An alternate approach for the numerical modeling of isothermal flash calculation using Peng-Robinson equation of state

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Abstract

In an industrial process for the design and simulation, the phase equilibrium of mixture and thermodynamic properties are required. Due to this reason, the flash calculation plays an important role to solve the industrial problem. In this research, the Peng-Robinson Equation of the state is applied which is widely used to find out the thermodynamic properties at phase equilibrium in the critical region for the system of hydrocarbon and related compounds. The behavior of four binary mixtures is observed by using mathematical modeling of Peng-Robinson Equation of the state. The pressure-volume behavior and pressure mole fraction behavior of both liquid and vapor phase at equilibrium are studied by mathematical modeling of isothermal flash calculation. The pressure mole fraction behavior is compared with the experimental data taken from literature which states that both mathematical modeling’s of isothermal flash calculations flow same behavior with the experimental data.

Keywords
Peng-Robinson equation of state; Mathematical modeling; flash calculation; methane; carbon dioxide; hydrogen

1. Introduction

In chemical industries for the operation and designing of the chemical process, the thermodynamic properties play an important role. For the prediction of the phase behavior of vapor-liquid equilibrium of mixture containing different compounds, the equation of state is used because these can be applied to a vast range of pressure and temperature for all cases of light gases and heavy liquids and also due to their reliable and robust solution for vapor-liquid equilibrium prediction (Voutsas, Magoulas, et al. 2004, Fateen, Khalil et al. 2013, Zivkovic, Bajic, et al. 2014). To calculate the density in precise manner by using cubic Equation of state the attribution of two parameters ‘a’ the temperature dependent variable and ‘b’ the effective volume pressure is needed that can calculate the density in a very much accurate way otherwise the density will be inaccurate in liquid phase over extensive temperature range and on critical points (Frey, Modell, et al. 2009, Shen, Liu, et al. 2014). The cubic equation of states such as Schmidt and Wenzel, Soave Redlich Kwong and Peng-Robinson are the modified form of van der Waal equation of state (Ziabakhsh-Ganji and Kooi 2012). This cubic equation of state is distinct from one and other due to pressure volume and temperature relationship (Nasrifar 2010). The limitation of a cubic equation of state is that for achieving chemical equilibrium for mixture the pressure, chemical potential and temperature for liquid-vapor equilibrium have to be equal for processes.

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mass transfer, boundary displacement and heat. The potential chemical satisfaction leads to the satisfaction of fugacity in both phases (Ghosh 1999). In chemical industries, the Peng-Robinson cubic equation of state is widely used because it predicts the more precise phase behavior at the liquid-vapor boundary, thermodynamic properties and also its prediction for VLE of a mixture containing hydrogen and nitrogen is more accurate as compared to other equation of state (Wei and Sadus 2000, Mingjian, Peisheng et al. 2007, Álvarez and Aznar 2008, Esmaeilzadeh and Samadi 2008, Ziabakhsh-Ganji and Kooi 2012, Abudour, Mohammad et al. 2014).

The PR EOS is most successful for calculation of vapor-liquid equilibrium for both kinds of fluids polar and non-polar by using critical properties, Pitzer acentric factor and assuming critical compressibility factor as a constant value for all components of the mixture all ranges of pressure. The Pitzer acentric factor which depends on the critical properties of a substance is used to calculate the parameter a which is used in PR (Lugo, Comunas et al. 2007, Ashour, Fatemi, et al. 2011, Zang, Zhu, et al. 2011, Martinez-Banos, Embid, et al. 2015). The critical properties temperature and pressure can be estimated more accurately as compared to the critical volume (Frey, Modell, et al. 2009).

The four mixtures Hydrogen n-propane, methane n-butane, carbon dioxide n-propane and methy n-decane are studied by the model. The mixture containing Hydrogen, methane or carbon dioxide plays an important role in fuel cells metal production of food and pharmaceutical industries, as fuel and in urea industry, biotechnology, and chemical fields. The information related to the prediction of gas solubility and phase equilibrium of hydrogen, methane, and carbon dioxide mixture is suitable for optimization of process design (Nasrifar 2010, Hussain, Ahsan, et al. 2013). There are numerous numerical techniques are available in the literature to do the flash calculation of a finite number of components present in the mixture. The isothermal flash calculation is applied to those systems where the feed is separated into liquid and vapor phase at volume liquid equilibrium as shown in figure 1.

Figure 1 Isothermal flash process

The purpose of this study is to overcome the challenging task of solving differential of PR EOS in flash calculation by iterating pressure to determine volumes for both phases which finally reveal to mole fraction for both phases and also to discuss the isothermal relationship of pressure and volume by applying an innovative mathematical model approach. In literature, the mole fraction of liquid and vapor phase are considered as input. In this model, the compressibility factor as the input of the algorithm and the value of liquid and vapor phase mole fractions are
calculated by the algorithm. The condition is applied to the ratio of liquid fugacity and vapor fugacity to determine the accurate K value which was supposed in the start of the process.
In this research the pressure-volume relationship is discussed at a specific range of temperature, pressure mole fraction relation for both phases are also observed for all four mixtures. The pressure mole fraction relationship is compared with the experimental data given in literature which states that numerical techniques results validate experimental data.

2. Mathematical Modeling

The iteration process is done by changing the pressure to find out the vapor fraction with the isothermal flash calculation for phase equilibrium. The independent variables for the system are temperature and pressure, and by iterating pressure the applied condition is satisfied.

Suppose K values, where

\[ k_i = \frac{y_i}{x_i} \]  

(1)

Empirical correlations are present which use the K-value to find out the phase fraction. Here the Wilson equation is applied, and if the K-value satisfied the equilibrium, the convergence of solution would occur.

\[ k_i = \exp \left[ \frac{5.37(1+\omega_i)(1-\frac{1}{T_{ri}})}{p_{ri}} \right] \]

(2)

For the calculation of both phases mole fraction, the Richford Rice procedure is applied. Newton-Raphson method is applied to equation (5), and the condition given in equation (7) is applied to find out the liquid mole fraction.

\[ x_i = \frac{z_i}{L+(1-L)k_i} \]

(3)

\[ y_i = k_i x_i \]  

(4)

\[ F(L) = \sum_{i=0}^{n_c} \frac{(1-k_i)k_i}{L+(1-L)k_i} \]  

(5)

\[ L_{\text{new}} = L_{\text{old}} - \frac{F(L_{\text{old}})}{\frac{dF}{dL}_{L_{\text{old}}}} \]  

(6)

\[ \left( \frac{L_{\text{new}}}{L_{\text{old}}} - 1 \right) < 10^{-5} \]  

(7)

\[ L = \frac{z_i-y_i}{x_i-y_i} \]  

(8)

Calculation of parameters for the equation of state

\[ (aa)_m = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j (aa)_{ij} \]  

(9)

\[ (aa)_{ij} = (1 - k_{ij}) \sqrt{(aa)_i(aa)_j} \]  

(10)

\[ b_m = \sum_{i=1}^{n_c} x_i b_i \]  

(11)

To get the applicable VLE behavior of mixture to solve the PR EOS for the liquid and vapor phase molar volumes (Soave, Gamba, et al. 2010). The roots of cubic EOS require two solutions because of different phases of composition.

An iterative procedure is applied to find out the cubic roots of PR EOS.

\[ p = \frac{RT}{v_m-b_m} - \frac{(aa)_m}{v_m(v_m+2b_m)+b_m} \]  

(12)

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Calculate the compressibility factor
\[ Z_L = \frac{pV_{ml}}{RT} \] (13)

For accurate chemical equilibrium, the fugacity is calculated for real gases instead of pressure and the fugacity is the effective pressure of real gases. The relationship between the fugacity and pressure is known as fugacity coefficient a dimensionless number because pressure and fugacity have same units. For the calculation of fugacity for all components of liquid phases use equation (14). For vapor phase change the xi with yi and L subscript with V.

\[
f_L = p \exp \left( \ln \left( \frac{V_{ml}}{V_{ml} - b_{ml}} \right) + \frac{b_i}{V_{ml} - b_{ml}} + \left( \frac{2 \sum_{j=1}^{n} x_j (aa)_{ij}}{RT b_{ml}} \right) \ln \left( \frac{V_{ml}}{V_{ml} + b_{ml}} \right) + \frac{b_i (aa)_{ml}}{RT b_{ml}} \ln \left( \frac{V_{ml} + b_{ml}}{V_{ml}} \right) - \frac{b_{ml}}{V_{ml} + b_{ml}} \right) - \ln \left( \frac{Z_L}{x_i} \right) \right)
\] (14)

The condition given in equation (15) is applied to get the convergence at specific vapor, and liquid composition which will satisfy the equilibrium (Sugahara, Murayama, et al. 2005) otherwise use equation (20) to update K-value and repeat the process to satisfy the equilibrium.

\[
\left( \frac{f_{w}}{f_{L}} - 1 \right) < 10^{-5}
\] (15)

\[
\tilde{\phi}_{iw} = \frac{f_{iw}}{y_i p}
\] (16)

\[
\tilde{\phi}_{il} = \frac{f_{il}}{x_i p}
\] (17)

\[
\tilde{\phi}_{iw} = \frac{f_{iw} y_i}{f_{iw} x_i}
\] (18)

\[
\tilde{\phi}_{iw} = \frac{y_i}{x_i}
\] (19)

\[
k_i^{new} = \frac{f_{iw}}{f_{iw}^{old}} k_i
\] (20)

The flow chart shown in Figure 2 has been used in the process to obtain results through mathematical modeling. It highlights the iterative procedure which is carried out to obtain accurate results. The operating parameters for PR EOS modeling are given in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Hydrogen</th>
<th>Propane</th>
<th>Methane n-butane</th>
<th>Carbon dioxide</th>
<th>Methane n-decane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrogen</td>
<td>Propane</td>
<td>Methane</td>
<td>n-butane</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Tc (K)</td>
<td>33.2</td>
<td>370</td>
<td>190.82</td>
<td>425.32</td>
<td>304.2</td>
</tr>
<tr>
<td>Pc (atm)</td>
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<td>41.8</td>
<td>45.8</td>
<td>37.42</td>
<td>73</td>
</tr>
<tr>
<td>\omega</td>
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<td>0.153</td>
<td>0.012</td>
<td>0.199</td>
<td>0.268</td>
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<tr>
<td>T (K)</td>
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<td>310.93</td>
<td>277.56</td>
<td>477.594</td>
<td>2190</td>
</tr>
<tr>
<td>P (atm)</td>
<td>13 - 433</td>
<td>3.536 – 136</td>
<td>5.4 - 37.9</td>
<td>3.536 - 136</td>
<td></td>
</tr>
</tbody>
</table>
3. Results and discussion

The parameters which are used in the PR modeling for the studied system are shown in table 1. The critical parameters are obtained from the literature. The phase behavior, mixing rule ability and behavior based on a mathematical model for the case of mixtures of hydrogen propane, methane n-butane, carbon dioxide propane and methane n-decane is discussed with a tolerance level of 10^{-7}. The mathematical model is also used to find out the pressure-volume behavior at a constant temperature (Nasri and Binous 2009). Figures 3-5 show isotherms of hydrogen, methane and carbon dioxide which demonstrate that when the temperature approaches to the critical temperature the ideality of gasses decrease. When the temperature is much below than critical temperature the gasses show ideal behavior. The isotherms clarify that by studying the graph from the right side, the pressure is increased gradually to the point up to that the

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volume becomes small at that point condensation occur. Below upper curve of graphs, both phases occur in equilibrium. The graphs show sudden pressure decrease which explains the unstable behavior of gasses. From the below point of pressure, it again starts increase but no effect on volume at that time all samples are in supercooled liquids.

In hydrogen propane mixture, the vast deviation is observed in the limited range of pressure due to the presence of hydrogen in the system. The accurate prediction of convergence to the phase equilibrium of hydrogen propane mixture is made by using binary interaction parameters as shown in figure 6. In the methane n-butane mixture, prediction of phase behavior calculated by modeling shows the same trend as experimental phase behavior trend of the mixture is shown in figure 7. It is observed that for hydrocarbon mixtures the phase behavior can be predicted accurately at critical conditions. The phase behavior of carbon dioxide and propane mixture show a deviation because of the presence of carbon dioxide in the mixture as in figure 8. But the vapor pressure of pure component can be regenerated more precisely. The system containing methane n-decane mixture validate EOS mixing rule. The model graphical and experimental graphical behavior is compared which states that phase behavior suggested by model follow almost accurate experimental phase behavior as shown in figure 9. Comparison based on the pressure of experimental (Soave 1972) and model for all the cases are given in Table 2.
Figure 4 Isotherms for Methane

Figure 5 Isotherms for Carbon dioxide
Figure 6 Mole fraction of hydrogen at various pressures

Figure 7 Mole fraction of methane at various pressures
Figure 8 Mole fraction of carbon dioxide at various pressures

Figure 9 Mole fraction of methane at various pressures
4. Conclusions
In this research, the mathematical modeling is applied on PR EOS for hydrogen n-propane, methane n-butane, carbon dioxide propane, and methane n-decane mixture to study the pressure-volume relationship and phase behavior. The hydrogen, methane, and carbon dioxide have an important role in the chemical industry, so the information related to phase equilibrium and thermodynamic properties. The prediction of phase behavior by PR EOS modeling accurately describes the experimental results for all these gases but in hydrogen propane mixture the deviation in liquid phase is noted due to low pressure and due to presence of lighter gas hydrogen and in carbon dioxide propane mixture the presence of carbon dioxide affect the VLE of mixture and it also shows the deviation in limited range of pressure but when pressure is moderate it show less deviation and at high pressure it shows almost negligible deviation from experimental behavior. The isotherms obtained between pressure and volume shows that when the pressure approaches zero the volume start continues to increase and gasses start to behave as ideal gases. In pressure mole fraction relationship, the mole fraction of all components of the mixture is obtained vapor-liquid equilibrium by iterating pressure in a specific range. The pressure mole fraction of components relationship in both phases obtained by model shows that prediction is given by model for the solution of problem accurate as experimental results.

5. Nomenclature
PR EOS = Peng-Robinson equation of state
\(\tilde{f}_i\) = fugacity of a component in a mixture, Pa
\(K_i\) = K-values of the nth component, dimensionless
\(k\) = binary interaction parameter, dimensionless
\(L\) = Liquid mole fraction, dimensionless

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