Experimental Equipment Validation for Methane (CH₄) and Carbon Dioxide (CO₂) Hydrates

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Abstract. Clathrate hydrates are eminent structures regard as a threat to the gas and oil industry in light of their irritating propensity to subsea pipelines. For natural gas transmission and processing, the formation of gas hydrate is one of the main flow assurance delinquent has led researchers toward conducting fresh and meticulous studies on various aspects of gas hydrates. This paper highlighted the thermodynamic analysis on pure CH₄ and CO₂ gas hydrates on the custom fabricated equipment (Sapphire cell hydrate reactor) for experimental validation. CO₂ gas hydrate formed at lower pressure (41 bar) as compared to CH₄ gas hydrate (70 bar) while comparison of thermodynamic properties between CH₄ and CO₂ also presented in this study. This preliminary study could provide pathways for the quest of potent hydrate inhibitors.

Keywords: CH₄ Hydrate; Compressibility Factor; CO₂ Hydrate; HLwVE; Thermodynamic Analysis.

1. Introduction

Gas hydrates are an ice-like crystalline structure shaped by water molecules through hydrogen bonding with suitable gas particles grasping inside polyhedral cavities. The key constituents, such as water particles (hosts), gas molecule (visitors), and thermodynamically appropriate environments including high pressure/low temperature are essential prerequisites for the formation of gas hydrate [1, 2]. The studies on the gas hydrates are ongoing in two fields; gas hydrate inhibitors for decreasing hydrate formation and gas hydrate promoters to enhance hydrate formation. Hydrates removals are industrially vital because the existence of gas hydrates in off-shore pipelines presents extraordinary financial losses with increased ecological and safety hazards. On the other hand, hydrates also have industrial significance in separation and storage processes of gases [3, 4]. Methane hydrates are also seen as a prospective fuel source in a future, for the reason that vast deposits of methane hydrate are found globally in continental margins and permafrost regions [5]. Other progressive applications of Gas hydrate incorporate; storage and transportation of gases in hydrate form (solid), separation of various gases via hydrates and carbon dioxide sequestration [6, 7]. At last, the utilization of their separation vitality can be applied in refrigeration procedures and cool stockpiling.
In petroleum industry, one of the topmost obstructions confronted in flow assurance engineering is the formation of gas hydrate in pipelines, which are the root cause of the impasse of the oil and gas production, transportation and processing [7–9]. Gas hydrate formation may possibly be a reason to appalling ecological and economic risks. Hydrate formations problem also arise during the offshore drilling operations when drilling fluids prone to hydrate formation could result in severe dangers towards the operational safety. Hydrates problems are regularly encountered in deep waters like Gulf of Mexico, North Sea and Caspian Sea alongside permafrost region like Alaska. Hydrate problem alone accounted the oil and gas industry billions of dollars annually to control hydrate formation with no perpetual solution in focus. Initially, Hammer Schmidt (1934) has found the hydrate blockage problem in the gas pipeline, and since then extensive investigations are being conducted to discover efficient and better mitigation solutions especially chemical inhibitors [2, 10].

Incrassating attention has been found of late in the gas hydrate of CO$_2$ and CH$_4$ due to the exploration of higher CO$_2$ content gas fields. One of the most significant prone for CO2 rich gas is the possibility of hydrate formation during production, transportation and processing stages [8]. Subsequently, CO$_2$ is more susceptible to form hydrate than CH$_4$, therefore increase quantities of CO$_2$ up to 70 mole % is additionally inclined to form gas hydrate mostly during the separation and transportation stages [11]. There are four conventional methods employed in oil and gas industry for preventing gas hydrate, which are (i) Dehydration (ii) Depressurization (iii) Heating and (iv) Chemical inhibitions. Dehydration refers as a preventive method for avoiding gas hydrate plug formation. Dehydration from offshore sources may not be liable for all the operations owing to constraints of physical footprints in the offshore production facilities. Depressurization also considered as a remedial method for hydrate plug removal; depressurization should be done in the cautious manner since sudden pressure drop caused a rapid increase in hydrate plug velocity can lead to catastrophic damages to plate form or engineering machinery. Similarly, thermal Heating involves insulation of entire pipeline which caused an enormous amount of economic losses since pipelines nowadays last for hundreds of miles, and capital cost of 1 million US$/mile contain it to the remedial method, once gas hydrate formed inside the pipeline. Therefore, the most efficient method for removal and prevention of gas hydrate is the insertion of chemicals [4], [12]. Chemical inhibition involves the addition of certain chemicals which make a hydrogen bond with the water molecule and delay /avoid gas hydrate plug formation. For that reason, under most of the circumstances, the application of gas hydrate inhibitors is the solitary practicable choice [6], [13]. From the knowledge of the chemical composition requirements and the thermodynamics of hydrates formation, the industry has tried to prevent the hydrate formation by using conventional hydrate prevention methods which are either ineffective or required an enormous quantity of chemicals resulting in extraordinary operational cost together with adverse environmental influence of operating gas and oil facilities. Thus, in numerous cases, the only viable solution for hydrate inhibition is the addition of chemical inhibitors in the pipelines [14]–[18]. An illustration of a gas hydrate plug is shown in Figure 1 [19].

Thermodynamic and kinetic inhibitors usually applied in the off-shore flow assurance strategies to avoid hydrate formation in the pipeline [20]. The purpose of these inhibitors to make sure the operational conditions in the transmission pipeline are set well beyond the hydrate formation region. Owing to this motive, accurate hydrate equilibrium data measurement and thermodynamic properties of the gas hydrates are essential [11] and measured in this initial study.
2. Methodology

In this experiments, CH$_4$ ($\geq$99.995%), CO$_2$ ($\geq$99.995%) gases were bought from Gas Walker Sdn Bhd. Malaysia. All gases and de-ionized water are used without any further purification in all experiments as listed in Table 1.

| No | Chemical Name         | Symbol | Purity          | Chemical Structure |
|----|-----------------------|--------|-----------------|--------------------|
| 1  | Methane               | CH$_4$ | 99.95 mole %    |                     |
| 2  | Carbon Dioxide        | CO$_2$ | 99.99 mole %    | O=C=O              |
| 3  | Water                 | H$_2$O | Deionized       | H$	ext-O-H$       |

2.1 Equipment

In this work, a specifically designed custom-made sapphire cell hydrate reactor was used. A PVT cell apparatus can perform formation/dissociation studies for the gas hydrates. Fig. 1 shows the complete schematic diagram of the experimental setup and Fig 2 provide the pictorial view of the sapphire cell. The sapphire apparatus consists of equilibrium cell with a volumetric capacity of 35 cm$^3$, with operatable temperature and pressure range from (253– 523) K 1-30 MPa respectively. Experimental conditions like pressure and temperature are recorded for every subsequent second with an accuracy of $\pm$0.01 MPa and $\pm$0.1K respectively. Furthermore, the equipment is fitted with a magnetic rod stirrer to provide adequate mixing of the sample in test conditions.
A well renowned T-cycle technique by isochoric step heating method was employed in this study [21]. Before experiments, the sapphire cell was thoroughly rinsed with water then vacuumed it to confirm there is no traces of the air remains in the cell. Now the cell was charged initially with 19 ml of deionized water into the cell, followed by gas sample. When temperature-pressure conditions stabilized, the mechanical stirrer was set at 300 rpm. Then the temperature of the cell was gradually condensed step-wise for a rate of 0.1 K/min up to hydrate formation regions. The span to each step usually differs from 2 to 6 hours. Hydrate formation was confirmed via both visibly from the sapphire frame along with sudden pressure drops seen in the data. As soon as the hydrate is entirely formed...
with no more pressure drip observed, then the cell was heated gradually for complete dissociation of
gas hydrate. Figure 3 represents the temperature-pressure profile and plotted by Bavoh et al. [22]. The
gas hydrate equilibrium point was reserved as the initial point, where cooling line encounters with the
heating line.

![Figure 3. Temperature-pressure profile measurement for hydrate dissociation point [22]](image)

2.2. Calculation
Pitzer correlation of gases [23] equation was employed for the determination of compressibility factor
Z shown in equation 1.

\[ Z = Z_\circ + \omega Z_1 \]  
\[ Z_\circ = 1 + B^\circ \left( \frac{Pr}{Tr} \right) \]  
\[ Z_1 = B_1 \left( \frac{Pr}{Tr} \right) \]  
\[ B^\circ = 0.083 - 0.422 / [Tr]^{1.6} \]  
\[ B_1 = 0.139 - 0.172 / [Tr]^{4.2} \]

Where; \( Z \) is the compressibility factor, \( Z_\circ \) and \( Z_1 \) are functions of reduced Pressure (Pr) and reduced
temperature (Tr). \( Z_\circ \) is a contribution for of simple fluid to compressibility factor, and \( Z_1 \) is the
generalized term for molecules with behaviour different from the simple fluid; \( \omega \) is known as acentric
factor and the values for CH\(_4\) and CO\(_2\) are 0.0115 and 0.228 respectively [24]. \( B^\circ \) and \( B_1 \) are function
of reduced temperatures. Then, some moles of methane were calculated by the general gas equation:

\[ PV = nZRT \]  
\[ n = \frac{PV}{ZRT} \]

Where; \( n \) is the number moles of methane, \( P \) is the pressure, \( T \) is the temperature, \( Z \) is the calculated
compressibility factor, \( V \) is the volume of the vessel (gas phase) = 20 cm\(^3\) and \( R \) is the universal gas
constant = 83.147.
3. Results and Discussion

3.1. H-Lw-V Equilibrium Curve

This study is for preliminary experimental validation of newly design apparatus (sapphire cell reactor) for gas hydrate thermodynamic and kinetic studies. Equilibrium data collected and compared with the existing literature data for CH₄ hydrate. Figure 4 shows the calibration data which revealed that the values remain within the range of hydrate.

For instance, it was stated earlier that Figure 4 refers to the numerous chronological work done on CH₄ hydrates. Besides this data also approaching in line with the preceding efforts, therefore, it can be said that the apparatus is ready for further experiments.

![Schematic diagram of Sapphire Autoclave Cell](image)

Figure 4. Schematic diagram of Sapphire Autoclave Cell

3.2 Thermodynamic Analysis of CH₄ and CO₂

In thermodynamic testing of methane hydrate equilibrium data was achieved and plot the pressure against temperature relation. HLwVE data shown in Figure 5 reflect that cooling line initially meeting with the heating line which also considered as HLwV equilibrium point at point E (285.1 K and 70.8 bar pressure) for CH₄ hydrate. Figure 6 further highlighted the different stages exists during the various parts of the HLwVE curve for CH₄ hydrate. Initially, at point A; only gas vapours and liquid water phases existed while cooling the system continues, the system then enters into B state where hydrate nucleation is started and considered as a metastable zone where conditions is favourable to hydrate formation. Sudden pressure drop observed (from 281 K at 41.4 Bar) reflect the starting of hydrate nucleation along with complete hydrate formation at point C. Point C and D possess three phases vapour, Hydrate, and liquid water which make ensure complete hydrate formation. Subsequently, step heating was initiated to dissociate hydrate by slowly increasing in pressure shown the dissociation curve until point E where no further increase in pressure was observed. Point E also possessed vapour phase, liquid and nucleation states. Finally, point F achieved after further heating for ensuring complete dissociation of hydrate. The temperature difference among point E to D considered as a degree of subcooling was around 11K due to complete hydrate formation around 274K.

Hydrate Equilibrium data of CO₂ hydrate was achieved and plotted as pressure and temperature profile. HLwVE data for CO₂ presented in Figure 6, reflects the meeting of cooling line with the heating line at 282.7 K and 41.1 bar pressure respectively. Furthermore, the degree of sub-cooling also deduced from this graph which almost is around 9.75 K due to complete hydrate formation around 272.95 K.
From figure 6 further detailed about the different existing states during the various parts of the HLwVE curve for CO₂ hydrates. Initially, at A position only gas vapours and liquid water exists while cooling the system continues, the system enters into B state where hydrate nucleation is started and considered as a metastable zone where conditions are favourable to hydrate formation. Sudden pressure drop observed (from 281 K at 41.4 MPa) reflect the starting of hydrate nucleation along with complete hydrate formation at point C. Point C and D possess three phases vapour, Hydrate, and liquid water which make certain complete hydrate formation. After that again step heating is performed to dissociate hydrate slowly, increase in pressure shown the dissociation curve until point E where no further increase in pressure was observed. Point E also has vapour, liquid and nucleation. As a final point, point F achieved after further heating for ensuring the complete dissociation of hydrate. The temperature differences among point E to D considered as a degree of subcooling; as subcooling temperature higher there is more chance of hydrate formation. In some cases; CO₂ not able to attain initial pressure due to the dissolution of CO₂ in the aqueous phase as evident above (Figure 6).
3.3. Determination of Compressibility vs Temperature for CH₄ and CO₂ Hydrate

A Compressibility factor describes the deviation of gas from the ideal state. Previously Qazi et al., [11] calculated the compressibility factors and enthalpies of CH₄ and CO₂ gas hydrate. Figure 7 describes the relationship of compressibility factor of CH₄ on temperature. From Figure 7, it is indicated that the value of Z increased when hydrate formation started while Z values depressed in the dissociation of hydrates. The values of Z for CH₄ alleged in between 0.85 to 0.91 which included in CH₄ boundary region.

![Figure 7. Compressibility Factor (Z) vs Temperature for CH₄ hydrate](image)

Figure 7. Compressibility Factor (Z) vs Temperature for CH₄ hydrate

Figure 8 discussed the relationship between compressibility factors of CO₂ gas on temperature. As mentioned earlier, figure 8 also provide the agreement that compressibility factor Z increased when hydrate formation started while Z values were depleted in the dissociation of CO₂ hydrate as well. However the Z values for CO₂ ranges between 0.73-0.79 which were lower than CH₄ compressibility values due to lesser pressure requirement for CO₂ hydrates.

![Figure 8. Compressibility Factor (Z) vs Temperature for CO₂ hydrate](image)

Figure 8. Compressibility Factor (Z) vs Temperature for CO₂ hydrate
4. Conclusion

In this preliminary work, H-Lw-V equilibrium data of CH₄ and CO₂ hydrates were measured along with the thermodynamic characterization. Obtained result were compared to existing literature data for CH₄ hydrate and found acceptable agreement for H-Lw-VE data. From thermodynamic results, it can clearly observe that CO₂ hydrates formed relatively low pressure compared to CH₄ hydrate at comparatively similar temperature conditions. Initial results revealed that the apparatus could route for extensive gas hydrate studies.

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