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CONTINUOUS THERMODYNAMICS OF PHASE EQUILIBRIA USING THE BETA DISTRIBUTION FUNCTION AND AN EQUATION OF STATE

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Abstract—Phase equilibrium calculation involving mixtures of very many components requires significant amounts of computation time. In this paper we considered the description of such mixtures as a collection of discrete components and a continuum distribution of species represented by the beta distribution function. Calculations are performed using the method of continuous thermodynamics and the Soave-Redlich-Kwong equation of state. Comparisons were made with the pseudocomponent method and gamma distribution function. The results showed that continuous thermodynamics with beta distribution function leads to better prediction of phase equilibria and shorter computing time compared to pseudocomponents. And more reasonable results were obtained by this method because of the flexibility of beta distribution function.

INTRODUCTION

For multicomponent systems which contain very many components having similar properties, there are generally two problems in predicting phase equilibrium: analysis and long computing time. The similarities of physical and chemical properties of components do not permit them to be identified and analyzed. And if they were identified and analyzed, another problem exists-long computing time because of very many components involved in the system.

Up to now two approximate methods have been used to solve these problems-pseudocomponent and key-component methods. These components, though different in definition, have been regarded to have the system properties and phase equilibrium calculations have been performed with them. But the thermodynamic properties of the systems represented by these components differ from researcher to researcher because they have chosen them with their experience and intuition.

Continuous thermodynamics is an another systematic approach to calculate phase equilibrium. In continuous thermodynamics, the composition of the system and the thermodynamic properties are expressed by the distribution function and distribution variables. This approach is not a new one. In 1949, Bowman [1] studied this method first, but his study was limited within Raoult's law. It was Gualtieri et al. [2] that introduced the equation of state in continuous thermodynamics and Cotterman et al. [3, 4] used Soave-Redlich-Kwong equation of state to calculate phase equilibrium. They used the gamma distribution function and the molecular weight as a distribution variable. But they treated only a linear system in which the constants of the equation of state are linear functions of molecular weight. Nonlinear system was treated by Shibata et al. [5] and they pointed out two problems-physical infeasibility and mathematical inconsistency-contained in the continuous thermodynamics. In addition Willman and Teja [6] used bivariate log normal distribution function and Wang and Whitting [7] introduced the activity model into the continuous thermodynamics.

Beta distribution function was already used by another researchers [8]. Their method, however, is restricted in the PHC (Perturbed hard chain) theory. In this paper, we presented more general method to calculate phase equilibrium.

The advantages of the continuous thermodynamics are the facts that all the components involved in the system can be considered and mathematical description of composition by distribution function decreases the computing time.

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CONTINUOUS THERMODYNAMICS

Thermodynamics that treats continuous mixture is called continuous thermodynamics. By continuous mixture, it is meant a mixture which contains very many components having similar physical and chemical properties, and its composition changes continuously.

In continuous thermodynamics, the composition of component can be represented by distribution function, e.g.

$$\int_I F(I)dI=1 \tag{1}$$

For the more general case of the system containing both discrete components and continuous mixture, the composition relationship is

$$\Sigma x_i+\eta\int_I F(I)dI=1 \tag{2}$$

where F(I) is the distribution function, I is the distribution variable, η is the total mole fraction of continuous mixture, and x_i is the composition of i component. Multivariate distribution function may be used to represent the composition of continuous mixture. But in such a case the number of components to be examined increases explosively [9], so does the computing time. Therefore univariate distribution function was used in this paper.

When a system contains both continuous and discrete components, general phase equilibrium conditions and mathematical relation were derived by Cotterman et al. [3, 4] and Kehlen et al. [10].

$$T^V=T^L \tag{3}$$

$$P^V=P^L \tag{4}$$

$$f^V(i)=f^L(i) \tag{5}$$

$$f^V(I)=f^L(I) \tag{6}$$

where the fugacities of the discrete components in each phase are given as

$$f(i)=x_i\varphi(i)P \tag{7}$$

and for the continuous components

$$f(I)=\eta F(I)\varphi(I)P \tag{8}$$

And fugacity coefficients are given as follows

$$RT\ln\varphi(i)=\int_0^v\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,V,j}-\frac{RT}{V}\right]dV-RT\ln z \tag{9}$$

$$RT\ln\varphi(I)=\int_0^v\left[\left(\frac{\delta G}{\delta F(I)}\right)_{T,V,I'}-\frac{RT}{V}\right]dV-RT\ln z \tag{10}$$

THE EQUATION OF STATE

In this paper, Soave-Redlich-Kwong (SRK) [11] equation of state was used to represent the behavior of gases and liquids.

$$P=\frac{RT}{v-b}-\frac{a}{v(v+b)} \tag{11}$$

$$a=a_c\alpha \tag{12}$$

$$a_c=0.42747\frac{(RT_c)^2}{P_c} \tag{13}$$

$$\alpha=[1+m(1-T_r^{1/2})]^2 \tag{14}$$

$$m=0.480+1.574\omega-0.176\omega^2 \tag{15}$$

$$b=0.08664\frac{RT_c}{P_c} \tag{16}$$

Since coefficient of Eq. (15) were developed by regressing vapor pressure data of low molecular weight hydrocarbon, it is unlikely that this equation will suffice for high molecular weight component. Sim and Daubert [12] determined new coefficients for the high molecular weight components as.

$$m=0.315+1.60\omega-0.166\omega^2 \tag{17}$$

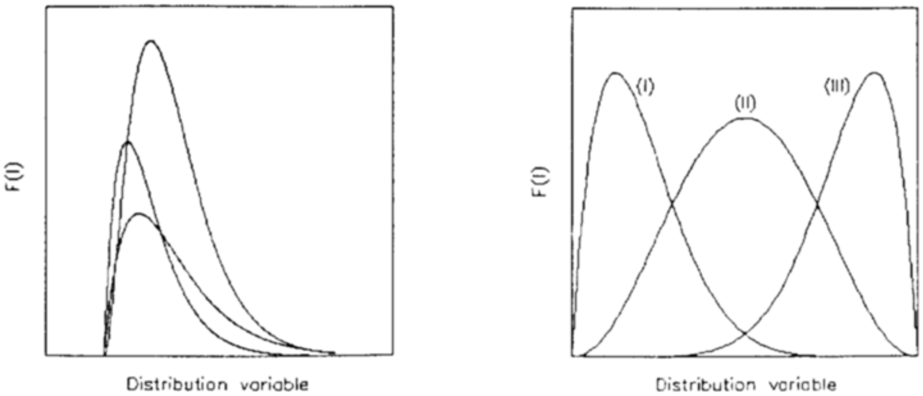
It was known that equation of state modified by Sim and Daubert is more accurate than original SRK equation [9] when applied to the system containing heavy fractions.

DISTRIBUTION FUNCTIONS AND DISTRIBUTION VARIABLES

It was generally known that as the molecular weight increases the composition of heavy fraction decreases exponentially [5, 13-15]. And components of heavy fraction can be identified by two physical properties (mainly boiling point, T_b and specific gravity, S.G.) [16].

Based on these facts, distribution functions involving exponential term was used and boiling point and specific gravity were used as distribution variables in previous studies [3-6].

But Shibata et al. pointed out two problems, mathematical inconsistency and physical infeasibility [5]. They suggested the method to overcome physical infeasibility. But their method was an approximate one, and requires additional numerical procedure to calculate quadrature points and weighting factors. And the problem of mathematical inconsistency also remains because it can be solved only when the considered



(a) Gamma distribution function

(b) Beta distribution function

Fig. 1. Comparison of gamma and beta distribution function.

system is linear and binary interactions are zeros.

In this paper, physical infeasibility was overcome by use of the beta distribution function.

$$F(I)=\frac{1}{B(p,q)}\frac{(I-a)^{p-1}(b-I)^{q-1}}{(b-a)^{p+q-1}} \tag{18}$$

The advantage of using beta distribution function is that the method suggested by Shibata to overcome physical infeasibility is not needed because beta distribution is bounded on both sides. In addition to this, beta distribution function is more flexible than gamma distribution function (Fig. 1), so it seems that beta distribution function can represent the composition of continuous mixture better than gamma distribution function.

For example, at equilibrium, light components are richer than heavier ones in the vapor phase. In this case gamma distribution can represent the composition of this phase [Fig. 1(a)] and so can the beta distribution [Fig. 1(b) I]. In contrast gamma distribution cannot exhibit the composition of liquid phase [Fig. 1 (a)] in which phase the heavier components are richer while beta distribution function can do because of its flexibility [Fig. 1(b) III].

RESULTS

1. The Comparison of Continuous Thermodynamics and Pseudocomponent Method

In this paper, beta distribution function was used to express the composition of continuous mixture. The coefficients of distribution function were calculated by performing optimization calculation. The optimization method was Powell method [17] and used object function is as follows

$$\text{obj. func.}=\Sigma\left|\,\Sigma x_i-\int_I f(I)dI\,\right|/\Sigma x_i \tag{19}$$

Numerical integration of beta and gamma distribu-

Table 1. Experimental TBP data for heavy oil [15]

(a) Pure component

Component	Mole fraction(%)
N_2	0.34
CO_2	0.84
Methane	49.23
Ethane	6.32
Propane	4.46
i-Butane	0.86
n-Butane	2.18
i-Pentane	0.93
n-Pentane	1.33
Hexane	2.06

(b) Component of C_{7+}

No.	Mole fraction	SP. GR.	T_b(°C)
1	3.33	0.7395	-100
2	4.06	0.7518	100-127
3	2.76	0.7756	127-152
4	1.33	0.7930	152-176
5	1.79	0.7902	176-197
6	1.70	0.8060	197-218
7	1.81	0.8203	218-237
8	1.46	0.8311	237-255
9	1.49	0.8446	255-272
10	1.08	0.8515	272-288
11	1.13	0.8542	288-304
12	0.99	0.8561	304-318
13	0.88	0.8663	318-332
14	7.64	0.9350	332-

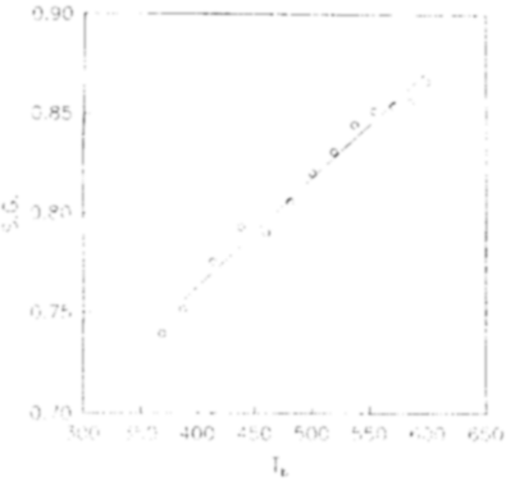


Fig. 2. Correlation of specific gravity with boiling point.

Table 2. Physical properties calculated for the case of 7 quadrature points

No	T_b(K)	S.G.	M.W.	T_c(K)	P_c(atm)	ω
1	372.4	0.749	97.4	560.2	31.8	0.278
2	403.2	0.766	113.6	589.2	27.7	0.330
3	453.1	0.793	142.0	634.0	22.5	0.432
4	513.5	0.826	179.6	691.8	18.5	0.590
5	573.8	0.859	220.7	766.1	17.1	0.737
6	623.7	0.886	257.2	856.9	18.9	0.762
7	654.5	0.903	280.9	926.5	22.3	0.713

tion was performed by use of Gaussian quadrature method. The detailed method was found in [5].

Experimental data used were for heavy oil data performed by Pedersen et al. [15]. The result of true boiling point experiment is shown in Table 1. In this paper the composition of C_{7+} components was represented by beta distribution function. Calculated parameters for beta distribution function are a = 364.8, b = 662.1, p = 0.544, and q = 0.665.

Generally at least two physical properties are required to identify a component from others in continuous mixture [16]. Mostly these are boiling point (T_b) and specific gravity (S.G.). But data obtained showed that specific gravity can be linearly related to boiling point (Fig. 2). So only boiling point was used as distribution variable.

Needed parameters (critical temperature and pressure, and acentric factor) were calculated with the data shown in Table 1 by use of Lin-Chao correlation [18]. In order to apply Lin-Chao correlation, the method of Gray et al. [19] were used and the results are shown in Table 2 for the case of 7 quadrature points.

Table 3. The binary interaction parameters used in this paper

	N_2	CO_2
N_2	0.000	−0.030
CO_2	−0.030	0.000
Methane	0.028	0.093
Ethane	0.041	0.136
Propane	0.076	0.129
i-Butane	0.094	0.128
n-Butane	0.070	0.143
i-Pentane	0.087	0.131
n-Pentane	0.088	0.131
Hexane	0.150	0.118

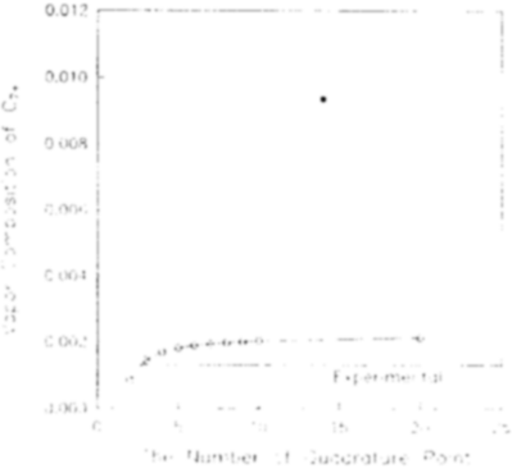


Fig. 3. Calculated vapor composition of C_{7+} with continuous thermodynamics (circle) and pseudocomponent (filled circle).

Binary interaction parameters used in this paper are listed in Table 3. In this paper, the binary interaction parameters between organic components, and between discrete components and continuous mixture are assumed to be zeros.

In continuous thermodynamic theory, as the number of quadrature points increases, the calculated result approaches a definite value. It is known that the number of quadrature points required to converge is from 6 to 10 [3]. In case of heavy oil studied in this paper, the general trend shows the results are converged for the number of the quadrature points greater than 7 (Fig. 3).

Calculated results are presented in Table 4. Both of the obtained results by continuous thermodynamics and pseudocomponent method seem to be reasonable. As shown in Table 4, the components with relatively

Table 4. Comparison of the results from continuous thermodynamics with the pseudocomponent method

Compn	Gas phase Expt	Cont	Thermodyn %dev	Pseudocompn	%dev	Liquid phase Expt	Cont	Thermodyn %dev	Pseudocompn	%dev
N_2	0.0059	0.0064	9.2	0.0065	9.56	0.0000	0.0004		0.0005	
CO_2	0.0133	0.0112	15.7	0.0113	14.88	0.0035	0.0057	61.7	0.0056	60.87
C_1	0.8484	0.8537	0.6	0.8492	0.10	0.1099	0.1393	26.8	0.1538	39.97
C_2-C_3	0.1113	0.1097	1.4	0.1072	3.71	0.0911	0.1060	16.4	0.1084	18.99
C_4-C_6	0.0198	0.0170	14.1	0.0165	16.81	0.1210	0.1289	6.5	0.1278	5.60
C_{7+}	0.0013	0.0019	49.4	0.0094	619.50	0.6745	0.6198	8.1	0.6039	10.47

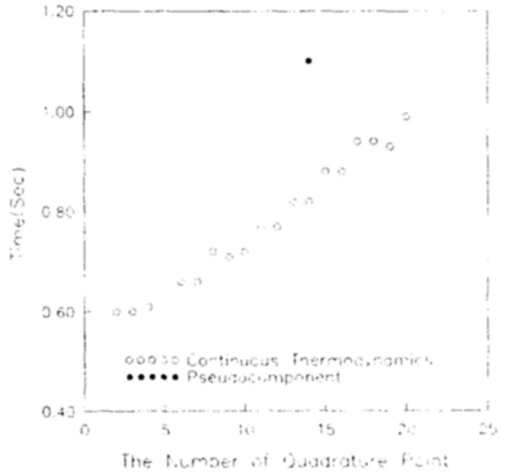


Fig. 4. Elapsed time to calculate phase equilibrium according to the number of quadrature point.

small quantity in each phase show large relative errors. Particularly pseudocomponent method fails to predict the composition of heavy component in gas phase though absolute error is very small. On the other hand, continuous thermodynamics can predicts the composition of the components in both phases better than the pseudocomponent method. Especially continuous thermodynamics can describe the behavior of the heavy component much better.

Fig. 4 shows the relation between calculation time and the number of quadrature points. Calculation time by continuous thermodynamics is shorter than that by pseudocomponent method. In particular calculation time by pseudocomponent is twice as long as that by continuous thermodynamics when the number of quadrature point is 7 where the calculation result converges.

It is generally known that computing time increases as the number of quadrature points considered and the difference of properties of each component increase. In Fig. 4, calculaion time increases stepwise. This is because the increase of the calculation time caused by the increment of the number of quadrature points is canceled a little bit by the decrement of the difference of the physical property between the components.

2. Comparison of Beta and Gamma Distribution Functions

In Table 5, beta and gamma distribution function were compared. As shown in Table 5 both beta and gamma distribution functions predicts liquid phase composition reasonably. But beta distribution function represents the composition of vapor phase than gamma distribution function, and original gamma distribution function and bounded gamma distribution function suggested by Shibata et al. make no difference

Table 5. Comparison of the beta and gamma distribution functions

(a) for vapor phase

	Expt	Beta distribution	dev(%)	Gamma distribution Cotterman*	dev(%)	Gamma distribution Shibata**	dev(%)
N_2	0.0059	0.0064	9.2	0.0062	5.8	0.0063	7.8
CO_2	0.0133	0.0112	15.7	0.0111	16.5	0.0110	17.1
C_1	0.8484	0.8537	0.6	0.8518	0.4	0.8581	1.1
C_2-C_3	0.1113	0.1097	1.4	0.1145	2.9	0.1100	1.2
C_4-C_6	0.0198	0.0170	14.1	0.0163	17.7	0.0146	26.2
C_{7+}	0.0013	0.0019	49.4	0.0000	100.0	0.0000	100.0
AARD			15.1		23.9		25.6

Table 5. Continued

(b) for liquid phase

	Expt	Beta distribution		Gamma distribution		Gamma distribution	
			dev(%)	Cotterman*	dev(%)	Shibata**	dev(%)
N_2	0.0000	0.0004		0.0002		0.0002	
CO_2	0.0035	0.0057	61.7	0.0053	53.7	0.0056	60.9
C_1	0.1099	0.1393	26.8	0.0090	17.3	0.1075	20.2
C_2-C_3	0.0911	0.1060	16.4	0.1003	10.1	0.1055	15.8
C_4-C_6	0.1210	0.1289	6.5	0.1376	13.7	0.1357	12.1
C_{7+}	0.6745	0.6198	8.1	0.6656	1.3	0.6454	4.3
AARD			23.9		19.2		19.1

(c) for K-value

	Expt	Beta distribution		Gamma distribution		Gamma distribution	
			dev(%)	Cotterman*	dev(%)	Shibata**	dev(%)
N_2		15.000		27.629		22.056	
CO_2	3.800	1.980	47.9	2.064	45.7	1.959	48.5
C_1	7.720	6.129	20.6	9.372	21.4	7.981	3.4
C_2-C_3	1.222	1.035	15.3	1.142	6.5	1.042	14.7
C_4-C_6	0.164	0.132	19.3	0.119	27.6	0.108	34.2
C_{7+}	0.002	0.003	62.5	0.000	100.0	0.000	100.0
AARD			33.1		40.2		40.1

*Continuous thermodynamic method by Cotterman

**Continuous thermodynamic method by Shibata

in both phase. As a whole gamma distribution function predicts only the composition of heavy oil rich phase, but beta distribution function can predicts the compositions of poth phase. This is because beta distribution function is more flexible than gamma distribution, so it can describe the composition of heavy oil of both phase.

CONCLUSION

Compared to pseudocomponent method, continuous thermodynamics can predict phase equilibrium more accurately because it can count the heavy fraction by using the distribution function. And in this paper, we showed that only one distribution variable is sufficient to characterize the heavy fossil fuel when its physical or chemical properties are interrelated each other like in this case. So it can reduce the computing time greatly.

In this paper, beta distribution function was used. The advantages of using beta distribution function are the facts that the physical infeasibility problem which arose in the case of gamma distribution function or other distribution functions containing exponential terms was overcome and therefore the method suggested by Shibata et al. [5] is not needed because beta distribution function is bounded on both sides. And the flexibility of beta distribution function leads to more accurate results for vapor phase in which phase the heavy fraction is nearly zero so gamma distribution function cannot predict its composition.

ACKNOWLEDGEMENT

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NOMENCLATURE

a : attraction energy parameter in SRK equation of state
a_c : attraction energy parameter in SRK equation of state at critical point
a, b : parameters used in beta distribution function
b : volume parameter in SRK equation of state [cm^3]
B : beta function
F : distribution function
G : Gibbs free energy
I : distribution variable
m : parameter defined in Eq. (15)
n : mole number [mol]
n_i : the mole number of component i [mol]

p, q : parameter used in beta distribution function
P : pressure [atm]
P_c : critical pressure [atm]
R : universal gas constant [atm·cm^3/Kmol]
S.G. : specific gravity [60°F/60°F]
T : temperature [K]
T_b : boiling temperature [K]
T_c : critical temperature [K]
T_r : reduced temperature (T/T_c)
v : molar volume [cm^3/mol]
V : total volume [cm^3]
x_i : mole fraction of i-component in liquid phase
z : compressibility factor
z_i : mole fraction of i-component

Greek Letters

α : temperature dependent parameter defined in Eq. (28)
μ : chemical potential
φ : fugacity coefficient
ω : Pitzer's acentric factor
η : mole fraction of continuous mixture

Superscripts

L : liquid phase
V : vapor phase

Subscripts

b : boiling point
i, j : any component
N : total number of component
c : critical property
r : reduced property

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