



# Simulation of Hydrate Phase Boundary for Natural Gas Mixture with High CO<sub>2</sub> Content through Simulation

Ali Qasim, Muhammad Saad Khan, Bhajan Lal, Mohd. Zamri Abdullah, Abdulhalim Shah Maulud

**Abstract:** Gas hydrates are solid crystalline structures in which water molecules trap small guest gas molecules and encage them through hydrogen bonding. Gas hydrates are known to be problematic in flow assurance applications as they can form plug inside the pipelines during oil and gas production, transportation and processing. In order to inhibit hydrate formation thermodynamically, various chemicals including some alcohols e.g. methanol (MeOH), mono- ethylene glycol (MEG) are used as thermodynamic hydrate inhibitors (THIs). In this paper, a simulation study is performed using PVTsim software wherein it predicts the hydrate formation for pure CO<sub>2</sub> solution mixture and CO<sub>2</sub>-MEG solution mixture systems using different equation of states. These equations of states include Soave-Redlich-Kwong (SRK), SRK-Peneloux, Peng- Robinson (PR) and Peng-Robinson Peneloux. The simulation results obtained using these equation of states were validated with the experimental data and PR-PenelouxEoS was found to be in better agreement. The hydrate formation regions are determined in between the pressure range of 10 to 110 bara for natural gas mixture containing high percentage of CO<sub>2</sub> in it. The inhibitors are used in 5, 10 and 20 wt% concentrations. The hydrate inhibition efficiency increased with the increase in concentration. Simulation results showed that methanol performed better in comparison to the other inhibitors at all concentrations.

**Keywords:** gas hydrates, phase boundary, PVTsim, equation of states.

## I. INTRODUCTION

In subsea pipelines, flow assurance risk management is an important factor that needs to be taken into consideration due to the formation of gas hydrates, corrosion, scaling and wax [1]–[6]. Among these dangers, the formation of gas hydrates is of the major concerns that cost millions of dollars per annum in mitigation [3], [7], [8].

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Gas hydrates are solid-crystalline structured compounds in which gas is trapped inside water molecules by forming hydrogen bond wherein the gas molecules are called as guest molecules while water as host molecules [4], [9]–[12]. The gases which generally make hydrates include propane, ethane, methane, hydrogen sulfide etc. at low temperature and high pressure conditions [13]–[15].

In Malaysia, some natural gas (NG) fields contain rich CO<sub>2</sub> content which in some cases is more than 70%. The high content of CO<sub>2</sub> may increase risk of hydrate formation and also makes it difficult to separate it from the NG. Gas hydrates can form in oil and gas transmission pipelines when suitable conditions are available for these to form.

While gas hydrates possess potential source of hydrocarbon energy and also medium for storage and transmission of natural gas, they can cause severe threats. Due to gas hydrates, the threat of breakage and plugging of flowlines in subsea cause spillage of containments instigating environmental catastrophe [16]–[22]. Once the pipeline is ruptured, the cost of repair and maintenance is high. In some cases, the use of mechanical techniques such as heating and insulation heating are preventive methods. But sometimes these methods prove to be impracticable and ineffective. In order to avert hydrate formation, kinetic and thermodynamic inhibitors are utilized. Kinetic inhibitor works on the principle of increasing the induction time [23]. Induction time is the time elapsed in hydrate formation and can be called as onset of hydrate formation time [13], [18], [24]. Whereas, thermodynamic inhibitors alter hydrate liquid vapor equilibrium (HLVE) phase equilibrium curve towards lower temperature and high pressure regions thus increasing the hydrate free zone [8]. To mitigate gas hydrates formation successfully, it is critically important to make a reliable prediction of hydrate phase equilibrium for industrial application. Usually four techniques are engaged in prediction of hydrate phase equilibrium for the NG systems: (1) manual calculation, but it has limited applicability and also suitable for single gas component (2) empirical correlations that are applicable to gaseous mixtures but also restricted in application, (3) methods involving experiment, but they may not be cost-effective and infeasible due to time consumption (4) methods involving simulation, which include the use of different phase generating softwares such as HYSYS (Hyprotech Systems), PVTsim (Pressure Volume Temperature Simulation) and EQUI phase (Equilibrium phase) [17]. For these reasons, the simulation approach is favored over other techniques.



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There are some softwares available commercially which are used for the prediction of hydrate liquid vapor equilibrium such as PVTsim and CSMGem. Though, PVTsim is used widely for the application. The HLVE of hydrogen sulfide was determined experimentally and validated using PVTsim. Ward et al. [25] showed that PVTsim can precisely define H<sub>2</sub>S hydrate phase equilibrium calculations. Moreover, Bavoh et al. [26] studied the HLVE of natural gas prepared synthetically in Canada and Ghana with H<sub>2</sub>S content and methanol inhibitor using PVTsim. The findings showed a good agreement between experiment and the simulation.

A previous study [27] involved the use of PVTsim in order to examine the phase behavior of hydrate in some parts of the world to ensure the operation safety. However, the studies on Malaysian natural gas systems are not widely available in literature. Therefore, in this paper a simulation method is used to predict the HLVE of synthetic NG system of Malaysia through PVTsim. Different equation of states including SRK Phenolux and PR Phenolux are used with 5, 10 and 20 wt% of inhibitor concentrations to observe the effect of inhibitors in shifting the equilibrium. The inhibitors which are taken into consideration involve methanol, ethanol and monoethylene glycol (MEG).

## II. METHODOLOGY

### Materials and Software

The composition of Malaysian NG system is mentioned in Table 1 which has been used for calculating HLVE in PVTsim software. The CO<sub>2</sub> content in gas system is more than 70% which makes it high CO<sub>2</sub> content NG system. The natural gas system mentioned in Table 1 is simulated to determine its hydrate phase equilibrium conditions by varying temperature from 5 °C to 25°C. The temperature range considered for validation is typical seabed temperature conditions.

**Table. 1 Composition of Malaysian NG field**

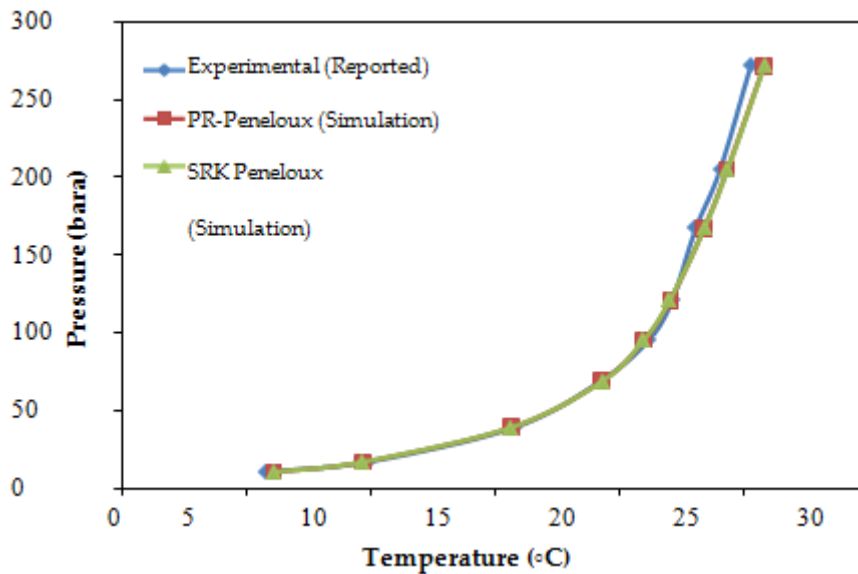
| Component        | Mol%  | Mol. Wt. |
|------------------|-------|----------|
| N <sub>2</sub>   | 0.10  | 28.01    |
| CO <sub>2</sub>  | 72.98 | 44.01    |
| H <sub>2</sub> S | 1.20  | 34.08    |
| C <sub>1</sub>   | 20.15 | 16.04    |
| C <sub>2</sub>   | 3.00  | 30.07    |
| C <sub>3</sub>   | 1.00  | 44.09    |
| iC <sub>4</sub>  | 0.20  | 58.12    |
| nC <sub>4</sub>  | 0.20  | 58.12    |
| iC <sub>5</sub>  | 0.10  | 72.15    |
| nC <sub>5</sub>  | 0.06  | 72.15    |
| C <sub>6</sub>   | 1.00  | 86.17    |

PVTsim is a modeling software established by Calsep which is used to simulate the properties of the fluid employing various equations of states (EoS). PVTsim is used to solve various industrial problems such as advanced flash regression algorithms, fluid characterization of reservoir, and self-regulating fluid regression for minimization of manual tuning. Different utilities and sub-packages are available in PVTsim related to unit operations,

flash operations, wax and hydrate. In order to simulate the HLVE phase behavior, hydrate structure utility was employed in this work. This is due to reason that this particular module can simulate the hydrate formation conditions and phase equilibrium in the absence and presence of inhibitors. The inhibitors used are methanol, ethanol and monoethylene glycol (MEG). All the inhibitors are employed in 5, 10 and 20 wt% concentrations. It can also be used in the presence of impurities due to its specified functions. In this work, two suitable fluid packages namely Peng Robinson (PR) Peneloux fluid package and SRK Peneloux are selected for the prediction of hydrate phase equilibrium for their capability to simulate results with higher accuracy. The hydrate phase boundary is determined within high pressure range of 10 to 110 bara. The equilibrium pressure values or the hydrate phase boundary is determined within this pressure range through PVTsim software. The results obtained using these equations are compared with the experimental results reported in the literature to examine the extent of agreement among them. The results obtained from PVTsim are further studied and compared at 5, 10 and 20 wt% inhibitor concentrations.

## III. RESULTS AND DISCUSSION

The results have been obtained using both PR-Peneloux and SRK-PenelouxEoS. The results are compared with each other for different inhibitors employed in different concentrations. Generally, thermodynamic inhibitors e.g methanol, ethanol and mono ethylene glycol (MEG) are used in industrial applications to prevent hydrate formation. Thermodynamic inhibitors inhibit hydrate formation by disrupting the activity of water in the process and generate hydrogen bonding with water molecules which pushes the hydrate liquid vapor equilibrium curve to the left of phase diagram i.e. keeping it at low temperature and/or high pressure conditions avoiding hydrate formation domain. This increases the hydrate free region and thus allowing the safe pipeline operation. Figure 1 shows the comparison between simulation results and experimental results reported in the literature[17].

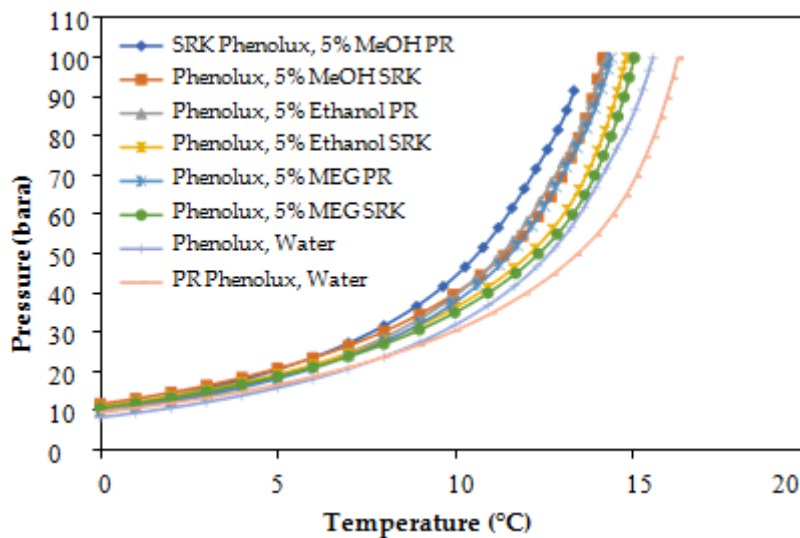


**Fig. 1 Comparison between Experimental and Simulation results [17]**

The results obtained using PR-Penolux and SRK Penolux equation of states using PVTSIM are compared with the experimental results in Figure 1. It can be observed from the Figure 1 that PR-PenoluxEoS in simulation works efficaciously and simulation and experimental results are in good agreement as compared to SRK-Penolux. The average absolute error (AAE) values obtained for PR-Peneolux is 2.10% whereas for SRK-Peneolux, the value is 2.18%. The values for AAE% show that PR-Peneloux equation of state is more suitable to predict the hydrate phase boundary. It is due to the reason that PR-PenoluxEoS is suitable to simulate the PVT relationship of hydrocarbons and defines the phase behavior of hydrocarbon mixtures more accurately.

The predictions made by PVTsim for 5 wt%

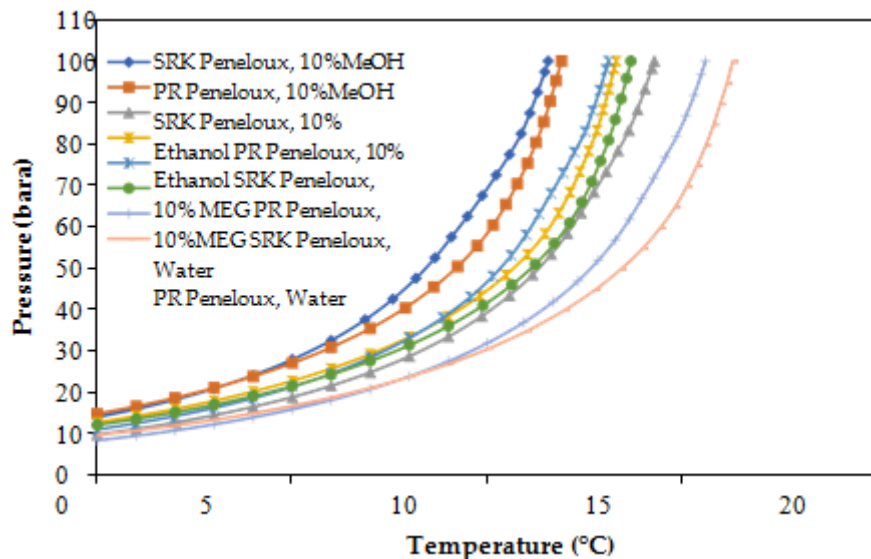
concentration of thermodynamic hydrate inhibitors; methanol, ethanol and MEG are shown in Figure 2. The results showed that the inhibition effect provided by methanol is highest among all the compounds in comparison to that of pure water. In the literature also, the inhibition provided by methanol is reported to be the highest [6], [23], [28]. The thermodynamic inhibition ability of methanol is due to its shorter alkyl chain length as shorter alkyl chain compounds provide better inhibition [28]. Also inhibitors such as methanol have polar molecules and they attract water molecules due to hydrogen bonds [29]. After methanol, the inhibition effect of ethanol is high while the inhibition offered by MEG is comparable to that of ethanol but still a little less than it.



**Fig. 2 HLVE prediction for 5 wt% MeOH, Ethanol and Water**

Figure 3 shows the results obtained for the NG system at 10 wt % inhibitor concentrations. The results show that inhibition performance of methanol is better compared to the other inhibitors. The extent of inhibition is concentration dependent and hydrate mitigation performance at 10 wt% is higher than at 5 wt%. The results are in line with the findings reported in literature [8], [16].

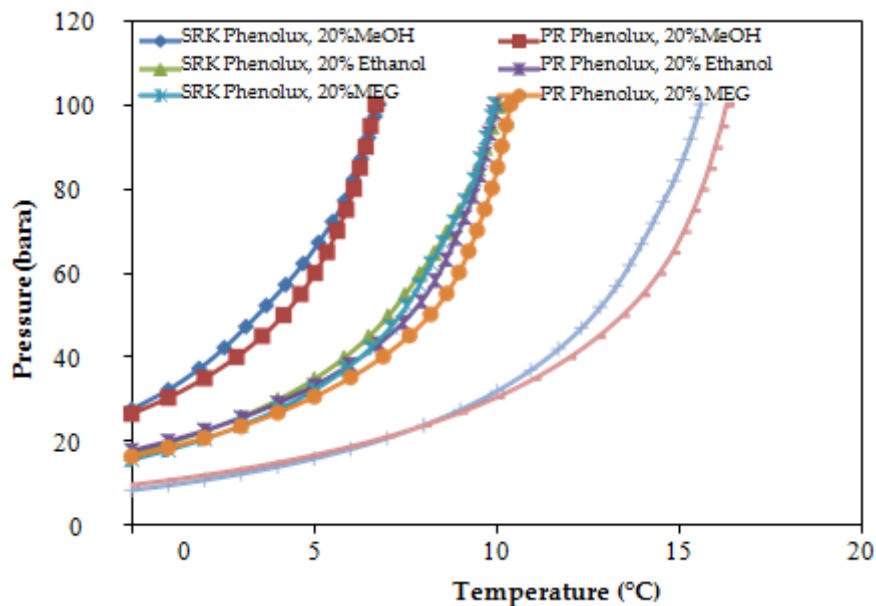
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**Fig. 3 HLVE prediction for 10 wt% MeOH, Ethanol and Water**

The inhibition effects calculated at 20 wt% of inhibitor concentrations are presented in Figure 4. The results reveal that PR-PenoluxEoS is more suitable to simulate the HLVE phase behavior of NG system and as observed previously, using 20% methanol has shifted the equilibrium as compared to the other solutions. According to the results obtained by PVTsim, the amount of thermodynamic

inhibition shown by SRK-Peneloux equation is higher as compared to PR-PenelouxEoS. Although the extent of inhibition is high but according to validation presented in Figure 1, results predicted by PR-PenelouxEoS are more accurate as it showed closer agreement with the experimental results.



**Fig. 4 HLVE prediction for 20 wt% MeOH, Ethanol and Water**

## IV. CONCLUSION

The paper evaluates the thermodynamic hydrate inhibition behavior of methanol, ethanol and MEG using two different equations of states namely PR-PeneoluxEoS and SRK-PenelouxEoS. The use of PR-PeneoluxEoS is found to be more suitable as it predicted the phase behavior accurately. The inhibition results revealed that methanol performed better in comparison to ethanol and MEG at 5, 10 and 20 wt% concentrations. Also, the inhibition performance was found to be increasing with the increase in concentration of the inhibitor.

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