Computation of Liquid-Vapor Critical Points for Multi-Component Mixtures

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Abstract

Liquid-vapor critical point for a thermodynamic mixture is an important parameter for the design of mixture transportation and processing. The classical critical points model for the multicomponent mixture is based on the tangent plane distance in terms of the Helmholtz energy. In this work, we have applied the damped Newton-Raphson scheme to solve the model using the critical temperature, critical specific volume and change in mole fraction of each component as independent variables. According to numerical experiments, the convergence criteria, initial guesses of variables and damped factor formulation were determined. The method was tested on twenty five mixtures containing two to eleven components using the SRK and PR equation of state. Comparisons between the calculated critical parameters and experimental values illustrated the overall accuracy of the solution method is satisfactory. This method can solve all the variables simultaneously using the whole iteration, which is more reliable than the nested two-singe variable loops method proposed by Heidemann and Khalil. Thus it can be used for practical purposes of locating the liquid-vapor critical points of multi-component mixtures.

Keywords: Liquid-vapor critical points; multicomponent mixtures; equation of state; mathematic model; damped Newton-Raphson method.

1. Introduction

A critical state of a thermodynamic mixture is an equilibrium state that is essentially between regions of stability and instability with regard to the number of phases. A critical state is characterized by its critical point. At the critical point, liquid phase and the vapor phase have the same thermophysic prosperities such as viscosity, density, compressibility factor (Mokhatab et al, 2006). Locating the critical point is important for both hydrocarbon pipeline transmission and the oil reservoir development. For example, the critical point helps to determine the safety operating pressure and temperature range of liquid petroleum gas (LPG) or CO_2 transmission pipeline (Li et al, 2010). Also, knowledge of vapor-liquid critical is useful in determining the type of gas reservoir and whether retrograde condensation of evaporation is possible (Tian et al, 2003).

Normally, there are three ways which are experiments, empirical correlations and theoretical models to determine the critical points (Hicks et al, 1977). As the critical points obtained by experiments are expensive and the applicable range is limited, the critical points are frequently calculated by mathematical models.

Gibbs proposed the first rigorous thermodynamic definition of critical points for n-component mixtures. The Gibbs criterion consists of two equations of partial composition derivatives of the Gibbs energy that must vanish at a critical point (Peng et al, 1977). Although the expressions are relatively simple for binary system, they become increasingly complex for the ternary and multicomponent system. Thus, the Gibbs criterion is less

useful for practical calculations. To make the Gibbs criterion suitable for use, Heidemann and Khalil (Heidemann et al, 1980, Michelsen et al, 1988) expressed the partial derivatives of the molar Gibbs energy in terms of partial derivatives of the molar Helmholtz energy through transformation of the independent variables. Heidemann and Khalil also proposed the solution method for their model. The method employs two nested single-variable iteration loops using Newton-Raphson and it has been adopted by API Technical Databook (API, 2005). Wang (1999) used homotopy continuation technique for calculating critical points in binary mixtures. Benito et al. (2001) also used the Heidmann and Khalil criteria for critical points of binary and ternary system in conjunction with a numerical technique based on the interval Newton analysis method. Henderson et al. (2004) formulated the critical points as an optimization problem, which was solved by the simulated annealing algorithm. In their method, the independent variables are the pressure and temperature. Their methods also tested on several ternary systems. Luo et al. (2000) solved the Heidmann and Khalil's model using five-point numerical differentiation method. Justo-Garcia et al. (2008) applied the simulated annealing algorithm for the calculation of critical points of binary and multicomponent mixtures by using appropriate cooling schedule parameters to minimize the computer time for the solution of a critical point formulated as an optimization problem. Recently, Henderson et al. (2010) used differential evolution algorithms for the first time in the prediction of critical points of several multicomponent

mixtures, but the critical points could be calculated in a few of hundredths of a second.

Sum of all, except for Justo-Garcia et al. (2008) and Henderson (2010), there are scarce literatures have applied their methods for the critical points calculation of multicomponent mixtures. However, lots of the hydrocarbon mixtures such as the condensed gas are consisted of more than seven components. Therefore, locating the liquid-vapor critical point is a problem worth studying.

The aim of this work is to research the liquid-vapor critical point calculation method for multicomponent mixutres. In Section 2, we introduced the critical points model developed by Heidemann, Khalil and Bentio. In Section 3, we applied the damped Newton-Raphson scheme to solve the model. In order to obtain the liquid-vapor critical point, the independent variables in the model, the iteration format, the convergence criteria, initial guesses of variables and damped factor were determined. Finally, the liquid-vapor critical points of twenty five mixtures from literatures are used to test the accuracy and robustness of the proposed solution method.

2. Critical Points Model

Gibbs presented a first critical point criterion which is in terms of the Gibbs free energy G. Heidemann and Khalil replaced the Gibbs free energy with Helmholtz free energy A. On the basis of a Taylor series expansion of A, and considering the second and third order terms, Heidemann, Khalil and Bentio et al formulated the critical condition for a mixture of C components as follows (Heidemann et al, 1980, Benito et al. 2001,):

$$\sum_{j=1}^{C}\sum_{i=1}^{C}\left(\frac{\partial\left(\ln f_{gi}\right)}{\partial n_j}\right)_{T,V}\Delta n_i \Delta n_j = 0 \qquad (1)$$

$$\sum_{m=1}^{C}\sum_{j=1}^{C}\sum_{i=1}^{C}\left(\frac{\partial^2\left(\ln f_{gi}\right)}{\partial n_j \partial n_m}\right)_{T,v}\Delta n_i \Delta n_j \Delta n_m = 0 \qquad (2)$$

Where, C is the total number of components, n_i and n_j are mole fraction of ith and j^{th} components, Δn_i, Δn_j, Δn_m are changes in mole fraction of ith, j^{th} and m^{th} components. f_{gi} is fugacity of ith component.

In equation (1) and equation (2), the fugacities are the most important parameters which are often derived from generalized cubic EoS. Equation (1) and equation (2) are transformed into the following equations using the Soave modification of the Redlich-Kwong (SRK) EoS and Peng-Robinson (PR) EoS.

$$RT\left(\frac{\Delta n_i}{n_i}+F_1\left(\beta_i\overline{N}+\overline{\beta}\right)+\beta_i F_1^2\overline{\beta}\right)+$$
$$\frac{a}{b}\left(\beta_i\overline{\beta}F_3-\frac{F_5}{a}\sum_{j=1}^{C}a_{ij}\Delta n_j+F_6\left(\beta_i\overline{\beta}-\alpha_i\overline{\beta}-\overline{\alpha}\beta_i\right)\right)=0 \qquad (3)$$

$$RT\left(-\sum_{i=1}^{C}\frac{\Delta n_i^3}{n_i^2}+3\overline{N}\left(\overline{\beta}F_1\right)^2+3\left(\overline{\beta}F_1\right)^3\right)$$
$$+\frac{a}{b}\left(3\overline{\beta}^2\left(2\overline{\alpha}-\overline{\beta}\right)\left(F_2+F_3+F_6\right)-2\overline{\beta}^3 F_4-3\overline{\beta}\overline{a}F_6\right)=0 \qquad (4)$$

Where, i is the number of mixtures ($i=1,2,\cdots,C$). F_1, F_2, F_3, F_4, F_5, F_6, a, b, β_i, $\overline{N}$, $\overline{\beta}$, a_{ij}, α_i, $\overline{\alpha}$ are parameters related to the EoS.

There is an error in the paper Benito et al.(2001). In Benito's paper, the first term in the first bracket of equation (4) is $-\sum_{i=1}^{C}\Delta n_i^3/n_i^2$ which means the equation represents C equations. Obviously, the total number of the equations is differ with that of Eq.(2). This work corrected the error, and the correct term is $-\sum_{i=1}^{C}\left(\Delta n_i^3/n_i^2\right)$.

$$\overline{N}=\sum_{i=1}^{C}\Delta n_i \qquad (5)$$

$$\alpha_k=\frac{\sum_{i=1}^{C}n_i a_{ik}}{a} \qquad (6)$$

$$\overline{\alpha}=\sum_{i=1}^{C}\Delta n_i \alpha_i \qquad (7)$$

$$\overline{a}=\frac{1}{a}\sum_{i=1}^{C}\sum_{j=1}^{C}\Delta n_i \Delta n_j a_{ij} \qquad (8)$$

$$\beta_i=\frac{b_i}{b} \qquad (9)$$

$$\overline{\beta}=\sum_{i=1}^{C}\Delta n_i \beta_i \qquad (10)$$

$$F_1=\frac{1}{K-1} \qquad (11)$$

$$F_2=\frac{2}{D_1-D_2}\left[\frac{D_1}{K+D_1}-\frac{D_2}{K+D_2}\right] \qquad (12)$$

$$F_3=\frac{2}{D_1-D_2}\left[\left(\frac{D_1}{K+D_1}\right)^2-\left(\frac{D_2}{K+D_2}\right)^2\right] \qquad (13)$$

$$F_4=\frac{2}{D_1-D_2}\left[\left(\frac{D_1}{K+D_1}\right)^3-\left(\frac{D_2}{K+D_2}\right)^3\right] \qquad (14)$$

$$F_5=\frac{2}{D_1-D_2}\ln\left(\frac{K+D_1}{K+D_2}\right) \qquad (15)$$

$$F_6=\frac{2}{D_1-D_2}\left[\left(\frac{D_1}{K+D_1}-\frac{D_2}{K+D_2}\right)-\ln\left(\frac{K+D_1}{K+D_2}\right)\right] \qquad (16)$$

$$K=\frac{V_c}{nb}=\frac{v_c}{b} \qquad (17)$$

$$a=\sum_{i=1}^{C}\sum_{j=1}^{C}\left(\frac{n_i n_j}{n^2}\right)a_{ij} \qquad (18)$$

$$b = \sum_{i=1}^{C} \left(\frac{n_i}{n} \right) b_i \tag{19}$$

$$a_{ij} = \left(a_i a_j \right)^{0.5} \left(1 - k_{ij} \right) \tag{20}$$

$$a_i = \frac{\left(RT_{ci} \right)^2 \eta}{P_{ci}} \left[1 + c_i \left(1 - \left(\frac{T_c}{T_{ci}} \right)^{0.5} \right) \right]^2 \tag{21}$$

$$D_1 = \frac{u_0 + \sqrt{u_0^2 - 4w_0}}{2} \tag{22}$$

$$D_2 = \frac{u_0 - \sqrt{u_0^2 - 4w_0}}{2} \tag{23}$$

For SRK EoS:

$$\eta = 0.42748 \quad , \quad c_i = 0.48 + 1.574 w_i - 0.176 w_i^2 \quad ,$$
$$b_i = 0.08664\, RT_{ci}/P_{ci} \, , \, u_0 = 1 \, , \, w_0 = 0 \, .$$

For PR EoS

$$\eta = 0.45724 \quad , \quad c_i = 0.37464 + 1.54226 w_i - 0.26992 w_i^2 \quad ,$$
$$b_i = 0.07780\, RT_{ci}/P_{ci} \, , \, u_0 = 2 \, , \, w_0 = -1 \, .$$

Where T_c is the critical temperature of the mixture, v_c is the critical specific volume of the mixture, T_{ci} is the critical temperature of ith component, P_{ci} is the critical pressure of ith component, w_i is the acentric factor of ith component, k_{ij} is the binary interaction coefficient. These parameters can be found in API Databook (API, 2005) or some commercial software such as Aspen HYSYS and SIMSCI PIPEPHASE.

Set $\Delta \mathbf{n} = \left[\Delta n_1, \Delta n_2, \cdots, \Delta n_C \right]^T$. To ensure that it is nonzero, the vector $\Delta \mathbf{n}$ is normalized.

$$\Delta \mathbf{n}^T \Delta \mathbf{n} - 1 = 0 \tag{24}$$

Equations (3) (4) and (24) construct the critical points model of defined mixtures. Equation (3) should apply to each component, thus the model represents a system of $C+2$ equations with the $C+2$ variables T_c, v_c and Δn_i ($i=1, 2, \cdots, C$). The critical temperature T_c, critical specific volume v_c and $\Delta \mathbf{n}$ can be gained by solving the equations. The critical pressure P_c can then be computed directly from the pressure-explicit EoS.

3 Model Solution
3.1 Damped Newton-Raphson Iteration Scheme
In order to calculate the critical point of a mixture, the above equations should be satisfied simultaneously. Heidemann and Khalil employed two nested single-variable iteration loops and the Newton iteration method to solve the model. The inner loop is holding v_c constant, and iterates T_c to find the equation (3) is equal to zero using a Newton iteration scheme. The outer loop is calculating the values of Δn_i and checking whether equation (4) is satisfied on the basis of T_c obtained from the inner loop. If it is satisfied, exit the iteration. Otherwise, repeat the inner loop and obtain the new values of T_c using Newton iteration scheme until equation (4) is satisfied (Michelsen et al, 1988; API,

2005).

This work replaced the two nested single-variable iteration with a whole iteration using Newton-Raphson iteration scheme. However, we found that if the total number of components is more than five and traditional Newton-Raphson method is employed to solve the critical points model, the Newton-Naphson method may not converge successfully. To overcome the problem, this work used the damped Newton-Naphson (Abbasbandy et al, 2003; Crisfield et al, 1984). Different with the traditional Newton iteration method, the convergence of damped Newton-Naphson is not only dependent on the initial guesses of variables, but also relates to the damped factor.

Nominate the equations (3) is f_{11}-f_{1c}, equation (4) is f_2 and equation (24) is f_3. Based on Taylor series expansion of the $C+2$ equations, and considering the first order terms, the iteration format can be built as follows:

$$\begin{bmatrix} \dfrac{\partial f_{11}}{\partial T_c} & \dfrac{\partial f_{11}}{\partial v} & \dfrac{\partial f_{11}}{\partial \Delta n_1} & \cdots & \dfrac{\partial f_{11}}{\partial \Delta n_C} \\ \dfrac{\partial f_{12}}{\partial T_c} & \dfrac{\partial f_{12}}{\partial v_c} & \dfrac{\partial f_{12}}{\partial \Delta n_1} & \cdots & \dfrac{\partial f_{12}}{\partial \Delta n_C} \\ & & \cdots & & \\ \dfrac{\partial f_{1C}}{\partial T_c} & \dfrac{\partial f_{1C}}{\partial v_c} & \dfrac{\partial f_{1C}}{\partial \Delta n_1} & \cdots & \dfrac{\partial f_{1C}}{\partial \Delta n_C} \\ \dfrac{\partial f_2}{\partial T_c} & \dfrac{\partial f_2}{\partial v_c} & \dfrac{\partial f_2}{\partial \Delta n_1} & \cdots & \dfrac{\partial f_2}{\partial \Delta n_C} \\ 0 & 0 & \dfrac{\partial f_3}{\partial \Delta n_1} & \cdots & \dfrac{\partial f_3}{\partial \Delta n_C} \end{bmatrix} \begin{bmatrix} \Delta T_c \\ \Delta v_c \\ \Delta \Delta n_1 \\ \Delta \Delta n_2 \\ \vdots \\ \Delta \Delta n_C \end{bmatrix} = - \begin{bmatrix} f_{11}\left(x^{(k)} \right) \\ f_{12}\left(x^{(k)} \right) \\ \vdots \\ f_{1C}\left(x^{(k)} \right) \\ f_2\left(x^{(k)} \right) \\ f_3\left(x^{(k)} \right) \end{bmatrix} \tag{25}$$

Where, ΔT_c, Δv_c, $\Delta \Delta n_i$ are the correction terms of the critical temperature, critical specific volume of the mixture and change in mole fraction of ith component respectively. $x(k)$ is the variables set of the kth iteration time, $x^{(k)} = \left(T^{(k)}, v^{(k)}, \Delta n_1^{(k)}, \cdots, \Delta n_c^{(k)} \right)$.

To ensure the results calculated are the vapor-liquid critical points, based on the method introduced in API Data Book and numerical experiments, we proposed the initial values of the variables can be set as follows.
Initial value of the critical specific volume:

$$v_c = \sum_{i=1}^{C} n_i v_{ci} \tag{26}$$

Initial value of the critical temperature:

$$T_c = 3 \sum_{i=1}^{C} n_i T_{ci} \tag{27}$$

Initial values of the change in mole fraction of each component:

$$\Delta n_i = n_i^{2/3} \tag{28}$$

Where, v_{ci} is the critical specific volume of ith component.

To ensure the iteration is convergent, the damped factor is calculated by equation (29).

$$x^{k+1} = x^k + \frac{1}{1 + Q\exp(-0.5k)}\Delta x \qquad (29)$$

If $Q=0$, the damped Newton-Raphson scheme is entirely equivalent to traditional Newton-Raphson scheme.

Considering there are magnitude difference between the temperature and the other variables, the different convergence criterion for each variable are proposed as follows:

$$|\Delta T| < 0.2 \qquad (30)$$

$$|\Delta v| < 0.01 \qquad (31)$$

$$|\Delta\Delta n_i| < 0.01 \quad i = 1, 2, \cdots, C \qquad (32)$$

When above convergence criteria are satisfied simultaneously, exit the iteration and output the results.

3.2 Determining the damped factor

In equation (29) the damped factor is dependent on Q which can be obtained by numerical experiments. We take a condensate gas which contains eleven components as a test sample. For different Q, the convergent curves of T_c and v_c are depicted in Figure 1 and Figure 2.

Table 1. Molar composition of the tested condensate gas.

Component	Mole fraction	Component	Mole fraction
CO_2	0.0150	nC_4H_{10}	0.0329
N_2	0.0033	iC_5H_{12}	0.0402
CH_4	0.5205	nC_5H_{12}	0.0458
C_2H_6	0.0823	C_6H_{14}	0.0503
C_3H_8	0.0633	$C_7H_{16}+$	0.1162
iC_4H_{10}	0.0302		

As depicted in Figure 1, the temperature cannot converge to a certain value if $Q=0$ (traditional Newton-Raphson scheme) and $Q=400$. However, the desired temperature can be obtained when Q is equal to or larger than 500. The similar phenomena also can be seen in Figure 2. Also, the critical specific volume cannot converge to a correct value if $Q=0$ or $Q=400$, while it converge to the same and correct value when $Q=500$ and $Q=600$. Then, we can give the correct liquid-vapor critical temperature is 407.6 K, critical specific volume is 1.523 m³/kmol, the critical pressure is 13706 kPa, corresponding changes in mole fraction of all components are 0.0055, -0.0056, -0.1936, 0.1100, 0.1650, 0.1065, 0.1271, 0.1926, 0.2310, 0.3102, 0.8420.

Note that the total iteration time is 35 when $Q=500$ and total iteration time is 36 when $Q=600$. That can be explained that the step length of each variable modification is decreasing with the increasing of Q. Finally, we choose 500 as the optimal value of Q. Then equation (29) is expressed as:

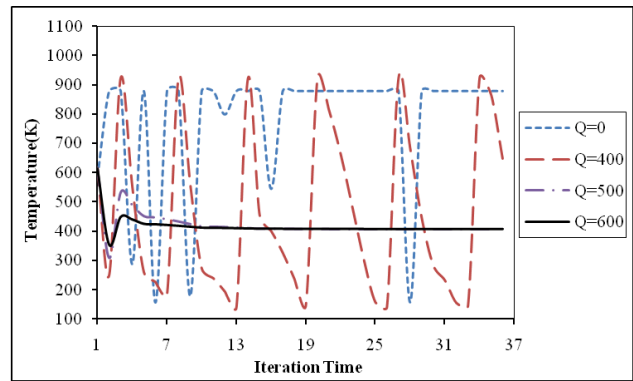$$x^{k+1} = x^k + \frac{1}{1 + 500\exp(-0.5k)}\Delta x \qquad (33)$$
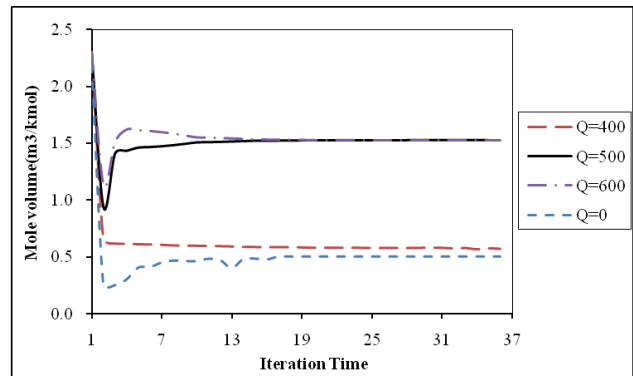

Figure 1. The critical temperature convegent curves.

Figure 2. The critical specific volume convegent curves.

The choice of the initial values, convergence criteria and damped factor is a very important aspect in the implementation of the solution method since it strongly affects the robustness of the method. The proposed initial values, convergence criterions and damped factor make the iteration method robust for locating critical points of multicomponent mixtures up to 11 components.

4. Results and Discussion

The solution procedures for locating the liquid-vapor critical point involve a large amount of matrixes calculation. In order to test the procedures presented, the computer program was developed using Microsoft Visual Basic and MATLAB hybrid programming technical (Li et al, 2010).

In this example, critical temperatures and pressures have been calculated for a total for twenty five mixtures which were gained from 11 literatures. This compositions for all the mixtures studied are given in Table 2. This table includes two two-component mixtures, eight three-component mixtures, four four-component mixtures, three five-component mixtures, one six-component mixture, one seven-component mixture , one ten-component mixture and four eleven-component mixtures, containing from methane to n-heptane, CO_2, N_2 were used to test the solution program.

The basic parameters, such as binary interaction parameters, molar weight, acentric factor and critical parameters of each component are obtained from the software named Aspen HYSYS 2006.

Table 3 presents the calculated critical pressures and temperatures for the twenty-five mixtures given in Table 2 using PR EoS and SRK EoS. To analyze the accuracy of the solution method, two kinds of error evaluation methods are defined. The first one is relative error (RE) defined by equation (34).

Table 2. Compositions of multicomponent systems studied.

Mixture no.	Mixture composition (mole fraction)										
	CO_2	N_2	CH_4	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}	iC_5H_{12}	nC_5H_{12}	C_6H_{14}	$C_7H_{16}+$
1			0.1000	0.9000							
2	0.9500	0.0500									
3		0.0700	0.4600							0.4700	
4				0.4290			0.3730				0.1980
5				0.7260			0.1710				0.1030
6				0.5140			0.4120				0.0740
7				0.8010				0.0640			0.1350
8				0.6120				0.2710			0.1170
9				0.6150				0.2960			0.0890
10		0.0465	0.4530		0.5005						
11		0.0490	0.4345	0.0835	0.4330						
12				0.6168			0.1376	0.0726			0.1730
13				0.2542	0.2547		0.2554		0.2357		
14				0.4858			0.3316		0.1213	0.0613	
15			0.2019	0.2029	0.2033		0.2038		0.1881		
16			0.7057	0.0669	0.0413		0.0508		0.1353		
17			0.6626	0.1093	0.1057				0.0616	0.0608	
18			0.1015	0.3573	0.2629				0.0657	0.0332	
19		0.0140	0.9430	0.0270	0.0074		0.0049		0.0010	0.0027	
20	0.0120		0.9089	0.0440	0.0191	0.0033	0.0060	0.0021	0.0013	0.0015	0.0018
21	0.0109	0.0884	0.8286	0.0401	0.0174	0.0030	0.0055	0.0019	0.0012	0.0014	0.0006
22	0.0091	0.2441	0.6870	0.0333	0.0144	0.0030	0.0040	0.0016	0.0010	0.0011	0.0014
23	0.0020	0.2400	0.7364	0.0120	0.0053	0.0010	0.0015	0.0005	0.0004	0.0004	0.0005
24	0.0030	0.1130	0.8580	0.0150	0.0060	0.0012	0.0018	0.0006	0.0004	0.0004	0.0006
25	0.0100	0.1611	0.7625	0.0369	0.0160	0.0028	0.0051	0.0018	0.0011	0.0012	0.0015

Table 3. Critical parameters obtained from calculation and experiments.

| Mixture no.	Number. of components	Experimental		SRK EOS		PR EOS		Data Source
		$T_c(K)$	$P_c(kPa)$	$T_c(K)$	$P_c(kPa)$	$T_c(K)$	$P_c(kPa)$	
1	2	299	5322	295	5235	299	5328	(API, 2005)
2	2	302	8300	301	8124	300	8092	(Seevam,2007)
3	3	462	1170	463	1168	459	1178	(Benito,2001)
4	3	438	6612	442	6375	439	6320	(Brunner,1990)
5	3	386	7605	390	7591	388	7462	(Brunner,1990)
6	3	400	6405	405	6298	404	6224	(Brunner,1990)
7	3	391	8101	396	8416	392	8260	(Brunner,1990)
8	3	421	7156	423	7085	420	7009	(Brunner,1990)
9	3	416	7060	417	6947	414	6879	(Brunner,1990)
10	3	313	9232	324	9205	321	9141	(Yarborough,1970)
11	4	313	8963	318	9093	316	9028	(Yarborough,1970)
12	4	423	7412	426	7477	423	7389	(Ekiner,1965)
13	4	406	5113	411	5095	409	5037	(Etter,1961)
14	4	418	4506	420	4443	419	4410	(Etter,1961)
15	5	387	7220	396	7091	393	6998	(Etter,1961)
16	5	308	13700	320	14884	316	14499	(Hanson,1945)
17	5	310	13748	324	14706	318	14443	(Hanson,1945)
18	6	376	6536	382	6508	380	6456	(Etter,1961)
19	7	201	5578	202	5938	202	5906	(Gonzalez,1968)
20	10	211	6378	211	6635	211	6602	(Gore,1952)
21	11	204	6584	204	6982	204	6704	(Davis,1954)
22	11	189	6708	180	6112	181	6238	(Davis,1954)
23	11	183	5618	184	6081	183	6108	(Davis,1954)
24	11	193	5829	193	5937	193	5916	(Davis,1954)
25	11	198	6674	192	6573	194	6878	(Davis,1954)
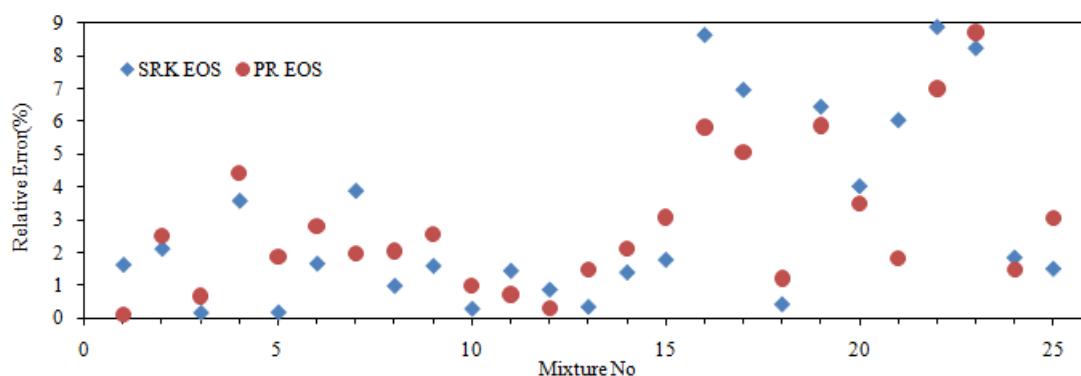
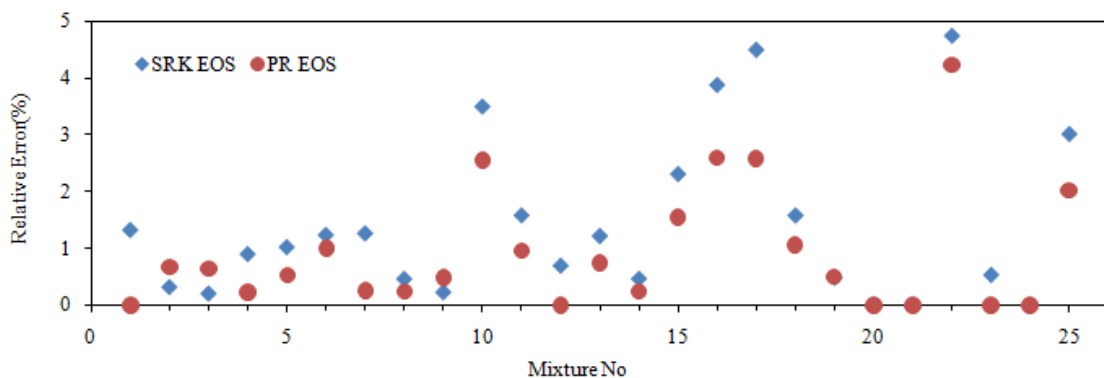*Figure 3. Relative errors for critical pressures*

Figure 4. Relative errors for critical temperatures

$$RE = \frac{\left|x_{cal} - x_{\exp}\right|}{x_{\exp}} \times 100\% \qquad (34)$$

Where, x_{cal} represents the calculated critical temperature or pressure, $x_{\exp}$ represents the critical temperature or pressure from experiments.

The relative errors between the experimental and calculated values are depicted in Figure 3 and Figure 4. The average relative error of critical pressures calculated using SRK EoS is 3.00%, while that calculated using PR EoS is 2.85%. The average relative error of critical temperatures calculated using SRK EoS is 1.43%, and the corresponding error of PR EoS is 0.92%. That means accuracy of the critical temperatures prediction is better than that of the critical pressures prediction. The overall critical parameters prediction accuracy of PR EoS is better than SRK EoS.

The second one is average absolute deviation (*AAD*) defined by equation (35).

$$AAD = \frac{1}{C} \sum_{i=1}^{N} \max \left|x_{cal} - x_{\exp}\right| \qquad (35)$$

The *AAD* of critical temperatures calculated using SRK EoS is 4.44K, and that calculated using PR EoS is 2.80K. The *AAD* of critical pressures calculated using SRK EoS is 240.28kPa, and that calculated using PR EoS is 209.40kPa. The overall accuracy of the solution method is slightly better than the simulated annealing technique reported by Justo-Garcia et al.(2008).

5. Conclusions

Based on the damped Newton-Raphson scheme, this paper researched the solution method of the critical model proposed by Hidemann and Khalil and developed by Stradi et al. This method used the critical temperature, critical specific volume and mole change in mole fraction of each component as independent variables. All the variables can be solved simultaneously through a whole iteration, which is more reliable than the nested two-singe variable loops method. Furthermore, the initial guesses of variables, convergence criteria of the iteration, and the damped factor were determined by using of numerical experiments. the choice of the values makes the iteration method robust for locating critical points of multicomponent mixtures.

The solution method was tested successfully on 25 mixtures which contain hydrocarbons from methane to n-heptane, CO_2, N_2. The analysis of errors presented the overall accuracy of the method is satisfactory. The method

provides a practical way to locating the liquid-vapor critical point of the multicomponent mixtures.

6. Nomenclature

C	total number of components
n	mole fraction of component
Δn	change in mole fraction
T	temperature
v	critical specific volume,
f_g	fugacity
T_c	critical temperature of the mixture
v_c	critical specific volume of the mixture
P_c	critical pressure of the mixture
T_{ci}	critical temperature of ith component
P_{ci}	critical pressure of ith component
v_{ci}	critical volume of ith component
w	accentric factor
k_{ij}	binary interaction coefficient.
ΔT	correction term of the critical temperature
Δv	correction term of the critical specific volume
$\Delta \Delta n$	correction term change in mole fraction
Q	parameter in damped Newton iteration method

F_1, F_2, F_3, F_4, F_5, F_6, a, b, β_i, $\overline{N}$, $\overline{\beta}$, a_{ij}, α_i, $\overline{\alpha}$ parameters related with equation of state.

Subscripts

i	i^{th} component
j	j^{th} component
m	m^{th} component
c	critical condition

Superscripts

k	k^{th} iteration step

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Appendix:The Derivation of Equations (3) and (4)

The general form of SRK EoS and PR EoS is

$$P = \frac{RT}{v-b} - \frac{a}{(v+bD_1)(v+bD_2)} \tag{A1}$$

The parameters in the equation are listed in the paper. Based on the EoSs, the fugacity of component i can be written as follows:

$$\ln(f_{gi}) = RT\left[\ln(n_i) + \frac{b_i}{v-b}\right] + \frac{ab_i}{b}\left[\frac{1}{b(D_1-D_2)}\left(\ln\left(\frac{v+bD_1}{v+bD_2}\right) - \left(\frac{bD_1}{v+bD_1} - \frac{bD_2}{v+bD_2}\right)\right)\right] - \frac{\partial a}{\partial n_i}\frac{1}{b(D_1-D_2)}\ln\left(\frac{v+bD_1}{v+bD_2}\right) \tag{A2}$$

The derivates in the quadratic form are:

$$\left(\frac{\partial \ln f_i}{\partial n_j}\right) = RT\left[\frac{\delta_{ij}}{n_j} + \frac{(b_i + b_j)}{v - b} + \frac{(b_i b_j)}{(v-b)^2}\right] + \frac{ab_i b_j}{b^2}\frac{1}{b(D_1 - D_2)}\left[\left(\frac{bD_1}{v + bD_1}\right)^2 - \left(\frac{bD_2}{v + bD_2}\right)^2\right]$$

$$+ \frac{2ab_i b_j - b\left(\dfrac{\partial a}{\partial n_i}b_j + \dfrac{\partial a}{\partial n_j}b_i\right)}{b}\frac{1}{b(D_1 - D_2)}\left[\frac{bD_1}{v + bD_1} - \frac{bD_2}{v + bD_2}\right] + \frac{-2ab_i b_j + b\left(\dfrac{\partial a}{\partial n_i}b_j + \dfrac{\partial a}{\partial n_j}b_i\right) - 2a_{ij}b^2}{b^3}\ln\left(\frac{v + bD_1}{v + bD_2}\right)$$

(A3)

The terms in the cubic form are

$$\left(\frac{\partial^2 \ln f_i}{\partial n_j \partial n_m}\right) = RT\left[\frac{\delta_{ijm}}{n_i^2} + \frac{(b_i b_j + b_j b_k + b_m b_i)}{(v-b)^2} + \frac{2b_i b_j b_m}{(v-b)^3}\right] - \frac{2ab_i b_j b_m}{b^3}\frac{1}{b(D_1 - D_2)}\left[\left(\frac{bD_1}{v + bD_1}\right)^3 - \left(\frac{bD_2}{v + bD_2}\right)^3\right]$$

$$+ \frac{b\left(\dfrac{\partial a}{\partial n_i}b_j b_m + \dfrac{\partial a}{\partial n_j}b_i b_m + \dfrac{\partial a}{\partial n_m}b_i b_j\right) - 3ab_i b_j b_m}{b^3}\frac{2}{b(D_1 - D_2)}\left[\left(\frac{bD_1}{v + bD_1}\right)^2 - \left(\frac{bD_2}{v + bD_2}\right)^2\right]$$

$$+ \frac{2\left[b\left(\dfrac{\partial a}{\partial n_i}b_j b_m + \dfrac{\partial a}{\partial n_j}b_i b_m + \dfrac{\partial a}{\partial n_m}b_i b_j\right) - 3ab_i b_j b_m\right] - 2b^2\left(a_{ij}b_m + a_{im}b_j + a_{jm}b_i\right)}{b^3}\frac{1}{b(D_1 - D_2)}\left[\frac{bD_1}{v + bD_1} - \frac{bD_2}{v + bD_2}\right]$$

$$+ \frac{2\left[b\left(\dfrac{\partial a}{\partial n_i}b_j b_m + \dfrac{\partial a}{\partial n_j}b_i b_m + \dfrac{\partial a}{\partial n_m}b_i b_j\right) - 3ab_i b_j b_m\right] - 2b^2\left(a_{ij}b_m + a_{im}b_j + a_{jm}b_i\right)}{b^4}\ln\left(\frac{v + bD_1}{v + bD_2}\right)$$

(A4)

Where

$$\frac{\partial a}{\partial n_i} = 2\sum_{j=1}^{c} n_j a_{ij}$$

(A5)

$$\delta_{ijm} = \begin{cases} 1 \ (i = j = m) \\ 0 \ (i \neq j,\ j \neq k \text{ or } i \neq m) \end{cases}$$

(A6)

$$\delta_{ij} = \begin{cases} 1 \ (i = j) \\ 0 \ (i \neq j) \end{cases}$$

(A7)

Considering the parameters defined in the main text of the paper, and reorganizing the same terms in the equations (A3) and (A4), the two equations can be written as Equations (3) and (4).