**Critical Point Analysis of Phase Envelope Diagram**

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**Abstract.** Phase diagram or phase envelope is a relation between temperature and pressure that shows the condition of equilibria between the different phases of chemical compounds, mixture of compounds, and solutions. Phase diagram is an important issue in chemical thermodynamics and hydrocarbon reservoir. It is very useful for process simulation, hydrocarbon reactor design, and petroleum engineering studies. It is constructed from the bubble line, dew line, and critical point. Bubble line and dew line are composed of bubble points and dew points, respectively. Bubble point is the first point at which the gas is formed when a liquid is heated. Meanwhile, dew point is the first point where the liquid is formed when the gas is cooled. Critical point is the point where all of the properties of gases and liquids are equal, such as temperature, pressure, amount of substance, and others. Critical point is very useful in fuel processing and dissolution of certain chemicals. Here in this paper, we will show the critical point analytically. Then, it will be compared with numerical calculations of Peng-Robinson equation by using Newton-Raphson method. As case studies, several hydrocarbon mixtures are simulated using by Matlab.

**Keywords:** Critical Point, Equation of State, Fugacity Equation, Phase Envelope

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**INTRODUCTION**

Ideal gas is composed of random particles, which is constructed by classical thermodynamic equation $PV = nRT$. In reality, real gases behave qualitatively like an ideal gas only at certain normal condition of temperature and pressure. Here, we simulate phase envelope using real gas model. Real gas exhibit properties that cannot be explained entirely using ideal gas law. Several aspects of real gas are considered here such as: interactions of gas molecules, compressibility effects, specific heat capacity, Van der Waals force, and composition of the gas[3].

**REAL GAS EQUATION AND EQUATION OF STATE**

The Equation of State (EOS) here is given by thermodynamic equation. It is describing state of matter in a certain physical conditions. This equation provides a mathematical relationship between two or more state variables, such as temperature, pressure, volume, or energy of the system. EOS is useful to describe physical properties of liquid, gas, or gas mixture. In general, real gas equation is modified in such a way to simplify the computational process. It is modified into a third order polynomial equation by using compressibility factor $Z = \frac{P}{RT}$. Here, we use Peng-Robinson real gas equation to simulate the Phase Envelope in this paper. Peng-Robinson real gas equation is[1]:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b) + b(V_m - b)}, \quad (1)$$

where $P$ is the pressure, $T$ is the temperature, $R$ the ideal gas constant, $V_m$ the molar volume, $a$ and $b$ are parameters that determined empirically for each gas and from their critical temperature ($T_c$), and critical pressure ($P_c$), $\alpha = (1 + m(1 - T_c^{3/5}))^2$ with $m$ is the parameter related to acentric factor $\omega$, which is fulfill $m = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3$ and $T_c = \frac{2}{\omega}$ is temperature reduction. The constant $a$ and $b$ in PR real gas equation are $a = \Omega_0\frac{RT^2}{\Omega_0} - 1$ and $b = \Omega_0\frac{RT}{\Omega_0}$, where $\Omega_0 = 0.427474$ and $\Omega_0 = 0.07780$. By substitute $V_m = \frac{2RT}{P}$ to Equation(1), we obtain PR EOS cubic equation[3]:

$$Z^3 - (B - 1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0, \quad (2)$$

where $A = \frac{(aa\alpha)P}{(RT)^2}$ and $B = \frac{bp}{RT}$. Meanwhile, mixing rule for variables A and B satisfy $A = \frac{(aa\alpha)P}{(RT)^2}$ and $B = \frac{bp}{RT}$. Variables $(aa\alpha)_m$ and $b_m$ apply[1]:

$$(aa\alpha)_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (a_i a_j \alpha_i \alpha_j)^{0.5} (k_{ij} - 1) \quad (3)$$
and

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

\[ a_i = \omega_i R T_i^2, \quad b_i = \omega_i RT_i \]  

\[ \alpha_i = \left[ 1 + m_i (1 - T_i^{0.5}) \right]^2, \quad T_i = \frac{T}{T_i} \]  

\[ m_i = 0.379642 + 1.48503 \alpha_i - 0.1644 \alpha_i^2 + 0.016667 \alpha_i^3 \]  

The parameter \( k_{ij} \) is a correction factor called the binary interaction coefficient, which can be determined empirically, characterizing the binary formed by i-component and j-component in the hydrocarbon mixture. The other parameter which is important to understand two-phase behavior is fugacity. The fugacity \( f \) is a represent the molar Gibbs energy of a real gas. It used to calculate bubble and dew point. In a mathematical form, the fugacity of a component is defined by

\[ f = P \cdot \exp \left[ \int_0^P \left( \frac{Z - 1}{P} \right) dP \right] \]  

The ratio of the fugacity to the pressure is called the fugacity coefficient \( \Phi \) is calculated from equation(8)

\[ \Phi = \frac{f}{P} = \exp \left[ \int_0^P \left( \frac{Z - 1}{P} \right) dP \right] \]  

**PHASE DIAGRAM**

According to thermodynamic definition phase diagram (phase envelope) is a graph showing the pressure at which transition of different phases from a compound, respect to temperature[1]. Here an example of phase envelope of a compound and its region phases.

**Bubble Line**

Bubble point which forms bubble line in FIGURE 1 is a point separating the liquid phase and the two phases region, namely the liquid phase and the gaseous phase. At bubble point conditions apply[1]:

\[ x_i = z_i, \quad 1 \leq i \leq n \]  

\[ n_L = 1, \quad n_v = 0 \]  

\[ \sum_{i=1}^{n} y_i = \sum_{i=1}^{n} [\omega_i K_i] = 1, \]  

where \( x_i \) is liquid mole fraction of i-component, \( y_i \) is gaseous molar fraction of i-component, \( z_i \) is mixing mole fraction of i-component, \( K_i \) is gas-liquid equilibrium ratio for i-component, \( n_L \) is total number of mole in the liquid phase, and \( n_v \) is total number of mole in the gaseous phase. While, \( K_i \) satisfy[4]:

\[ K_i = \frac{y_i}{x_i} = \frac{\Phi_i^L}{\Phi_i^V} = \frac{\frac{f_i^L}{(x_i P_b)}}{\frac{f_i^V}{(y_i P_b)}} = \frac{f_i^L}{f_i^V} \]  

Equation (12) can be rewritten as:

\[ \sum_{i=1}^{n} \left[ \frac{z_i \Phi_i^L}{\Phi_i^L} \right] = \sum_{i=1}^{n} \left[ \frac{z_i f_i^L}{f_i^V} \Phi_i^V \right] = \sum_{i=1}^{n} \left[ \frac{f_i^L}{f_i^V} \Phi_i^V \right] = 1 \]  

or

\[ P_b = \sum_{i=1}^{n} \left[ \frac{f_i^L}{f_i^V} \Phi_i^V \right] \]  

So, equation(15) can be simplify as[1]:

\[ f(P_b, T) = \sum_{i=1}^{n} \left[ \frac{f_i^L}{\Phi_i^V} \right] - P_b = 0, \]  

where \( P_b \) is bubble point pressure, \( T \) is temperature, \( f_i^L \) is fugacity component i in liquid phase, and \( \Phi_i^V \) is fugacity coefficient component i in gaseous phase. We need to calculate Bubble Pressure\( (P_b) \) in Equation(16). Equation (16) can be solved by using Newton-Raphson method[5]:

\[ P_{b+1} = P_b - \frac{f(P_b, T)}{\frac{\partial f(P_b, T)}{\partial P_b}} \]  

To this end, first derivative of \( f(P_b, T) \) respect to \( P_b \). We carry out as follow:

\[ \frac{\partial f}{\partial P_b} = \sum_{i=1}^{n} \left[ \frac{\Phi_i^V (\partial f_i^L / \partial P_b) - f_i^L (\partial \Phi_i^V / \partial P_b)}{\Phi_i^V / (\Phi_i^V)^2} \right] - 1 \]  

Using center difference, discretize equation (18) as:

\[ \frac{\partial f_i^L}{\partial P_b} \approx \left[ \frac{f_i^L (P_b + \Delta P_b) - f_i^L (P_b - \Delta P_b)}{2 \Delta P_b} \right] \]  

\[ \frac{\partial \Phi_i^V}{\partial P_b} \approx \left[ \frac{\Phi_i^V (P_b + \Delta P_b) - \Phi_i^V (P_b - \Delta P_b)}{2 \Delta P_b} \right] \]
**Dew Line**

Dew point which forms dew line in FIGURE 1 is a point separating the gaseous phase and the two phases region, namely the liquid phase and the gaseous phase. At dew point, the follow conditions must be satisfied[1]:

\[
y_i = z_i, \quad 1 \leq i \leq n
\]  
(21)

\[
n_L = 0, \quad n_y = 1
\]  
(22)

\[
\sum_{i=1}^{n} x_i = \sum_{i=1}^{n} \left[ \frac{z_i}{K_i} \right] = 1
\]  
(23)

Using gas-liquid equilibrium ratio, we simplify Equation (23) to become[2]:

\[
\sum_{i=1}^{n} \left[ \frac{z_i \Phi_i}{\Phi_i} \right] = \sum_{i=1}^{n} \left[ \frac{z_i f_i}{z_i P_d \Phi_i} \right] = \sum_{i=1}^{n} \left[ \frac{f_i}{P_d \Phi_i} \right] = 1
\]  
(24)

or

\[
P_d = \sum_{i=1}^{n} \left[ \frac{f_i}{\Phi_i} \right]
\]  
(25)

Since \( P_d \) is independent of \( n \). For the need of computation, we rewrite (25) as[1]:

\[
f(P_d, T) = \sum_{i=1}^{n} \left[ \frac{f_i}{\Phi_i} \right] - P_d = 0
\]  
(26)

where \( P_d \) is dew point pressure, \( T \) is temperature, \( f_i \) is fugacity component \( i \) in gaseous phase, and \( \Phi_i \) is fugacity coefficient component \( i \) in liquid phase. Equation (26) can be solved for determine \( P_d \) by using Newton-Raphson method as (17) to (20)[5]. We replace the variables \( P_b \) with \( P_d \), \( f_i \), with \( f_i \), and \( \Phi_i \) with \( \Phi_i \).

**Critical Point**

State of pressure and temperature at which all properties of the gas and liquid phases are equal at a certain point is known as critical point. It is satisfying[1]:

\[
\left( \frac{\partial P}{\partial V} \right)_{T} = \left( \frac{\partial^2 P}{\partial V^2} \right)_{T} = 0
\]  
(27)

From condition (27), Chueh and Prausnitz simplified Critical Temperature as follow:

\[
T_{cm} = \sum_{j=1}^{n} (\Theta_j T_{c,j}) + \sum_{j=1}^{n} \sum_{i=j+1}^{n} (\Theta_j \Theta_i \tau_{ij})
\]  
(28)

with

\[
\Theta_j = \frac{x_j (V_{c,j})^{\frac{3}{2}}}{\sum_{i=1}^{n} x_i (V_{c,i})^{\frac{3}{2}}}
\]  
(29)

Hydrocarbon composition of the first case is a mixture of hydrocarbons with light component to moderate component, while the second case of hydrocarbon composition is a mixture of light component to heavy component. Here, we will see the difference of the phase envelope properties between the first and second case such as Critical Pressure, Critical Temperature, Cricondenbar and Cricondenterm.

**NUMERICAL SIMULATION**

In the following simulation, we use composition:

**TABLE 1. Composition data**

<table>
<thead>
<tr>
<th>No</th>
<th>Component</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO₂</td>
<td>1.857</td>
</tr>
<tr>
<td>2</td>
<td>N₂</td>
<td>2.201</td>
</tr>
<tr>
<td>3</td>
<td>C₁</td>
<td>84.796</td>
</tr>
<tr>
<td>4</td>
<td>C₂</td>
<td>6.437</td>
</tr>
<tr>
<td>5</td>
<td>C₃</td>
<td>2.73</td>
</tr>
<tr>
<td>6</td>
<td>i-C₄</td>
<td>0.598</td>
</tr>
<tr>
<td>7</td>
<td>n-C₄</td>
<td>0.643</td>
</tr>
<tr>
<td>8</td>
<td>i-C₅</td>
<td>0.278</td>
</tr>
<tr>
<td>9</td>
<td>n-C₅</td>
<td>0.164</td>
</tr>
<tr>
<td>10</td>
<td>C₆</td>
<td>0.198</td>
</tr>
<tr>
<td>11</td>
<td>C₇</td>
<td>0.098</td>
</tr>
<tr>
<td>12</td>
<td>C₈</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>C₉</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>C₁₀</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>C₁₁</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>C₁₂</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>C₁₃</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>C₁₄</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>C₁₅</td>
<td>0</td>
</tr>
</tbody>
</table>

Where

\( T_{cm} \) : Mixture critical temperature

\( T_{c,j} \) : Critical temperature of component \( j \)

\( V_{c,j} \) : Critical volume of component \( j \)

\( \Theta_j \) : Surface fraction of component \( j \)

\( \tau_{ij} \) : Binary interaction coefficient

In the next section, we are simulating phase envelope of hydrocarbon mixtures, by solving Equation(16) and Equation(26) which satisfy Equation(2) and Equation(28).
The simulation result are given:

**Case 1**

![Figure 2. Case 1](image1)

**Case 2**

![Figure 3. Case 2](image2)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical Pressure</td>
<td>1149.17 psia</td>
<td>1694.61 psia</td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>408.66 R</td>
<td>430.14 R</td>
</tr>
<tr>
<td>Cricondenbar</td>
<td>1428.23 psia</td>
<td>2298.9 psia</td>
</tr>
<tr>
<td>Cricondentherm</td>
<td>515.97 R</td>
<td>677.08 R</td>
</tr>
</tbody>
</table>

Simulation results show that the composition involved will affect the shape and properties of phase envelope is formed. From the simulation above, we can determine in which areas, liquid, gas, or a mixture of liquid and gas are formed in both cases.

**CONCLUSION**

We calculated bubble point and dew point, which build bubble line and dew line. Critical temperature was calculated using Chueh and Prausnitz correlation. While, critical pressure was calculated using dew function. The results of numerical simulation for Peng-Robinson real gas equation obtained:

- The greater number of C components are involved in a composition of hydrocarbons, critical temperature, Cricondenbar and Cricondentherm are greater.
- The greater number of C components are involved in a composition of hydrocarbons, more extensive two-phase region is formed.

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**REFERENCES**