Continuous Thermodynamics of Petroleum Fluids Fractions

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Abstract

A method based on continuous thermodynamics has been presented for calculating the vapor pressure of undefined composition mixtures. In order to verify the proposed method the experimental data of an Indonesian petroleum fluid as well as a detailed true boiling point data on the lube-oil cut SAE 10 of Tehran Refinery have been used. In this work by using the combination of the Trouton's rule and the Clausius–Clapeyron equation in the well-known equation of Antonie, the continuous version of the Raoult's law has been developed and the results of the modeling and calculations have been compared with the experimental data and good agreement was found. Moreover, for improving the results of the ideal continuous mixture, modeling of non-ideal behaviour of such mixtures has been carried out by introducing the continuous version of the UNIFAC activity coefficient in the formulation and a better result has been obtained. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are many mixtures in different industries which have a complex compositions and expressing the compositions of these mixtures in the form of conventional quantities such as mole or weight fractions is not possible. Examples of these complex mixtures are petroleum fluids, vegetable oils and polymer solutions [1]. For phase equilibrium calculations of such mixtures a powerful method which has been developed in the past two decades is continuous thermodynamics [2,3,7,8].

The main idea of this method is the application of a continuous distribution function instead of mole or weight fraction for representation of the mixture composition. Therefore, all thermodynamic functions such as enthalpy and entropy come to the form of functionals instead of ordinary functions [5]. It is evident that because of the assumption of infinite number of components in the continuous or semi-continuous mixtures, the formulation of phase rule has been changed to the

special form, which could be consistent with the basic assumptions of continuous thermodynamics [8].

Various distribution functions have been presented for the application in continuous thermodynamics by a number of researchers. One of the well-known equations for continuous description of the petroleum fluids is the gamma distribution function [14],

$$F(M) = \frac{(M - \eta)^{\alpha - 1} \exp[(M - \eta)/\beta]}{\beta^{\alpha} \Gamma(\alpha)}. \tag{1}$$

Another well-known equation which has been used in continuous thermodynamics is the Gaussian distribution function [11],

$$f(N) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{(N - \bar{N})^2}{2\sigma^2}\right). \tag{2}$$

Besides the two above mentioned distribution functions, a simple exponential decay function also has been used [8] which is:

$$F(M) = \frac{1}{\eta} \exp\left(-\frac{M - M_o}{\eta}\right). \tag{3}$$

Notwithstanding the simplicity of this function it could be a good representative for the gas condensates.

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Recently, Riazi [9,10] have proposed a general distribution function for characterization of petroleum fluids fractions in the following form:

$$\frac{p - p_o}{p_o} = \left[\frac{A}{B} \ \ln \ \frac{1}{1 - x} \right]^{1/B} \tag{4}$$

In the present work using these distribution functions, a method for the boiling point calculation of the complex petroleum fluids fractions has been proposed using the concepts of continuous thermodynamics.

2. Modeling and calculations

Here we have carried out the boiling point calculations for two cases (i) ideal mixtures; and (ii) non-ideal mixtures. In the first case the continuous version of the Raoult's law has been presented and in the second case the continuous version of the UNIFAC model was used for developing the results of the ideal mixtures to the non-ideal mixtures.

2.1. Case one: ideal mixtures

In general, the equilibrium vapor pressure of a multicomponent mixture with N distinct species can be calculated by the following equation [12]:

$$P = \sum_{i=1}^{N} x_i P_i^{\text{sat}} \gamma_i, \tag{5}$$

where, P is the total pressure, x_i is the mole fraction of the ith component, P_i^{sat} is the saturation pressure and γ_i is the activity coefficient of the ith component in the mixture. For the ideal mixtures because of the unity of all activity coefficients, this equation can be reduced to the following simple form:

$$P = \sum_{i=1}^{N} x_i P_i^{\text{sat}}. \tag{6}$$

This equation is known as the Raoult's law and indicates that the partial pressure of the ith component in the mixture is equal to the product of its mole fraction by the saturated vapor pressure (at the mixture temperature).

If the number of components in the mixture goes to a very large number, in such a way that the composition of the mixture cannot be presented in usual forms of mole or mass fractions, a continuous distribution function can be applied for defining the composition of the mixture. In such cases the continuous version of the Eq. (6) may be written as follows:

$$P = \int F(I) P^{\text{sat}}(I) \ \text{d}I, \tag{7}$$

where, $F(I)$ is a suitable distribution function of a proper characterization index 'I' such as the molecular weight or boiling point.

In application of Eq. (7), an equation for expressing P^{sat} is required. In this work the well-known equation of Antonie has been applied [15],

$$\log_{10} P^{\text{sat}} = A_A - \frac{B_A}{t + C_A}, \tag{8}$$

where, P^{sat} is the vapor pressure of a pure component at temperature t and A, B and C are the special constants for each component.

It is obvious that for the application of Eq. (7) the continuous form of the Antonie's equation is needed. If we combine the Trouton's rule with the Clapeyron–Clausius equation, the following equation can be obtained:

$$P^{\text{sat}}(T) = P_{\text{atm}} \ \exp[10.58(1 - T/T_s)], \tag{9}$$

where T is the boiling point in distribution functions (in Kelvin) and T_s, is the temperature at which distillation occurs. Therefore, by combining Eq. (7) and Eq. (9) we have,

$$P = \int_{\text{IBP}}^{\text{FBP}} P_{\text{atm}} \exp[10.58(1 - T/T_s)] \, F(T) \text{d}T. \tag{10}$$

The lower and upper limits of the integral (IBP and FBP) are the initial and final boiling points of the petroleum fluids fractions, respectively. Therefore, if we have the distribution function of the mixture, we will be able to calculate the equilibrium vapor pressures of such complex mixtures.

To verify the proposed method we have examined various distribution functions represented by Eqs. (1)–(4). These equations were used in the Eq. (10) for calculating the normal boiling point of the lube-oil cut SAE 10 of the Tehran Refinery. The error analysis based on these distribution functions is presented in Table 2. As it can be seen from Table 2, Eq. (11) has the minimum absolute average deviation (AAD) compared with the other distribution functions. The probability density function obtained from Eq. (4) which has been used for our calculations can be expressed in the following form [10]:

$$F(T) = \frac{1}{T_o} \frac{B^2}{A} \left(\frac{T - T_o}{T_o} \right)^{B-1} \exp\left[-\frac{B}{A} \left(\frac{T - T_o}{T_o} \right)^B \right]. \tag{11}$$

All the parameters of this equation which have been calculated by the regression analysis method based on the results of Table 1 can be given as:

$$A = 0.01862 \tag{12}$$

$$B = 3.5298 \tag{13}$$

$$T_o = 554.45 \ \text{K} \tag{14}$$

$F(T)$ from Eq. (11) was introduced in Eq. (10) and the integral was calculated by numerical methods. The results of the calculations are:

$$T = 674.45 \ \text{K} \tag{15}$$

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Table 1

True boiling point (TBP) vs. weight percent of distilled lube-oil cut SAE 10 of Tehran Refinery produced by the Simdis GC Chrompac system Model 438

Wt%	TBP (K)	Wt%	TBP (K)	Wt%	TBP (K)	Wt%	TBP (K)
0	554.5	26	650.8	52	672.9	78	691.8
2	581.5	28	653.1	54	674.5	80	693.4
4	597.9	30	654.9	56	675.8	82	694.9
6	609.0	32	656.7	58	677.2	84	696.5
8	618.0	34	658.5	60	678.5	86	698.5
10	623.8	36	660.5	62	680.1	88	700.6
12	629.2	38	662.3	64	681.4	90	702.6
14	633.0	40	663.9	66	682.8	92	705.1
16	636.9	42	665.5	68	684.4	94	708.2
18	640.5	44	667.0	70	685.7	96	711.8
20	643.4	46	668.4	72	687.1	98	717.7
22	645.6	48	670.0	74	688.6	100	737.9
24	648.3	50	671.5	76	690.0	–	–

$$P = 1.014 \times 10^5 \ Pa \tag{16}$$

In order to in make a comparison of the calculated results with the experimental data, we can refer to the Table 1. As it can be seen from this table, the calculated temperature corresponds to the 54% distillation. Therefore, the relative error is 0.45%.

As mentioned above, various distribution functions (Eqs. (1)–(4)) have been examined in a similar way and the results of calculations have been summarized in Table 2.

2.2. Case two: non-ideal mixtures

It is evident that the proposed formulation for ideal mixture could not handle the related calculations for the non-ideal mixtures, therefore, we have to generalize the results of the non-ideal mixtures. In this case the equilibrium vapor pressure of the continuous mixture can be written as:

$$P = \int_{IBP}^{FBP} F(I) P^{\overline{sat}}(I) \gamma(I, T) \ dI, \tag{17}$$

where $\gamma(I, T)$ is the continuous version of the activity coefficient of the mixture components.

The composition of the complex mixtures such as petroleum fractions are not well defined therefore, in this work we have used the predictive model of UNIFAC. For applying this model for the petroleum fluids fractions its continuous version is required, but when using the continuous form of the UNIFAC model for phase equilibrium calculations, it is necessary to know the analytical expressions for the number of the various functional groups in the mixture. A polynomial of order 2 has been used by some researchers [6] for calculating the number of different functional groups in the light petroleum fractions but these equations are not suitable for heavier petroleum fractions such as

lube-oil cut which is our interest in the present work. Therefore, we have proposed higher order polynomials (up to 8) for this purpose [13] in the following forms:

$$v^A(N) = a_1 + b_1 N + c_1 N^2 + d_1 N^3 + e_1 N^4, \tag{18}$$

and

$$v^{P+N}(N)$$
$$= a_2 + b_2 N + c_2 N^2 + d_2 N^3 + e_2 N^4 + f_2 N^5 + g_2 N^6$$
$$+ h_2 N^7 + i_2 N^8. \tag{19}$$

The coefficients of these equations have been obtained using the detailed experimental data on lube-oil cut SAE 10 of Tehran Refinery and an Indonesian oil [4] by using the powerful numerical software of TABLE CURVE (TC) and the results have been given in Table 3 and Table 4.

Since a petroleum fraction have been made mainly from three different homologue series as paraffinic, naphthenic and aromatic hydrocarbons, we have divided these hydrocarbon homologues to two parts, i.e. aromatic hydrocarbons and paraffinic + naphtenic hydrocarbons. The number of different functional groups of type 'm' in each of these parts can be obtained in the following form [6]:

$$v_m(N) = x_a v_m^A(N) + x_{n+p} v_m^{p+n}(N). \tag{20}$$

Using Eqs. (18)–(20) along with the continuous form

Table 2

Comparison of the average absolute deviations percent (AAD%) of different distribution functions

Distribution type	AAD% of the calculated boiling point
Exponential decay	1.21%
Gaussian distribution	0.83%
Gamma distribution	0.79%
General distribution Eq. (4)	0.45%

Table 3
Calculated coefficients according to Eq. (18) as well as the correlation coefficients (r^2)

Constants	Functional groups					
	CH_{aro}	C_{JC}	C_{aro}	CH_{aro}	CH_{2aro}	CH_{3ro}
a_1	−53.6758	−59.8886	53.0061	18.9138	4.7696	18.0086
b_1	9.7321	8.6852	−8.5985	−2.5342	−0.8678	−2.1733
c_1	−0.5812	−0.4300	0.5408	0.1157	0.0534	0.0970
d_1	0.0150	0.0088	−0.0146	−0.0016	−0.0007	−0.0013
e_1	−0.0014	0.0000	0.0001	0.0000	0.0000	0.0000
r^2	0.9263	0.9359	0.9677	0.9330	0.9670	0.9250

of UNIFAC model, the activity coefficient for a continuous mixture such as aromatic or paraffinic + naphthenic parts can be obtained as follows.

At first using Eqs. (18)–(20) we can write the continuous version of the required parameters of the UNIFAC model, i.e. r_A and q_A or r_{n+p} and q_{n+p}, the molecular volume and surface size parameters of the continuous ensembles present in the continuous mixture in the following form:

$$r_A(N) = \sum \nu_{Am}(N)R_m, \tag{21}$$

$$q_A(N) = \sum \nu_{Am}(N)Q_m, \tag{22}$$

$$r_{n+p}(N) = \sum \nu_{n+p,m}(N)R_m, \tag{23}$$

$$q_{n+p}(N) = \sum \nu_{n+p,m}(N)Q_m. \tag{24}$$

In the UNIFAC model the activity coefficient comprises of two parts, i.e. combinatorial and residual, therefore, by using Eq. (22) and Eq. (23), the activity coefficient of the continuous ensembles of aromatic or naphthenic + paraffinic parts can be obtained by the following equations:

$$\ln\gamma^A(N) = \ln\gamma^{C,A}(N) + \ln\gamma^{R,A}(N) \tag{25}$$

$$\ln\gamma^{p+n}(N) = \ln\gamma^{C,p+n}(N) + \ln\gamma^{R,p+n}(N). \tag{26}$$

For the ideal mixtures it has been demonstrated that the best distribution function for the examined mixture was Eq. (11), therefore for the non-ideal mixture too we used this function and the following results were obtained:

$$T = 390.94 \text{ K} \tag{27}$$

$$P = 1.502 \times 10^7 \tag{28}$$

In order to verify the accuracy of the proposed method here we have compared this theoretical results with the experimental data of an Indonesian petroleum fluid [4]. This comparison indicated a good agreement between theoretical results and experimental data. Thus it can be said that the proposed formulation based on the application of the continuous form of the activity coefficient model can improve the accuracy of the calculations.

3. Conclusion

Based on the concepts of continuous thermodynamics a method has been proposed for the vapor pressure calculation of the complex petroleum fluids fractions. At first the continuous version of the Raoult's law has been developed for applying in those mixtures that comprise of similar species and their behaviour can be considered as ideal mixtures. Comparison between modeling and experimental data on the lube-oil cut SAE 10 of the Tehran Refinery showed that for these types of petroleum fractions the proposed modelling and calculations give the best results with the Riazi distribution function.

The above mentioned method has been developed to the case of non-ideal mixtures using the continuous version of the UNIFAC-model and the results have been compared with the experimental data of an Indonesian oil, and better accuracy has been obtained.

Appendix A. Nomenclature

A	parameter in Eq. (4) and Eq. (11)
A_A	parameter in the Antonie's equation
a_1, a_2	parameters in Eq. (18) and Eq. (19)
B	parameter in Eq. (4) and Eq. (11)
B_A	parameter in the Antonie's equation
b_1, b_2	parameters in Eq. (18) and Eq. (19)
C_A	parameter in the Antonie's equation
c_1, c_2	parameters in Eq. (18) and Eq. (19)
d_1, d_2	parameters in Eq. (18) and Eq. (19)
e_1, e_2	parameters in Eq. (18) and Eq. (19)
$F(I)$	distribution function
f_2	parameter in Eq. (19)
g_2	parameter in Eq. (19)
h_2	parameter in Eq. (19)

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Table 4
Calculated coefficients according to Eq. (19) as well as the correlation coefficients (r^2)

Constants	Functional groups					
	CHN	CH$_3$N	CH$_2$N	CHA	CH$_2$A	CH$_3$A
a_2	−85870.6	21.1	−11361.5	−2871.4	−15.0	−204160.8
b_2	30874.0	−2.6	3468.6	733.8	1.7	79714.2
c_2	−4808.2	0.1	−447.2	−77.0	0.0	−13757.5
d_2	423.7	0.0	31.6	4.3	0.0	1377.3
e_2	−23.1	0.0	−1.3	−0.1	0.0	−88.1
f_2	0.8	0.0	0.0	0.0	0.0	3.7
g_2	0.0	0.0	0.0	1.4	0.0	−0.1
h_2	0.0	0.0	0.0	0.0	0.0	0.0
i_2	0.0	0.0	0.0	0.0	0.0	−2.0
r_2	0.8144	0.8815	0.9262	0.8524	0.9889	0.9209

I	a characterization parameter such as boiling point or molecular weight
i_2	parameter in Eq. (19)
M	molecular weight
N	number of carbon atoms
p	general property in Eq. (4)
P	absolute pressure
q	surface area parameter
Q	parameter defined in Eq. (22) and Eq. (24)
R	volume size parameter
r	parameter defined in Eq. (21) and Eq. (23)
T	absolue temperature in kelvin
t	temperature in C
x	cumulative mole or mass fraction

Greek letters

α	parameter in Eq. (1)
β	parameter in Eq. (1)
Γ	gamma function
γ	activity coefficient
η	parameter in Eq. (1) and Eq. (3)
σ	parameter in Eq. (2)

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