The Effect of Acidic Gases and Thermodynamic Inhibitors on the Hydrates Phase Boundary of Synthetic Malaysia Natural Gas

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Abstract. In this work, PVTSim was used to predict the hydrate phase equilibrium boundaries of a Malaysia synthetic natural gas (SNG) composition with increasing CO_2 and H_2S compositions in the presence of commonly used hydrate thermodynamic inhibitors such as methanol (MeOH), ethanol (EtOH), mono-ethylene glycol (MEG), diethylene glycol (DEG), tri-ethylene glycol (TEG). The increasing CO_2 and H_2S concentrations studied ranged from 5 – 50 mol%, while the inhibitors were tested at 10 wt%. To validate the accuracy of PVTSim, a validation test was conducted by predicting the phase behavior of a natural gas in the open literature. The predicted results were in good agreement with the literature data with a percentage deviation of 0.08% from the experimental data. From the predicted hydrate phase equilibrium for pure SNG field, it was found that, when the SNG composition was modified, the hydrate formation region shrank at increasing CO_2 composition, reducing the hydrate formation risk whereas the hydrate formation region expanded at increasing H_2S composition, increasing the hydrate formation threat. TEG was found to best inhibit hydrate formation in the studied gas compositions.

1. Introduction

As exploration and production move further into the deeper sea, flow assurance risk management in subsea pipelines becomes crucial due to problems such as gas hydrates, slugging, corrosion, wax, and scales [1], [2]. Among these flow risks, gas hydrate formation is of major concern to which millions of dollars are spent annually combating its effects [3], [4]. Gas hydrates are solid-crystalline compounds formed by hydrogen-bonded water molecules (host molecules) forming solid crystalline lattice structure by the engaging of gas molecules (guest molecules) such as methane, ethane, propane and etc. at low temperature and high pressure conditions [5], [6], [7], [8]. In Malaysia, a natural gas field situated in the South China Sea offshore of the Sarawak Province holds more than 13.2 trillion cubic feet (tcf) of natural gas with 70% of CO_2 [9]. The high content of CO_2 not only makes it difficult for the operator to separate CO_2 from the natural gas and condensate but also subjects the field to hydrate formation threat [10]. On the other hand, gas hydrates also potentially form inside production facilities whenever the formation conditions are fulfilled.

Although gas hydrates may have potential both as a source of hydrocarbon energy and as a medium for storing and transmitting natural gas, they create major threats. Gas hydrates plug subsea flowlines and can rupture the pipeline which leads to spills of containments causing environmental disasters, high costs of repair and maintenance or even loss of assets. [11]–[15]. Mechanical methods such as insulation and active heating are some existing control measures. However, these methods are impractical and ineffective under some conditions [16]–[20]. For this reason, kinetic and thermodynamic inhibitors are introduced to prevent hydrate formation. A kinetic inhibitor prolongs the induction time of hydrate formation more than the residence time of free water in pipeline while the widely used technique; thermodynamic inhibition shifts the hydrate envelope to the left side of the Pressure-Temperature Diagram to displaces the hydrate formation region to a lower temperature and/ or higher pressure conditions as shown in figure 1 [17], [21].
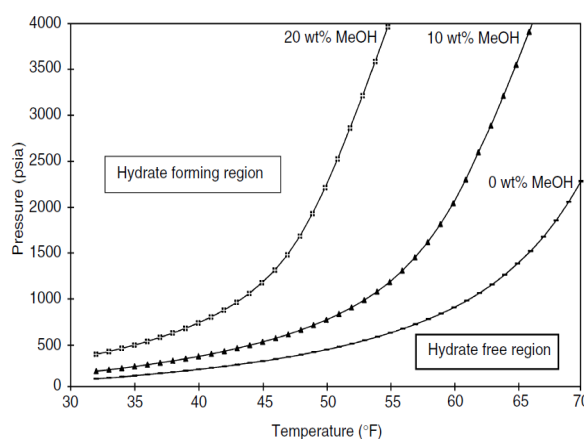
Figure 1. Effect of methanol thermodynamic inhibitor [5]

In order to successively inhibit gas hydrates formation, prediction of hydrate phase equilibrium becomes critical in industrial application. Four available methods are employed for predicting hydrate phase equilibrium in the natural gas systems: (1) hand calculation- suitable for single gas component but limited applicability, (2) empirical correlations- though can be applied to gas mixture, but also limited applicability, (3) experimental method- costly, time consuming and limited apparatus available currently and (4) simulation- easily accessible, fast and reliable using software such as PVTSim, HYSYS, EQUIphase, PIPEphase and etc. [11], [22], [23]. Due to these reasons, the simulation method is nowadays more preferred than other methods.

There are various types of hydrate simulation software such as CSMGem and PVTSim. However, PVTSim is the widely used software. Ward et al. [24] studied the hydrate equilibrium phase of H_2S experimentally and validated his work using PVTSim and reported that PVTSim could be accurately used for H_2S hydrate equilibrium phase studies. In addition, Sule and Rahman [25] and Bavoh et al [26] predicted the hydrate equilibrium phase of synthetic natural gas in Canada and Ghana in the presence of H_2S and inhibitor (methanol) using PVTSim. Their results suggested that PVTSim gives an accurate prediction. More so, the presence of H_2S increased the hydrate formation threat in the studied natural gas systems.

Several studies [27], [28] have to use PVTSim to study the hydrate phase behave is some regions around the world for safe field operation. However, such studies have not been reported on Malaysia field in the open literature. Therefore, this paper seeks to implement simulation method to predict the hydrate phase equilibrium of a synthetic natural gas system in Malaysia using PVTSim and to study the resulting effects on the hydrate phase equilibrium when the gas composition is modified and/ or when commercial gas hydrate inhibitors such as methanol (MeOH), ethanol (EtOH), mono-ethylene glycol (MEG), diethylene glycol (DEG), tri-ethylene glycol (TEG) and glycerol is present.

2. Methodology

2.1. Materials
A set of experimental data as shown in Table 1 was taken from reference [5] to validate the accuracy of PVTSim in predicting hydrate phase equilibrium. Table 2 shows the main data used in this work.

Table 1. Experimental data from literature [5]

CH_4	C_2H_6	C_2H_8	iC_4H_{10}	nC_4H_{10}	nC_5H_{12}	N_2
8.41	6.47	3.57	0.99	1.14	0.78	0.64

Table 2. Synthetic natural gas composition (SNG)

CO_2	H_2S	N_2	CH_4	C_2H_6	C_2H_8	iC_4H_{10}	nC_4H_{10}	iC_5H_{12}	nC_5H_{12}	H_2O
2.13	-	3.91	88.92	4.42	0.50	0.05	0.05	0.01	0.01	2.59

2.2. Applied Software Model

PVTSim owned and developed by Calsep is an adaptable equation of state (EOS) modeling software used for the simulation of fluid properties and experimental PVT data. PVTSim is designed to suit a variety of processes and problems in the industry as it includes features such as advanced flash and regression algorithms, reliable and predictive reservoir fluid characterization, self-regulating fluid regression for minimization of manual tuning, user-friendly interface designed for fast and efficient workflow, etc. [29] PVTSim is divided into a few modules such as characterized fluid, flash and unit operations, asphaltene, wax, hydrate, hydrate open structure, etc. The hydrate and hydrate open structure modules were employed in this work due to its specialized functions in the simulation of hydrate formation conditions, with and without inhibitors as well as the effect of impurities (such as acidic gases) on hydrate formation. [29] A suitable fluid package, Peng Robinson (PR) Peneloux fluid package was selected for the prediction of hydrate phase equilibrium for its capability to cater for a wide range of operating conditions and to simulate result with higher accuracy compared to the Soave-Redlich-Kwong (SRK) Peneloux fluid package [28].The PVTSim predicted results were tabulated and analyzed using Microsoft Excel.

2.3. Simulation Contents and Methods

To set up the modeling environment in PVTSim, every gas composition to be used in this work was registered and stored in the fluid database. Next, the hydrate module was selected in order to employ the hydrate calculations.

For validation analysis, the natural gas composition of the experimental data from open literature [5] was selected from the fluid database. In the hydrate open structure module, the hydrate formation temperature function was selected, and the phase equilibrium pressures of the experimental data were inputted to predict the corresponding phase equilibrium temperatures. The predicted temperatures were compared to the experimental temperatures in Microsoft Excel and the average absolute percentage error (APE) between the predicted result and the experimental result was calculated.

In the first part of the main study, pure SNG composition was selected from the fluid database. The hydrate formation PT curve function in the hydrate open structure module was selected to predict the hydrate phase equilibrium at a pressure range of 16 bar – 200 bar and a temperature range of 2 ℃ – 20 ℃, with reference to the good design pressure, 49.63bar, and temperature, 37.76℃. From this prediction, the hydrate-forming region and hydrate free region can be determined for the safe operation of the field.

The second part of the main work consists of two case studies: The effect of increasing CO_2 and H_2S composition in the synthetic natural gas composition and the effect of thermodynamic inhibitors for effective hydrate inhibition. In case study 1, the CO_2 composition in SNG was increased by 5mol%, 10mol%, 15mol%, 20mol%, 30mol%, 40mol% and 50mol%. Firstly, SNG with additional 5mol% of CO_2 was selected from the fluid database and the hydrate phase equilibrium was predicted at a pressure range of 16 bar – 200 bar using the hydrate formation temperature function. Under the same pressure range, the hydrate phase equilibrium for the increasing CO_2 compositions in the SNG was predicted and compared to that of pure SNG. Next, the average temperature deviation of the hydrate phase equilibrium curves between pure SNG and SNG with increasing CO_2 composition was calculated for each increment and was plotted in Excel. Finally, the CO_2 effect on the hydrate phase equilibrium were analyzed and discussed. The same procedure was repeated for increasing H_2S composition under the same pressure and temperature conditions.

In case study 2, the composition of pure SNG with the addition of methanol (MeOH) at 10wt% concentration was selected from the fluid database. The hydrate phase equilibrium was then predicted under the same pressure range used in case study 1. This step was repeated with ethanol (EtOH), mono-ethylene glycol (MEG), diethylene glycol (DEG), tri-ethylene glycol (TEG) and glycerol. The hydrate phase equilibrium curves generated for each inhibitor were plotted in the same graph in Excel to analyze and discuss the inhibition effect for the pure SNG so as to determine the best inhibitor for the particular composition. The same procedure was repeated for SNG + 30mol% CO_2 and SNG + 30mol% H_2S to study the effect of the inhibitors incorporating the effect of change in gas composition.

3. Results and Discussions

Prior to the simulation, the accuracy of PVTSim in predicting the hydrate phase equilibrium curve was validated by predicting the experimental hydrate equilibrium phase data of the natural gas composition taken from reference [5]. Fig. 2 shows the comparison of the hydrate phase equilibrium curves between the experimental and PVTSim predicted results. A close agreement is observed between the two curves with an average absolute percentage error of 0.08%, which verifies the accuracy of PVTSim in the prediction of hydrate phase equilibrium conditions.

Figure. 3 shows the hydrate phase equilibrium curve of pure SNG composition predicted by PVTSim. In Fig. 3, the area above the curve (to the left) shows the hydrate-forming region whereas the area below the curve (to the right) shows the hydrate free region. Based on the predicted hydrate phase equilibrium data of the SNG system, the gas field flow assurance operations must be conducted within the temperatures and pressures conditions in Fig. 3 to avoid flow assurance problems such as hydrate formation in the pipelines.
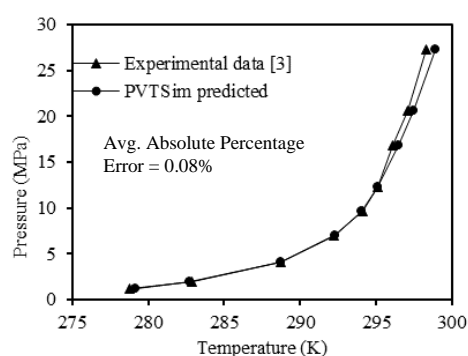
**Figure 2.** Comparison of PVTSim predicted result and experimental result
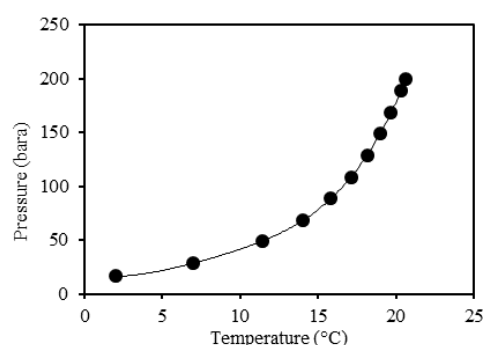
Figure 3. PVTSim predicted hydrate phase equilibrium of pure synthetic natural gas (SNG) composition

3.1 Case Study 1: The effect of CO_2 and H_2S on SNG composition

The addition of acidic gases such as CO_2 and H_2S makes the gas mixture sour. In the life of a field, the gas composition may change which can affect the hydrate equilibrium phase curve of the mixed gas system. Hence, the prediction of the hydrate equilibrium phase curve of the SNG system when some of its gas composition change is necessary for gas hydrate formation prevention strategies in natural gas field flow assurance operations. Fig. 4 shows the effect of increasing CO_2 composition in the SNG system at CO_2 increasing concentrations of 5mol%, 10mol%, 15mol%, 20mol%, 30mol%, 40mol% and 50mol%. From Fig. 4, it is observed that the pure SNG hydrate phase equilibrium curves shift to the left as CO_2 concentration increases. This shows that CO_2 behaves like an inhibitor by shrinking the hydrate formation zone, decreasing the risk of hydrate formation in the system. However, the inhibiting effect is observed to be minimal with an average temperature depression of 1°C at all studied increasing CO_2 concentration. In addition, the SNG hydrate phase equilibrium shifts to the left more at higher pressures.

To further scrutinize the effect of CO_2 increasing concentration on the SNG hydrate equilibrium phase, the average temperature deviations of the SNG hydrate equilibrium phase in the presence of

increasing CO_2 concentrations are calculated and presented in Fig. 5. The negative value of the average temperature deviation is an indication that the hydrate phase equilibrium curves are shifted to the left.
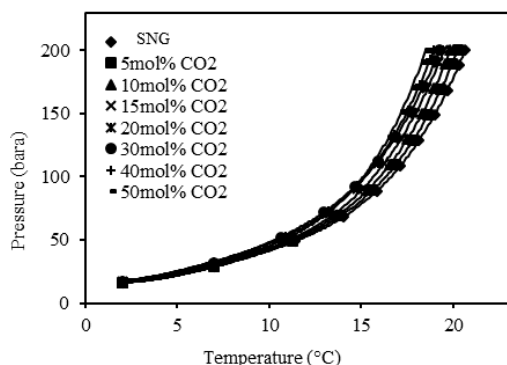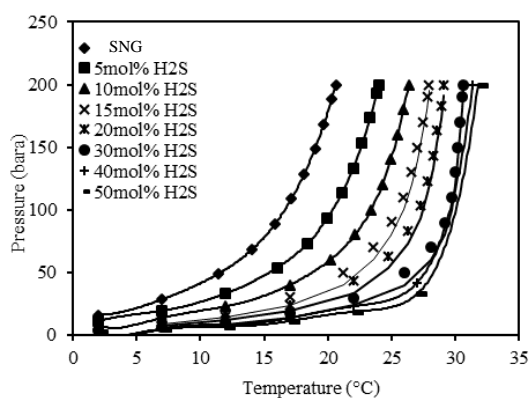

Figure 4. PVTSim predicted hydrate equilibrium phase curve of pure SNG composition and SNG + different CO_2 concentration ranging from 5mol% to 50mol%
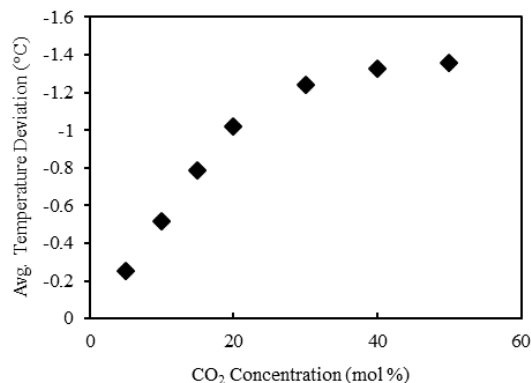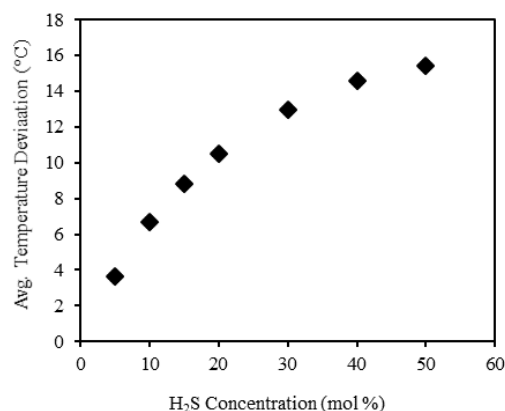

Figure 5. Average temperature deviation between pure SNG composition and SNG + different CO_2 concentration ranging from 5mol% to 50mol%

However, it is noticed that the inhibiting effect of increasing CO_2 composition in the SNG system stabilizes at 30mol%. Increasing CO_2 concentration above 30mol% exhibits small or negligible temperature deviation compared to CO_2 concentrations lower than 30mol%. This means that adding more CO_2 to the SNG system will not have any further significant effect on its hydrate equilibrium phase curves. Therefore, it is deduced that hydrate formation risk in the SNG system relatively / slightly reduces significantly with increasing CO_2 concentration until 30mol% CO_2 concentration. Fig. 6. shows the effect of increasing H_2S composition on the SNG system at concentrations of 5mol%, 10mol%, 15mol%, 20mol%, 30mol%, 40mol% and 50mol% predicted by PVTSim. In contrary to the increasing effect of CO_2 concentration in the SNG system, increasing H_2S concentration further expands the hydrate formation region by shifting the SNG hydrate phase equilibrium curve to higher temperatures and lower pressures region. This signifies that, the presence of H_2S increases in gas hydrate formation threat in the system as H_2S concentration increases as shown in Fig. 6. Surprisingly, it is seen that H_2S gives a more significant effect than CO_2 when added to the SNG system. For example, with 50mol% of H_2S in the SNG mixture, the hydrate phase equilibrium is shifted to the right of the PT diagram for an average temperature difference of 10°C, which is about ten times more than the shift that occurs in the case of 50mol% of CO_2 added to the gas mixture that gives only an average temperature difference of 1°C (see Fig. 4).

Figure 6. PVTSim predicted hydrate equilibrium phase curve of pure SNG composition and SNG +

Figure 7. Average temperature deviation between pure SNG composition and SNG + different H_2S concentration ranging from 5mol%

different H_2S concentration ranging from 5mol% to   to 50mol%
        50mol%

Furthermore, it can be observed from the trend of the hydrate phase equilibrium curves of each H_2S concentration that the curve shifts drastically to the right of the PT diagram when pressure is below 100 bar and the shifting starts to retard as pressure increases causing the curves to incline more vertically. Fig. 7 shows the average temperature deviation of the SNG composition and SNG + different H_2S concentration ranging from 5mol% to 50mol%. The positive value of the average temperature deviation represents the right-hand side shifting of the hydrate phase equilibrium curves. The deviation in temperatures increases consistently and is observed to decrease at 40mol% H_2S, indicating the stabilization of the H_2S effect on the SNG hydrate equilibrium curve. However, the concentration of H_2S above 50mol% is seen to have a negligible effect in shifting the hydrate phase equilibrium.

In case study 1, it can be inferred that SNG + CO_2 or H_2S hydrate phase equilibrium curves tends to shift towards the hydrate equilibrium curve of pure CO_2 or H_2S component as CO_2 or H_2S concentration increases in the system, agreeing to similar finding reported by Lee and Kang in their study of the hydrate-phase equilibria for gas mixture ($CH_4 + C_2H_4$) and ($C_2H_6 + C_2H_4$) with various concentrations along with the equilibrium curves of the pure components. [30] Also, explained in their work that the shifting of the hydrate phase equilibrium is affected by the cavity filling of mix gases present in the system. On the other hand, Ripmeester and others also studied on the $H_2S - CH_4$ hydrates cage occupancy and found out that occupancy of cavities of Structure I by H_2S increases as the concentration of H_2S increases, which is also represented by the shifting of the hydrate phase equilibrium to the right of the $H_2S - CH_4$ hydrates PT diagram [31].

3.2. Case Study 2: The effect of thermodynamic inhibitors
Commonly, thermodynamic inhibitors such as methanol, ethylene glycol, glycerol and etc. are used in the industry to prevent hydrate formation. Thermodynamic inhibitors generally inhibit hydrate formation by distracting the activity of water in hydrate formation by forming hydrogen bonding with water molecules which results in shifting the hydrate phase equilibrium curve to lower temperatures and higher pressures conditions to keep the system out of the hydrate formation zone.
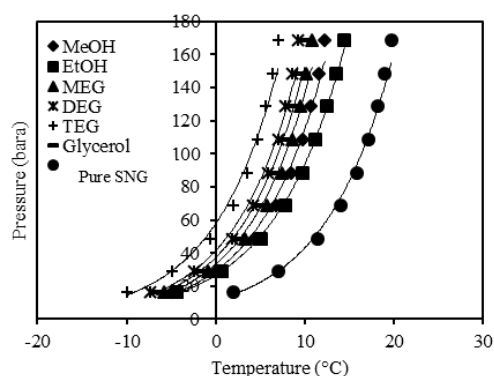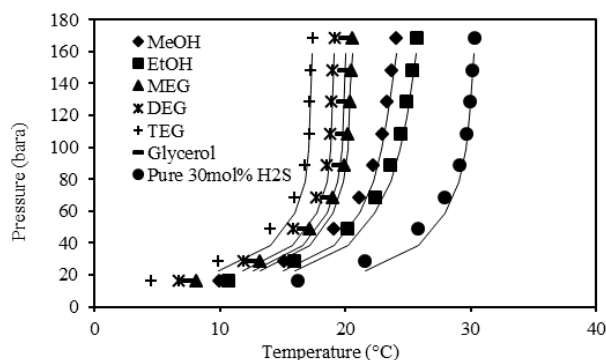

Figure 8. PVTSim prediction of hydrate phase equilibrium of SNG composition + different types of thermodynamic inhibitors at 10wt%
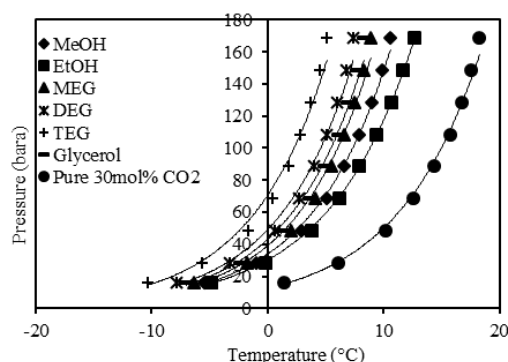
Figure 9. PVTSim prediction of hydrate phase equilibrium of SNG + 30mol% of CO_2 in the presence of commonly used gas hydrate thermodynamic inhibitors at 10wt%

Figure 10. PVTSim prediction of hydrate phase equilibrium of SNG + 30mol% of H_2S + in the presence of commonly used gas hydrate thermodynamic inhibitors at 10w%

The PVTSim predicted effect of six commonly used thermodynamic inhibitors namely: methanol, ethanol, mono ethylene glycol (MEG), diethylene glycol (DEG), tri-ethylene glycol (TEG) and glycerol on pure SNG composition, SNG + 30mol% of CO_2 and SNG + 30mol% of H_2S at a concentration of 10wt% are as shown in Fig. 9, Fig. 10 and Fig. 11 respectively. In Fig. 9, it is seen that all inhibitors shift the SNG hydrate phase equilibrium to the left. It is also observed that the inhibitors increase in inhibition in an ascending order of magnitude of EtOH, MeOH, MEG, Glycerol, DEG, and TEG. Therefore, TEG can best inhibit hydrate formation as it incurs the greatest shift of the hydrate phase equilibrium to the left of the PT diagram. The presence of different gas in the SNG composition can affect the inhibition outcome. For optimum results, the effect of thermodynamic inhibitors on the hydrate equilibrium curves of SNG + 30mol% CO_2 and SNG + 30mol% H_2S were also studied and presented in Fig. 10 and 11 respectively. From Fig. 10 and 11, similar inhibiting performances as presented in Figure 4.7 are observed in which TEG can best reduce the hydrate formation zone. However, some slight changes of inhibition in the SNG +30mol% H_2S composition + inhibitor equilibrium curve, suggest that the performance of a thermodynamic inhibitor can be affected by the type of gas composition.

4. Conclusions
PVTSim was applied to predict the hydrate phase equilibrium conditions of a synthetic natural gas composition of a field in Malaysia. Based on the study, the hydrate formation risk in the SNG system relatively reduces significantly with increasing CO_2 concentration until 30mol% CO_2 concentration. In contrary, increasing H_2S expands the hydrate formation region in a greater extent but starts to stabilize at 40mol% H_2S concentration and shows negligible phase boundary increasing effect at 50mol% H_2S concentration. Furthermore, it was found that TEG can best inhibit hydrate formation in pure SNG, SNG + 30mol% CO_2 and SNG + 30mol% H_2S compared to other inhibitors. This study is significance to ensure the safe operation of natural gas wells.

5. Acknowledgments

6. References
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