference vapor pressure. Sensitivity analysis rather than regression must be used when dealing only with the one point.

Using only a three-parameter formulation, some properties of highly polar and/or hydrogen-bonding compounds such as ammonia and water are not well predicted over an extended range of temperature and pressure (such as in the cryogenic region where many hydrogen and ammonia data are reported). For these problem fluids, the value of $\omega$ can usually be substituted for that of $\gamma$ in order to make a calculation. Although densities for these compounds may be poorly predicted, other properties, such as vapor pressure are sufficient for making VLE or enthalpy calculations for coal fluids in which the concentrations of these components are relatively small and mostly in the vapor phase.

## CORRELATION OF CORRESPONDING-STATES CHARACTERIZATION PARAMETERS WITH FRACTION AVERAGE MEASURABLE PROPERTIES

To obtain reliable estimates of MPCS characterization parameters for undefined, distillable coal-fluid fractions, correlations have been developed according to common practices of dealing with petroleum fractions. Most established correlations for distillable fluids are based on petroleum hydrocarbons (e.g., Riazi and Daubert, 1980; Sim and Daubert, 1980). In order to be successful for coal fluids, these correlations must be re-evaluated and modified using a data base which includes PCAHs typical of coal fluids.

For most of the distillable coal chemicals for which data are available, the average normal boiling point $T_b$ and specific gravity $S$ are the typically reported inspection data (Lin et al., 1980a,b,c). Additional inspection data such as viscosity could potentially improve correlation accuracy; e.g., petroleum fluids and coal fluids with the same Watson characterization factor can have very different viscosities at ambient temperature and pressure. Average molecular weight $M$ is apparently needed for characterizing high-molecular-weight fluids, as heavy organic-compound $S$ changes only slightly as $M$ increases (however, *molar* density continues to decrease uniformly as $M$ increases). $M$ is also needed to distinguish between organic compounds with and without nitrogen, oxygen, and sulfur (NOS) substituted groups. For example, a heterocyclic with $T_b$ about the same as that of a homocyclic may have a much lower $M$ than the homocyclic.

Unfortunately, additional inspection data such as viscosity and $M$ have not generally been available; thus, most of the empirical formulas presented herein express corresponding-states parameters as empirical functions of only $T_b$ and $S$. These characterization correlations are based on data for more than 130 pure aromatic hydrocarbons as well as NOS-substituted aromatic compounds. Using these correlations, estimates can be obtained for critical temperature $T_c$, critical molar volume $V_c$, and orientation parameter $\gamma$—the characterization parameters used for the 3PCS correlation presented herein. Note that these correlations are generally not applicable to nondistillables, which must be treated using different procedures (e.g., Brulé et al., 1981).

### Average Critical Temperature, Critical Volume, Orientation Parameter, and Molecular Weight

The equation used for many years in the petroleum industry (Cavett, 1962) has been modified for predicting $T_c$ of distillable coal-fluid fractions:

$$\begin{aligned} T_c = {} & 429.138 + 0.886861\ T_b - 4.596433 \times 10^{-4}\ {T_b}^2 \\ & - 2.410089 \times 10^{-3}\ API \times T_b + 1.630489 \times 10^{-7}\ {T_b}^3 \\ & - 9.323778 \times 10^{-7}\ API \times {T_b}^2 - 1.430628 \times 10^{-8}\ API^2 \times {T_b}^2 \end{aligned} \quad (27)$$

TABLE 2. PREDICTION OF THERMODYNAMIC PROPERTIES USING GENERALIZED 3PCS-MBWR EQUATION OF STATE[1]

| Coal Chemicals | | Characterization parameters[3] | | | | | No. of Data pts | Range | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Emp Form. | Fluid Name | Mol wt. | Crit temp $T_cK$ | Crit vol $V_c$ cm³/mol | Orient. param $\gamma$ | Prop. | | Temp. °C | Pres. kPa | %AARD | Data References |
| $H_2$ | Hydrogen[2] | 2.016 | 32.95 | 64.14 | 0. | | 180 | 100~600 | 100~20,000 | 1.46 | Vargaftik 1975 |
| $N_2$ | Nitrogen | 28.01 | 126.17 | 90.10 | 0.0263 | $P_s$ | 19 | −184~−147 | 200~3392 | 0.90 | Canjar & Manning 196 |
| | | | | | | $\rho$ | 41 | −196~116 | 101~61,611 | 0.27 | Friedman and White 1 |
| | | | | | | $H-H^o$ | 79 | −184~10 | 1379~17237 | 2.02 | |
| $CH_4$ | Methane | 16.042 | 190.69 | 99.50 | 0.01289 | $P_s$ | 30 | −199~−82 | 1~4613 | 0.68 | Douslin et al. 1964 |
| | | | | | | $\rho$ | 41 | −148 3~50 | 889~16,030 | 0.65 | Vennix 1966 |
| | | | | | | $H-H^o$ | 35 | −157~10 | 1724 ~ 13,789 | 1.34 | Yesavage 1968 |
| $H_2O$ | Water | 18.015 | 647.3 | 56.0 | 0.344 | — | — | — | — | — | Reid et al. 1977 |
| CO | Carbon monoxide | 28.011 | 132.89 | 93.04 | 0.04385 | $P_s$ | 25 | −203~−143 | 20~3039 | 1.52 | Vargaftik 1975 |
| | | | | | | $\rho$ | 40 | −205~−143 | 20~3039 | 1.06 | |
| $H_2S$ | Hydrogen sulfide | 34.076 | 373.56 | 95.00 | 0.1092 | $P_s$ | 24 | −60~101 | 101~9004 | 0.72 | Reamer et al. 1950 |
| | | | | | | $\rho$ | 41 | 4 ~ 171 | 689 ~ 13,789 | 1.85 | |
| $CO_2$ | Carbon dioxide | 44.01 | 304.17 | 94.00 | 0.2093 | $P_s$ | 33 | −56 ~ 29 | 517~7115 | 0.76 | Canjar & Manning 1967 |
| | | | | | | $\rho$ | 41 | −30~140 | 1517~31923 | 0.65 | |
| | | | | | | $H-H^o$ | 39 | −30~140 | 3041~50,678 | 3.16 | |
| COS | Carbonyl sulfide | 60.070 | 378.78 | 135.13 | 0.1070 | $P_s$ | 23 | −103~106 | 2~6349 | 1.22 | Robinson & Senturk 197 |
| $C_6H_6$ | Benzene | 78.115 | 562.09 | 257.97 | 0.2180 | $P_s$ | 37 | 16~283 | 8 ~ 4895 | 0.53 | API-44/TRC Project |
| | | | | | | $\rho$ | 36 | 132~289 | 396~4923 | 3.75 | Chao 1978 |
| $C_6H_{12}$ | Cyclohexane | 84.163 | 553.44 | 307.53 | 0.2159 | $P_s$ | 26 | 10~270 | 6~3565 | 0.72 | API-44/TRC |
| | | | | | | $\rho$ | 9 | 10~80 | 6~99 | 0.16 | |
| | | | | | | $H-H^o$ | 112 | 149~360 | 1379~9653 | 1.59 | |
| $C_7H_8$ | Toluene | 92.142 | 591.72 | 315.29 | 0.2665 | $P_s$ | 42 | 60~316 | 19~4068 | 1.45 | Vargaftik 1975 |
| | | | | | | $\rho$ | 23 | 0~110 | 101 | 0.91 | API-44/TRC |
| | | | | | | $H-H^o$ | 84 | 10~371 | 346~17,237 | 3.03 | |
| $C_7H_80$ | m-Cresol | 108.140 | 705.83 | 312.14 | 0.4667 | $P_s$ | 20 | 100~432 | 2~4550 | 0.74 | Kudchadker et al. 1978a |
| | | | | | | $\rho$ | 25 | 58~433 | 0.1~4557 | 7.26 | |
| $C_7H_{16}$ | n-Heptane | 100.21 | 540.29 | 426.13 | 0.3499 | $P_s$ | 43 | −68~258 | 0.004~2413 | 0.75 | API-44/TRC |
| | | | | | | $\rho$ | 41 | −68~238 | 101~21,243 | 0.65 | |
| | | | | | | $H-H^o$ | 16 | 267~374 | 545~16,292 | 2.13 | |
| $C_8H_{10}$ | m-Xylene | 106.169 | 616.97 | 376.07 | 0.2950 | $P_s$ | 30 | 138~343 | 106~3516 | 1.53 | API-44/TRC |
| | | | | | | $\rho$ | 59 | 20~275 | 100~40,000 | 1.20 | |
| $C_8H_{10}$ | 2,4-Xylenol | 122.166 | 707.67 | 380.66 | 0.4590 | $P_s$ | 15 | 200~434 | 76~4400 | 4.04 | Kudchadker et al. 1978b |
| $C_8H_{18}$ | n-Octane | 114.224 | 568.59 | 486.20 | 0.4004 | $P_s$ | 63 | 57~293 | 0.002~2413 | 1.16 | API-44/TRC |
| | | | | | | $\rho$ | 54 | −57~266 | 101~1655 | 1.18 | |
| | | | | | | $H-H^o$ | 66 | 24~316 | 1379~9653 | 3.17 | |
| $C_8H_6S$ | Thianaphthene | 134.20 | 752.0 | 405.72 | 0.3092 | $P_s$ | 29 | 158~357 | 19~1060 | 0.55 | Wieczorek et al 1980 |
| $C_9H_7N$ | Quinoline | 129.163 | 782.15 | 364.52 | 0.3258 | $P_s$ | 29 | 164~428 | 15~1979 | 1.16 | Wilson et al. 1979 |
| | | | | | | $\rho$ | 9 | 100~240 | 1~107 | 0.46 | Viswanath 1979 |
| $C_9H_{12}$ | Mesitylene | 120.196 | 637.28 | 433.53 | 0.3767 | $P_s$ | 12 | 35~164 | 1~101 | 3.79 | API-44/TRC |
| $C_9H_{20}$ | n-Nonane | 128.24 | 594.56 | 542.85 | 0.4463 | $P_s$ | 26 | −49~179 | 0.001~207 | 1.46 | API-44/TRC |
| $C_{10}H_8$ | Naphthalene | 128.175 | 748.33 | 410.71 | 0.2796 | $P_s$ | 17 | 199~371 | 3~1345 | 3.37 | Kudchadker et al. 1978d |
| | | | | | | $\rho$ | 18 | 218~316 | 106~586 | 4.95 | |
| $C_{10}H_{12}$ | Tetralin | 132.207 | 720.0 | 439.63 | 0.3232 | $P_s$ | 22 | 93~446 | 3~3296 | 1.10 | Nasir et al. 1980 |
| | | | | | | $\rho$ | 20 | 94~400 | 3~3296 | 1.89 | Kudchadker et al. 1978c |
| $C_{10}H_{22}$ | n-Decane | 142.276 | 617.56 | 602.01 | 0.4880 | $P_s$ | 24 | −29~204 | 0.001~207 | 0.77 | API-44/TRC |
| | | | | | | $\rho$ | 32 | 38~238 | 1379~41,368 | 1.09 | |
| $C_{11}H_{10}$ | 1-Methylnaphthalene | 142.202 | 772.22 | 445.91 | 0.3538 | $P_s$ | 17 | 142~246 | 6~103 | 1.27 | Boublik et al. 1973 |
| $C_{12}H_9N$ | Carbazole | 167.200 | 900.0 | 624.28 | 0.4650 | $P_s$ | 33 | 253~358 | 9~108 | 3.98 | Boublik et al. 1973 |
| $C_{12}H_{10}$ | Acenaphthene | 154.214 | 805.56 | 542.85 | 0.3759 | $P_s$ | 11 | 147~288 | 3~125 | 1.70 | Boublik et al. 1973 |
| $C_{12}H_{10}$ | Biphenyl | 154.214 | 788.89 | 503.45 | 0.3022 | $P_s$ | 11 | 160~360 | 7~655 | 4.38 | Vargaftik 1975 |
| | | | | | | $\rho$ | 11 | 180~360 | 14~655 | 1.36 | |
| $C_{12}H_{22}$ | Bicyclohexyl | 166.31 | 731.4 | 576.97 | 0.4078 | $P_s$ | 23 | 151~304 | 10~347 | 1.55 | Wieczorek et al. 1980 |
| $C_{13}H_9N$ | Acridine | 179.211 | 905.56 | 542.85 | 0.4044 | $P_s$ | 9 | 166~346 | 1~101 | 4.82 | McNeil 1965 |
| $C_{13}H_{10}$ | Fluorene | 166.225 | 822.22 | 594.55 | 0.4136 | $P_s$ | 12 | 161~300 | 2~108 | 1.85 | Boublik et al. 1973 |
| $C_{13}H_{12}$ | Diphenylmethane | 168.241 | 770.22 | 567.36 | 0.4358 | $P_s$ | 30 | 152~374 | 4~670 | 1.17 | Wieczorek et al. 1980 |
| $C_{14}H_{10}$ | Phenanthrene | 178.236 | 922.22 | 524.60 | 0.3299 | $P_s$ | 51 | 199~382 | 3~200 | 0.80 | Kudchadker et al. 1978 |
| | | | | | | $\rho$ | 8 | 100~320 | 1~101 | 0.67 | |
| $C_{14}H_{12}$ | 9,10-Dihydrophenanthrene | 180.25 | 846.1 | 606.1 | 0.4181 | | | | | | |
| $C_{16}H_{10}$ | Pyrene | 202.258 | 938.33 | 657.14 | 0.5532 | $P_s$ | 12 | 262~444 | 5~200 | 5.32 | Kudchadker et al. 1979 |
| $C_{16}H_{10}$ | Fluoranthene | 202.258 | 979.44 | 594.55 | 0.3251 | $P_s$ | 11 | 296~494 | 3~101 | 4.23 | Boublik et al. 1973 |
| $C_{16}H_{14}$ | 1,2,3,4-Tetrahydrofluoranthene | 206.3 | 954.4 | 625.5 | 0.3211 | $P_s$ | 5 | 127~196 | 0.1~1.4 | 0.34 | API-42, 1942–1966 |
| $C_{16}H_{34}$ | n-Hexadecane | 226.43 | 717.22 | 975.44 | 0.7122 | $P_s$ | 10 | 190~280 | 7~88 | 0.29 | Vargaftik 1975 |
| | | | | | | $\rho$ | 10 | 190~270 | 7~70 | 2.12 | |
| $C_{18}H_{12}$ | Triphenylene | 228.296 | 1013.3 | 734.45 | 0.5176 | $P_s$ | 13 | 296~494 | 5~200 | 4.78 | API-42 |
| $C_{18}H_{24}$ | 1,2,3,4,5,6,7,8,-13,14,14,16-Dodecahydrochrysene | 240.4 | 923.3 | 781.3 | 0.4795 | $P_s$ | 5 | 149~217 | 0.1~1.4 | 0.61 | API-42 |

TABLE II (*continued*)

| Coal Chemicals |  | Characterization parameters[3] |  |  |  |  | No. |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Emp Form. | Fluid Name | Mol wt. | Crit temp $T_cK$ | Crit vol $V_c$ cm³/mol | Orient. param $\gamma$ | Prop. | of Data pts | Range Temp. °C | Range Pres. kPa | %AARD | Data References |
| $C_{20}H_{26}$ | 1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-Tetradecahydroperylene | 266.4 | 929.4 | 889.3 | 0.6591 | $P_s$ | 5 | 184~252 | 0.1 ~ 1.4 | 1.66 | API-42 |

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[1] $\%AARD = 1/N \sum_{1}^{N} |(\text{exp-calc})|/\text{exp} \times 100$

[2] Parameters estimated for supercritical hydrogen corresponding to typical coal-liquefaction conditions.

[3] Some of the compounds listed are components present in the VLE systems studied by Watanasiri et al. (1981). Other coal chemiclas shown are in addition to those previously reported by Brulé et al. (1979).

[4] Water exhibits hydrogen bonding and the correlation of water properties within a 3PCS framework is difficult over wide ranges of $T$ and $P$. For making VLE calculations, $\gamma$ has been assumed to be the same as $\omega$.

[5] No pure-fluid data were found with which to determine characterization parameters via multiproperty analysis, so the parameters have been estimated in order to make VLE calculations (Watanasiri et al., 1981).

where $T_c$ is in kelvins, $T_b = 1.8\, T_b(°\text{C}) + 32$ or $T_b = T_b(°\text{F})$, and $\text{API} = 141.5/S - 131.5$. This correlation is based on $S$ @ 20/20°C (68/68°F) since most PCAH specific-gravity data reported in the literature are usually for fluids at 20°C, rather than the U.S. customary reference temperature of 60°F (15.6°C). The difference between $S$ for most aromatic hydrocarbons at the two reference temperatures is small, about 0.3%; and therefore can be neglected for most engineering calculations. The behavior of Eq. 27 for $T_c$ vs. $T_b$ at different $S$ is shown in Figure 1.

Hall and Yarborough's correlation for $V_c$ (1971) has been modified using a coal-compound data base:

$$V_c = 3.01514\, M^{1.02247}\, S^{-0.054476} \tag{28}$$

where $V_c$ is in cm³/gmol. Figure 2 illustrates that $V_c$ generated using Eq. 28 is a very weak function of $S$. If $M$ is not available, $M$ can be estimated using Eq. 30.

Estimates for $\gamma$ can be obtained from:

$$\gamma = 333.333 + 151.244(T_c/T_b) - 519.841(T_b/T_c) + 38.9063(T_b/T_c)^4 + 1255.01 \log_{10}(T_b/T_c) \tag{29}$$

where both $T_b$ and $T_c$ are in the same absolute units, i.e., in kelvins or degrees Rankine. Figure 3 gives a plot of $\gamma$ vs. the relative reduced normal boiling temperature $T_{b_r} = T_b/T_c$ generated from Eq. 29.

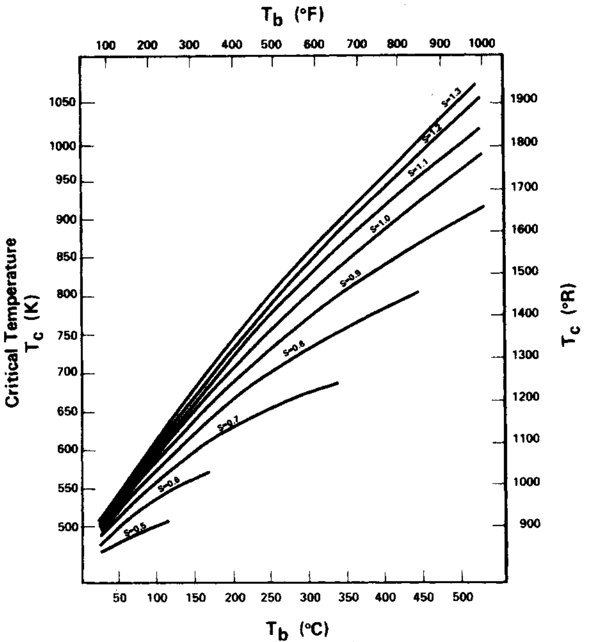

**Figure 1. Critical temperature vs. average boiling temperature of distillable coal-fluid fractions at different specific gravities.**

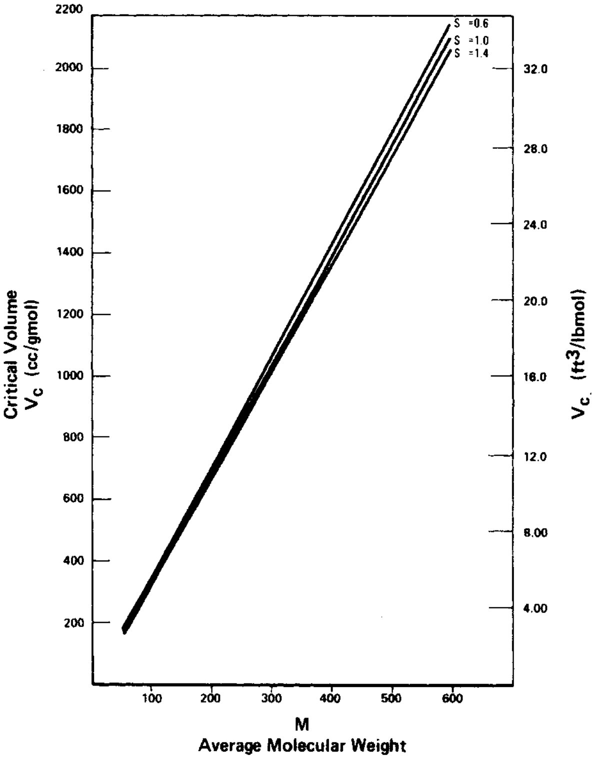

**Figure 2. Critical volume vs. fraction average molecular weight at different specific gravities.**

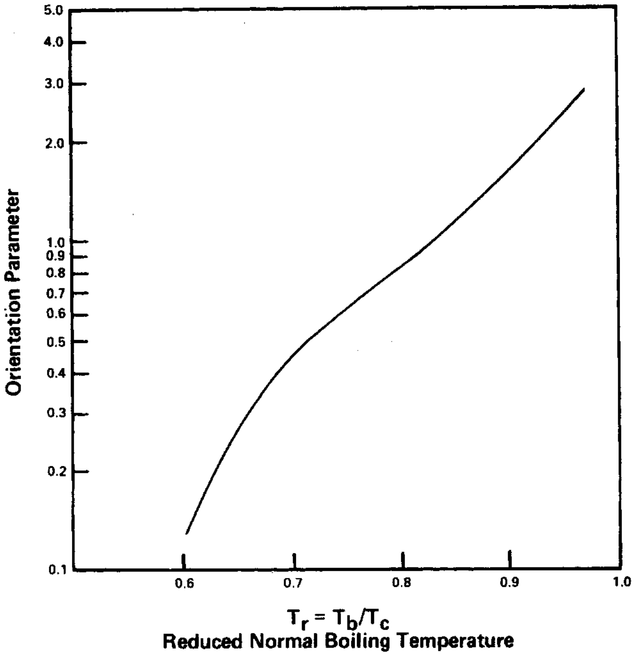

**Figure 3. Orientation parameter vs. reduced normal boiling temperature.**

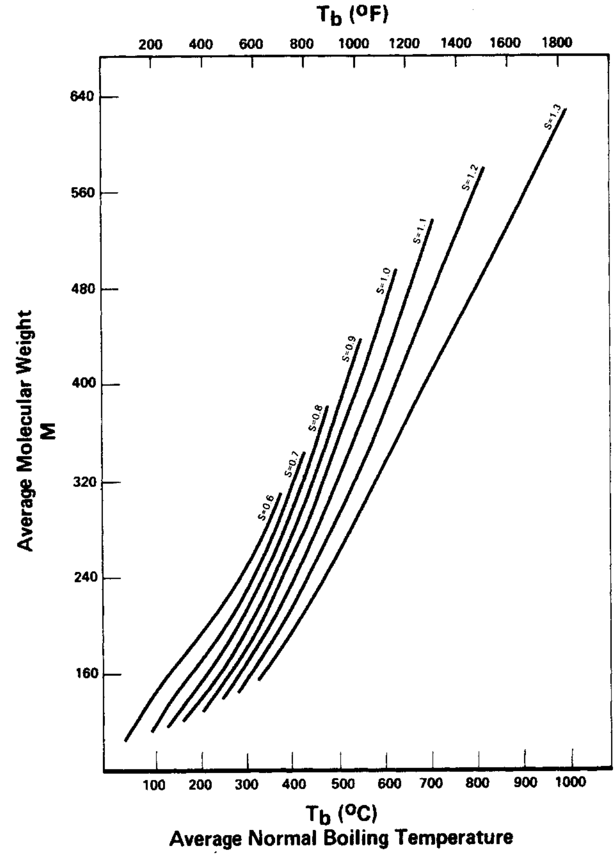

**Figure 4. Molecular weight vs. average boiling temperature at different specific gravities.**

The expression given by Kesler and Lee (1976) for calculating $M$ for petroleum fractions has been modified for coal fluids:

$$\begin{aligned} M = {} & -12421.7 + 9316.25\,S + (7.753212 - 5.362614\,S)T_b \\ & + (1.0 - 0.753344\,S - 0.0173543\,S^2)(1.42072 \\ & - 405.3994/T_b)(5.5556 \times 10^6/T_b) + (1.0 - 0.888972\,S \\ & + 0.118591\,S^2)(1.66192 - 46.75250/T_b)(1.714678 \times 10^{11}/T_b{}^3) \end{aligned} \tag{30}$$

where $T_b$ is in kelvins. Equation 30 behaves according to the plot of $M$ vs. $T_b$, at different $S$, given in Figure 4.

Equations 27, 28, 29, and 30 have been successfully used to estimate the characterization parameters for distillable, nonassaociating coal-fluid fractions in calculations of thermophysical properties. Caution should be exercised when extrapolating beyond a boiling temperature of about 350°C because little data were available for correlation development beyond this temperature.

### Ideal-Gas Thermodynamic Properties

For calculating heat capacity, enthalpy, or entropy changes during a real process, the ideal-gas heat capacity is required. The Kesler-Lee correlation (Kesler and Lee, 1976), which is designed to calculate the ideal-gas heat capacities for petroleum fluids, has been modified herein for distillable coal fluids. Most of the data used are from the API-44/TRC Data Project (1978). The expression for heat capacity, which serves as the base equation for deriving other ideal-gas properties, such as enthalpy and entropy, is

$$C_p^* = a + bT + cT^2 \tag{31}$$

where:

$$\begin{aligned} a = {} & [0.612562 \cdot 10^{-1} - 0.197528 \cdot 10^{-1}\,K + CF(0.102898 \cdot 10^1 \\ & - 0.808608S)] \cdot SI_2 \end{aligned}$$

$$\begin{aligned} b = {} & [0.140324 \cdot 10^{-2} - 0.202885 \cdot 10^{-3}\,K + 0.145194 \cdot 10^{-4}\,K^2 \\ & + CF\,(-0.153599 \cdot 10^{-2} + 0.120644 \cdot 10^{-2}\,S)] \cdot SI_1 \cdot SI_2 \end{aligned}$$

$$\begin{aligned} c = {} & [-0.198065 \cdot 10^{-6} + CF(0.496214 \cdot 10^{-6} \\ & - 0.388487 \cdot 10^{-6}\,S)] \cdot SI_1^2 \cdot SI_2 \end{aligned}$$

$$\text{and } CF = \left[\left(\frac{9.0}{K} - 1\right)\left(\frac{11.5}{K} - 1\right) \cdot 100\right]^2$$

In Eq. 31, $K$ is the Watson characterization factor defined as 1.2164 $\sqrt[3]{T_b}/S$, $T_b$ and $T$ are both in kelvins, and $SI_1 = 1.8$ and $SI_2 = 4.1868$. Ideal-gas heat capacity $C_p^*$ is in kJ/(kg · K). For U.S. customary engineering units of Btu/(lb · °F), use $K = \sqrt[3]{T_b}/S$ and $T_b$ and $T$ in °R, and set $SI_1 = SI_2 = 1$.

## CALCULATION OF THERMODYNAMIC PROPERTIES OF UNDEFINED, DISTILLABLE COAL FLUIDS

Application of the 3PCS thermodynamic correlation presented herein, to distillable coal fluids, requires the use of the characterization parameters for the undefined fluid. The characterization parameters, $T_c$, $V_c$, and $\gamma$, as well as $M$, can be estimated using Eqs. 27 through 30. For a given coal-fluid fraction, all the information required to estimate the parameters, i.e., $T_b$, $S$, and $M$, may not always be available. The following procedures are recommended for these cases:

- When $T_b$, $S$, and $M$ are available, use Eqs. 27, 28, and 29 to estimate $T_c$, $V_c$, and $\gamma$.
- When only $T_b$ and $S$ are available, use Eq. 30 to estimate $M$. Then use the estimated $M$ and Eqs. 27, 28, and 29 to calculate $T_c$, $V_c$, and $\gamma$.

Depending on what inspection data are available, the coal fluid may be treated either as a single pseudocomponent or as a mixture. Generally, more pseudocomponents need to be specified when calculating properties for multiphase systems rather than for bulk (single-phase) systems. When the $T_b$, $S$, and $M$ for just the whole fluid are given, the fluid can be treated as a single pseudocomponent having characterization parameters estimated by using the procedures prescribed above. If the whole coal fluid is characterized by separating it into different TBP fractions, with inspection data for each fraction, the fluid can be treated as a mixture with each fraction represented as a pseudocomponent. Characterization parameters for each pseudocomponent in the mixture are estimated by using the above prescribed procedures if $T_b$, $S$, and/or $M$ are available. If $S$ of each fraction is not available, but $S$ of the whole fluid is given, use the whole-fluid $S$ to calculate the $M$ of each fraction using Eq. 30; then estimate $T_c$, $V_c$, and $\gamma$ from $M$ and Eqs. 27, 28, and 29. The mole fraction of each pseudocomponent in the coal-fluid mixture can be estimated by various procedures depending on the available information:

If the weight percent (wt%) and $M$ of each fraction are given, then

TABLE 3. COMPARISON OF COAL-FLUID DENSITY DATA WITH PREDICTION VIA THE CSM-3PCS-MBWR EQUATION OF STATE[1]

| Coal liquid Designation[2] | $N$ No. of Points | $T_b$ at 50 wt% Distilled | Avg. mol wt | %AARD |
|---|---|---|---|---|
| IHS | 33 | 271°C (520°F) | 179 | 1.04 |
| IA—10 | 32 | 244 (471) | 164 | 1.58 |
| IA—6 | 36 | 260 (500) | 172 | 1.05 |
| IA—3 | 30 | 246 (475) | 167 | 4.18 |
| WA—5 | 30 | 248 (478) | 167 | 2.93 |
| WA—6 | 26 | 253 (488) | 169 | 4.52 |
| WV—1 | 29 | 276 (528) | 192 | 4.40 |
| IA—6 + $H_2$ | 18 | 260 (500) | 172 | 1.61 |
| IA—3 + $H_2$ | 18 | 246 (475) | 167 | 4.21 |
| WA—5 + $H_2$ | 22 | 248 (478) | 167 | 8.36 |
| WA—6 + $H_2$ | 30 | 253 (488) | 169 | 5.05 |
| WV—1 + $H_2$ | 28 | 276 (528) | 192 | 5.32 |
| WA—2 + $H_2$[3] | 22 | 366 (690) | 242 | 8.82 |

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[1] Data of Hwang et al. (1980).
[2] $I$ = Illinois No. 6 coal; $W$ = Wyoming Wyodak Coal.
[3] Wide-boiling fluid for which little characterization data were available.

TABLE 4. COMPARISON OF AVERAGE ABSOLUTE DEVIATIONS[1] OF ENTHALPY DIFFERENCES PREDICTED USING DIFFERENT METHODS[4]

| System[4] | Number of Data Points | Johnson-Grayson Method | Kesler-Lee Graphical Method | Huang Correlation | Lee-Kesler Equation of State | CSM-3PCS MBWR[2] (This Work) |
|---|---|---|---|---|---|---|
| | | AAD kJ/kg | | | | |
| Utah Syncrude Distillate | 21 | 26.3 | 30.2 | 25.8 | 38.1 (43)[3] | 13.9 |
| Western Kentucky Light Distillate | 16 | 9.30 | 14.0 | / | 33.5 (41) | 28.8 |
| Synthoil Distillate | 19 | 84.7 | 83.1 | 75.4 | 94.4 (42) | 28.1 |
| Western Kentucky Syncrude | 12 | 5.58 | 6.28 | 12.8 | 23.0 (43) | 20.4 |
| SRC-I Naphtha | 51 | 6.75 | 9.54 | / | / | 6.23 |
| Col #878 | 36 | 57.9 | 62.1 | / | / | 5.28 |
| Total pts | 155 | | | | (169) | |
| Overall AAD for method | kJ/kg (Btu/lb) | 31.0 (13.3) | 33.8 (14.5) | 40.9 (17.6) | 47.2 (20.3) | 13.2 (5.66) |

---

[1] AADA = $1/N\Sigma_1{}^N|H_{exp} - H_{calc}|$.

[2] Modified Kesler-Lee correlation used for ideal-gas heat capacity (Eq. 31).

[3] Number of data points (in parentheses) calculated using the method.

[4] See Kidnay and Yesavage (1979).

$$x_i = \frac{wt\%_i/M_i}{\sum\limits_j (wt\%_j/M_j)} \tag{32}$$

If only the wt% of each fraction is available, but not $M$, use $T_b$ and $S$ to estimate $M$ using Eq. 30. Then, calculate $x_i$ per Eq. 32.

If percent volume distilled, v%, $S$, and $T_b$ of each fraction distilled are given, which is the usual inspection data included in an ASTM-distillation analysis, use $T_b$ and S to estimate $M$ using Eq. 30. Then, the mole fraction, $x_i$, is calculated by:

$$x_i = \frac{v\%_i S_i/M_i}{\sum\limits_j (v\%_j S_j/M_j)} \tag{33}$$

If v% and $T_b$ of each fraction and S of the whole fluid before analysis are given, use the whole-fluid S for all the fractions. The $x_i$ can then be estimated by using Eqn. 33.

## Coal-Liquid Density Prediction

The CSM-3PCS-MBWR has been used in conjunction with characterization Eqs. 27 through 30 to predict the density of several coal liquids. The experimental data reported were measured at conditions ranging from 21 to 454°C and 6.8 to 218 atm (70 to 850°F and 100 to 3200 psia) (Hwang et al., 1980). The $T_b$ and $M$ for each liquid are given. An approximate $S$ was extrapolated from the density data. Each coal fluid was treated as a single pseudocomponent (not as a mixture), with characterization parameters calculated using Eqs. 27, 28, and 29. The density predictions summarized in Table 3 are for seven coal liquids without hydrogen and six liquids with hydrogen. The six systems of coal liquid + hydrogen were each treated as binary mixtures in equation-of-state calculations.

The good prediction results corroborate the previous observation that bulk thermodynamic properties are not strongly dependent on the resolution of the coal fluid to pseudocomponents.

## Coal-Fluid Enthalpy-Difference Prediction

Experimental enthalpy-difference data for six coal fluids have been reported by Kidnay and Yesavage (1979), in the range from 50 to 360°C (120 to 680°F) and pressures from 3.4 to 100 atm (50 to 1500 psia). The $S$ of each whole coal fluid, before resolution to pseudocomponent fractions via ASTM distillation, is reported; however, the $S$ for each fraction is not, except for one coal fluid. Herein, when only the whole-coal-fluid $S$ was available, the same $S$ was used for each fraction to calculate characterization parameters via Eqs. 27, 28, and 29. The mole fraction of each pseudocomponent was estimated herein using the procedures described for Eqs. 32 and 33. The BIPs for each binary pair were taken to be unity.

The coefficients in Eq. 31 for the ideal-gas heat capacity were determined from the experimental enthalpy-difference data, treating Eq. 21 for the enthalpy departure as being exact. Because the 3PCS correlation does not account for association effects, it is expected that predicted heats of vaporization for associating coal-fluid mixtures will be too small. Therefore, $C_p^*$ is expected to be too large when coefficients determined as above for Eq. 31 are used. However, when the original Kesler-Lee correlation (Kesler and Lee, 1976) for $C_p^*$ was used, inaccurate predictions resulted (Figure 5). It was beyond the scope of this work to fully account for association effects. The results presented herein must, therefore, be considered provisional and use should be limited to coal-fluid mixtures of the types studied to date (e.g., Kidnay and Yesavage, 1979). Nevertheless, the present correlation is probably the most accurate correlation presently available for heat-exchanger-duty calculations for coal-fluid mixtures above 300°F (Table 5 and Figures 6 and 7). Because compressor and other gas-phase calculations accentuate the errors in $C_p^*$ these calculations will be of lower

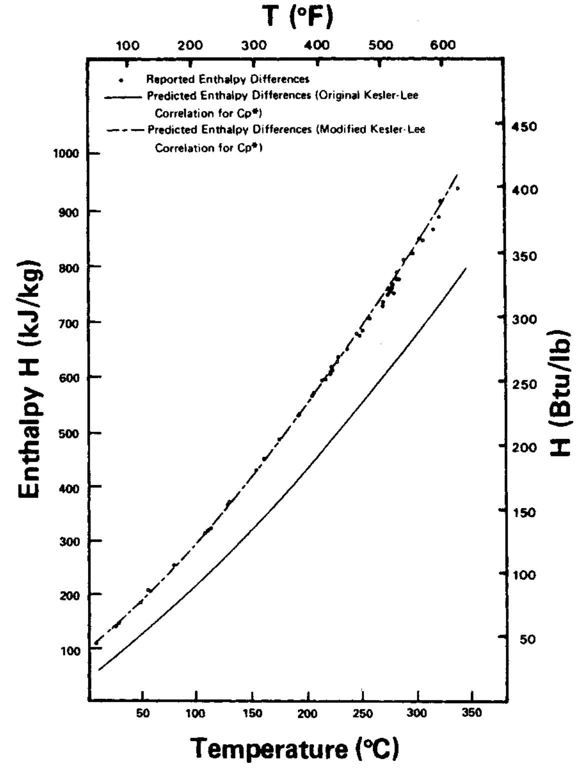

**Figure 5. Comparison of enthalpy differences predicted, using the CSM-3PCS-MBWR and Eq. 31 integrated with respect to temperature for ideal-gas enthalpy, with experimental data for a synthoil distillate.**

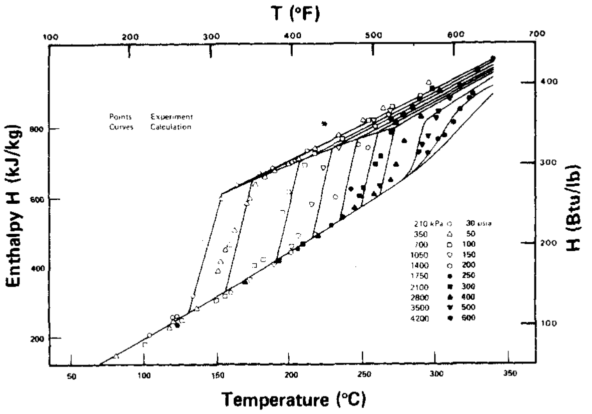

**Figure 6. Comparison of the predicted enthalpy differences with experimental measurements for SRC-1 naphtha.**

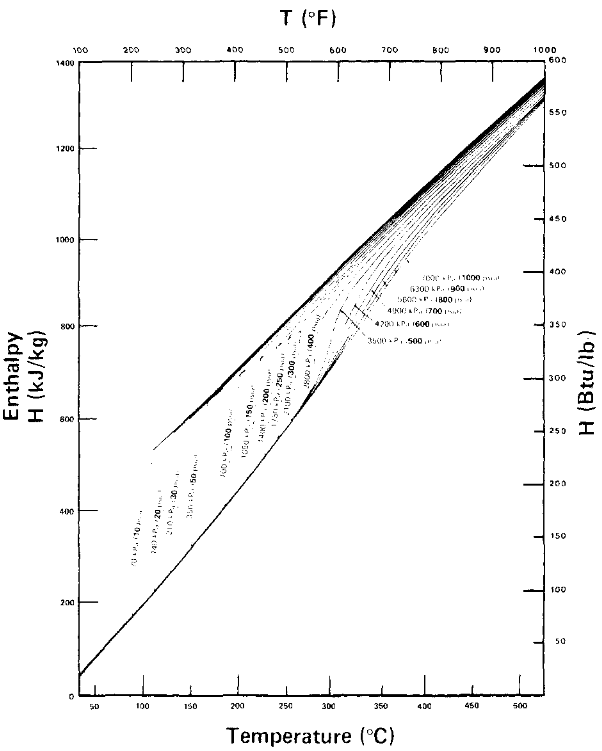

**Figure 7. T-H diagram for SRC-1 naphtha generated by using the CSM-3PCS-MBWR.**

accuracy than heat-exchanger-duty calculations. Future correlations for enthalpy departures accounting for association effects will provide further improvements. The use of these future correlations for coal-fluid mixtures will require the development of compositional analysis and characterization methods that yield characterization of the degree of association for pseudocomponent fractions. Also, compositional-analysis methods that yield information for molecular-structure characterization of fractions are needed because $T_b$ and $S$ are insufficient for correlation of ideal-gas calorimetric properties, since ideal-gas properties cannot be related using the corresponding-states principle.

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## Notation

API = °API = 141.5/S-131.5
$C_p^o$ = heat capacity in ideal-gas state
$E_i$ = generalized ith equation-of-state parameter
$a_i,b_i$ = universal constants in expression for $E_i$
$\hat{f}_i,f_i^o$ = fugacity of component $i$, standard-state reference fugacity
$H - H^o$ = specific enthalpy departure of fluid
$H^o$ = specific enthalpy of fluid in ideal-gas state, $H^o = H_T^o - H_0^o$
$ij$ = subscript denoting binary pair
$k$ = Boltzmann constant ($1.38054 \times 10^{-23}$ J/K)
$K$ = Watson characterization factor
$M$ = fraction average molecular weight
$P$ = absolute pressure
$P_c$ = critical pressure
$P_s$ = vapor pressure
$Q^*$ = reduced quadrupole moment
$S$ = specific gravity
$S - S^o$ = specific entropy departure of fluid
$S^o$ = specific entropy of fluid in ideal-gas state, $S^o = S_T^o - S_0^o$
$T$ = absolute temperature
$T^*$ = reduced temperature, $T^* = kT/\epsilon$
$T_b$ = normal boiling temperature
$T_{b_r}$ = relative reduced normal boiling temperature, $T_{b_r} = T_b/T_c$
$T_c$ = critical temperature
$T_r$ = relative reduced temperature, $T_r = T/T_c$
$v\%$ = average volume percent distilled
$V_c$ = critical volume
$x$ = subscript denoting mixture
$x_i$ = liquid-phase mole fraction
$Z$ = fluid compressibility factor
$Z_o$ = isotropic-reference-fluid compressibility factor
$Z_\omega$ = first-order perturbation contribution to compressibility factor

## Greek Letters

$\epsilon$ = characteristic molecular-energy parameter
$\gamma$ = molecular orientation parameter
$\mu^*$ = reduced dipole moment
$\rho$ = density
$\rho_c$ = critical density
$\rho^*$ = reduced number density, $\rho^* = \rho\sigma^3$
$\rho_r$ = relative reduced density, $\rho_r = \rho/\rho_c$
$\omega$ = acentric factor
$\sigma$ = characteristic molecular-size parameter
$\xi_{ij}$ = molecular-size binary-interaction parameter
$\zeta_{ij}$ = molecular-energy BIP
$\hat{\phi}_i$ = fugacity coefficient of component $i$

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