Investigation on Thermodynamic Equilibrium Conditions of Methane Hydrates in Multiphase Gas-Dominant Pipelines

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ABSTRACT: The estimation of thermodynamic equilibrium conditions of methane hydrates in the presence of crude oil based on experiments is shown in this research work. This pipeline system replicated the gas-dominant multiphase transmission pipelines at deep-sea regions. An experimental study is done by the usage of a Raman gas hydrate reactor. The pressure was maintained in the range of 3–8 MPa for the experimental study. The water cut is kept constant throughout the system as 30%. Initially, the experimental setup is calibrated by using carbon dioxide gas. Then, methane hydrates are formed with and without crude oil. The methane hydrates that are created without the presence of crude oil are validated with simulation that is performed using CSMGEM, PVTSIM software, and literature data. Then, the thermodynamic conditions are found for the methane hydrate formation in the presence of crude oil with an addition of a 15% oil cut to the system. From these results, the phase behavior of a multiphase system is evaluated. The formation of methane hydrates in the system was found to be affected by the presence of an additional oil phase that exhibited an inhibition behavior. This research validates all the multiphase systems that contain similar hydrocarbon and gas compositions.

1. INTRODUCTION

Gas hydrates are solid ice-like compounds, which, in the presence of gas molecules and water at low temperatures and high pressures, form in the flow lines. The most commonly known gas hydrate-forming gases are CO2 (carbon dioxide), CH4 (methane), C2H6 (ethane), C3H8 (propane), and C4H10 (butane). When these gas molecules interact with water at suitable conditions, they get clathrate in water cages forming ice-like compounds, and these are referred as clathrates or gas hydrates. As they come across in different flow assurance applications, especially in the oil & gas industry, gas hydrates are one of the most prominent flow assurance problems.

In the oil & gas industry, the production lines consist of various phase materials like oil, water, gas, emulsions, etc. that are usually referred to as multiphase flow lines at deep-sea conditions. These flow lines are typically operated at high pressures, and the operating temperatures are relatively low. So, in these multiphase pipelines, there is a high potential for the formation of gas hydrates. When the gas production is done from gas reservoirs, the possibility of dominant gas pipelines is quite high. The formation of gas hydrates in such pipelines is therefore more viable, as the supply of gas is greater. Due to these typical scenarios, the gas hydrates are of high importance when it comes to challenges faced in multiphase transmission pipelines.

The presented work represents the methane hydrate formation in a gas-dominant multiphase environment that usually comes across in deep-sea situations. Over the years, there are plentiful prediction models developed and proposed on the gas hydrate formation at various conditions as well as in the presence of different chemical inhibitors. However, in a gas-dominant multiphase framework, research focused on the formation of gas hydrates is limited. There is also very marginal literature data available, which discussed the degree of blockage caused by the formation of gas hydrates in multiphase pipelines.

The first research work on the formation of gas hydrates in multiphase pipelines was implemented in 1980. Parametric research on the formation of gas hydrates concentrated on the system’s phase behavior in the multiphase pipeline. The amounts of liquid, pressure, and temperature have been found to play a major role in the formation of gas hydrates.
Furthermore, the study showed that the flow velocity in transient pipelines is a crucial contributing factor in the gas hydrate formation. This is because the flow velocity tends to create a disturbance within the flow, which will lead to the additional mixing of the gas in the system leading to the gas hydrate formation.

The use of chemical inhibitors became more important for the prevention of gas hydrate formation in pipelines with the advances in chemical applications in the oil and gas industry in the late 90s. In the initial study for the chemical inhibition method, in a multiphase system, the usage of low-cost surfactants like trichlorofluoromethane (CCl3F) was proposed. Further, interest was more on the study of various flow regimes in multiphase pipelines that cause the gas hydrate formation. This was studied to estimate the safer flow velocity conditions as in the literature. It was proposed that the flow velocity influences the gas hydrate formation. Various studies have been carried out in flow loops and other flow simulation devices to understand the impact of water on the formation of gas hydrates in multiphase pipelines, marking the importance of water cuts and emulsion activity in the pipelines. Water cut can simply be defined as the percentage of water available in the flow of a multiphase system. However, technically, the water cut is the ratio of water produced compared to the volume of total liquids produced from an oil well.

Interest has been shifted toward the product pipelines as there is a possibility of hydrate formation even when the processed fuels like gasoline and diesel are being transported in subsea pipelines due to the favorable conditions for gas hydrate formation. With the increase in software computational facilities, the modeling became more significant as well in the gas hydrate prediction, especially for multiphase scenarios. The methane hydrate formation in oil dispersed media and other pilot-scale experimental works contributed to the dynamic prediction capability development. However, in the prediction of the formation conditions of gas hydrates in multiphase gas-dominant pipelines, there is a research gap.

This research study demonstrates the thermodynamic conditions during which the methane hydrates are formed in the multiphase gas-dominant scenario when the crude oil is present in the system.
2. RESULTS AND DISCUSSION

2.1. Carbon Chain Analysis. To assess the carbon chain existence in the crude oil sample used for the experimental investigation, the HPLC test was performed. The results are displayed in Figure 1.

Then, an elemental test for carbon, hydrogen, nitrogen, and sulfur (CHNS) test has been performed to evaluate the quality of the crude oil used. This test will determine the amount of sulfur present in crude oil, which will help in estimating the quality of crude oil as sweet or sour crude. The results of CHNS analysis are presented in Figure 2. The carbon content is highest with less sulfur, as per this understanding. The results of the CHNS legitimize the fact that the sample of crude oil used for this analysis is sweet and highly used because of its commercial value. Because of this, the probability of transportation of crude oil via pipelines is also greater.

2.2. Validation of the Experimental Apparatus. The experimental apparatus is first calibrated and tested initially with carbon dioxide for the accuracy of the results. With the data produced during the formation of gas hydrate and dissociation in the reactor cell, the T-cycle curves are plotted. Based on these T-cycles, thermodynamic equilibrium conditions are found. The pressure and temperature conditions are recorded during the heating, cooling, and stabilization steps for the gas hydrate formation and dissociation. The T-cycle is obtained by the cyclic plotting of these conditions. The temperature and pressure point on the T-cycle where the cooling and heating curves intersect is drawn as the thermodynamic equilibrium point. The representation of the T-cycle curve is done in Figure 3. At various pressure conditions, the thermodynamic equilibrium points are obtained for the carbon dioxide gas. These points are used to generate the HLVE curve. This HLVE curve is compared to the HLVE curves generated with simulation tools CSMGEM and PVTSIM and the literature17−19 to verify the performance in accuracy of the experimental apparatus. For CSMGEM, the 2001 version is used, and for PVTSIM, the 2011 version is used. The results are presented in Figure 4. From this analysis, the results from the apparatus are in accordance with the simulation results as well as the literature.

2.3. Thermodynamic Equilibrium Conditions and Phase Behavior Study. The methane hydrates formed at various pressure conditions are dissociated through slow step heating maintaining a difference of 0.5 °C for each step for approximately 120 min at each level. The data recorded using the PLC data logging system is used to plot the T-cycle. These conditions are used further to plot the HLVE curves. The plots of the HLVE curves based on experiments of a simple system and multiphase system alongside the simulation and literature are presented in Figure 5. The results captured from the experimental evaluation are mentioned in Table 1. It is clearly observed from the plot that there is a definite change in the HLVE curve when the thermodynamic gas hydrate data, which is generated using a multiphase method consisting of crude oil, is analyzed.

From the calibration results, the simple system’s HLVE curve is almost in line with the results of the simulation and literature. It can be observed that there is a certain shift in the HLVE curve for the multiphase system, which contains crude oil. The curve moves toward the lower temperature region at a chosen pressure as opposed to that of the pure system. This result can be concluded as the inhibition effect of the multiphase system. Since crude oil is an unprocessed raw fuel, which, along with some big inhibiting groups such as aromatics and OH groups, contains a lot of impurities, the formation of gas hydrate in the multiphase system is seen as an inhibition effect.20,21 It was observed from the literature, the phase transitions are affected rapidly due to the presence of impurities in the third phase.21 Due to its impurities, the presence of crude oil in the environment influences physical properties such as the freezing point and the melting point as the crude oil is an unprocessed fuel oil.22 This results in an understanding of the effects of impurities playing a role in the conditions of gas hydrate formation. The presence of crude oil influences the thermodynamic conditions by affecting the gas hydrate dissociation.23 Here, the influence of oil cut also can be justified. According to the literature, oil cut plays a very minute role in gas hydrate formation/dissociation studies in oil−water emulsions compared to that of water cut.24−27 The increase in oil cuts in the system increases the inhibition of gas hydrate formation. This is due to the presence of a mixture of various inhibition mechanisms and possibly a rivalry between mechanisms for inhibition promotion.28

2.4. Variance in Temperature (T) and Enthalpy. The thermodynamic inhibition effect and phase behavior study is done by the calculation of the temperature variance (T) between the pure and multiphase system. The following equation is used for the computation of the temperature variance (T).

\[
T = \frac{\Delta T}{n} = \frac{\sum_{i=1}^{n} (T_{0,p_i} - T_{1,p_i})}{n}
\]  

where the equilibrium temperatures of pure and multiphase systems are represented by \( T_{0,p_i} \) & \( T_{1,p_i} \) respectively. The pressure must be maintained constant when the calculation of dissociation temperature is done. The total number of pressure conditions considered for this study is represented by \( n \). In Table 2, the variance in temperature for pure and multiphase systems is presented.

The equation of Clausius−Clapeyron is used to determine dissociation enthalpies and is expressed by \( \Delta H \). By using the Clausius−Clapeyron equation, the slope of the HLVE curves is calculated, and the \( \Delta H \) is determined. The Clausius−Clapeyron equation (eq 2) is presented below.
where the thermodynamic equilibrium temperature is represented by $T$, and $P$ represents the thermodynamic equilibrium pressure. The universal gas constant and the compressibility factor of the gas are denoted by $R$ and $z$, respectively. Every gas has a different compressibility factor ($Z$) at different pressures. In this work, the constant slope and varying $Z$ are considered to calculate the enthalpy.

The $\Delta H$ values for the pure and multiphase systems are shown in Table 3 alongside the pressure vs enthalpy graph in Figure 6.

From the graph, it can be seen clearly that the multiphase system exhibits a higher enthalpy of dissociation when compared to the system without crude oil. From this, it can be concluded that the multiphase system exhibits the inhibition effect due to the presence of crude oil. When the oil phase is added into the system, the enthalpy required to
The multiphase system has a different thermodynamic equilibrium curve due to the presence of crude oil. The crude oil impurities disrupt the dissociation of the gas hydrate, which is higher than that of the simple system, with the presence of crude oil. The crude oil impurities disrupt the dissociation of the gas hydrate due to their stability in the presence of crude oil. The crude oil samples were collected from the Terengganu Crude Oil Terminal (TCOT) and were delivered by Linde Malaysia Sdn. Bhd. The crude oil sample was also tested for the CHNS test to understand the carbon chain presence in the oil. Alongside this, the crude oil sample was also tested for the high-performance liquid chromatography (HPLC) system to characterize the components in the crude oil. The crude oil sample was also tested for the CHNS test to understand the carbon chain presence in the oil.

### 3. CONCLUSION

This research work demonstrates the estimation of thermodynamic equilibrium conditions of methane hydrates in the presence of crude oil using experiments. By the experimental investigation, the thermodynamic equilibrium conditions are found, and the HLVE curve has been plotted for both pure and multiphase systems. From the comparison between the curves, it can be inferred that relative to that of the simple system, the multiphase system has a different equilibrium curve due to the presence of crude oil. The crude oil impurities disrupt the dissociation of the gas hydrate, which is higher than that of the simple system.

### 4. METHODOLOGY

#### 4.1. Materials

For the experimental study, the below listed materials were used to replicate the gas-dominant multiphase transmission pipelines:

1. **CH₄ (methane gas)**
2. **deionized water**
3. **crude oil**

The methane gas (CH₄) sample with a purity of 99.97% was delivered by Linde Malaysia Sdn. Bhd. The crude oil sample is collected from the Terengganu Crude Oil Terminal (TCOT), Petronas Carigali Sdn. Bhd. The deionized water is prepared in the gas hydrate laboratory.

#### 4.2. Experimental Setup

The details for this experimental study of the experimental apparatus used have been adapted from the literature [29–32] and are presented in Figure 7. Dixson FA Engineering Sdn. Bhd. fabricates equipment used. The experimental apparatus is a high-pressure stainless-steel cell with a 650 mL volume size. It is intended for operation at a maximum pressure of 20 MPa, and the operating temperature range is 253–523 K. It is equipped with a PLC data logging system to record the data in every subsequent 3 s. This is with an accuracy of ±0.001 mL, ±0.01 MPa, and ±0.1 K, respectively. The reactor is also equipped with a magnetic stirrer to provide sufficient agitation in the reactor cell, which simulates the real-time flow conditions in pipelines.

#### 4.3. Experimental Procedure

Initially, the materials characterization is carried out to understand the components in the crude oil. The crude oil sample is tested with a high-performance liquid chromatography (HPLC) system to understand the carbon chain presence in the oil. Alongside this, the crude oil sample is also tested for the CHNS test to understand the carbon chain presence in the oil.

### Table 1. Methane Hydrate Thermodynamic Equilibrium Conditions

| Pressure (MPa) | Temperature (K) | CSMGEM | PVTsim | Saad et al. | Bavoh et al. | experiments (pure) | experiments (multiphase) |
|---------------|----------------|--------|--------|-------------|--------------|--------------------|-------------------------|
| 3             | 274.59         | 274.11 | 0.480  |             |              |                    |                         |
| 3.5           | 276.29         | 275.87 | 0.420  |             |              |                    |                         |
| 4             | 277.35         | 276.88 | 0.470  |             |              |                    |                         |
| 4.5           | 278.89         | 278.11 | 0.780  |             |              |                    |                         |
| 5             | 279.81         | 279.99 | 0.820  |             |              |                    |                         |
| 5.5           | 280.26         | 279.89 | 0.370  |             |              |                    |                         |
| 6             | 281.54         | 280.35 | 1.190  |             |              |                    |                         |
| 6.5           | 282.31         | 280.79 | 1.520  |             |              |                    |                         |
| 7             | 282.59         | 281.95 | 0.640  |             |              |                    |                         |
| 7.5           | 283.13         | 282.31 | 0.820  |             |              |                    |                         |
| 8             | 284.32         | 283.6  | 0.720  |             |              |                    |                         |

### Table 2. Variance in Temperature between Pure and Multiphase Systems

| Temperature Variance | Pressure (MPa) | Temperature (K) |
|----------------------|---------------|-----------------|
| 0.740                | 3             | 274.59          |
| 0.720                | 3.5           | 276.29          |
| 0.710                | 4             | 277.35          |
| 0.680                | 4.5           | 278.89          |
| 0.670                | 5             | 279.81          |
| 0.640                | 5.5           | 280.26          |
| 0.640                | 6             | 281.54          |
| 0.720                | 6.5           | 282.31          |
| 0.720                | 7             | 282.59          |
| 0.600                | 7.5           | 283.13          |
| 0.600                | 8             | 284.32          |

### Table 3. Enthalpy

| Pressure (MPa) | Water (kJ/mol) | Multiphase (kJ/mol) |
|---------------|---------------|---------------------|
| 3             | 62.16509582   | 65.36324367         |
| 3.5           | 61.42212821   | 64.58205332         |
| 4             | 60.50844323   | 63.62136191         |
| 4.5           | 59.83543777   | 62.91373935         |
| 5             | 59.14821902   | 62.19116052         |
| 5.5           | 58.4478698    | 61.45478111         |
| 6             | 57.8881884    | 60.86630632         |
| 6.5           | 57.30975505   | 60.25811486         |
| 7             | 56.70352974   | 59.62070166         |
| 7.5           | 56.17203328   | 59.06186182         |
| 8             | 55.783154     | 58.65297623         |

Average (ΔHₘₐₜ) (kJ/mol): 61.68966321
evaluate the economic significance of the crude oil by evaluating the sulfur content.

In order to determine the phase behavior of the multiphase system, the experiments are performed in the apparatus. The T-cycle method is applied in this work to determine the thermodynamic equilibrium conditions. The T-cycle is plotted by analyzing the temperature and pressure variation at a constant volume condition, which is an isochoric process. The hydrate liquid–vapor equilibrium (HLVE) curves are drawn by using these thermodynamic equilibrium points. Also, the HLVE curves helps in understanding the phase behavior of both the systems.33,34

The gas hydrate reactor cell in which the samples would be injected is sprinkled with refined water altogether to stay away from any pollutants that might affect the study and afterward fully dried. Then, this reactor cell is attached to the system, and it was made sure that the system is properly aligned. This reactor cell is then purified from any air pollutants by operating the vacuum pump attached to the system. For the experimental study on the simple system, which is the study without crude oil, the deionized water of volume 200 mL is loaded into the reactor cell. Then, the rapid cooling effect is created with the help of a water bath that is attached to the system for stabilization at a certain temperature. Once the stability in temperature is reached, a minor volume of the gas sample is pumped into the reactor cell by using the high-pressure boosting pump. Then, the vacuum pump is again operated to remove this gas sample as well to make sure that the reactor cell is empty from any gas molecules. This process could cause a disturbance in the temperature of the reactor cell. So, the system is once again allowed to stabilize at the initial chosen temperature. Once the stability in temperature is achieved, the gas sample was allowed to flow into the reactor cell. This process is continued till the pressure in the reactor cell and initial chosen temperature are constant. Once temperature and pressure stabilization conditions have been achieved, the activity of the magnetic stirrer was implemented by setting it at 400 rpm to interrupt the interface of the gas–liquid boundary, and during the formation of gas hydrates, sufficient mixing is achieved. Due to this, there is a pressure drop in the reactor cell. So, the gas inlet is still left open for the pressure and temperature conditions to stay constant. Then, the cooling

Figure 6. Enthalpy plot: water vs multiphase.

Figure 7. Schematic depiction of the experimental setup.
duty is implemented by allowing the system to cool rapidly to a certain lower temperature. This will create the sudden temperature drop for the reactor cell that simulates the pipeline operating conditions. Due to this cooling effect, the gas hydrates are formed in the reactor cell. The reactor cell is maintained at this lower temperature condition for around 4 to 8 h. As the gas hydrate formation is an exothermic reaction, when the reactor temperature is spotted to increase for a drop in pressure, it can be confirmed as the gas hydrate formation in the reactor cell. The data logging system is closely observed, and when the pressure drop is constant, then, it can be concluded that the gas hydrate formation is complete. Then, the temperature is increased at the rate of 0.5 K/h to make sure that the dissociation of the hydrate is slow and steady. For the determination of the equilibrium point of the hydrate, the duration of each phase must be between 2 and 6 h. The accomplishment of each experiment analysis required roughly 48 h. A similar cycle is followed for the multiphase framework also, aside from the method of stacking samples into the reactor cell fluctuates. The crude oil used for the experimental study is warmed up for making sure about the precipitants dissociating or melting back into the oil. Then, this oil sample of volume 100 mL is loaded into the reactor cell. Then, the procedure is followed the same for attaining thermodynamic equilibrium conditions for the multiphase system.

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Notes
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