Fluid Phase Equilibria 437 (2017) 69-82

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Calculation of critical points for natural gas mixtures with the GERG-2008 equation of state



FI UID PHASE

David Guerrero-Zárate¹, Alejandro Estrada-Baltazar^{**}, Gustavo A. Iglesias-Silva^{*}

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Celaya, Gto. CP 38010, Mexico

ARTICLE INFO

Article history: Received 8 September 2016 Received in revised form 13 January 2017 Accepted 13 January 2017 Available online 17 January 2017

Keywords: Natural gas Critical point Mixtures Equation of state

ABSTRACT

Critical points of natural gas mixtures containing linear alkane molecules (C_1 -n- C_8), branch alkanes (i- C_4 -i- C_5), nitrogen (N₂), and carbon dioxide (CO₂) are calculated using a criterion based upon the Helmholtz free energy. We use the GERG equation of state with its mixing rules together with needed derivatives evaluated numerically. A multivariable iterative method is used to solve the system of non-linear equations that appear in this procedure. Results are checked for stability using mechanical, diffusional and global stability tests. Our results are compared with the literature values. Maximum error for the temperature and pressure are 1.301 and 11.087% respectively. The predictive capability of the GERG-2008 equation of state are capable of representing global phase behavior types I to IV. Results show that the GERG-2008 equation of state with binary interaction parameters is adequate for the prediction of critical points.

© 2017 Elsevier B.V. All rights reserved.

2. Introduction

In the natural gas industry, accurate prediction of thermodynamic properties is important from an economical point of view. Recently, the Groupe Européen de Recherchers Gazières (GERG) [1,2] has developed an accurate equation of state for natural gas. This equation is based upon reference equations of state of the constituents. The success of the GERG equation of state has been shown in different applications: optimization of the Rankine cycle [3], calculation of Joule-Thompson inversion curve [4], prediction of thermodynamic properties at supercritical conditions [5,6], modeling liquefaction of natural gas [7], validation of models for fluid transport in pipelines [8], prediction of phase equilibria including formation of carbon hydrates in pipelines [9-11] and the used of its mixing rules for the prediction of transport and thermophysical properties of different fuels [12–17]. The GERG equation of state has even been used together with a geochemical model to calculate the solubility of gases in liquid hydrocarbons at cryogenic conditions of Titan, Saturn's moon [18].

The critical point of a natural gas mixture is of special interest because it allows us to know the global phase behavior indirectly if the mixture is in the retrograde region [1]. Calculation of critical points using reference equations of state is reported by Akasaka [19–21]. Heidemann and Khalil (HK) [22] have developed an algorithm for the calculation of critical conditions of mixtures based upon a Taylor series expansion of the Helmholtz energy. Their method has been successfully used in the calculation of critical points [23–32] using different equations of state and different mixing rules. Also, their method has been solved with many numerical techniques [33–39].

In this work, we estimate critical points of natural gas mixtures containing linear alkanes (C_1-n-C_8) , branch alkanes $(i-C_4-i-C_5)$, nitrogen (N₂), and carbon dioxide (CO₂), using an existing algorithm with our own modification to improve its convergence. We use the method proposed by Heideman and Khalil [22] where they performed a Taylor series expansion of Helmholtz free energy around the critical point. The unknowns with this procedure are the critical temperature and the critical volume. Derivatives of the Helmholtz energy are evaluated numerically using the GERG equation of state [2] and a nonlinear system of two equations is solved with a multivariable Newton-Raphson method [19]. Mechanical, diffusional and global stability [30] tests are performed to the solution to check stability of the critical point. Results are compared with



^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: alest@iqcelaya.itc.mx (A. Estrada-Baltazar), gais@iqcelaya.itc. mx (G.A. Iglesias-Silva).

¹ Present address: División Académica Multidisciplinaria de Jalpa de Méndez, Universidad Juárez Autónoma de Tabasco, Jalpa de Méndez, Tab. CP 86205, Mexico.

experimental critical temperatures and pressures reported in the literature. Furthermore, a comparison of the prediction of critical loci is performed using GERG-2008, Peng-Robinson (PR) and Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equations of state for 42 binary systems. Alfredique and Castier [25] have shown that the PR and PC-SAFT equations of state can predict the global phase behavior types I to V and I to IV (van Konynenburg and Scott classification [40]), respectively. Results for critical points of five natural gas mixtures for GERG-2008 is compared with results reported in literature for PR, PC-SAFT, Soave-Redlich-Kwon (SRK), Predictive Soave-Redlich-Kowng (PSRK), and Simplified Perturbed Hard-Chain Theory (SPHCT) equations of state.

2. Methodology

The criterion to find the critical conditions consists of solving simultaneously a system of two non-linear equations that involves the second and third derivatives of the Helmholtz energy with respect to the number of moles. The unknowns are the critical volume and the critical temperature. For a multicomponent mixture,

$$\mathbf{Q} \cdot \overline{\Delta n} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{\partial^2 A}{\partial n_j \partial n_i} \right) \Delta n_i \Delta n_j = 0 \tag{1}$$

$$C = \sum_{k=1}^{N} \sum_{j=1}^{N} \sum_{i=1}^{N} \left(\frac{\partial^{3} A}{\partial n_{k} \partial n_{j} \partial n_{i}} \right) \Delta n_{i} \Delta n_{j} \Delta n_{k} = 0$$
⁽²⁾

Subject to

$$Q = |\mathbf{Q}| = \begin{vmatrix} \frac{\partial^2 A}{\partial n_1^2} & \cdots & \frac{\partial^2 A}{\partial n_N \partial n_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 A}{\partial n_1 \partial n_N} & \cdots & \frac{\partial^2 A}{\partial n_N^2} \end{vmatrix} = 0$$
(3)

where *A* is the total Helmholtz energy, n_i , n_j , and n_k are the number of moles of component *i*, *j*, and *k* present in the mixture and the vector Δn is a perturbation in the moles number. A problem exists in solving Eqs. (2) and (3) for multicomponent systems at small molar fractions since we encounter a stiff problem due to the difference in the magnitude of the derivatives of the Helmholtz energy in Eq. (3). We have modified Eq. (3) by multiplying the second derivative by the y_i mole fraction,

$$Q = |\mathbf{Q}| = \begin{vmatrix} y_1 \frac{\partial^2 A}{\partial n_1^2} & \cdots & y_1 \frac{\partial^2 A}{\partial n_N \partial n_1} \\ \vdots & \ddots & \vdots \\ y_N \frac{\partial^2 A}{\partial n_1 \partial n_N} & \cdots & y_N \frac{\partial^2 A}{\partial n_N^2} \end{vmatrix} = 0$$
(4)

which is allowed because multiplying a row by a constant does not change equality of the determinant with zero.

In this work, we use the GERG-2008 EOS [2] to evaluate the Helmholtz energy and their derivatives,

$$\frac{a(\tau,\delta,\mathbf{x})}{RT} = \alpha(\tau,\delta,\mathbf{x}) = \alpha^{0}(T,\rho,\mathbf{x}) + \alpha^{r}(\tau,\delta,\mathbf{x})$$
(5)

where α° is the non-dimensionalized Helmholtz energy for the ideal gas mixture, α^{r} is the non-dimensionalized residual

Helmholtz energy. Kunz et al. [1] and Kunz and Wagner [2] propose the following mixing rules for the Hemholtz energies,

$$\alpha^{0}(T,\rho,\mathbf{x}) = \sum_{i=1}^{N} x_{i} \alpha_{i}^{0}(T,\rho) + \sum_{i=1}^{N} x_{i} \ln(x_{i})$$
(6)

and

$$\alpha^{r}(\tau,\delta,\mathbf{x}) = \sum_{i=1}^{N} x_{i} \alpha_{i}^{r}(\tau,\delta) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_{i} x_{j} F_{ij} \alpha_{ij}^{r}(\tau,\delta)$$
(7)

where α_i^0 is the non-dimensionalized ideal gas Helmholtz energy for pure substance *i*, α_i^r is the non-dimensionalized residual Helmholtz energy and α_{ij}^r is the non-dimensionalized interaction residual Helmholz energy between species *i* and *j*. Expressions of the non-dimensionalized Helmholtz energy for the pure components are

$$\alpha_{i}^{0}(T,\rho) = \ln\left(\frac{\rho}{\rho_{C_{i}}}\right) + \frac{R^{*}}{R} \left[n_{i,1}^{0} + n_{i,2}^{0} \frac{T_{C_{i}}}{T} + n_{i,3}^{0} \ln\left(\frac{T_{C_{i}}}{T}\right) + \sum_{k=4,6} n_{i,k}^{0} \ln\left(\left|\sinh\left(\vartheta_{i,k}^{0} \frac{T_{C_{i}}}{T}\right)\right|\right) - \sum_{k=5,7} n_{i,k}^{0} \ln\left(\left|\cosh\left(\vartheta_{i,k}^{0} \frac{T_{C_{i}}}{T}\right)\right|\right) \right]$$

$$(8)$$

$$K_{\text{ford}}$$

$$K_{\text{exp}}$$

$$\sum_{i}^{r}(\tau,\delta) = \sum_{k=1}^{K_{Pol}} N_k \tau^{t_k} \delta^{d_k} + \sum_{k=K_{Pol}+1}^{K_{exp}} N_k \tau^{t_k} \delta^{d_k} \exp(-\delta^{c_k})$$
(9)

and

۵

$$\alpha_{ij}^{r}(\tau,\delta) = \sum_{k=1}^{K_{Pol}} N_{ij,k} \tau^{t_{ij,k}} \delta^{d_{ij,k}} + \sum_{k=K_{Pol}+1}^{K_{exp}} N_{ij,k} \tau^{t_{ij,k}} \delta^{d_{ij,k}} \exp\left(b_{ij,k}\right)$$
(10)

where

$$b_{ij,k} = -\eta_{ij,k} \left(\delta - \varepsilon_{ij,k}\right)^2 - \beta_{ij,k} \left(\delta - \gamma_{ij,k}\right)$$
(11)

In Eq. (8), $n_{i,k}^0$ and $\vartheta_{i,k}^0$ are parameters for calculation of the ideal heat capacity at the reference state, according to Jaeschke and Schley [41]. It is common to consider the ideal gas enthalpy and entropy of the reference state equal to zero [2] at $T_0 = 298.15$ K and $P_0 = 0.101325$ MPa with a density equal to $\rho_0 = P_{0/R} \cdot T_0$. The ratio R/R^* is used to relate the actual molar gas constant R = 8.314598 J·mol⁻¹·K⁻¹ [42] and molar gas constant $R^* = 8.314510$ J·mol⁻¹·K⁻¹ used by Jaeschke and Schley [41]. Residual Helmholtz energy equations for pure components, α_i^r , have been developed previosuly by Span and Wagner [43], Kunz et al. [1] and Kunz and Wagner [2]. The characteristic parameters, N_k , d_k , t_k , and c_k , are reported the parameters for 21 pure components including hydrocarbons, water, nitrogen, hydrogen, etc. They define the reduced density and temperature of the mixture as

$$\delta = \frac{\rho}{\rho_{\rm red}} \tag{12}$$

$$\tau = \frac{T_{\text{red}}}{T} \tag{13}$$

With

Download English Version:

https://daneshyari.com/en/article/6473363

Download Persian Version:

https://daneshyari.com/article/6473363

Daneshyari.com