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Direct Prediction of Cricondentherm and Cricondenbar Coordinates of Natural Gas Mixtures using Cubic Equation of State

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Abstract A numerical algorithm is presented for direct calculation of the cricondenbar and cricondentherm coordinates of natural gas mixtures of known composition based on the Michelsen method. In the course of determination of these coordinates, the equilibrium mole fractions at these points are also calculated. In this algorithm, the property of the distance from the free energy surfaces to a tangent plane in equilibrium condition is added to saturation calculation as an additional criterion. An equation of state (EoS) was needed to calculate all required properties. Therefore, the algorithm was tested with Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and modified Nasrifar-Moshfeghian (MNM) equations of state. For different EoSs, the impact of the binary interaction coefficient (k_{ij}) was studied. The impact of initial guesses for temperature and pressure was also studied. The convergence speed and the accuracy of the results of this new algorithm were compared with experimental data and the results obtained from other methods and simulation softwares such as Hysys, Aspen Plus, and EzThermo.

Keywords Cricondenbar · Cricondentherm · Critical point · Equation of state · Phase envelope · Natural gas

1 Introduction

The phase envelope is a pressure-temperature diagram which describes the state of a petroleum fluid, namely, gas, liquid, gas plus liquid, solid, or dense phase, at various

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conditions of pressure and temperature. A proper analysis of many petroleum problems requires a knowledge of at least a portion of the phase envelope. For a petroleum fluid, the shape of the phase envelope depends on the composition and the nature of components making up the system. The phase envelope has numerous applications in petroleum production and process design ranging from reservoir simulation, pumping liquids, transportation of natural gas by pipeline or in liquefied natural gas (LNG) form, ethane plus recovery, refrigeration processes, and operation near the critical point or in the supercritical region. In short, sound process design requires a good knowledge of the phase envelope.

For a petroleum fluid, the phase envelope may be constructed by experimental measurements of a series of bubble points and dew points. However, this is very time-consuming and expensive. With a little care and experience, an accurate phase envelope may be constructed using equation-of-state calculations based on a limited number of experimental measurements [1].

For a gas condensate reservoir, there are two important points on the phase envelope from production, transportation, and processing viewpoints. These two points are the cricondenbar, the maximum pressure at which a fluid may exist in the two-phase region and the cricondentherm, the maximum temperature at which a fluid can be in the two-phase region.

This article presents a new algorithm for predicting the cricondenbar and cricondentherm coordinates for multicomponent hydrocarbon mixtures based on the facts that the derivatives of pressure with respect to temperature at the cricondenbar and the derivative of temperature with respect to pressure at the cricondentherm are equal to zero. These two derivatives are calculated by use of the tangent plane distance function. This function has been used in stability analysis by Michelsen [2] and suggested for direct prediction of the cricondenbar or cricondentherm by Michelsen [3].

Also, the equality of the fugacity for each component in the two phases (equilibrium criteria) is another criterion for this calculation. The equation of state (EoS) is used for calculating the fugacity of each component in both phases. Using these criteria and those two derivatives, the governing equations for these two points are obtained. The equations form a nonlinear set which are solved by Newton's method and the Jacobian matrix for simultaneous nonlinear equations.

2 Equations for Two-Phase Equilibrium

For a gas mixture with n components and known composition (z_i), at the cricondenbar and cricondentherm, there are $n+2$ variables, consisting of the n liquid mole fractions, temperature, and pressure. For this mixture, $n+2$ equations can be arranged as follows,

n equations can be derived from equilibrium criteria:

$$f_i^{\mathrm{v}} = f_i^l \qquad (i = 1, 2, \ldots, n) \tag{1}$$

These equations can be rewritten as follows:

$$g_n = \ln(z_i) - \ln(x_i) + \ln(\phi_i^{\mathrm{v}}) - \ln(\phi_i^l) = 0 \tag{2}$$

In the above equations, f_i^{v}, f_i^l, ϕ_i^{v}, and ϕ_i^l represent the fugacity and fugacity coefficients of component i in the vapor and liquid phases, respectively. The terms z_i and x_i represent the mixture and liquid-phase composition of component i, respectively. In addition, g_n is the error function. As suggested by Michelsen [3], by treating mole fractions as independent variables, an additional equation is obtained:

$$g_{n+1} = 1 - \sum_{1}^{n} x_i = 0 \tag{3}$$

For the additional equation at the cricondenbar,

$$\mathrm{d}P/\mathrm{d}T = 0 \tag{4}$$

and at the cricondentherm,

$$\mathrm{d}T/\mathrm{d}P = 0 \tag{5}$$

However, Michelsen [3] has suggested using the tangent plane distance; therefore, $\mathrm{d}P/\mathrm{d}T = 0$ and $\mathrm{d}T/\mathrm{d}P = 0$ are replaced by the following equations, respectively.

At the cricondenbar,

$$g_{n+2} = \mathrm{d}Q/\mathrm{d}T = 0 \tag{6}$$

At the cricondentherm,

$$g_{n+2} = \mathrm{d}Q/\mathrm{d}P = 0 \tag{7}$$

where Q can be one of the modified tangent plane distances (Michelsen [3]),

$$Q_1 = 1 - \sum_{i=1}^{n} x_i - \sum_{i=1}^{n} x_i (\ln z_i - \ln x_i + \ln \phi_i^{\mathrm{v}} - \ln \phi_i^l) = 0 \tag{8}$$

$$Q_2 = 1 - \sum_{i=1}^{n} z_i \phi_i^{\mathrm{v}} / \phi_i^l = 0 \tag{9}$$

3 Conventional Solution Methods

As suggested by Michelsen [3], two solution methods can be applied for solving these equations. The straightforward Newton's iteration can be used for solving simultaneously $n+2$ Eqs. 2, 3, and 6 for the cricondenbar and Eqs. 2, 3, and 7 for the cricondentherm. This solution method will be called Method A. Another method is a direct substitution procedure for which x_i is reevaluated subsequently from the equations:

$$\ln X_i = \ln z_i + \ln \phi_i^{v} - \ln \phi_i^{l(k)} \tag{10}$$

$$x_i^{(k+1)} = X_i \Big/ \sum X_i \tag{11}$$

for which the temperature and pressure are determined by the Newton's correction using Eqs. 6 and 8 for the cricondenbar and Eqs. 7 and 8 for the cricondentherm. In this article this method is called Method B.

4 New Algorithm

Equations 2 and 3 with Eq. 6 or 7 must be solved simultaneously for the cricondenbar or cricondentherm calculation for a gas mixture with a known composition of z_i. For this purpose, the following algorithms are suggested.

4.1 Cricondentherm

(a) Make initial guesses for pressure and temperature.
(b) To generate initial liquid mole fractions (x_i), n Eq. 2 must be solved simultaneously using initial guesses for temperature and pressure in the previous step.
(c) Using these values of temperature and x_i, solve ${}^{\partial Q}\!/_{\partial P} = 0$ for new pressure.
(d) Perform a Newton's iteration using Eqs. 2 and 3 with new pressure which was obtained in step 3 for updating the temperature and x_i.
(e) Go back to step 3 if the temperature and x_i have not converged.

4.2 Cricondenbar

(a) Make initial guesses for pressure and temperature.
(b) To generate initial liquid mole fractions (x_i), n Eq. 2 must be solved simultaneously using initial guesses for temperature and pressure in the previous step.
(c) Using these values of pressure and x_i, solve ${}^{\partial Q}\!/_{\partial T} = 0$ for new temperature.
(d) Perform a Newton's iteration using Eqs. 2 and 3 with new temperature which was obtained in step 3 for updating pressure and x_i.
(e) Go back to step 3 if the pressure and x_i have not converged.

4.3 Explanations

As is clear from the above, the variables in Newton's iterations are $x_1, x_2, \ldots, x_n$ and T for the cricondentherm and $x_1, x_2, \ldots, x_n$ and P for the cricondenbar. In most calculations during the convergence, the liquid mole fractions may become negative, especially when these values are very close to zero. In this situation the use of a very small relaxation factor [4] cannot prevent this difficulty and it causes the divergence. This situation also may occur in solving n Eq. 2 for finding the initial liquid mole fractions (variables are $x_1, x_2, \ldots, x_n$). To prevent this difficulty, as suggested by Michelsen [3], it is better to use variables in logarithmic form as

$\ln x_1, \ln x_2, \ldots, \ln x_n, \ln T$ for the cricondentherm and $\ln x_1, \ln x_2, \ldots, \ln x_n, \ln P$ for the cricondenbar and $\ln x_1, \ln x_2, \ldots, \ln x_n$ for finding initial liquid mole fractions.

By considering these new variables, the convergence criteria have been set to

$$\sum_{i=1}^{n}\left[\ln x_i^{(k)} - \ln x_i^{(k-1)}\right]^2 < 10^{-10}, \quad \left|\ln T^{(k)} - \ln T^{(k-1)}\right| < 10^{-7},$$
$$\text{and } \left|\ln P^{(k)} - \ln P^{(k-1)}\right| < 10^{-8}$$

5 Application of New Algorithm

Using the above algorithms, the cricondentherm and cricondenbar coordinates are calculated directly for the same mixture used by Michelsen [5], see Table 1. In the proceeding section, the Soave-Redlich-Kwong [6] (SRK) EoS is used. The cricondentherm and cricondenbar coordinates for this mixture were calculated by Michelsen [5] during the saturation calculations to predict the entire phase envelope.

To calculate the cricondentherm with an initial guess of 5 MPa and 255 K, initial liquid mole fractions are generated (Table 1). By using these liquid mole fractions, the initial guess of temperature, and solving ${}^{\partial Q_1}/_{\partial P} = 0$ for pressure, the modified pressure of 3.113 MPa is obtained. Using this new value of pressure and performing Newton's iteration, the values of liquid mole fractions and temperature are adjusted. Convergence to the cricondentherm at 270.46 K and 3.980 MPa is achieved in 10 iterations. The final liquid-phase composition at the cricondentherm point is listed in Table 1.

To calculate the cricondenbar with an initial guess of 6 MPa and 236 K, initial liquid mole fractions are generated (Table 1). By using these initial mole fractions, the initial guess of pressure, and solving ${}^{\partial Q_1}/_{\partial T} = 0$ for temperature, the modified temperature of 222.09 K is obtained. Using this new value of temperature and performing Newton's iteration, the values of mole fractions and pressure are adjusted. Convergence to the cricondenbar at 9.02 MPa and 239.02 K is achieved in seven iterations. The final liquid mole fractions at the cricondenbar point are listed in Table 1.

Table 1 Composition of mixture and final calculated values of x_i at cricondentherm and cricondenbar points

Component	Mix. 1	Calculated initial guess of x_i based on assumed P and T		Final calculated x_i	
	z_i	Cricondentherm	Cricondenbar	Cricondentherm	Cricondenbar
C_1	0.9430	0.183754	0.164717	0.231538	0.616765
C_2	0.0270	0.035774	0.035663	0.038771	0.062061
C_3	0.0074	0.036937	0.037623	0.037832	0.040806
$n-C_4$	0.0049	0.091514	0.094696	0.089060	0.064555
$n-C_5$	0.0010	0.065231	0.067626	0.061311	0.030209
$n-C_6$	0.0027	0.585949	0.598985	0.540289	0.181298
N_2	0.0140	0.000837	0.000686	0.001194	0.004303

6 Comparison of Methods

To test the accuracy and reliability of the proposed method, the cricondenbar and cricondentherm were calculated using these three different methods for the mixture shown in Table 1. As expected, the same accuracy and uniqueness were obtained, because the same equations and the same convergence criteria were used in all the methods. Therefore, the convergence speed of the methods was compared using different initial guesses of temperature and pressure. For all the three methods, the initial liquid mole fractions are calculated by solving n Eq. 2 with identical initial conditions. The numbers of iterations for these three methods are listed in Tables 2 and 3 for the cricondentherm and cricondenbar, respectively. Tables 2 and 3 indicate that method A is very sensitive with respect to the initial guess. For initial guesses close to the answer, this method is fast; otherwise, it is very slow or diverges, Michelsen [3]. Analysis of Tables 2 and 3 also indicates that method B in the cricondentherm calculation is as fast as the new algorithm, but in the cricondenbar calculation, its convergence is slower than the new algorithm. Therefore, the new algorithm is faster than the other two and it is reliable for these calculations. Comparisons of the reported cricondentherm and cricondenbar by Michelsen [5] and the calculated values by this new procedure are shown in Table 4.

This proposed algorithm is checked for seven more hydrocarbon mixtures shown in Table 5. The calculated results for these seven mixtures and the Michelsen mixture are compared with the calculated results by EzThermo [7], Hysys [8], and Aspen Plus [9] software in Table 6. The temperature and pressure of the cricondenbar and cricondentherm of mixtures 7 and 8 are reported by Etter and Kay [10] and are compared with the calculated results of the algorithm in Table 7.

Also, this algorithm is tested against five synthetic natural gas mixtures for which their dew points are measured experimentally by Jarne et al. [11] and Avila et al. [12]. The compositions of these synthetic natural gas mixtures and their reported

Table 2 Comparison of cricondentherm convergence iteration number for three methods using different initial guesses

Initial guesses			Cricondentherm iteration number		
No.	Temperature (K)	Pressure (MPa)	Method A [3]	Method B [3]	New method
1	200	4.5	155	13	12
2	240	4	20	12	11
3	220	5	61	12	12
4	260	5	15	11	10
5	260	4	5	11	10
6	200	4	99	13	12
7	230	8	57	12	12
8	230	4	27	12	12
9	200	3	65	13	12
10	265	4	7	11	10
11	240	8.5	41	11	11
Iteration number summation			552	131	124
Average iteration number			50.2	11.9	11.3

Table 3 Comparison of cricondenbar convergence iteration number for three methods using different initial guesses

Initial guesses			Cricondenbar iteration number		
No.	Temperature (K)	Pressure (MPa)	Method A [3]	Method B [3]	New method
1	230	8	11	20	5
2	220	6	11	21	6
3	200	5	NC	21	7
4	260	5	NC	20	7
5	230	4	NC	21	8
6	220	7	32	21	6
7	240	8.5	7	20	6
8	210	6	354	20	7
Iteration number summation			415	164	52
Average iteration number			51.9	20.5	6.5

Table 4 Comparison of calculated cricondentherm and cricondenbar with literature values

	Calculated values by this work	Reported values Michelsen [5]
Cricondentherm (K)	270.46	269.9
Cricondenbar (MPa)	9.02	8.87

Table 5 Compositions of hydrocarbon mixtures used in this work

Component	Composition (mol%)						
	Mix. 2	Mix. 3	Mix. 4	Mix. 5	Mix. 6	Mix. 7	Mix. 8
C_1	79.14	85.34	75.44	81.13	69.59	–	–
C_2	7.48	7.90	15.40	7.24	5.31	0.254	–
C_3	3.29	4.73	6.95	2.35	4.22	0.255	0.486
$n-C_4$	0.51	0.85	0.98	0.22	0.85	0.255	0.332
$i-C_4$	1.25	0.99	1.05	0.35	0.76		
$n-C_5$	0.36	0.10	0.09	0.09	0.67	0.236	0.121
$i-C_5$	0.55	0.09	0.09	0.03	1.12	–	–
$n-C_6$	0.61	–	–	–	1.22	-	0.061
$n-C_7$	4.80	–	–	–	14.64	–	–
N_2	0.29	–	–	6.25	0.12	–	–
CO_2	1.72	–	–	2.34	1.50	–	–

experimental cricondentherm and cricondenbar are listed in Table 8. In Tables 9 and 10, the average absolute error for the new algorithm and EzThermo, Hysys, and Aspen Plus software with respect to the experimental data are shown.

To verify the impact of the initial guesses of temperature and pressure, the calculation for the Michelsen mixture (Table 1) is performed by this algorithm with 30 different initial points. The points are shown in Fig. 1. For all points where convergence is realized, the results have the same accuracy for the cricondentherm and cricondenbar coordinates. The iteration numbers are listed in Table 11. It is clear that the initial guess should be located in the two-phase region. When the initial guess is outside the

Table 6 Comparison between calculated cricondentherm and cricondenbar coordinates by several methods

System	New algorithm				EzThermo				Hysys				Aspen Plus			
	Cricondentherm		Cricondenbar		Cricondentherm		Cricondenbar		Cricondentherm		Cricondenbar		Cricondentherm		Cricondenbar	
	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
Mix. 1	270.46	3.980	239.02	9.020	272.6	4.068	240.0	9.135	270.5	4.017	239.1	9.005	270.0	3.362	235.7	8.931
Mix. 2	388.7	7.537	316.9	18.02	386.3	7.653	314.6	18.346	387.1	7.984	313.1	19.06	386.5	7.832	308.8	18.47
Mix. 3	267.43	5.681	248.7	8.923	267.1	5.585	248.8	8.816	267.2	5.644	248.5	8.867	267.2	5.220	250.3	8.855
Mix. 4	277.9	6.275	260.8	9.061	277.7	6.274	261.0	8.961	277.7	6.213	260.6	9.020	277.7	5.872	262.1	9.006
Mix. 5	246.8	4.977	231.0	7.981	245.6	4.757	229.7	7.791	245.6	4.817	229.5	7.817	246.8	4.966	232.0	7.917
Mix. 6	443.4	8.597	353.7	19.33	440.9	8.894	349.9	20.070	441.9	9.095	345.7	21.13	440.8	9.756	361.0	20.30
Mix. 7	413.2	4.861	410.7	5.091	413.3	4.895	409.8	5.076	413.2	4.906	410.3	5.113	412.9	4.700	407.6	5.058
Mix. 8	421.1	4.361	420.5	4.443	418.4	4.403	418.4	4.403	420.8	4.361	419.8	4.433	420.9	4.405	420.7	4.417

Table 7 Cricondenbar and cricondentherm values for this work and reported values [10]

		Temperature (K)		Pressure (MPa)	
		Cricondentherm	Cricondenbar	Cricondentherm	Cricondenbar
Mix. 7	Etter and Kay [10]	410.0	403.3	–	–
	This Work	413.2	410.7	4.8615	5.0917
Mix. 8	Etter and Kay [10]	–	–	4.3782	4.5092
	This Work	421.1	420.59	4.3611	4.4436

Table 8 Synthetic natural gas mixtures reported by Jarne et al. [11] and Avila et al. [12]

Composition	mol%				
	SNG 1	SNG 2	SNG 3	SNG 4	SNG 5
C_1	69.114	90.483	84.446	88.1882	83.3482
C_2	2.620	8.038	8.683	2.720	7.526
C_3	0.423	0.801	3.297	0.850	2.009
$i-C_4$	0.105	0.081	0.293	0.170	0.305
$n-C_4$	0.104	0.123	0.589	0.320	0.520
$i-C_5$	0.034	0.010	0.084	0.085	0.120
$n-C_5$	0.023	0.0079	0.086	0.094	0.144
$n-C_6$	0.110	0.0047	0.050	0.119	0.068
$n-C_7$	–	0.0011	–	0.0258	0.0138
$n-C_8$	–	–	–	0.018	0.011
N_2	1.559	0.313	0.772	6.900	5.651
$C0_2$	25.908	0.202	1.7	0.510	0.284
Cricondentherm T(K)	252.2	229.1	261.4	277.3	273.5
Cricondentherm P(MPa)	3.68	2.98	5.1	3.5	4.5
Cricondenbar, T(K)	246.4	221.1	251.4	245.3	241.9
Cricondenbar P(MPa)	6.02	6.97	7.78	10.59	9.23

Table 9 Average absolute of the relative errors from experimental cricondentherm using the new method and three software packages

	This work		Hysys		EzThermo		Aspen Plus	
	Temp	Pres	Temp	Pres	Temp	Pres	Temp	Pres
SNG 1	2.78	25.46	0.40	6.77	0.16	8.21	2.70	22.01
SNG 2	0.13	21.30	0.52	18.75	0.39	17.98	0.22	20.10
SNG 3	0.11	3.941	0.15	5.73	0.19	6.73	0.11	7.31
SNG 4	0.18	2.971	0.14	4.40	0	4.40	0.04	15.60
SNG 5	0.04	13.97	0.15	13.84	0.15	12.66	0.18	2.51
AARE (%)[a]	0.65	13.53	0.27	9.90	0.18	10.00	0.65	13.50

[a] Average Absolute of Relative Error %: $AARE\% = \frac{100}{Number\ of\ Mixtures} \sum \left| \frac{Calculated\ value}{Experimental\ value} - 1 \right|$

Table 10 Average absolute errors from experimental cricondenbar using the new method and three software packages

Gas	This work		Hysys		EzThermo		Aspen Plus	
	Temp	Pres	Temp	Pres	Temp	Pres	Temp	Pres
SNG 1	0.69	35.46	4.22	26.34	4.95	25.08	0.49	34.18
SNG 2	1.67	8.84	1.95	9.63	1.67	9.99	1.22	9.80
SNG 3	3.42	7.65	3.82	5.94	3.82	5.54	3.70	6.92
SNG 4	2.24	9.69	2.24	8.99	2.24	10.27	1.71	10.10
SNG 5	0.29	1.84	0.17	2.32	0.17	2.63	0.04	2.43
AARE%	1.66	12.69	2.48	10.64	2.57	10.70	1.43	12.68

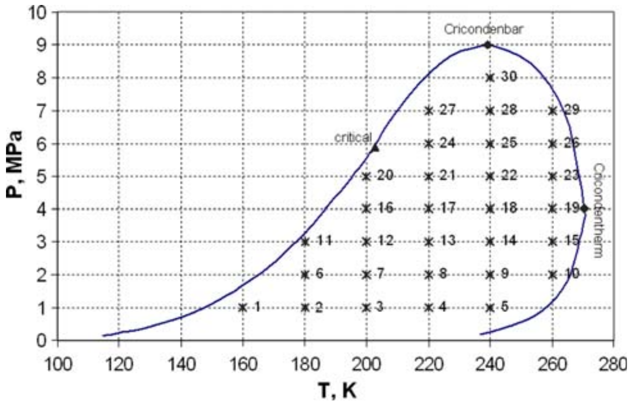

Fig. 1 Phase diagram for Michelsen [5] mixture and point coordinates for initial guess

Table 11 Iteration number for Mix. 1 [5] with different initial guesses shown in Fig. 1

Point	Cricondentherm	Cricondenbar	Point	Cricondentherm	Cricondenbar
	Iteration number			Iteration number	
1	12	over 100[a]	16	12	8
2	12	over 100[a]	17	12	8
3	12	over 100[a]	18	11	8
4	12	over 100[a]	19	10	8
5	11	27[b]	20	12	8
6	12	9	21	11	7
7	12	8	22	11	7
8	12	8	23	10	7
9	11	9	24	11	6
10	10	19[c]	25	11	6
11	12	8	26	9	7
12	12	8	27	11	6
13	12	8	28	11	6
14	11	8	29	10	6
15	10	8	30	11	6

[a] Convergence results using relaxation factor equal to 0.05
[b] Convergence results using relaxation factor equal to 0.6
[c] Convergence results using relaxation factor equal to 0.7

Table 12 Iteration number for new algorithm using Eq. 3 or 8 in Newton's iterations for Mix. 1

Relaxation factor		Using Eq. 3	Using Eq. 8					
		1	1	0.8	0.6	0.5	0.3	0.1
Itr. No.	Cricondentherm	10	NC[a]	23	29	NC	74	124
	Cricondenbar	7	NC	NC	24	30	82	142

[a]NC = No Convergence

Table 13 Experimental [11,12] and predicted cricondentherm coordinates using $k_{ij} = 0.0$

System	Exp. Data		SRK			MNM			PR		
	T(K)	P(MPa)	T(K)	P(MPa)	Itr.No	T(K)	P(MPa)	Itr.No	T(K)	P(MPa)	Itr.No
SNG 1	252.2	3.68	259.2	4.617	21	258.0	4.479	20	257.3	4.551	21
SNG 2	229.1	2.98	228.8	3.615	20	228.1	3.333	20	227.2	3.62	23
SNG 3	261.4	5.1	261.7	4.899	18	260.0	4.664	17	260.2	4.759	18
SNG 4	277.3	3.5	277.8	3.604	12	276.6	3.400	11	275.2	3.397	12
SNG 5	273.5	4.5	273.6	3.871	15	272.2	3.621	14	271.3	3.702	15

Table 14 Experimental [11,12] and predicted cricondenbar coordinates using EoSs with $k_{ij} = 0.0$

System	Exp. Data		SRK			MNM			PR		
	T(K)	P(MPa)	T(K)	P(MPa)	Itr.No	T(K)	P(MPa)	Itr.No	T(K)	P(MPa)	Itr.No
SNG 1	246.4	6.02	244.7	8.155	13	243.5	8.224	15	243.9	8.085	12
SNG 2	221.1	6.97	217.4	6.354	12	216.3	6.319	11	216.7	6.299	11
SNG 3	251.4	7.78	242.8	8.375	10	240.5	8.288	11	241.3	8.244	10
SNG 4	245.3	10.59	239.8	9.564	7	236.5	9.743	7	237.1	9.225	7
SNG 5	241.9	9.23	242.6	9.060	9	240.1	9.000	9	240.2	8.842	10

two-phase region, it causes a trivial convergence for initial equilibrium mole fractions in the stability test $K_i = 1$ and the wrong convergence, or divergence, is the result. For the cricondentherm, it is sufficient that the initial guess is located in the two-phase region. As shown in Table 11, for all initial guesses in the two-phase region, convergence is obtained but cricondenbar initial guesses at a low pressure may result in divergence. For low-pressure initial guesses, the correction vector and subsequently the step size will be increased. Therefore, divergence may occur for this large step size. This difficulty may be prevented by applying a small relaxation factor. The molar average of the critical pressure and the critical temperature (pseudo-critical P and T) or their values multiplied by 1.1 to 1.3 are good initial guesses.

In the new algorithm using the Newton iteration, Eqs. 2 and 3 must be solved simultaneously. However, as an alternative method, Eq. 8 or 9 can be used instead of Eq. 3. For the mixture listed in Table 1, calculations were performed using the new algorithm and Eq. 8 instead of Eq. 3. Results are shown in Table 12 and indicate that the use of Eq. 8 in Newton's iteration makes calculations unstable with an increase in the probability of divergence.

Table 15 Comparison of average absolute of relative errors in %[a] for cricondentherm and cricondenbar of SNG 1–5 using three EoSs

		SRK			MNM			PR		
		Temp. Error	Pres. Error	Itr. No.[b]	Temp. Error	Pres. Error	Itr. No.	Temp. Error	Press. Error	Itr. No.
Cricondentherm	With $k_{ij} = 0$	0.65	13.53	17.2	0.80	12.90	16.4	0.97	14.50	17.8
	With $k_{ij} \neq 0$ [15]	0.54	11.27	16.2	0.71	11.66	15.4	0.88	11.42	15.6
Cricondenbar	With $k_{ij} = 0$	1.66	12.70	10.2	2.40	12.59	10.6	2.21	13.40	10
	With $k_{ij} \neq 0$ [15]	2.13	11.95	9.6	2.86	11.99	9.8	2.79	12.51	9.2

[a] Average Absolute of Relative Error %: $AARE\% = \frac{100}{Number\ of\ Mixtures} \sum \left| \frac{Calculated\ value}{Experimental\ value} - 1 \right|$

[b] Average iteration number

To study the robustness of this algorithm for different equations of state, the modified Nasrifar-Moshfeghian (MNM) [13] and Peng-Robinson (PR) [14] equations of state are applied in addition to the SRK EoS and calculations were performed for the five synthetic natural gas mixtures listed in Table 8. The results for the cricondentherm and cricondenbar are listed in Tables 13 and 14, respectively. Also, the impact of binary interaction parameters (k_{ij}) [15] on the accuracy of the results and speed of convergence was studied. The results are shown in Table 15 and indicate that binary interaction parameters (k_{ij}) improve the accuracy of the results and decrease the number of iterations to achieve convergence.

7 Conclusions

A numerical algorithm for solving the cricondentherm and cricondenbar governing equations has been proposed. In this algorithm, the modified tangent plane distance was applied with simplification of $(\partial T/\partial P) = 0$ and $(\partial P/\partial T) = 0$ to $(\partial Q/\partial P) = 0$ and $(\partial Q/\partial T) = 0$ as suggested earlier by Michelsen [3].

This algorithm was checked against two other solution methods; the results from all of these methods have the same accuracy, but it was found that the new algorithm is faster and more reliable. The accuracy of this method was evaluated by comparison with experimental data and common simulation software, and excellent agreement has been found.

The algorithm was tested for 30 different initial guesses, and the impact of the initial guess was studied. It has been found that a good initial guess must be located in the two-phase region.

The algorithm was tested with SRK, MNM, and PR EoSs to study the impact of binary interaction parameters (k_{ij}). As expected, the optimized binary interaction parameters increased the speed of convergence.

List of Symbols

f_i	Fugacity of component i
k_{ij}	Binary interaction parameter between components i and j
n	Number of components
g	Error function
P	Pressure, MPa
Q, Q_1, Q_2	Modified tangent plane distance, subscripts represent Eq. number
T	Temperature, K
x	Component liquid-phase mole fraction
X	Recalculated component liquid-phase mole fraction during iterations
y	Component vapor-phase mole fraction
z	Component mole fraction in mixture
ϕ_i	Fugacity coefficient of component i

Superscript

k	Iteration number
l	Liquid phase
v	Vapor phase

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