

PHASE EQUILIBRIUM COMPUTATIONAL ALGORITHMS OF CONTINUOUS MIXTURES

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ABSTRACT

Two continuous mixture phase equilibrium algorithms which can be used for vapor-liquid equilibrium calculation involving very-many-component fluid mixtures are proposed. The algorithms are applied to the case of simulated gas-condensate systems with analytical results. The proposed continuous mixture techniques reduce the required computer time significantly while they retain accuracy of the predictions. In addition, the proposed continuous mixture algorithms are applicable to varieties of multicomponent mixtures, equations of state, and mixing rules.

INTRODUCTION

There have been a number of new development in the theory of continuous mixtures: Blum and Stell (1979) have introduced a diameter distribution to characterize a hard-sphere continuous mixture, they also have extended the Percus-Yevick approximation for hard-sphere mixture to the continuous fluids of hard-spheres. Aris and Gavalas (1966) have introduced functional analysis into the thermodynamic description of polydisperse system and into the kinetics of continuous reactions such as polymerization or cracking. Concerning petroleum distillation, Hoffman (1968) have presented a numerical integration method in which he adopts an integrated form of the Clausius-Clapeyron equation and Raoult's law to compute vapor pressures of petroleum fluids. He uses a Gaussian distribution, with the normal boiling temperature as the independent variable, to describe the vapor and liquid phases. Similar procedures as Hoffman's have been presented by Kehlen et al. (1985) whose treatment is based on Raoult's law and compositions described by normal density function to derive thermodynamic properties of continuous mixtures.

An approach using an equation of state for solving phase equilibrium problems in continuous mixtures, has been developed by Gualtieri et al. (1982). They use the van der Waals equation of state to solve the fractionation of a polydisperse impurity dissolved in a solvent and the shift of the critical point due to the presence of a polydisperse impurity. Similar results for flash calculation of continuous mixtures which are based on the Redlich-Kwong equation of state have been reported by Briano (1983). Cotterman and Prausnitz (1985) have introduced two techniques for phase equilibrium calculation of reservoir fluids, one of which is a continuous model and the other is a semi-

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continuous model. In both of their techniques they use the Soave equation of state to perform phase equilibria calculation.

Due to the lack of a general algorithm for continuous mixture phase equilibrium calculation, a number of simplifying assumptions have been made in the past. Such assumptions have hampered the effective use of continuous mixture theory in practical phase equilibrium calculations and development of accurate prediction techniques. In order to perform phase equilibrium calculations when the species of a continuous mixture have a wide range of molecular weight distribution, we have developed three computational algorithms. (one of these techniques was discussed in a paper which was presented in the 1986 SPE California Regional Meeting, U.S.A.) Due to space limitation, in the present report we introduce only the other two computational algorithms by which we can also predict phase behavior of continuous mixtures such as petroleum reservoir fluids, polymer solutions, or vegetable oils. In part II we introduce the basic theories behind these two new algorithms. In part III we illustrate VLE flash calculations using the proposed techniques which includes the continuous Peng-Robinson equation of state and the computational results as compared with simulated gas-condensate VLE flash data.

THEORY OF PHASE EQUILIBRIUM OF CONTINUOUS MIXTURES

For a mixture with a large number of components, composition may be replaced with a composition distribution function $F(I, I_0, \eta)$ whose independent variable I is some measurable property such as molecular weight, boiling point, or the likes, with mean value of I_0 and variance of η . The composition distribution function $F(I, I_0, \eta)$ is normalized such that

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

over the entire range of I . Since distribution functions are not additive, $F_f(I)$, $F_L(I)$, and $F_V(I)$ can not possess the same functional forms in a specific flash calculation scheme.

In the case of continuous mixtures, an expression for the chemical potential of a fraction in a continuous mixture is generally needed for the phase equilibrium calculation (e.g., Gualtieri et al., 1982; Briano, 1983; Cotterman and Prausnitz, 1985). It can be derived as the following form.

$$\mu(I) = \mu^0(I) + \int_V \left[\frac{\partial P}{\partial F(I)} - \frac{RT}{V} \right] dV - RT \ln \frac{V}{RTF(I)} + RT \quad (1)$$

or

$$\mu(I) = \mu^0(I) + \delta(V, T, I_0, \eta; \{I\}) - RT \ln \frac{V}{F(I, I_0, \eta)} \quad (2)$$

where $\mu^0(I)$ is the chemical potential of the continuous reference state at temperature T . With regard to the above equation we have assumed that there is only one family of continuous mixtures in the system. Extension of the above formulas to the case of a multi-family continuous mixture is

straightforward.

According to classical thermodynamics for multi-phase equilibrium calculations, it is necessary to equate temperatures, pressures, and chemical potentials of components in every phase. For vapor-liquid equilibrium of a continuous mixture, this means the following conditions must be satisfied:

$$T = T^L = T^V \quad (3)$$

$$P = P^L(T, v_L, I_{\circ L}, \eta_L) = P^V(T, v_V, I_{\circ V}, \eta_V) \quad (4)$$

$$\begin{aligned} \delta^L(T, v_L, I_{\circ L}, \eta_L: \{I\}) - RT \ln \frac{v_L}{F(I_{\circ L}, \eta_L: \{I\})} \\ = \delta^V(T, v_V, I_{\circ V}, \eta_V: \{I\}) - RT \ln \frac{v_V}{F(I_{\circ V}, \eta_V: \{I\})} \end{aligned} \quad (5)$$

Considering the fact that distribution function variable I changes from some initial value of I_1 to very large values, eqn.(5) is representative of a multitude of equations. Generally, it is impossible to solve these equations simultaneously for the liquid and vapor equilibrium calculations of continuous mixtures.

In order to extend the application of continuous thermodynamics to practical cases such as reservoir fluids, polymer solutions, or vegetable oils, we have presented one computational algorithm (1986) for phase behavior predictions of continuous mixtures with wide ranges of molecular weight distribution. Now, two other computational algorithms, based on the following theories, are developed for continuous mixtures.

Direct Minimization of the Gibbs Free Energy Algorithm

Based on the classical thermodynamics for a system in equilibrium (constant T & P), the total Gibbs free energy of the system is minimal with respect to all possible changes. In other words, at the equilibrium state, differential variations can occur in the system at constant T and P without producing any change in the total Gibbs free energy. Thus, a general criterion for a system to be at equilibrium is,

$$(dG)_{TP} = 0 \quad (6)$$

To apply this criterion to continuous mixture phase equilibrium calculations, we restrict consideration only to a one continuous mixture family of compounds in vapor-liquid equilibrium. In such cases, the total Gibbs free energy of the system is

$$G = G_L + G_V \quad (7)$$

Generally, the Gibbs free energy of a one-family continuous mixture can be presented as the following expression.

$$G = \int_V^{\infty} \left[P - \frac{NRT}{v} \right] dv - NRT \int_I^V F(I) \ln \left[\frac{v}{NF(I)RT} \right] dI + PV + G^{\circ} \quad (8)$$

Where N is the number of moles and G° is the Gibbs free energy of the continuous reference state at temperature T . Thus the total Gibbs free energy of eqn.(7) is a function of temperature, volume, mean values, and variances. Since the system is in phase equilibrium, the equilibrium criterion, eqn.(6), is imposed on the system. Then, all of the first derivatives of the total Gibbs free energy G with respect to each variable, such as variance or mean value, will equal zero, thus, G is minimized at constant T and P .

$$(\partial G / \partial \eta_L)_{T, P, \eta_V, I_{\circ L}, I_{\circ V}} = 0 \quad (9)$$

$$(\partial G / \partial \eta_V)_{T, P, \eta_L, I_{\circ L}, I_{\circ V}} = 0 \quad (10)$$

$$(\partial G / \partial I_{\circ L})_{T, P, \eta_L, \eta_V, I_{\circ V}} = 0 \quad (11)$$

$$(\partial G / \partial I_{\circ V})_{T, P, \eta_L, \eta_V, I_{\circ L}} = 0 \quad (12)$$

To perform flash calculations for a one-family continuous mixture, eqn's.(9)-(12) and eqn.(4) will form a set of 5 nonlinear equations which must be solved simultaneously.

Equilibrium Ratio Algorithm

Another criterion for a two-phase system to be in equilibrium is that the following condition must be satisfied for the system at a given temperature and pressure.

$$\psi_i^L x_i = \psi_i^V y_i \quad (13)$$

ψ_i^L and ψ_i^V are fugacity coefficients of component i in liquid and vapor phases, respectively. By analogous arguments, as in the discrete mixtures, the following equation results for phase equilibrium calculations of a one-family continuous mixture.

$$\psi^L(I, I_{\circ L}, \eta_L) \cdot F_L(I, I_{\circ L}, \eta_L) = \psi^V(I, I_{\circ V}, \eta_V) \cdot F_V(I, I_{\circ V}, \eta_V) \quad (14)$$

Generally, the fugacity coefficient of component I is expressed in the following form:

$$RT \ln \psi(I) = \int_V^\infty \left[\frac{\partial P}{\partial F(I)} - \frac{RT}{v} \right] dv - RT \ln Z \quad (15)$$

At this stage, we may define an equilibrium ratio $K(I)$ which is the ratio of two fugacity coefficients of component I such that

$$K(I) = \psi^L(I, I_{\circ L}, \eta_L) / \psi^V(I, I_{\circ V}, \eta_V) \quad (16)$$

By using the concept of material balance for continuous mixture, the following expressions for describing the composition of component I result

$$F(I, I_{\circ L}, \eta_L) = \frac{F(I, I_{\circ f}, \eta_f)}{1 + \phi_V [K(I) - 1]} \quad (17)$$

and

$$F(I, I_o_v, \eta_v) = \frac{F_f(I, I_o_f, \eta_f) \cdot K(I)}{1 + \phi_v [K(I) - 1]} \quad (18)$$

By integrating eqn's. (17) and (18) over the entire range of I, the following expressions are derived

$$\int_I \frac{F_f(I, I_o_f, \eta_f)}{1 + \phi_v [K(I) - 1]} dI = 1 \quad (19)$$

$$\int_I \frac{F_f(I, I_o_f, \eta_f) K(I)}{1 + \phi_v [K(I) - 1]} dI = 1 \quad (20)$$

The other two equations are derived for flash calculations of a one-family continuous mixture by multiplying each term of eqn. (17) and (18) by $[1 + \phi_v [K(I) - 1]] \cdot I$, and integrating over the entire range of I.

$$\int_I F_L(I, I_o_L, \eta_L) \{1 + \phi_v [K(I) - 1]\} I dI = \int_I F_f(I, I_o_f, \eta_f) I dI \quad (21)$$

$$\int_I \frac{F_v(I, I_o_v, \eta_v) \{1 + \phi_v [K(I) - 1]\} I}{K(I)} dI = \int_I F_f(I, I_o_f, \eta_f) I dI \quad (22)$$

The equality of pressures, eqn. (4), together with eqn's. (19)-(22) will constitute a system of 5 equations. This system of equations must be solved simultaneously for phase behavior prediction of a one-family continuous mixture. In what follows we introduce the proposed algorithms for the Peng-Robinson equation of state which is extensively used for reservoir fluid phase behavior calculation.

CONTINUOUS PENG-ROBINSON EQUATION OF STATE

To illustrate the utility of the proposed algorithms, the Peng-Robinson equation of state of mixtures,

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (23)$$

$$a(T) = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} = [\sum_i x_i a_{ii}]^2 \quad (24)$$

$$b = \sum_i x_i b_i \quad (25)$$

$$a_{ii}(T) = a(T_{Ci}) [1 + k_i (1 - T_{ri}^{1/2})]^2 \quad (26)$$

$$a(T_{Ci}) = 0.45724 R^2 T_{Ci}^2 / P_{Ci} \quad (27)$$

$$b_i = 0.0778 R T_{Ci} / P_{Ci} \quad (28)$$

$$k_i = 0.37464 + 1.54226w - 0.26992w^2 \quad (29)$$

joined with the exponential-decay distribution function, which is suitable for gas-condensate reservoir fluids,

$$F(I) = (1/\eta) \exp[-(I - I_o)/\eta] \quad (30)$$

is used to perform the flash calculations of continuous gas-condensate mixtures. In order to extend this equation of state

to continuous mixtures, we modify eqn. (24) to the following form:

$$[a(T)]^{1/2} = a_1 - a_2 T^{1/2} \quad (31)$$

where

$$a_1 = \sum_i x_i a_{i1}, \quad a_1 = \int_I F(I) a_1(I) dI \quad (32)$$

$$a_2 = \sum_i x_i a_{i2}, \quad a_2 = \int_I F(I) a_2(I) dI \quad (33)$$

and

$$a_{i1} = [a(T_{ic})]^{1/2} (1 + k_i) \quad (34)$$

$$a_{i2} = [a(T_{ci}) / T_{ci}]^{1/2} k_i \quad (35)$$

Graphical representation of a_{i1} , a_{i2} , and b_i for paraffinic hydrocarbons versus molecular weight have been reported by Du and Mansoori (1986). Thus, $a_1(I)$, $a_2(I)$, and $b(I)$ of paraffins are represented by the following third order polynomials with respect to molecular weight I :

$$a_1(I) = a_{10} + a_{11}I + a_{12}I^2 + a_{13}I^3 \quad (36)$$

$$a_2(I) = a_{20} + a_{21}I + a_{22}I^2 + a_{23}I^3 \quad (37)$$

$$b(I) = b_0 + b_1I + b_2I^2 + b_3I^3 \quad (38)$$

To introduce the exponential-decay distribution function, eqn. (30), into eqn's. (32) and (33), we can derive continuous mixture expressions for parameters a_1 , a_2 , and b of the Peng-Robinson equation of state.

Using the continuous mixture Peng-Robinson equation of state, the required equations, based on the proposed algorithms for a one-family continuous mixture, have been derived. The derivation follows.

(i) In order to utilize the direct minimization of the Gibbs free energy algorithm for VLE calculations of continuous mixtures, we need to derive an expression of the Gibbs free energy. To introduce eqn. (23) into eqn. (8), the Gibbs free energy of the system can be derived in the following form:

$$G = -\frac{\eta_f - \eta_v}{\eta_L - \eta_v} g_L + \frac{\eta_L - \eta_f}{\eta_L - \eta_v} g_v \quad (39)$$

where

$$g_L = -RT \ln(v_L - b_L) + \frac{a_L}{2.828b_L} \ln \frac{v_L - 0.414b_L}{v_L + 2.414b_L} - RT \ln \eta_L + \frac{v_L RT}{v_L - b_L} - \frac{a_L v_L}{v_L(v_L + b_L) + b_L(v_L - b_L)} \quad (40)$$

and g_v will have a similar expression.

To perform VLE flash calculations, we need to substitute eqn. (39) into eqn's. (9)-(12). But, since $I_{of} = I_{oL} = I_{ov}$ = the molecular weight of methane, we will only need to solve eqn's. (9) and (10). Using eqn's. (4), (9), and (10), the P-T diagram, the equilibrium ratios, K_i , and the vapor-liquid

ratios of a hypothetical gas-condensate reservoir fluid with $\eta_f = 25.0$ are calculated and are reported in Fig. (1), (2), and (3), respectively. Also reported in these figures are the P-T diagram, equilibrium ratios, and vapor-liquid ratios of the same fluid assumed to contain very-many pseudocomponents. This figure shows that the proposed algorithm can accurately predict the phase behavior of a many-component mixture.

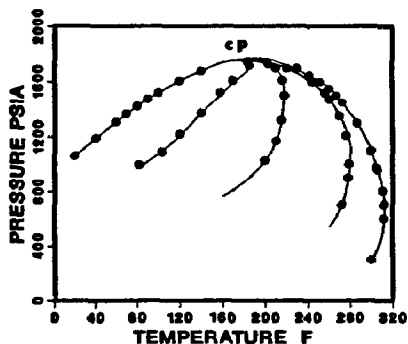


Fig. (1)

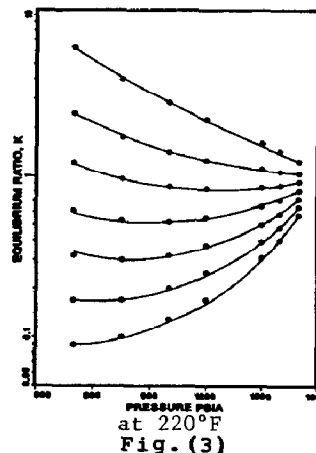


Fig. (3)

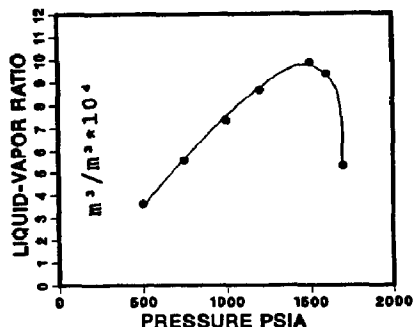


Fig. (2)

Figure (1)-(3): Phase diagrams of a continuous mixture with $\eta_f=25.0$ as compare with the results by using a pseudocomponent method (dots).

(ii) In order to utilize the equilibrium ratio algorithm for VLE calculations of continuous mixtures, we need to introduced eqn.(23) into (15). As a result, fugacity coefficient of component I can be derived in the following form:

$$\psi(I) = \exp(D_0 + D_1 I + D_2 I^2 + D_3 I^3) \quad (42)$$

where

$$D_0 = \ln \frac{RT}{p(v-b)} + b_0 Q_1 + (a_{10} - a_{20} T^{1/2}) Q_2 \quad (43)$$

$$D_1 = b_1 Q_1 + (a_{11} - a_{21} T^{1/2}) Q_2 \quad (44)$$

$$D_2 = b_2 Q_1 + (a_{12} - a_{22} T^{1/2}) Q_2 \quad (45)$$

$$D_3 = b_3 Q_1 + (a_{13} - a_{23} T^{1/2}) Q_2 \quad (46)$$

$$Q_1 = \frac{1}{v-b} \frac{a}{RT} \left[\frac{1}{b(v^2 + 2bv - b^2)} + \frac{1}{2.828b^2} \ln \frac{v-0.414b}{v+2.414b} \right] \quad (47)$$

$$Q_2 = \frac{Q_3}{1.414bRT} \ln \frac{v-0.414b}{v+2.414b} \quad (48)$$

$$\begin{aligned} Q_3 = & (a_{10} - a_{20}T^{\frac{1}{2}}) + (a_{11} - a_{21}T^{\frac{1}{2}})(I_0 + \eta) + (a_{12} - a_{22}T^{\frac{1}{2}}) \\ & (I_0^2 + 2I_0\eta + 2\eta^2) + (a_{13} - a_{23}T^{\frac{1}{2}})(I_0^3 + 3I_0^2\eta + 6I_0\eta^2 + 6\eta^3) \end{aligned} \quad (49)$$

By substituting eqn. (42) into eqn. (16), the following equation for $K(I)$ will result.

$$K(I) = \exp[(D_{0L} - D_{0V}) + (D_{1L} - D_{1V})I + (D_{2L} - D_{2V})I^2 + (D_{3L} - D_{3V})I^3] \quad (74)$$

Based on the above expression for $K(I)$, the P-T diagram of a hypothetical gas-condensate reservoir fluid with $\eta_f = 25.0$ is calculated by using eqn's. (19)-(22). The computational results are identical with the results of the previous algorithm as it was reported in Fig. (1).

CONCLUSIONS

Accurate prediction of very-many-component mixture phase behavior by using the conventional methods requires the assumption of a large number of pseudocomponents, as a result, excessive amount of computer time. The proposed algorithms have been successful in reducing the computer time significantly while retaining the basic characteristic of the mixtures under consideration. Practical application of the proposed schemes for realistic very-many-component mixtures requires the use of unlike interaction parameters in the equation of state. The authors (Mansoori and Du, 1986) have solved this problem for realistic gas-condensate mixtures which will be reported in a forthcoming publication.

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REFERENCES

- Aris, R. and Gavalas, G.R., 1966. On the Theory of Reaction in Continuous Mixtures. *Phil. Trans. Soc.*, A260: 351-93.
- Blum, L., and Stell, G., 1979. Polydisperse System I. Scattering function for polydisperse fluids of hard or permeable spheres. *J. Chem. Phys.*, 71(1): 42-46.
- Briano, J.G., 1983. Classical and Statistical Thermodynamics of Continuous Mixtures, Ph. D. Thesis, University of Pennsylvania. Thesis, University of Pennsylvania.
- Cotterman, R.L. and Prausnitz, J.M., 1985. Flash Calculation for Continuous or Semicontinuous Mixtures Using an Equation of State. *Ind. Eng. Chem. Process Des. Dev.*, 24: 434-443.
- Du, P.C., and Mansoori, G.A., 1986. A Continuous Mixture Computational Algorithm for Reservoir Fluids Phase Behavior. SPE California Regional Meeting, U.S.A.
- Gualtieri, J.A., Kinacid, J.M., and Morrison, G.J., 1982. Phase Equilibria in Polydisperse Fluids. *Chem. Phys.*, 77: 121-36.
- Hoffman, E.J., 1968. Flash Calculations for Petroleum Fractions. *Chem. Eng. Sci.*, 23: 957-64.
- Kehlen, H., Rätzsch, M.T., and Bergmann, J., 1985. Continuous Thermodynamics of Multicomponent System., *AIChE J.*, 31(7): 1136-1148.