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## Gas Hydrate Equilibrium Measurement of Methane + Carbon Dioxide + Tetrahydrofuran+ Water System at High CO<sub>2</sub> Concentrations

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### Abstract

Application of gas hydrate in separation of carbon dioxide (CO<sub>2</sub>) from nitrogen in Carbon Capture and Storage (CCS) chain is recently studied by many researchers. Tetrahydrofuran (THF) is suggested as promoter for this process. The same process can be suggested for separation of CO<sub>2</sub> from methane (CH<sub>4</sub>) for gas treatment and sweetening, especially for high CO<sub>2</sub> content mixtures such as landfill gas. The first step in development of such process is understanding of the phase boundary of this mixture at different pressure-temperature condition and gas/liquid composition. In this work, gas hydrate phase boundary of CH<sub>4</sub>, CO<sub>2</sub>, THF and water at different pressure from 4.5 to 8.1 MPa is experimentally measured. CO<sub>2</sub> mole fraction in gas phase is fixed at 0.7 and THF concentration in the liquid phase set at 0.03 mole fraction. Results show that presence of THF in the mixtures shift the phase boundary to the lower pressure / higher temperature condition. This effect is favorable for industrial applications.

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**Keywords:** gas hydrate; phase boundary; thermodynamic; high CO<sub>2</sub> content.

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### 1. Introduction

Clathrate hydrates are solid crystalline complex materials which consist of mostly water molecules as host and suitable-sized gas, i.e., CH<sub>4</sub>, ethane (C<sub>2</sub>H<sub>6</sub>), nitrogen (N<sub>2</sub>), hydrogen (H<sub>2</sub>), and CO<sub>2</sub>. This compound is a good sample of stabilized structure due to the minimization of energy, where the clathrate hydrate has lower energy compared to accompanying liquid water and gas mixture [1]. Due to the limitation of guest molecule sizes, hydrate formation process is nominated for gas separation [2]. Especial attention is made in separation of CO<sub>2</sub> from N<sub>2</sub> for CCS application [3-7]. However, as the hydrate formation process is a thermodynamically driven process, pressure and temperature of process are playing an important role. The hydrate, liquid water and flue gas equilibrium phase in the absence of chemical occurs at moderate to high pressures (1.5-22.0 MPa) and low temperatures (4-10 °C) [8], meanwhile flue gas exist nearly at atmospheric pressure and temperatures much higher than the flue gas hydrate equilibrium phase boundary. Utilization of gas hydrate process in such condition is required lots of compression

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power and cooling duty and consequently increasing the process cost. Therefore, it was recommended to utilize promoters to shift the hydrate equilibrium boundary to higher temperature/lower pressure condition. The water soluble organic solvents, such as acetone, Tetrahydrofuran (THF) and 1,4-dioxane are good candidates for such application [9]. Presence of these additives in the mixture could increase the equilibrium temperature of gas hydrate at a certain pressure. This stabilization effect on hydrate formation was found to be the highest for THF solution [10]. THF is completely miscible with water and can easily access to hydrate cavities due to the existence of oxygen atom. Thus, THF occupies all the large cages of sII at atmospheric pressure. Later, many researchers have used THF as a promoter for different systems. The most studied systems are  $\text{CO}_2 + \text{THF} + \text{water}$  [11-20],  $\text{CO}_2 + \text{H}_2 + \text{THF} + \text{water}$  system [21-24] and  $\text{CO}_2 + \text{N}_2 + \text{THF} + \text{water}$  system [24, 25]. As mentioned before, these systems are especially interested for CCS applications in capturing  $\text{CO}_2$  from flue and fuel gas streams in post combustion and pre-combustion capturing scenarios respectively. However, utilization of hydrate formation process for capturing  $\text{CO}_2$  is not limited to these scenarios. Non-conventional resource of fuel gas, such as biogas, mainly landfill gas [26] or high  $\text{CO}_2$  content natural gas [27] are also have appreciable  $\text{CO}_2$ -content. Capturing  $\text{CO}_2$  is an essential stage of both gas treatment and CCS application. But as the amount of  $\text{CO}_2$  in these gas mixtures are normally more than 40%, normal gas treatment processes cannot be used for such system. Gas hydrate process can be used for such condition also. However, equilibrium data for  $\text{CH}_4 + \text{CO}_2 + \text{THF} + \text{water}$  is very limited [20]. Lee et al. [28] suggested the hydrate formation in production of landfill gas (LFGH) process recently and studied the equilibrium condition of  $\text{CO}_2 + \text{CH}_4 + \text{N}_2$  in the presence of THF for such application. There is no hydrate equilibrium data for  $\text{CH}_4 + \text{CO}_2 + \text{THF} + \text{water}$  system containing high concentration of  $\text{CO}_2$  in the open literature. In this work, hydrate, gas and liquid equilibrium for this system is experimentally measured.

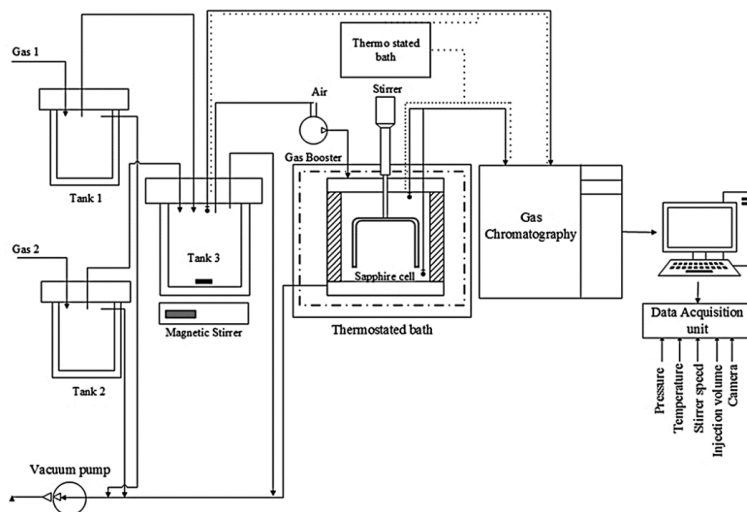
## 2. Methodology

The chemical used in this work is presented in Table 1. All gases are used without further purification. Deionized water is used in all experiments. Deionized water was produced and purified with RO membrane TKA-LabTower from Thermo Scientific. The Resistivity of produced deionized water was 18 M $\Omega$ .

**Table 1:** Chemical used in this work

No	Chemical	Supplier	Purity
1	Methane	Gas Walker Sdn Bhd	99.995%
2	Carbon dioxide	Gas Walker Sdn Bhd	99.95%
3	Tetrahydrofuran	Merck Chemical	99 %

The schematic diagram of experimental equipment used in this study is shown in Figure 1. The setup consists of a constant-volume sapphire cell with an internal volume of 60 cm<sup>3</sup>. Pressure transducer (model PAA-33X/80794) and platinum resistance (Pt-100 $\Omega$ ) thermometer probes are used to measure pressure and temperature inside the equilibrium cell. Pressure, temperature, and volume are measured and recorded continuously in 2 s interval with an accuracy of  $\pm 0.1$  K,  $\pm 0.01$  MPa, and  $\pm 0.001$  cm<sup>3</sup>, respectively. The cell is immersed in thermostatic bath with Lauda thermostats to control the temperature. A magnetic stirrer with a 2000 rpm motor is placed inside the equilibrium cell. This equipment is described in more details by Sabil et al. [29].



**Figure 1.** Schematic diagram of experimental apparatus [29].

A standard T-cycle with step heating technique isochoric process is employed in this work. At the beginning of each run, the sapphire cell is washed with deionized water, dried, and vacuumed. The cell is charged with 25 cm<sup>3</sup> of 3 mole% THF solution. The gases are mixed with each other at ratio of 70 mol% CO<sub>2</sub> and 30 mol% CH<sub>4</sub> in the Tank 3. The mixing is based on PVT calculation and the non-ideality of gases are calculated by Peng and Robinson equation of state [30]. The mixed gas was sent to gas chromatograph for confirmation of concentration. The cell was pressurized by mixed gas through gas booster to the experiment pressure. To achieve uniform temperature condition inside the cell stirrer, mixture is stirred at 500 rpm. Then, the temperature of the system is reduced to 5 °C and held until gas hydrate is formed. Once the hydrate is fully formed and pressure stabilized, the cell is heated up by increasing the temperature of the system with a stepwise method of 0.5 K/step. The length of each step varies between (2 to 4) hours maximum based on the stability of pressure and temperature. The hydrate equilibrium point is achieved when the last particle of hydrate is completely dissociated. On a P-T diagram, this point is taken at the first point where the heating curve meets with the cooling curve.

### 3. Results Discussion

The accuracy of the experimental apparatus and procedures adapted in this work was verified previously by Sabil et al. [29]. Therefore, the same method is used for performing the experiments. The 7/3 ration of CO<sub>2</sub>/CH<sub>4</sub> is selected based on the composition of the Malaysian K5 Field sour gas reservoir located offshore of Sarawak. The Hydrate- Liquid- Vapor (H-L<sub>w</sub>-V) equilibrium data of CH<sub>4</sub> + CO<sub>2</sub> + THF + water system are reported in Table 2.

**Table 2:** H-L<sub>w</sub>-V equilibrium of CH<sub>4</sub> + CO<sub>2</sub> + THF + water system

Temperature (K)	Pressure (MPa)
294.95	4.53
295.35	5.02
295.75	5.77
297.35	7.94
297.75	7.98
297.95	8.11

Figure 2 shows the comparison between the H-L<sub>w</sub>-V of this system with the equilibrium data reported by Sabil et al. for CH<sub>4</sub> + CO<sub>2</sub> + water system [29]. The water free concentration of gas mixture reported by Sabil et al. [29] is 72.49 mol% CO<sub>2</sub> and 27.51 mol% CH<sub>4</sub>. As shown in Figure 2, the presence of THF in the mixture increases the equilibrium temperature around 10 °C at constant pressure. It should be noticed that CH<sub>4</sub> and CO<sub>2</sub> mixture are forming structure I gas hydrate. However, THF can only occupy the large cavities of structure II. Therefore, presence of THF in the solution is changing the structure from structure sI to structure sII. The occupancy of large cavities of structure sII with THF molecules is resulted in more stable structure. Consequently, the mixed gas hydrate is forming at higher temperature. This behavior is also reported for CO<sub>2</sub> + THF and CH<sub>4</sub>+ THF hydrate as well [20]. These data are also presented in Figure 2. As it is also illustrated in this figure, the impact of THF on CH<sub>4</sub> hydrate is more significant compared to CO<sub>2</sub> hydrate. This behavior is very important for utilization of THF as a promoter for selective capturing of CH<sub>4</sub> from this gas mixture. As mentioned before, according to the size ratio between THF molecules and cavity sizes, the large cavities of structure sII is the only possible cavity for THF molecules to occupy. Therefore, in the presence of THF, only structure sII hydrate can be formed. The suitable size of methane molecules let them to occupy both small and large cavities of sII hydrate. Nevertheless, CO<sub>2</sub> molecules are slightly big for small cavities of structure sII and they prefer to fill the large cavities. Therefore, in the presence of THF, the CH<sub>4</sub> hydrate is more stable and the hydrate equilibrium line of CH<sub>4</sub> + THF hydrate is shifted more towards the higher temperatures. On the other hand, CO<sub>2</sub> molecules have to combat with THF molecules for occupying the large cavities of structure sII. Comparing the hydrate equilibrium line of CO<sub>2</sub> + CH<sub>4</sub> with CO<sub>2</sub> and CH<sub>4</sub> hydrates indicated that in the presence of THF, the equilibrium temperature of mixed CO<sub>2</sub> and CH<sub>4</sub> hydrate is more similar to CH<sub>4</sub> hydrate. This means that the captured gas composition is also affected by the presence of THF in the system. Further investigations are required to study this impact of THF.

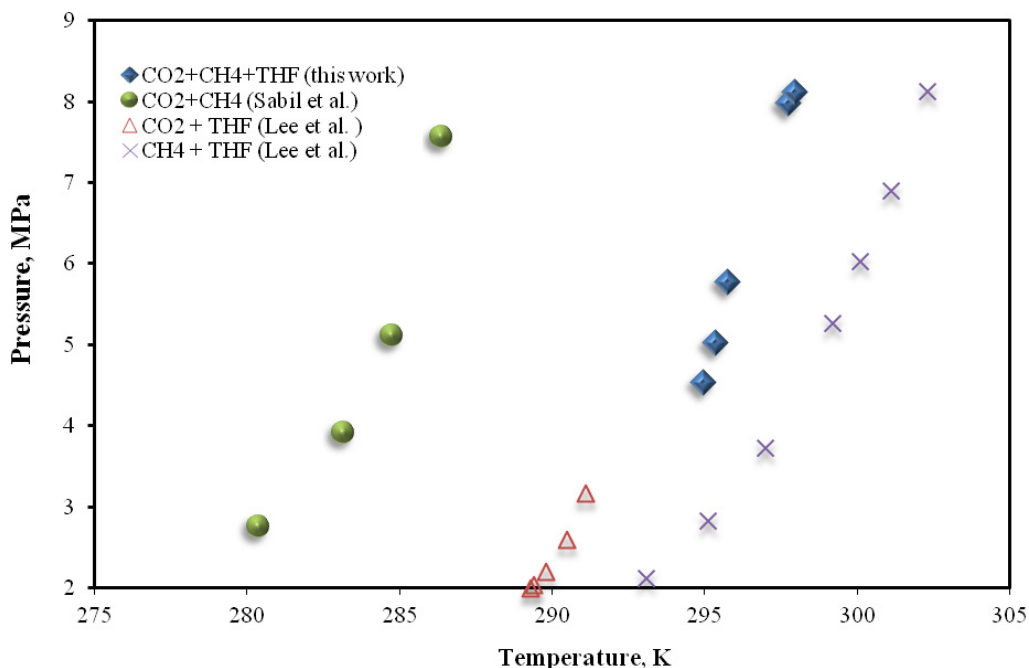


Figure 2. Phase boundary of CH<sub>4</sub> and CO<sub>2</sub> hydrates in the presence of 3 mol% THF aqueous solution.

#### 4. Conclusion and Recommendations

In this work new experimental hydrate equilibrium H–L<sub>w</sub>–V data for system of THF + CO<sub>2</sub> + CH<sub>4</sub> + water has been reported. Results indicated that presence of THF can increase the temperature of the hydrate phase boundary of CO<sub>2</sub> + CH<sub>4</sub> hydrate approximately by about 10 °C toward right as a particular pressure. This effect is very favorable for introducing hydrate based process for separation of CO<sub>2</sub> from CH<sub>4</sub>/ CO<sub>2</sub>. However, presence of THF is also changing the formed hydrate structure from structure I to structure II. Therefore, it is recommended to extend this work to understand the kinetic of hydrate formation and cage occupancy analysis for rich CH<sub>4</sub>/ CO<sub>2</sub> systems.

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