



Recovery of CH₄ from coal mine model gas mixture (CH₄/N₂) by hydrate crystallization in the presence of cyclopentane

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HIGHLIGHTS

- ▶ Cyclopentane is confirmed to be an effective promoter for CH₄ separation.
- ▶ The hydrate equilibrium data in the presence of cyclopentane are reported.
- ▶ The effect of cyclopentane concentration on methane recovery is investigated.
- ▶ Nitrogen competes with methane to enter hydrate crystals at a higher overpressure.

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ABSTRACT

This work presents how water containing cyclopentane (CP) can facilitate the recovery of methane from the CH₄/N₂ coal mine gas mixture through hydrate crystallization. Gas hydrate formed in the CH₄/N₂/CP/H₂O system has more favorable equilibrium conditions than that formed in pure water with the same gas mixture. The incipient equilibrium conditions at 4.0 and 13.0 wt% CP were measured and are reported. The dynamics of hydrate formation using a 30 mol% CH₄/N₂ gas mixture were studied at 283.4 K, two CP concentrations (4.0 and 13.0 wt%) and at 2.6 and 3.8 MPa. These hydrate formation pressures correspond to 2.3 and 3.5 MPa overpressures (driving forces) respectively. It was found that CH₄ is preferentially incorporated into the hydrate crystal compared to N₂. However, N₂ competes with CH₄ to enter the hydrate crystal at the higher driving force. The CH₄ recovery substantially increases as the CP concentration is increased from 4.0 to 13.0 wt%. The experimental condition of 283.4 K, 2.6 MPa, and 13.0 wt% CP is preferred for the separation of CH₄ from the 30 mol% CH₄/N₂ gas mixture. The CH₄ recovery obtained at this condition is approximately 46.1% and the corresponding CH₄ content in the hydrate is 47.2 mol%. A methane-rich stream (72 mol% CH₄/N₂) is obtained after two stages of gas hydrate formation in the presence of cyclopentane.

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1. Introduction

Coal mine methane (CMM) gas is a mixture of coal mine methane and air, which emits continuously from coal mines [1]. The concentration of CH₄ in this mixture is approximately in the range 30–50 mol%, that of O₂ is around 10 mol% and the balance is N₂. Methane is found to be a contributing factor in underground coal mine explosions. The recovery of methane from such mixtures is a desire to promote safety, reduce emission of greenhouse gases, and provide an additional source of energy [2,3].

Recently, significant progress has been made in gas hydrate separation technology to capture CO₂ from flue gas or fuel gas [4–8], recover SF₆ [9], or separate noble gases (Ar, Kr, Xe) from air [10]. Gas hydrate crystallization is a potentially low-cost method for methane separation from the CH₄/N₂/O₂ mixture when a small amount of a suitable additive like tetrahydrofuran (THF) is added to reduce the incipient equilibrium hydrate formation pressure (thermodynamic promoter). The lower formation pressure reduces the gas compression cost of the hydrate-based separation method [8,11]. An alternative way to carry out the process is to use tetra-*n*-butyl ammonium bromide (TBAB) instead of THF [12,13]. Zhong and Englezos [13] presented a conceptual process that employs TBAB with simulated low-concentration CMM gas (30 mol% CH₄/N₂) and produced a methane-rich stream (70 mol% CH₄/N₂) after two stages of hydrate formation. Simulated gas is used because

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the hydrate formation conditions of O₂ and N₂ hydrate are close [14], and hence it is assumed that the mixture contains only N₂. However, the CH₄ recovery of this process is relatively low and thus an additive is needed that will not only reduce the hydrate formation pressure but will also capture CH₄ from CMM gas more effectively.

Cyclopentane (CP) is a suitable candidate to be investigated because it is an effective thermodynamic promoter. The phase equilibrium pressure of gas hydrates (CH₄, CO₂, N₂, etc.) formed at a given temperature in the presence of cyclopentane is greatly reduced compared to those obtained in pure water and in the presence of TBAB [15–17]. Therefore, gas hydrates formed in the presence of CP are stable at lower pressures and higher temperatures, which are commercially viable conditions for the gas hydrate separation technology. In addition, cyclopentane is relatively inexpensive and is much cheaper than TBAB and THF. Therefore, in this work, we selected cyclopentane as a desired promoter for methane separation from CMM gas (30 mol% CH₄/N₂) by gas hydrate crystallization. The purpose of this work is to investigate how water containing cyclopentane (CP) can facilitate the recovery of methane from the CH₄/N₂ coal mine gas mixture through hydrate crystallization. First, the four phase equilibria of the hydrate (solid)/aqueous liquid/CP (liquid)/vapor system containing CH₄, N₂, CP, and water were determined. Subsequently, the separation of CH₄ from the 30 mol% CH₄/N₂ gas mixture by hydrate formation in a semi-batch crystallizer was assessed at different CP concentrations and overpressures (driving force).

2. Experimental section

2.1. Materials

The CH₄/N₂ gas mixture (30 mol% CH₄/70 mol% N₂) used was ultra high purity (UHP) grade and was supplied by Praxair Technology Inc. Cyclopentane (CP) was supplied by Acros Organics (catalog number: AC11148-0010) with a certified mass purity of 99.0%. Deionized water was used in all experiments.

2.2. Apparatus and procedures

The apparatus (Apparatus #1) used for the measurement of incipient equilibrium hydrate formation conditions was described elsewhere [18]. The isothermal pressure search method to determine the incipient equilibrium hydrate formation pressure at a given temperature was employed in this work [19]. The phase equilibrium data are necessary for the design of the separation process (selection of operating conditions). Since there were no gas hydrate phase equilibrium data for CMM gas in the presence of cyclopentane available in the literature the incipient equilibrium data of such system were determined first.

Another apparatus (Apparatus #2) was used to carry out gas hydrate formation (kinetic) experiments to assess the separation of CH₄ from the 30 mol% CH₄/N₂ gas mixture. Apparatus #2 is described by Daraboina et al. [20]. Briefly, the experiments were conducted as follows [13]. The crystallizer (CR) was filled with 20 cm³ water and 4 cm³ CP (13.0 wt%) or 1 cm³ CP (4.0 wt%) and purged three times with the 30 mol% CH₄/N₂ gas mixture to remove the air remaining in the system. Once the temperatures of the gas and liquid phase reached the desired values the crystallizer was pressurized with the CH₄/N₂ gas mixture. Then the magnetic stirrer was started at a constant speed (400 rpm) and the data acquisition system was initiated to collect and record the temperatures of the gas and liquid phase (T_{gas} , T_{liq}) and the pressure of the gas phase. This is time zero for the experiments. The crystallizer was connected with the reservoir (R) and maintained at a constant

temperature and pressure during the formation process of hydrate crystals. Thus, a continuous supply of the 30 mol% CH₄/N₂ gas mixture was provided to the crystallizer. The experiments were kept running for approximately 20 h. The composition of the gas phase at the end of the experiments was measured using a Varian CP-3800 gas chromatograph (GC). Then the crystallizer was quickly vented to atmospheric pressure and the hydrate was dissociated. The composition of the gas mixture released from the hydrate was also measured with GC.

2.3. Calculation of the amount of gas mixture for hydrate formation

Because hydrate crystallization is an exothermic process, the nucleation point can be detected by a sudden temperature rise in the water or gas phase. This point coincides with a sudden increase in gas consumption. The time it takes for the onset of nucleation is the induction time (t_{ind}) [21]. The number of moles of the CH₄/N₂ gas mixture consumed for gas hydrate formation (Δn_{H}) is calculated as follows:

$$\Delta n_{\text{H}} = n_{\text{g},0} - n_{\text{g},t} = \left(\frac{PV}{zRT}\right)_{\text{CR},0} - \left(\frac{PV}{zRT}\right)_{\text{CR},t} + \left(\frac{PV}{zRT}\right)_{\text{R},0} - \left(\frac{PV}{zRT}\right)_{\text{R},t} \quad (1)$$

where n_{g} is the number of moles of gas mixture in the crystallizer (CR) and reservoir (R) at time 0 and time t , z is the compressibility factor calculated by Pitzer's correlation [22], and V is the volume of gas phase in the crystallizer and the volume of reservoir.

Subsequently, moles of the gas mixture consumed at nucleation point can be obtained when the induction time is determined. Rate of hydrate growth (R_{f}) is defined as the gas consumption rate for the first 30 min after hydrate nucleation, which is calculated by Eq. (2). The final gas consumed is defined as the gas consumption per mole of water at the end of the experiments, and calculated by Eq. (3).

$$R_{\text{f}} = \frac{\Delta n_{\text{H}}|_{t_{\text{ind}}+30 \text{ min}} - \Delta n_{\text{H}}|_{t_{\text{ind}}}}{t|_{=30 \text{ min}}} \quad (2)$$

$$\text{final gas consumption} = \frac{\Delta n_{\text{H}}}{n_{\text{H}_2\text{O}}} \quad (3)$$

where $n_{\text{H}_2\text{O}}$ is the number of moles of water added into the reactor.

The CH₄ recovery or split fraction of methane from the mixture, and the separation factor (SF) are determined by the following equations [23,13]:

$$\text{CH}_4 \text{ recovery} = \frac{n_{\text{CH}_4}^{\text{H}}}{n_{\text{CH}_4}^{\text{feed}}} \times 100\% \quad (4)$$

$$SF = \frac{n_{\text{CH}_4}^{\text{H}} \times n_{\text{N}_2}^{\text{gas}}}{n_{\text{N}_2}^{\text{H}} \times n_{\text{CH}_4}^{\text{gas}}} \quad (5)$$

where $n_{\text{CH}_4}^{\text{feed}}$ is defined as the moles of CH₄ in feed gas, $n_{\text{CH}_4}^{\text{H}}$ is the moles of CH₄ captured in the hydrate at the end of experiments, $n_{\text{CH}_4}^{\text{gas}}$ is the moles of CH₄ in the gas phase at the end of the kinetic experiment, $n_{\text{N}_2}^{\text{gas}}$ is the moles of N₂ in the gas phase at the end of the kinetic experiment, and $n_{\text{N}_2}^{\text{H}}$ is the moles of N₂ incorporated into the hydrate.

3. Results and discussion

3.1. Incipient equilibrium hydrate formation conditions for the CH₄/N₂/CP/H₂O system

Galfre et al. [17] reported equilibrium points for CO₂/CP hydrate formed at 5.0 and 20.0 vol% CP and found that CP remarkably

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