Phase identification of natural gas system with high CO₂ content through simulation approach using Peng-Robinson model

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Abstract: The phase behavior for natural gas mixtures with high CO₂ content and heavier hydrocarbons up to pentane for cryogenic separation has been obtained through simulation using Peng-Robinson (PR) model. The bubble point and dew point curves which define the liquid-vapor and solid-vapor domains for separation are obtained by generating the pressure-temperature phase diagram. The simulations are performed using Aspen HYSYS. The validation for the use of PR model is done by comparing the results of CO₂ freeze-out temperature predictions for PR and Soave-Redlich-Kwong (SRK) model with the experimental data available in the literature.

1. Introduction

The energy consumption and demand throughout the world is increasing. Also the increase in population calls for an increase in energy usage. Natural gas serves as a clean and sustainable source of energy, so for this reason it is widely employed in industrial and household applications [1, 2]. It was reported in 2010 that natural gas fulfills almost a quarter of the world’s total energy requirements [3]. Although natural gas is considered a clean fuel in comparison with the fossil fuels but raw natural gas contains impurities such as CO₂, water and other hydrocarbons. Regarding natural gas reservoirs, it is estimated that almost 33% of these reservoirs are acrid. In Malaysia, some of the reserves contain more than 70% of CO₂ in natural gas [4, 5]. In these impurities, removal of CO₂ is of utmost importance as it significantly decreases the calorific content of natural gas and causes erosion in delivery pipelines [6, 7].

In order to predict the phase behavior of natural gas mixture, a number of equation of states are used for modeling and simulation purposes such as Peng-Robinson (PR), Soave-Redlich-Kwong (SRK) and Benedict-Webb-Rubin-Starling (BWRS). Among these equations, Peng-Robinson equation of state model is suitable to be used in oil, gas and petrochemical applications. It is extensively used to model VLE behavior of natural gas in cryogenic gas processing systems. Peng-Robinson equation of state also holds high degree of efficiency and reliability for its use in low pressure and higher temperature conditions [8, 9]. The cryogenic separation method, among the other CO₂ removal processes, is a resourceful technique for CO₂ capture. Cryogenic separation method involves the removal of CO₂ impurity at lower temperatures of up to -120°C or below [10]. In hybrid cryogenic separation technique, conventional distillation columns and packed beds are incorporated and separation of the components can be performed in both liquid-vapor and solid-vapor regions of the phase [11].
In this work, the phase behavior of two natural gas mixtures with high CO₂ content is determined through simulation using the suitable equation of state that predicts it more accurately, which in this case is PR equation of state. The investigation of phase behavior is done to determine the vapor, liquid and solid boundaries for cryogenic based separation. Simulations are performed in Aspen HYSYS. The phase behavior obtained through the use of PR and SRK equations of states for binary gas mixture containing CO₂ and CH₄ are compared with the experimental data for validation.

2. Methodology

The composition of the natural gas feed gas mixtures is shown in Table 1. It is based on the maximum available amount of higher hydrocarbons that exists in Malaysian wells [12]. Also, in both mixtures, more than half of the total amount of gas constitute of CO₂.

| Component | Gas Mixture 1 | Gas mixture 2 |
|-----------|---------------|---------------|
| CH₄       | 30            | 20            |
| CO₂       | 60            | 70            |
| C₂H₆      | 5             | 5             |
| C₃H₈      | 2.8           | 2.8           |
| C₄H₁₀     | 1.2           | 1.1           |
| C₅H₁₂     | 1             | 1             |

The VLE behavior of gas mixtures has been predicted through the generation of pressure-temperature phase diagram using Aspen HYSYS 8.0. Bubble point and dew point curves along with the CO₂ freeze out line construe the boundaries for liquid-vapor and solid-vapor regions. Figure 1 shows the simulation environment where the feed enters the separator and is separated in vapor and liquid states.

![Figure 1. HYSYS simulation for phase identification.](image)

In order to determine the accuracy of the software and suitability of the equation of state, the Solid-Liquid-Vapor (SLV) locus is obtained through simulation for both the PR and SRK models. It is obtained at the same pressure and temperature conditions that were used experimentally in previous study. Donnelly et al. had reported the experimental data for SLV locus of CO₂-CH₄ binary gas mixture which is
available in literature [13]. The comparison between the predicted and experimental SLV locus is reported in Table 2 of the next section along with the discussion.

3. Results and discussion

The simulation results for phase separation of the selected compositions of natural gas mixtures are obtained by using PR and SRK equation of states. In case of gaseous mixture composed of hydrocarbons, previous studies suggest the use of PR equation of state for the accurate prediction and description of vapor-liquid, vapor-solid and liquid-solid phase behavior [14, 15]. Some studies also involved SRK model to investigate the thermodynamic behavior of natural gas for the optimization of a cryogenic system in a large scale natural gas processing plant [16]. In this work, for validation purposes, the SLV locus predicted by these equilibrium relationships through simulation is compared with the available experimental data. The experimental range of pressure at which the CO$_2$ freeze out temperatures and SLV locus are determined vary from 9 bar to 38 bar. Donnelly et al. determined experimentally the three phase locus describing the equilibria wherein solid CO$_2$ came in coexistence with the liquid and vapor phases. Their experimental setup consisted of a glass-windowed pressure cell in an alcohol bath used to confine the system [13]. For validation, Table 2 shows the comparison between experimental set of values at which CO$_2$ freeze out occurs and the phase exists in liquid, vapor and solid states with the predicted values for SLV locus considering both the PR and SRK equation of states.

| P (bar) | Experimental Temp (°C) | PR Model Predicted Temp (°C) | SRK Model Predicted Temp (°C) | AAE for PR Model (%) | AAE for SRK Model (%) |
|---------|------------------------|-----------------------------|-------------------------------|----------------------|-----------------------|
| 9       | -57.7                  | -60                         | -57.4                         | 3.846                | 0.602                 |
| 10.7    | -58.3                  | -57.8                       | -57.8                         | 0.914                | 0.928                 |
| 12.8    | -57.5                  | -58.2                       | -58.2                         | 1.217                | 1.163                 |
| 18      | -59.1                  | -59.3                       | -59.3                         | 0.225                | 0.205                 |
| 24.3    | -59.7                  | -60.6                       | -60.6                         | 1.47                 | 1.48                  |
| 29.7    | -60.5                  | -61.7                       | -61                           | 1.89                 | 0.706                 |
| 31.2    | -61.1                  | -62.1                       | -61                           | 1.618                | 0.208                 |
| 32      | -61.3                  | -62.3                       | -61                           | 1.484                | 0.659                 |
| 38      | -61.3                  | -63.7                       | -61                           | 3.765                | 0.654                 |
| 39.5    | -61.6                  | -64                         | -61                           | 3.784                | 1.1                   |
| 40.2    | -62.2                  | -64.2                       | -61                           | 3.179                | 1.983                 |
| 41.8    | -63                   | -64.6                       | -61                           | 2.449                | 3.277                 |
| 44.2    | -62.7                  | -65.4                       | -61                           | 4.177                | 2.847                 |
| 44.6    | -63                   | -65.5                       | -61                           | 3.877                | 3.275                 |
| 44.9    | -64.1                  | -65.6                       | -61                           | 2.234                | 4.949                 |
| 46.9    | -64.7                  | -66.3                       | -61                           | 2.438                | 5.764                 |
| 47.8    | -66.9                  | -66.7                       | -61                           | 0.365                | 8.891                 |
| 46.4    | -69.7                  | -67.8                       | -61                           | 2.678                | 12.522                |
| 44.7    | -71.1                  | -69.7                       | -61                           | 1.909                | 14.232                |
| 43      | -72.7                  | -71.6                       | -61                           | 1.507                | 16.197                |
| 37.5    | -78.6                  | -78.1                       | -61                           | 0.578                | 22.419                |

MAE=2.172% MAE=4.955%
The average absolute error in terms of percentage for the predicted temperature values for both the models is calculated and mean absolute error (MAE) is also determined. The mean absolute error for SRK model is about 5% while for PR model, it is only 2.172%. The comparison between the results predicted by PR model and SRK model clearly shows that the ability of PR model to predict the actual phase behavior is much better as compared to that of SRK model. The results also show the imprecision of SRK model to predict the phase behavior and the actual CO$_2$ freeze out temperatures at higher pressures and the model is not suitable to simulate the phase behavior for natural gas in high pressure applications. So the phase identification for the feed gas mixtures mentioned in Table 1 is done by using PR equation of state and the Figure 2 shows the boundaries of liquid, vapor and solid phases for both the gas mixtures.

![Figure 2. Phase regions for natural gas mixtures.](image)

From the above figure it can be noticed that the liquid-vapor (L-V) region starts from about 0°C to around -60°C and solid-vapor (S-V) domain lies in the temperature range starting from about -60°C to -120°C. Bubble point and dew point curves are obtained in order to determine the phase behavior.

Figure 2 also indicates that from the temperature range of 40°C to 0°C, the gas mixture is in vapor state. It is also be noticed that the vapor-liquid region lies between the temperature range of 0 to -60°C and beyond -60°C, the phase enters into solid-vapor region. The solid-vapor region has been worked upon by Davis et al. and it is reported that in this region only CO$_2$ exists in solid form while CH$_4$ is all vapor as the freezing point of methane is much lower than that of CO$_2$ [17]. At very low temperatures as -120°C and at both lower and higher pressures, phase enters into solid-liquid region. It is feasible to do separation in liquid-vapor and solid-vapor regions. The energy requirements for separation in liquid-solid region is high as more energy is needed to lower the temperatures to enter this region. Also the solidification of methane is avoided in this region as it is possible at very lower temperatures therefore it is not recommended to separate CO$_2$ in solid-liquid region.

4. Conclusion

The liquid-vapor and solid-vapor phase regions are identified for natural gas systems with high CO$_2$ content through simulation using PR model. These domains are determined in order to separate natural gas components at lower temperatures for cryogenic applications. PR equation of state was selected due to more accurate prediction of the phase behavior of natural gas with the data available in literature in
comparison to that of SRK model. PR model predicts the VLE phase behavior and CO₂ freeze out temperatures more accurately.

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