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Continuous Mixture Computational Algorithm of Reservoir Fluid Phase Behavior Applicable for Compositional Reservoir Simulation

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ABSTRACT

Development of compositional reservoir simulators is presently hampered due to the complexity of the existing computational algorithms of reservoir fluid phase behavior calculations. Through the application of the theory of polydisperse fluid mixtures we have been able to develop a number of algorithms for phase behavior calculations. In the present report we introduce one of such algorithms. In this algorithm reservoir fluid is considered to consist of a continuous mixture with a defined molecular weight/composition distribution function. Computational computer time required for the new algorithm is shown to be one order of magnitude smaller than the existing algorithms. As an example, the new algorithm is used to perform retrograde condensation calculations for two different gas-condensate reservoir fluids. Comparisons of experimental data with the calculated results indicate good agreement between the two.

INTRODUCTION

In conventional Gibbsian thermodynamics for multiphase equilibrium calculations, it is assumed that each component of the mixture can be identified and its concentration can be determined by ordinary chemical analysis. This assumption is feasible if the system contains only a few components. The species concentrations for highly complex mixtures cannot be determined by ordinary chemical analysis. Examples of such mixtures are petroleum reservoir fluids, vegetable oils, polymer solutions or the like. In these cases, the assumption of known mole fractions is invalid, and phase predictions using conventional Gibbsian thermodynamics is not feasible.

References and illustrations at end of paper.

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Another method which is an extension of Gibbsian thermodynamics, generally called continuous thermodynamics, has been used extensively to perform phase equilibrium calculations for complex mixtures. Instead of using the mole fractions of components or of pseudocomponents (e.g., Yarborough¹), a continuous distribution function is used for describing the composition of such complex mixtures.

A number of earlier efforts in the direction of continuous thermodynamics are known. To introduce continuous distribution functions to complex mixtures such as reservoir fluids, some investigators have presented a number of theories which can be applied within the framework of thermodynamics and statistical mechanics (e.g., Gal-Or et al.²; Vrij³; Blum and Stell⁴; Dickinson⁵). Studies based on the concept of continuous thermodynamics have been presented by another group of investigators for petroleum distillations and polymer separations (e.g., Bowman⁶; Scott⁷; Hoffman⁸; Komingsveld⁹; Taylor and Edmister¹⁰; Flory and Abe¹¹). All the contributions mentioned above have been restricted to specific models (Raoult's law). These studies can not be applied to the general problem of continuous thermodynamics whose fundamentals do not necessarily rely on the ideal solution models of the chemical potentials.

In recent years, a number of advances in the direction of phase equilibrium calculation of non-ideal continuous mixtures have been made: Gualtieri et al.¹² have used the continuous van der Waals equation of state to solve the fractionation of a polydisperse impurity dissolved in a solvent and to predict the shift of the critical point. Based on the Redlich-Kwong equation of state, Briano¹³ had similar results for flash calculations of continuous mixtures. Kehlen et al.¹⁴ have reviewed the concept of

continuous thermodynamics in generating general thermodynamic property relations for such properties as chemical potential, entropy, enthalpy and Gibbs free energy of continuous mixtures. Cotterman and Prausnitz¹⁵ have developed two techniques for performing phase equilibrium calculations of both continuous and semicontinuous mixtures utilizing the technique proposed by Gualtieri et al.¹² and with the use of the Soave equation of state. In our previous reports (Du and Mansoori^{16,17}) we have presented three different computational algorithms by which the phase equilibrium calculations of continuous mixtures, consisting of species with a wide molecular weight distribution can be performed effectively. The algorithms are proved to be applicable to varieties of complex mixtures, equations of state, and mixing rules.

In this report, a general technique which is based on one of our three algorithms, namely "The Minimization of The Total Gibbs Free Energy Algorithm", will be introduced. Flash calculations of a complex mixture containing both discrete components and a continuous fraction will be performed by using this proposed technique. The reason for the choice of this algorithm in the present calculations is because it produces analytical equations for continuous reservoir fluid mixtures which will reduce the computational time even more than the other existing algorithms.

THEORY OF PHASE EQUILIBRIUM OF CONTINUOUS MIXTURES

For a mixture with many components being continuous in character, the compositions can be described by a density distribution function, $F(I, I_0, \eta)$ whose independent variable I is some measurable property such as molecular weight, boiling point or density with a mean value of I_0 and a variance of η . The normalizing condition of the density distribution function is defined by

$$\int_I F(I) dI = 1 \quad (1)$$

The distribution functions are not additive, as a result, $F_F(I)$, $F_L(I)$ and $F_V(I)$ will not possess the same functional forms in a specific flash calculation scheme. There exists another class of complex mixtures which are, in part, continuous and contain sufficiently large amounts of components which should be considered as discrete components. In such cases, eqn.(1) will be valid for the continuous fraction of the mixture, while for the whole mixture the following normalizing condition will hold:

$$\sum_i^d x_i + x_c = 1 \quad (2)$$

where x_i and x_c are the mole fraction of discrete component i and the continuous fraction, respectively and d is the total number of discrete components in the mixture. Regarding the material

balance of component I in continuous fraction, we get

$$z_c F_F(I) = x_c \phi_L F_L(I) + y_c \phi_V F_V(I) \quad (3)$$

If we were going to follow the conventional Gibbsian thermodynamics, the conditions of identical temperatures, pressures and chemical potentials of components in each phase would form the fundamental basis for multicomponent phase equilibrium calculations. Thus for the vapor-liquid equilibrium calculations for a mixture consisting of both discrete components and a continuous fraction, it would mean that the following conditions should be satisfied:

$$T = T^L = T^V \quad (4)$$

$$P = P^L = P^V \quad (5)$$

$$\mu_i^L = \mu_i^V \quad i (1, d) \quad (6)$$

$$\mu^L(I) = \mu^V(I) \quad I (1, \infty) \quad (7)$$

However, considering the fact that the continuous fraction contains a large number of components, eqn.(7) will have to represent a multitude of equations. Therefore, simultaneous solution of eqn's.(4)-(7) for continuous mixtures in vapor-liquid equilibrium would be very difficult or technically impossible. Because of this difficulty we are proposing the phase equilibrium technique presented below.

In order to extend continuous thermodynamics to engineering applications we introduce a general technique which is based on one of our previous proposed algorithms (Du and Mansoori¹⁷) namely "The Minimization of The Total Gibbs Free Energy Algorithm". Using this technique, flash calculations of complex mixtures containing discrete components and a continuous fraction, which has a wide molecular weight distribution, are performed here.

For a system in equilibrium (constant T and P), for any differential "virtual displacement" occurring in the system, a general criterion of equilibrium should be imposed on the system such that the total Gibbs free energy is minimal.

$$(\delta G)_{T, P=0} = 0 \quad (8)$$

To restrict our consideration only to the vapor-liquid equilibrium, we write the total Gibbs free energy of the system as:

$$G = G_L + G_V \quad (9)$$

For a mixture consisting of discrete components and a one-family continuous fraction, we derive an expression of the Gibbs free energy for the liquid phase;

$$G_L = \int_{V_L}^{\infty} \left[P - \frac{N_L RT}{V} \right] dV - RT \sum_i^d N_i \ln \frac{V_L}{N_i RT} - N_c RT \int_{I_{oL}}^{\infty} F_L(I) \ln \left[\frac{V_L}{N_c F_L(I) RT} \right] dI + PV_L + G_L^* \quad (10)$$

where G_L^* is the Gibbs free energy of the reference state. A similar expression will hold for the vapor phase. The Gibbs free energies of the liquid and vapor phases above provide the key relations for representing the total Gibbs free energy of the system as a function of temperature, volumes, mole fractions of components, the mean values, and the variances of distribution functions in the liquid and vapor phases. Since, the system is in equilibrium, according to eqn. (8), all of the first derivatives of the total Gibbs free energy, G , with respect to the system variables must be equal to zero, i.e.

$$(\partial G / \partial \eta_L)_{T, P, x_i, y_i, \eta_V, I_{oL}, I_{oV}} = 0 \quad (11)$$

$$(\partial G / \partial \eta_V)_{T, P, x_i, y_i, \eta_L, I_{oL}, I_{oV}} = 0 \quad (12)$$

$$(\partial G / \partial I_{oL})_{T, P, x_i, y_i, \eta_L, \eta_V, I_{oV}} = 0 \quad (13)$$

$$(\partial G / \partial I_{oV})_{T, P, x_i, y_i, \eta_L, \eta_V, I_{oL}} = 0 \quad (14)$$

To perform flash calculations for a system composed of discrete components and a continuous fraction, eqn's. (5) and (6), coupled with eqn's. (11)-(14), will form a set of nonlinear equations which must be solved simultaneously.

To illustrate the application of the proposed technique, in what follows we will use the Peng-Robinson equation of state and perform flash calculations for gas-condensate reservoir fluids.

The Peng-Robinson equation of state is

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (15)$$

where

$$a(T) = a(T_c) [1 + \kappa(1 - T_r^{-1/2})]^2 \quad (16)$$

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c \quad (17)$$

$$b = 0.0778 R T_c / P_c \quad (18)$$

$$\kappa = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad (19)$$

For mixtures consisting of m components, it has been very common to represent parameters a and b with the following expressions which are known as the mixing rules

$$a = \sum_i^m \sum_j^m x_i x_j a_{ij} \quad (20)$$

$$b = \sum_i^m x_i b_i \quad (21)$$

where

$$a_{ij} = (1 - k_{ij}) (a_{ii} a_{jj})^{1/2} \quad \text{when } (i=j) \quad (22)$$

and k_{ij} is the binary interaction parameter.

In order to extend the Peng-Robinson equation of state to a mixture containing d discrete components and a continuous fraction with a wide molecular weight distribution, we need to rewrite the mixing rules in the following forms:

$$a = \sum_i^d \sum_j^d x_i x_j a_{ij} + 2 \sum_i^d x_i x_c \int_I F(I) a(i, I) dI + x_c^2 \int_I \int_J F(I) F(J) a(I, J) dJ dI \quad (23)$$

$$b = \sum_i^d x_i b_i + x_c \int_I F(I) b(I) dI \quad (24)$$

where

$$a(i, I) = a_i^{1/2} a^{1/2}(I) (1 - k_{iI}) \quad (25)$$

$$a(I, J) = a^{1/2}(I) a^{1/2}(J) (1 - k_{IJ}) \quad (26)$$

and where x_i and x_c are the mole fractions of component i and the whole continuous fraction, respectively. Parameters $a^{1/2}(I)$ and $b(I)$ can be accurately represented by third-order polynomials with respect to molecular weight I for a homologous series of paraffinic hydrocarbons as given below.¹⁶

$$a^{1/2}(I) = \alpha_1 + \alpha_2 I + \alpha_3 I^2 + \alpha_4 I^3 \quad (27)$$

where

$$\alpha_1 = 0.4771 + 0.0157 T^{1/2}; \quad \alpha_2 = 0.1055 + 0.0017 T^{1/2};$$

$$\alpha_3 = -0.4066 \times 10^{-4} + 0.2960 \times 10^{-5} T^{1/2};$$

$$\alpha_4 = 0.2700 \times 10^{-6} - 0.1318 \times 10^{-8} T^{1/2}$$

and

$$b(I) = \beta_1 + \beta_2 I + \beta_3 I^2 + \beta_4 I^3 \quad (28)$$

where $\beta_1 = 0.0071$, $\beta_2 = 0.0013$, and $\beta_3 = -0.1371 \times 10^{-5}$, $\beta_4 = 0.9586 \times 10^{-8}$.

We may further introduce the exponential-decay distribution function

$$F(I) = (1/\eta) \exp[-(I - I_o)/\eta] \quad (29)$$

which is a proper distribution function for describing the composition of gas-condensate

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fluids.^{16,17} In applying the proposed technique to the phase equilibrium calculations of a gas condensate system, we need to derive an expression for the total Gibbs free energy of the system. Knowing that methane constitute a large fraction of every gas condensate system, it is appropriate to treat the system as a mixture of methane and a continuous fraction of the rest of hydrocarbons. As a result, by substituting eqn. (15) into eqn. (9) and considering eqn. (29) as the continuous fraction distribution function, the total Gibbs free energy of a system containing a single discrete component and a continuous fraction will be of the following form:

$$\bar{G} = \phi_L \bar{g}_L + \phi_V \bar{g}_V \quad (30)$$

where

$$\begin{aligned} \bar{g}_L = & -RT \ln(v_L - b_L) + \frac{a_L}{2.828b_L} \ln \frac{v_L - 0.414b_L}{v_L + 2.414b_L} + RT(x_1 \ln x_1 + x_c \ln x_c \\ & - x_c - x_c \ln \eta_L) + \frac{v_L RT}{v_L - b_L} - \frac{a_L v_L}{v_L(v_L + b_L) + b_L(v_L - b_L)} \quad (31) \end{aligned}$$

and \bar{g}_V will have a similar expression. The analytical expressions for parameters a_L and b_L of the Peng-Robinson equation of state are as the following:

$$a_L = x_1^2 a_{11} + x_c^2 a_{cL}^2 + 2x_1 x_c (a_{11})^{1/2} (a_{cL})^{1/2} a_{11} \quad (32)$$

where

$$\begin{aligned} a_{11} = & \exp(-70.0/\eta_L) (q_1 + q_2 \eta_L + q_3 \eta_L^2 + q_4 \eta_L^3 \\ & + q_5 \eta_L^4) \\ a_{cL} = & [a_1 + a_2 (I_0 + \eta_L) + a_3 (I_0^2 + 2I_0 \eta_L + 2\eta_L^2 \\ & + a_4 (I_0^3 + 3I_0^2 \eta_L + 6I_0 \eta_L^2 + 6\eta_L^3))]^2 - 0.02 \{ \\ & (a_{22})^{1/2} [\exp(-70.0/\eta_L) - \exp(-84.0/\eta_L)] + (a_{33})^{1/2} \\ & [\exp(-84.0/\eta_L) - \exp(-98.0/\eta_L)] \} (s_1 + s_2 \eta_L \\ & + s_3 \eta_L^2 + s_4 \eta_L^3) \\ q_1 = & -0.0579\alpha_1 - 5.344\alpha_2 - 5.344 \times 10^2 \alpha_3 \\ & - 5.345 \times 10^4 \alpha_4 \\ q_2 = & 0.441 \times 10^{-4} \alpha_1 - 0.0491 \alpha_2 - 10.257 \alpha_3 - 1.662 \times 10^2 \alpha_4 \\ q_3 = & 0.8822 \times 10^{-4} \alpha_2 + 2.5308 \alpha_3 - 34.398 \alpha_4 \\ q_4 = & 2.6466 \times 10^{-4} \alpha_3 - 0.393 \alpha_4 \\ q_5 = & 1.0586 \times 10^{-3} \alpha_4 \\ s_1 = & \alpha_1 + \alpha_2 \times 10^2 + \alpha_3 \times 10^4 + \alpha_4 \times 10^6 \\ s_2 = & \alpha_2 + 2\alpha_3 \times 10^2 + 3\alpha_4 \times 10^4 \end{aligned}$$

$$s_3 = 2\alpha_3 + 6\alpha_4 \times 10^2$$

$$s_4 = 6.0\alpha_4$$

and

$$\begin{aligned} b_L = & x_1 b_1 + x_c [\beta_1 + \beta_2 (I_0 + \eta_L) + \beta_3 (\\ & I_0 + 2I_0 \eta_L + 2\eta_L^2) + \beta_4 (I_0^3 + 3I_0^2 \eta_L \\ & + 6I_0 \eta_L^2 + 6\eta_L^3)] \quad (33) \end{aligned}$$

In the above equations b_1 is the (b) parameter of the Peng-Robinson equation of state for methane and s_{11} , s_{22} , and s_{33} are the (a) parameter of the Peng-Robinson equation of state for methane, ethane, and propane, respectively. Similar relations will hold for parameters a_V and b_V .

To perform flash calculations, we need to substitute eqn. (30) into eqn's. (11)-(14). Since for gas-condensates $I_0^2 = I_0 L = I_0 V$, eqn's. (13) and (14) will vanish, we only need to solve eqn's. (5) and (6), coupled with eqn's. (11) and (12), simultaneously. The analytic expressions of the resulting equations are given as the following:

$$\begin{aligned} \frac{RT}{v_L - b_L} - \frac{a_L}{v_L(v_L + b_L) + b_L(v_L - b_L)} \\ = \frac{RT}{v_V - b_V} - \frac{a_V}{v_V(v_V + b_V) + b_V(v_V - b_V)} \quad (34) \end{aligned}$$

$$\begin{aligned} RT \ln \left[\frac{v_L}{v_L - b_L} \right] + \frac{RT b_1}{v_L - b_L} + \frac{a_L v_L b_1}{b_L (v_L^2 + 2v_L b_L - b_L^2)} \\ + \left[\frac{x_1 a_{11} + x_c (a_{11})^{1/2} (a_{cL})^{1/2} a_{11}}{1.414 b_L} + \frac{a_L b_1}{2.828 b_L^2} \right] \\ \ln \left[\frac{v_L - 0.414 b_L}{v_L + 2.414 b_L} \right] - RT \ln \left[\frac{v_L}{x_1 RT} \right] \\ = RT \ln \left[\frac{v_V}{v_V - b_V} \right] + \frac{RT b_1}{v_V - b_V} + \frac{a_V v_V b_1}{b_V (v_V^2 + 2v_V b_V - b_V^2)} \\ + \left[\frac{y_1 a_{11} + y_c (a_{11})^{1/2} (a_{cV})^{1/2} a_{11}}{1.414 b_V} + \frac{a_V b_1}{2.828 b_V^2} \right] \\ \ln \left[\frac{v_V - 0.414 b_V}{v_V + 2.414 b_V} \right] - RT \ln \left[\frac{v_V}{y_1 RT} \right] \quad (35) \end{aligned}$$

$$\begin{aligned} \frac{x_c (\bar{g}_L - \bar{g}_V)}{y_c \eta_V - x_c \eta_L} + \left\{ \frac{RT}{v_L - b_L} - \frac{a_L}{2.828 b_L^2} \ln \left[\frac{v_L - 0.414 b_L}{v_L + 2.414 b_L} \right] \right. \\ \left. - \frac{v_L a_L}{b_L (v_L^2 + 2v_L b_L - b_L^2)} + \frac{v_L RT}{(v_L - b_L)^2} \right. \\ \left. + \frac{2a_L v_L (v_L - b_L)}{[v_L (v_L + b_L) + b_L (v_L - b_L)]^2} \right\} \left(\frac{\partial b_L}{\partial \eta_L} \right)_{P, T, \eta_V} - \frac{RT x_c}{\eta_L} \\ + \left[\frac{1}{2.828 b_L} \ln \left[\frac{v_L - 0.414 b_L}{v_L + 2.414 b_L} \right] \right. \end{aligned}$$

$$-\frac{v_L}{v_L^2 + 2b_L v_L - b_L^2} \left\{ \frac{\partial a_L}{\partial \eta_L} \right\}_{P, T, \eta_V} = 0 \quad (36)$$

and

$$\begin{aligned} & \frac{y_c (g_L - g_V)}{y_c \eta_V - x_c \eta_L} + \left\{ \frac{RT}{v_V - b_V} - \frac{v^a}{2.828 b_V} \ln \left[\frac{v_V - 0.414 b_V}{v_V + 2.414 b_V} \right] \right. \\ & - \frac{v_V a_V}{b_V (v_V^2 + 2b_V v_V - b_V^2)} + \frac{v_V RT}{(v_V - b_V)^2} \\ & + \left. \frac{2a_V v_V (v_V - b_V)}{[v_V (v_V + b_V) + b_V (v_V - b_V)]^2} \right\} \left(\frac{\partial b_V}{\partial \eta_V} \right)_{P, T, \eta_L} - \frac{RT y_c}{\eta_V} \\ & + \left\{ \frac{1}{2.828 b_V} \ln \left[\frac{v_V - 0.414 b_V}{v_V + 2.414 b_V} \right] \right. \\ & - \left. \frac{v_V}{v_V^2 + 2b_V v_V - b_V^2} \right\} \left(\frac{\partial a_V}{\partial \eta_V} \right)_{P, T, \eta_L} = 0 \quad (37) \end{aligned}$$

In what follows the proposed algorithm is used for calculation of properties of two different gas-condensate systems.

COMPARISON OF CALCULATED AND EXPERIMENTAL RESULT

In our calculations, we use the Peng-Robinson equation of state to perform flash calculations for two different gas-condensate systems.^{18,19} Each of the two gas-condensate systems is treated as a fluid with a discrete component of methane and a continuous fraction of other hydrocarbons. The continuous fraction is described by an exponential-decay distribution function starting from the molecular weight of ethane. In performing phase equilibrium calculations based on an equation of state we will need to define the unlike pair-interaction parameters appearing in eqn.(22). For calculation of the binary interaction parameter k_{ij} of gas-condensate systems, the following procedure is used:

- (i) It is assumed that $k_{ij}=0$ for all binary pairs except for methane-C₇+, ethane-C₇+, and propane-C₇ interactions.
- (ii) It is assumed that $k_{ij}=0.01$ for ethane-C₇ and propane-C₇ binary pairs as proposed by Katz and Firoozabadi.²⁰
- (iii) Katz and Firoozabadi have also proposed the following expression relating k_{ij} of methane-C₇ to the specific gravity of the C₇ hydrocarbons:

$$k_{i,i} = -0.129 (SG)_i - 0.055855 \quad (38)$$

From the data reported by Hoffmann et al.¹⁸, the following expression relating the specific gravity to molecular weight of pseudocomponent hydrocarbons can be deduced.

$$(SG)_i = 0.3419 \times 10^{-3} I - 0.01585 \quad (39)$$

By joining the above two equations the following expression relating the pair-interaction parameter of methane-C₇ to molecular weight of hydrocarbons will be derived.

$$k_{i,i} = -0.057 + 0.4411 \times 10^{-4} I \quad (40)$$

In what follows flash calculations for two different gas-condensate systems are reported and the results are compared with the available experimental data.

(i) Comparison of calculated and experimental results for Hoffmann et al. gas-condensate system: Hoffmann et al.¹⁸ have reported a gas-condensate data set in which the crude oil composition, equilibrium condensate phase equilibrium data and liquid-vapor volume ratios at different pressures are given. As mentioned above, this system is treated as a mixture of methane (with a mole fraction of 0.9135) and a continuous fraction of other hydrocarbons. The continuous fraction is described by an exponential-decay distribution function (with a variance of $\eta=22.3$). In Fig.(1) and (2) the component mole fraction equilibrium ratio (K-value) and liquid-vapor volume ratio as calculated by the present algorithm are compared with experimental data (dots) at 201°F, respectively. Also reported in these figures are the results (squares) of calculations based on a pseudocomponent method²⁰. According to these figures, flash calculations based on the present technique produce results which are in good agreement with the experimental data. Also, the results calculated by our proposed technique show that they are as accurate as those obtained using a pseudocomponent technique.

(ii) Comparison of calculated and experimental results for Ng et al. gas-condensate system: Ng et al.¹⁹ have reported another set of data for a gas-condensate reservoir system. This system is also treated as a mixture of methane (with a mole fraction of 0.74133) and a continuous fraction of other hydrocarbons described by an exponential-decay distribution function (having a variance of $\eta=48.9$). In our calculation, we use a treatment which is similar to the previous calculation to predict the phase behavior of the system. In Fig's.(3), (4) and (5) the component mole fraction equilibrium ratio (K-value), liquid volume percent (with respect to total volume of the system), and the P-T diagram as calculated by the present technique are compared with the experimental data (dots) of Ng et al.¹⁹ As shown in Fig's.(3)-(5), the flash calculations performed by using the proposed continuous mixture technique are in good agreement with the experimental data.

CONCLUSIONS

The proposed technique provides a general and convenient procedure for performing flash calculations for a reservoir fluid mixture consisting of both discrete and continuous components. Compared to the conventional pseudocomponent methods, the proposed technique can reduce the required computer time and overcome the complexity for solving a multitude of simultaneous

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equations. Also, this technique is capable of predicting properties of gas-condensate systems accurately. The present technique is applicable to varieties of complex reservoir fluid mixtures, equations of state, mixing rules, and combining rules. Based on the present technique, a versatile computer program has been developed by the authors which can be used to predict phase behavior of varieties of reservoir fluids containing discrete and continuous components.

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REFERENCE

1. Yarborough, L.: "Application of a Generalized Equation of State To Petroleum Reservoir Fluid," in the ACS Symposium Series #182, American Chemical Society, Washington D. C. (1979), 383-439.
2. Gal-Or, B., Cullinan, H. T. and Galli, R.: "New Thermodynamic-Transport Theory for Systems With Continuous Component Density Distributions," Chem. Eng. Sci. (1975) 30, 1085-1092.
3. Vrij, A.: "Light Scattering of a Concentrated Multi-component System of Hard Spheres in the Percus-Yevick Approximation," J. Chem. Phys. (1978) 69, 1742-1747.
4. Blum, L. and Stell, G.: "Polydisperse System. I. Scattering function for polydisperse fluids of hard or permeable spheres," J. Chem. Phys. (1979) 71, 42-46.
5. Dickinson, E.: "Statistical Thermodynamics of Fluid Phase Equilibrium in A Conformal Polydisperse System," J. Chem. Soc. Faraday II (1980) 76, 1458-1467.
6. Bowman, J.R.: "Distillation of an Indefinite Number of Components," Ind. Eng. Chem. (1949) 41, 2004-2007.
7. Scott, R.L.: "The Thermodynamics of High-Polymer Solutions," J. Chem. Phys. (1949) 17, 268-279.
8. Hoffman, E.J.: "Flash Calculations for Petroleum Fractions," Chem. Eng. Sci. (1968) 23, 957-64.
9. Koningsveld, R.: "Phase Relationships and Fractionation in Multicomponent Polymer Solutions," Pure Appl. Chem. (1969) 20, 271-307.
10. Taylor, D.L. and Edmister, W.C.: "Solutions for Distillation Processes Treating Petroleum Fractions," AIChE J. (1971) 17, 1324-29.
11. Flory, P.J., and Abe, A.: "Statistical Thermodynamics of Mixtures of Rodlike Particles," Macromolecules (1979) 11, 1119-1126.
12. Gualtieri, J.A., Kinacid, J.M., and Morrison, G.J.: "Phase Equilibria in Polydisperse Fluids," J. Chem. Phys. (1982) 77, 121-36.
13. Briano, J.G.: Classical and Statistical Thermodynamics of Continuous Mixtures, Ph. D. Thesis, University of Pennsylvania (1983).
14. Kehlen, H., Rätzsch, M.T. and Bergmann, J.: "Continuous Thermodynamics of Multicomponent System," AIChE J. (1985) 31, 1136-1148. [Kehlen and Rätzsch have published numerous other papers in the area of continuous thermodynamics previous to this paper. However, due to the large number of conceptual errors which exists in those other papers, we do not recommend their study to a first-timer. However, this last paper is a review of the basic concepts of continuous thermodynamics.]
15. Cottersman, R.L. and Frausnitz, J.M.: "Flash Calculation for Continuous or Semicontinuous Mixtures Using an Equation of State," Ind. Eng. Chem. Process Des. Dev. (1985) 24, 434-443.
16. Du, P. C. and Mansoori, G. A.: "A Continuous Mixture Computational Algorithm for Reservoir Fluids Phase Behavior," (1986) SPE Paper #15082.
17. Du, P. C. and Mansoori, G. A.: "Phase Equilibrium Computational Algorithms of Continuous Mixtures," Proceedings of Fourth International Conference on Fluid Properties & Phase Equilibria for Chemical Process Design, Lo-Skolen, Denmark (1986) 8/58-8/64.
18. Hoffmann, A. E., Crump, J. S. and Hocott, C. R.: "Equilibrium Constants for A Gas-Condensate System," Pet. Trans., AIME (1953) 198, 1-8.
19. Ng, H. J., Chen, C. J. and Robinson, D. B.: "Vapor Liquid Equilibrium and Condensing Curves in The Vicinity of the Critical Point for A Typical Gas Condensate," Project 815-A-84, GPA Research Report #RR-96, Gas Processors Association (Nov. 1985) Tulsa, Ok.
20. Katz, D.L., and Firoozabadi, A.: "Predicting Phase Behavior of Condensate/Crude Oil systems Using Methane Interaction Coefficients," J. Pet. Tech. (1978) 228, 1649-55.

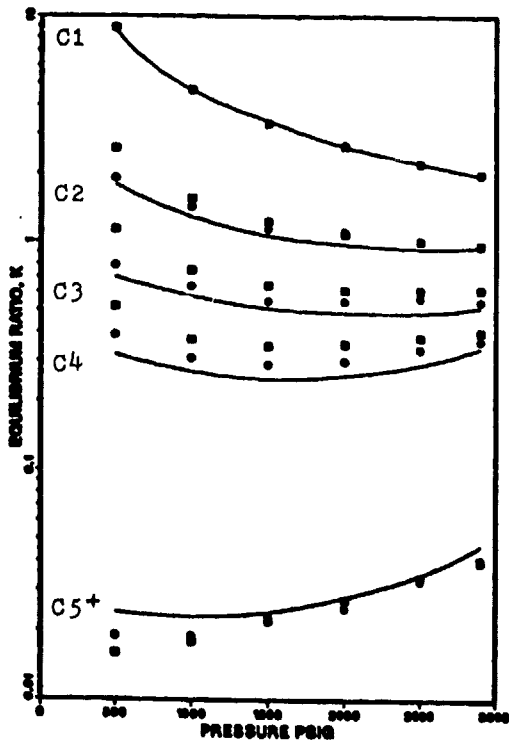


Fig. 1—Component mole fraction equilibrium ratio (K-value) of a gas condensate¹⁸ at 201°F.

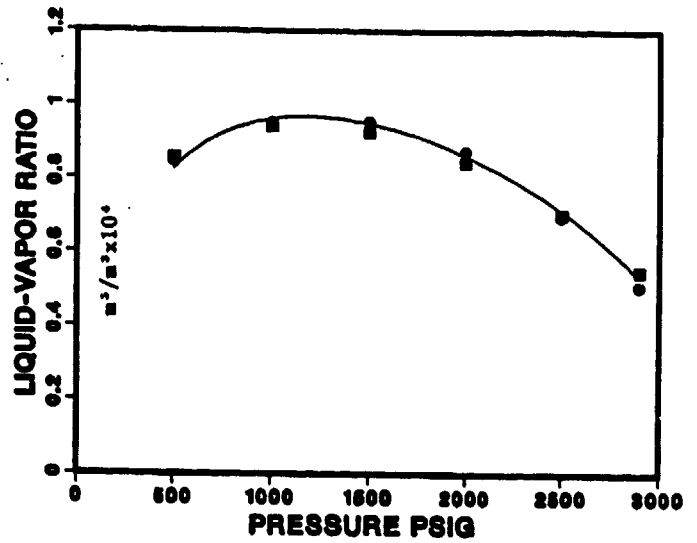


Fig. 2—Liquid-vapor volume ratio of a gas-condensate reservoir fluid¹⁸ at 201°F.

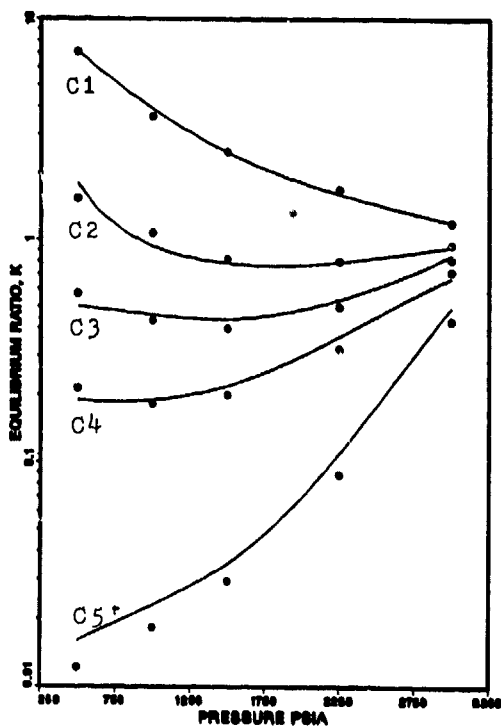


Fig. 3—Component mole fraction equilibrium ratio (K-value) of a gas-condensate reservoir fluid¹⁹ at 100°F.

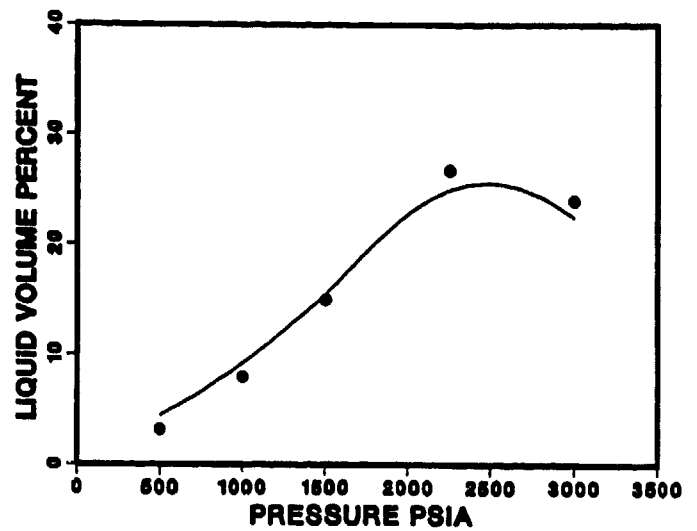


Fig. 4—Liquid volume percent of a gas-condensate reservoir fluid¹⁹ at 100°F.

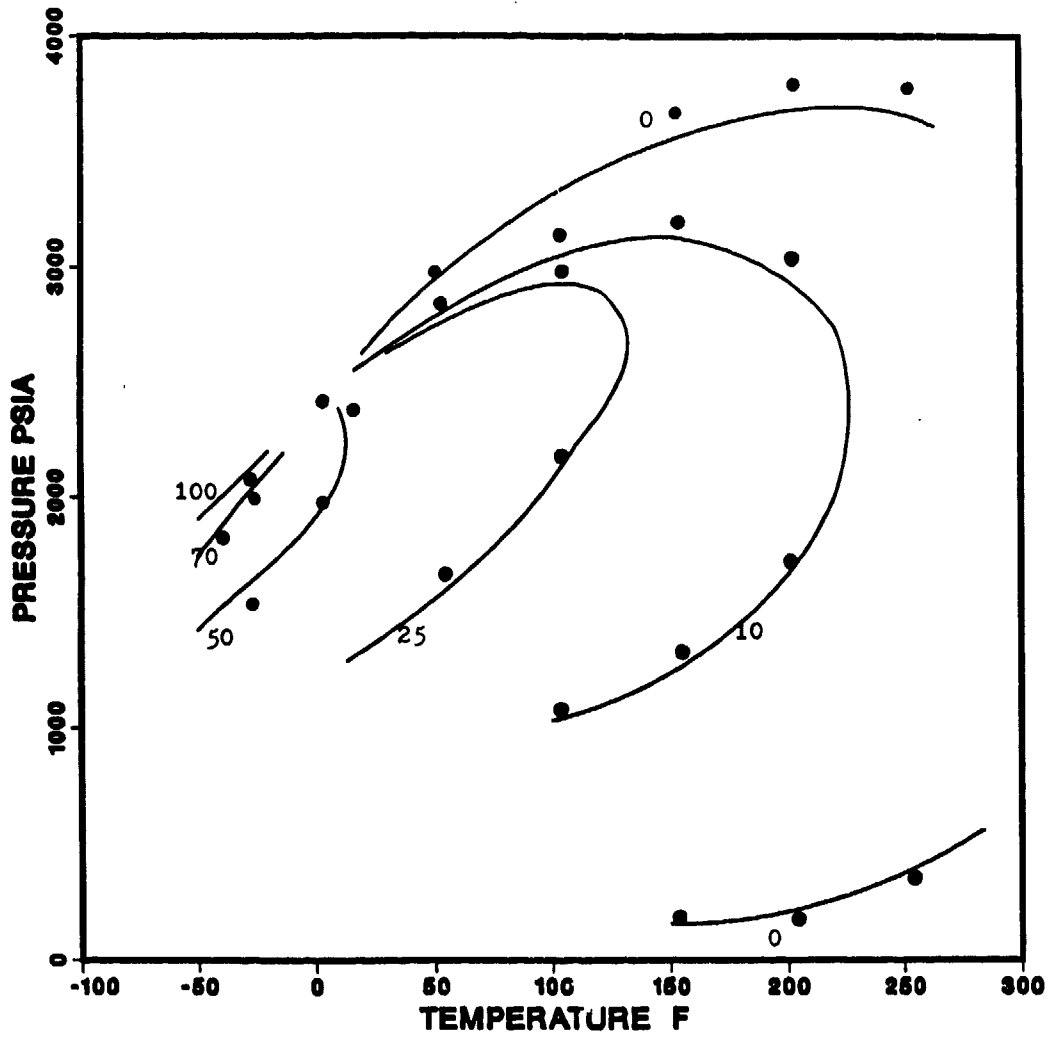


Fig. 5—P-T diagram of a gas-condensate reservoir fluid¹⁹ at 100°F.