

Research Article

CH₄ Separation from Coal Bed Methane by Hydrate in the SDS and THF Solution

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Hydrate-based separation experiments on simulate coal bed methane gas have been conducted in THF solution and SDS solution. In this work, a novel hydrate-based gas separation process was used to enhance CH₄ separation from a 65.7% CH₄/20.2% N₂/O₂ gas mixture in the presence of 300 ppm SDS and 19% THF solution. The characteristics of the CH₄ separation efficiency, fluctuation of temperature, and pressure were studied at different promoter solution. It was found that hydrate formation was induced by promoter in the solution and occurred immediately as the experiments were started. THF performed better than SDS for CH₄ separation from the CH₄/N₂/O₂ gas mixture. In particular, the separation coefficients of CH₄ and N₂ were compared in two solutions. The gas mixture S.Fr. or CH₄ recovery is increased from 1.056 to 1.259 while SF of N₂ is decreased from 1.183 to 0.634 in THF solution.

1. Introduction

Coal bed methane (CBM) is an unconventional natural gas and usually mixed with air during the process of coal mining gas drainage [1]. It can be recovered as a supplementary energy resource because it exists abundantly in coal mines [2–4]. However, it is hard to utilize the CBM gas as low concentration of methane. Methane separation is recognized as a possible way to use the low-concentration CBM gas mixture. This method can also mitigate global warming and climate change because CH₄ is a stronger greenhouse gas than CO₂. Recently, gas hydrate formation has been employed for CH₄ separation from the low-concentration CBM gas mixture in experimental studies [5, 6].

Gas hydrates (clathrate hydrates) are crystalline solid structures consisting of water and small molecules such as CO₂, N₂, CH₄, and H₂, which are formed under certain thermodynamic conditions [7, 8]. When a gas mixture forms hydrate with water, the concentration of each gas in the hydrate phase and that in the exhaust vapor phase will be different. The gas that forms hydrate more easily can be enriched in the hydrate phase. Hydrate-based gas separation

(HBGS) is one of the novel and promising technologies for gas separation from gas mixture [9, 10]. The basis for separation is the selective partition of gas component such as CH₄ or CO₂ between the hydrate phase and the gaseous phase upon hydrate formation. When gas mixture contacts water at a suitable temperature and pressure to form hydrates, the hydrate phase is enriched with CH₄ or CO₂. So it is considered possible to separate gas mixtures by forming hydrate. Hydrate-based gas separation concepts have been proposed for many fields: (1) recovering sulfur hexafluoride (SF₆) from nitrogen and CO₂ and H₂S from flue gas; (2) recovering hydrogen from hydrogen-containing light hydrocarbon gas mixtures; and (3) recovering methane from low-concentration coal mine methane. The hydrate-based gas separation is more effective and has many advantages over conventional separation methods, such as cryogenic fractionation, selective adsorption, gas absorption, and membrane process.

The high-pressure requirement for hydrate formation is one of the decisive obstacles to commercialize the hydrate-based separation process. To solve this inherent problem and to compete with other conventional methods, some

hydrate promoters, such as SDS (sodium dodecyl sulfonate), THF (tetrahydrofuran), TBAB (tetra-*n*-butyl ammonium bromide), and CP (cyclopentane) [11–16] which remarkably reduce the required hydrate formation pressure, have been used as additives, without compromising the separation efficiency or gas recovery of the process. According to Zhang et al. [17], CP has a potential to be a better thermodynamic promoter than THF for a hydrate-based precombustion CO₂ capture. To remove H₂S from biogas, Kamata et al. [18] have conducted separation experiments using TBAB semiclathrate hydrate. Among all of the additives mentioned above, SDS and THF are widely used as promoters. Even if these additives are used, N₂ will inevitably enter the hydrate cage, which leads to a low separation efficiency. In this study, separation effect, temperature, and pressure changes were analyzed during hydrate formation in SDS and THF solution. In particular, the separation coefficients of CH₄ and N₂ were compared in two solutions as N₂ will directly affect the separation efficiency of methane in CBM gas mixture.

2. Experiment

2.1. Materials. Experimental mixed gas was prepared in proportion by standard gas and compressed air. The volume of the gas component is CH₄: 65.7%, N₂: 20.2%, O₂: 13.3%, and CO₂: 0.8%. Purity of the THF is more than 99% which is prepared as the solution in the quality proportion of 19:81 (19%) with water (i.e., the best theoretical molar ratio of THF hydrate THF:H₂O = 1:17). The purity of sodium dodecyl sulfate (SDS) is more than 99% and is prepared to the 300 ppm (mg/L) water solution. Distilled water was used for preparing the aqueous solution that was boiled for half an hour to expel the dissolved air.

Gas mixture was supplied by Beijing AP BAIF Gases Industry Co., Ltd., which was used for hydrate formation with distilled water and additives. All chemicals were used as received. All other chemicals were used without further purification.

2.2. Apparatus and Procedure. The type of hydrate experimental device is PW30-14 Test Bed for hydrate formation which was designed by Taiyuan University of Technology. The experimental device includes pressure supply system, constant temperature bath system, cyclic reaction system, and measurement test system, as shown in Figure 1. The details of the system are as follows:

- (1) Pressure supplying system mainly includes gas cylinder 1, buffer tank 2, plunger pump 3, pressure transmitter, and electrical control modules. The experimental gas flows from the gas cylinder 1 to the buffer tank 2 and then is pressurized by the plunger pump 3 with flow rate of 60 L/h.
- (2) Low temperature bath system includes refrigerator, bath, circulating pump 4, and control valve. The temperature of bath is controlled by cooling system in bath 5. A circulation pump 4 is installed in bath to reduce temperature fluctuations.
- (3) Cyclic reaction system consists of two sections: low-temperature high-pressure reactor 6 and fluids circulating pump 7. The maximum working pressure of the reactor is 30 MPa (internal size of $\Phi 150 \times 800$ mm and thickness of 30 mm). The flow rate of the circulating pump is 36 L/h.

TCD detector of Shimadzu GC-17A gas chromatograph is used to monitor the feed gas. The gas is injected from the last six-way valve. Reactor pressure is measured by a piezoresistive pressure transmitter with range of 0.01–100 MPa and with accuracy of $\pm 0.25\%$ FS (full scale). Temperature is measured by the metal platinum resistance.

2.3. Experimental Method. Constant volume reaction mode was used in which the fixed volume solution (2.0 L) was injected into the reactor. The gas phase volume of the reaction was kept constant during the hydrate formation reaction process. As the hydrate formed, the gas was converted into hydrate, which causes the pressure drop of the reactor. Detailed experimental procedures are as follows:

- (1) Reactor was washed by the distilled water and then purged with the experimental gas about 3 min. Experimental gas mixture was added to the reactor by pressure gas supplying system until the initial setting pressure was achieved (6.0 MPa in SDS solution and 2.3 MPa for THF solution; at this time according to the hydrate phase equilibrium condition, the two solution systems have the same pressure difference (the reaction driving force) with the phase equilibrium pressure in 275.8 K).
- (2) The refrigeration system was opened and the liquid of the bath was cooled to the experimental setting temperature and keeping about 30 min. Experimental accelerator solution is also placed in the bath to maintain consistency with the experimental setting temperature. Reaction temperature was set to be 275.8 K in the low temperature bath.
- (3) Cooled solution is injected into the reactor by the circulation pump 7. And then the solution was circulated in the reactor. The solution was drawn from the bottom of the reactor and then was injected into the reactor gas phase.
- (4) Temperature and pressure in the reactor were recorded on time. Gas concentrations of each component were monitored every 40 min in the reactor. The dissociation gas after hydrate decomposition was collected and analyzed by chromatography.

3. Discussions

3.1. Hydrate Experiment in SDS Solution. SDS is an anionic surface active agent which is recognized as a good accelerator of hydrate formation. It promotes hydrate formation by increasing water surface tension. A large number of experiments have confirmed that SDS solution in 300 ppm has the best effect for promotion of hydrate formation. The gas

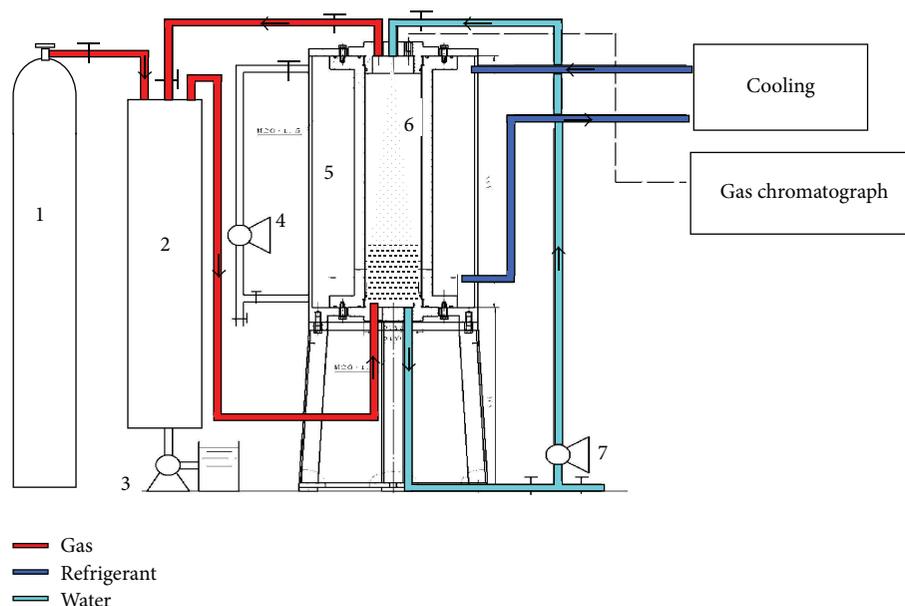


FIGURE 1: Process flow diagram hydrate formation experiment device.

mixture of 65.7% CH₄ concentration was selected to analyze change of content and the pressure of phase equilibrium during the hydrate formation of coal bed methane gas by the SDS solution. The concentration of the gas component is CH₄: 65.7%, N₂: 20.2%, O₂: 13.3%, and CO₂: 0.8%. The initial pressure of hydrate formation was set to be 6.0 MPa in SDS solution.

Temperature and pressure of the two stages in the reactor are shown in Figure 2. At the beginning of reaction, temperature fluctuated greatly and then continued to reach 275.5 K–278.3 K. The pressure in the reactor began to drop with the reaction and the pressure drop rate was sped up in this stage. This stage lasts about 350 min. The change of temperature and pressure became slower in the later stage. The temperature of reactor changed from 276.5 K to 277.5 K in the second stage within the cyclic reaction. Pressure also declined and was maintained at 5.5 MPa until the end of reaction. It is indicated that there was no more hydrate formatted.

The concentrations of various gas are shown in Figure 3 in gas phase of reactor during the process of SDS solution hydrate formation. The final concentrations of each feed gas are CH₄: 57.2%, N₂: 19.2%, O₂: 23.4%, and CO₂: 0.2% in the gas phase. The concentration of CH₄ decreases 8.5%; the concentration of N₂ decreases 1.0%, and the concentration of CO₂ decreases 0.6% while the concentration of O₂ increases 10.1% during the hydrate formation process. At the same time, the analysis results of each component in the gas hydrate are CH₄: 69.4%, N₂: 23.9%, and O₂: 4.1%. It can be seen from comparison that concentration of N₂ in the hydrates is not reduced but increased about 3.7% which indicates that part of N₂ participates in the hydrate reaction and transforms into hydrate. The concentration of CH₄ rises only from 65.7% up to 69.4%. So hydrate separation efficiency is not too good in economic and technology factor by adding SDS solution.

Linga et al. [19] introduced two metrics, namely, *separation factor* (SF) and *CO₂ recovery* or *split fraction* (S.Fr.).

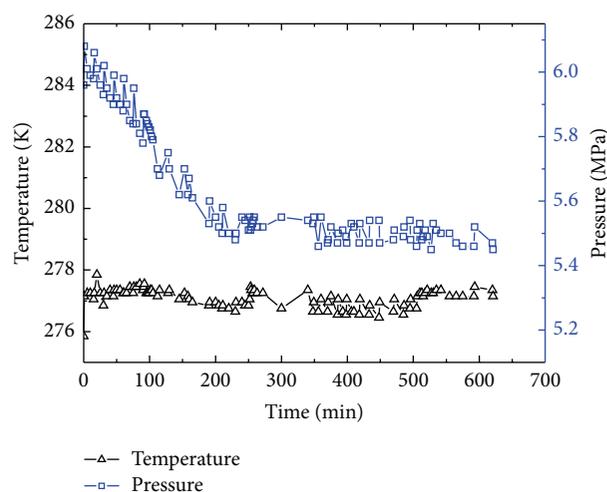


FIGURE 2: Temperature and pressure of hydrate formation in SDS solution.

Separation factor is equivalent to the term selectivity used in traditional separation processes. According to their methods CH₄ recovery or split fraction (S.Fr.) is defined as

$$\text{S.Fr. or CH}_4 \text{ recovery} = \frac{n_{\text{CH}_4}^{\text{H}}}{n_{\text{CH}_4}^{\text{Feed}}}, \quad (1)$$

where $n_{\text{CH}_4}^{\text{H}}$ and $n_{\text{CH}_4}^{\text{Feed}}$ are the number of moles of CH₄ in hydrate and feed gas. And SF of CH₄ is 1.056 in SDS solution.

Accordingly, the N₂ entrainment or split fraction (S.Fr.) is defined as

$$\text{S.Fr. or N}_2 \text{ recovery} = \frac{n_{\text{N}_2}^{\text{H}}}{n_{\text{N}_2}^{\text{Feed}}}, \quad (2)$$

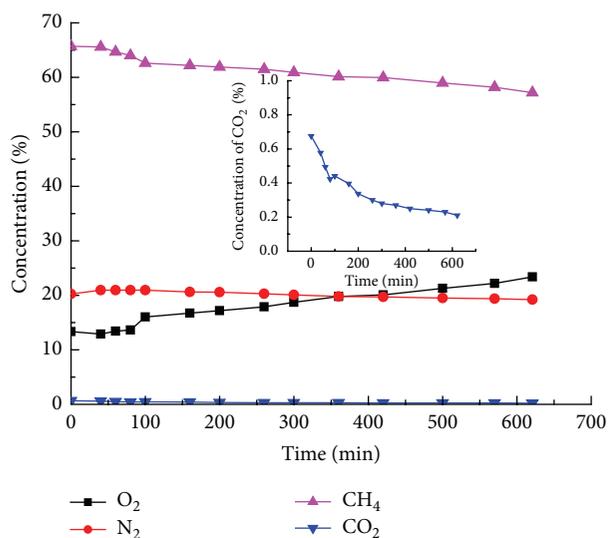


FIGURE 3: Gas concentration of hydrate formation in SDS solution.

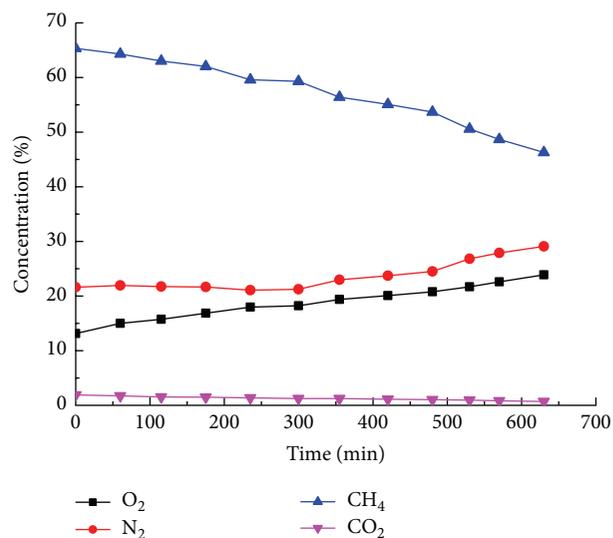


FIGURE 5: Gas concentration of hydrate formation in THF solution.

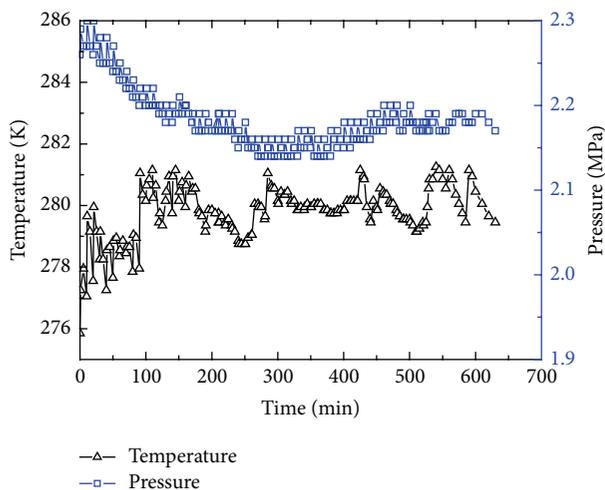


FIGURE 4: Temperature and pressure of hydrate formation in THF solution.

where $n_{N_2}^H$ and $n_{N_2}^{Feed}$ are the number of moles of N_2 in hydrate and feed gas. And SF of N_2 is 1.183 in SDS solution.

3.2. Hydrate Experiment in THF Solution. THF is a water soluble polymer and itself can generate hydrate. When THF solution formed hydrate with gas it can reduce the phase equilibrium pressure of gas hydrate. Different promotion mechanism determines the difference in reaction characteristics from SDS solution. The temperature and pressure of gas hydrate formation process in THF solution were shown in Figure 4. The temperature fluctuation of THF solution is more obvious than that of the SDS solution, because SDS makes the gas-liquid interface more adequate and uniform during the process of promoting reaction. The temperature in the reactor is always fluctuating between 279.15 K and 281.15 K. This change was greater than that in the SDS solution.

But the reaction rate at 2.3 MPa in THF solution is not inferior to the SDS solution at 6.0 MPa from the fluctuation of the temperature and pressure. So THF solution can effectively reduce the hydrate formation pressure. Temperature fluctuations are frequent until the end of the hydrate reaction.

The final concentrations of each gas are CH_4 : 46.3%, N_2 : 29.1%, O_2 : 23.9%, and CO_2 : 0.4% in the gas phase. The concentration of CH_4 decreases 19.4%, the concentration of N_2 increases 8.9%, and the concentration of CO_2 decreases 0.4% while the concentration of O_2 increases 10.6% during the hydrate formation process. At the same time, the analysis results of each component in the gas hydrate are CH_4 : 82.7%, N_2 : 12.8%, and O_2 : 3.2%. It can be seen from comparison that concentration of N_2 in the hydrates reduced 16.3%. The concentration of CH_4 rises from 65.7% up to 82.7%. So hydrate separation efficiency is better in THF solution than SDS solution. The concentration changes with time as shown in Figure 5. The decrease rate and the value of CH_4 concentration were significantly higher than those in the SDS solution. The concentration of N_2 was obviously increased during the process of hydrate formation. The gas mixture S.Fr. or CH_4 recovery is 1.259 and SF of N_2 is 0.634 in THF solution.

Details of the each gas content are shown in Figure 6 during the hydrate formation process in SDS (a) and THF (b) solution. From Figure 6 the most obvious difference is that the content of N_2 was decreased in SDS solution while it was increased in THF solution. And then the decrease of CH_4 content in THF solution is bigger than that in the SDS solution. The change of O_2 and CO_2 content is not obvious in two kinds of solution. THF solution for separation effect of CH_4 was better than SDS solution.

The results presented in Figure 6 indicate that the separation of CH_4 from a $CH_4/N_2/O_2$ gas mixture is greatly enhanced by the THF solution in this study. The gas mixture S.Fr. or CH_4 recovery is increased from 1.056 to 1.259 while SF of N_2 is decreased from 1.183 to 0.634 in THF solution.

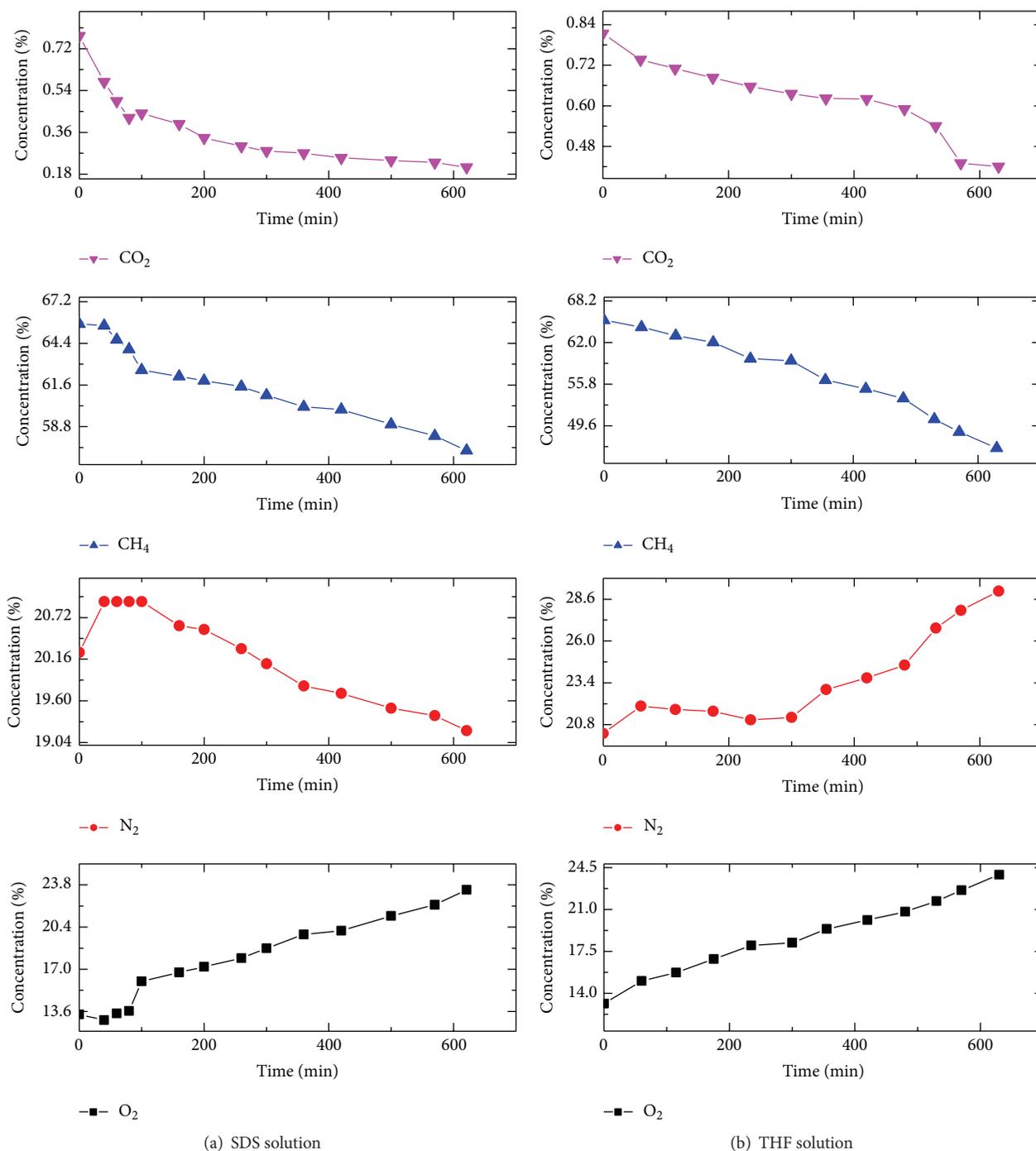


FIGURE 6: Gas concentration of hydrate formation in SDS and THF solution.

Therefore, gas hydrate formation coupled with other chemical promoters such as THF might become a promising method for increasing the CH₄ separation efficiency from CH₄/N₂/O₂ gas mixtures in the near future.

4. Conclusions

In this work, a novel hydrate-based gas separation process was used to enhance CH₄ separation from a 65.7 mol%

CH₄/20.3 mol% N₂/O₂ gas mixture in the presence of 300 ppm SDS and 19% THF solution. The characteristics of the CH₄ separation efficiency, fluctuation of temperature, and pressure were studied at different promoter solution. It was found that hydrate formation was induced by promoter in the solution and occurred immediately as the experiments were started. THF performed better than SDS for CH₄ separation from the CH₄/N₂/O₂ gas mixture. The gas mixture S.Fr. or CH₄ recovery is increased from 1.056 to 1.259

while SF of N_2 is decreased from 1.183 to 0.634 in THF solution.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper. The authors declare no competing financial interest.

Acknowledgments

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