CO₂ Capture from CH₄/CO₂ Mixture Gas with Tetra-n-butylammonium Bromide Semi-clathrate Hydrate through a Pressure Recovery Method

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ABSTRACT: In this study, CO₂ capture from (67.00 mol %) CH₄/CO₂ mixed gas with tetra-n-butylammonium bromide (TBAB) solution at 281.3 K through a pressure recovery of hydrate separation method were studied. During the experiment, pressure was recovered by TBAB solution injected into the cell to improve the separation efficiencies of CO₂ and the effects of the concentration of TBAB solution and the operating conditions was investigated. The results showed that the CH₄ concentration in the gas phase could achieve 93.52 mol % with a pressure recovery method at 1.14 MPa and 0.293 mol % TBAB. Under the pressure of 1.14 MPa and 0.1 mol % TBAB, the maximum CO₂ separation factor was 52.87 and the CH₄ separation and recovery factor was 2.050. The results demonstrated that the pressure recovery method can significant enhance the separation efficiency of hydrate separation. It is an effective method to cut down energy consumption of hydrate-based gas separation.

1. INTRODUCTION

Natural gas is considered to be the cleanest fossil fuel, producing less carbon dioxide (CO₂) than coal or oil. Unconventional natural gases, such as biogas, landfill gas, etc., as the important gas resource have attracted attention as a result of their renewability. However, these gases consist of approximately 15–60 mol % CO₂ and other trace components (e.g., hydrogen sulfide). CO₂ reduces the caloric value of biogas or landfill gas and corrosion of the pipeline. To obtain methane, CO₂ needs to be separated from biogas or landfills. Hydrate-based CO₂ capture (HBCC) technology from gas mixtures was considered as a promising gas separation technology for its low cost and simple operation.

Denderen et al. studied CO₂ removal from contaminated biogas. The concentration of CO₂ reduced from 50 to 39% at 275 K. Although hydrate can be used to purify biogas by equilibrium separation, the selectivity of CO₂ hydration was low, which is the main bottleneck in HBCC from biogas. To overcome the barrier, the use of chemical additives can enhance the hydrate formation kinetics and selectivity of CO₂. For example, sodium dodecyl sulfate (SDS) is an anionic surfactant which can increase the hydrate formation rate. Tetrahydrofuran (THF) and tetra-n-butylammonium bromide (TBAB) can enhance the selectivity of CO₂ hydration and moderate the operating conditions at the same time. TBAB has significantly attracted attention as a hydrate promoter as a result of the fact that it can form hydrates at milder experimental conditions compared to the gas hydrates, where small gas molecules, such as CH₄ and CO₂, can occupy the small cages. Linga et al. reported a high CO₂ capture capacity among all liquid promoters reported thus far and also did a comparison to TBAB as a promoter. In our previous work, CH₄ in the biogas were enriched from 67 to 84% at 278 K and 3 MPa with TBAB solution in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate by one-stage hydrate separation, and the maximum CO₂ separation factor was 10.3.

In several studies for hydrate-based gas separation, separation processes are a batch or semi-batch operation. During a batch process, the pressure of the system will gradually reduce to the equilibrium pressure of hydrate formation with the hydration reaction, resulting in the hydration termination. Zhong et al. designed a semi-batch operation. They connected the crystallizer to their reservoir and kept it at a constant temperature and pressure. They found that the semi-batch operation is more effective than the batch operation for the separation of CH₄ from the 30 mol % CH₄/N₂ gas mixture. A CH₄-rich stream (70 mol % CH₄/N₂) was obtained. Tomita et al. performed continuous gas separation experiments for HBCC from the (40 mol %) CH₄/CO₂ gas mixture. The concentration of CH₄ in the gas phase and CO₂ in the hydrate slurry reached 61 and 76 mol % at the steady state, respectively. However, the bad selectivity of CO₂ is still the major obstacle for HBCC. Pressure reduction during the formation of hydrate crystals was considered as one of the major factors for low HBCC separation efficiency.

In the present paper, a pressure recovery method of HBCC was used for CO₂ capture from the CH₄/CO₂ gas mixture to enhance the selectivity of CO₂. The influences of the operating pressure and TBAB concentration were investigated. The experimental temperature was 281.3 K, and the initial reaction pressures were 1.14 and 3 MPa. The mole fraction of TBAB was fixed at 0.1, 0.293, and 0.9 mol %. A 67.00 mol % CH₄/33.00 mol % CO₂ gas mixture was used to simulate biogas with a high CH₄ content.

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2. EXPERIMENTAL SECTION

2.1. Materials. The gas mixtures containing CH₄ (67.00 mol %) and CO₂ (33.00 mol %) were supplied by Zhaqing Gaoneng Gas Co., Ltd., China. TBAB with a purity of 99% (Guangzhou Jinke Chemical Co., Ltd., China) was weighed on an electronic balance with an uncertainty of ±0.001 g. Distilled water was used to prepare all solutions.

2.2. Apparatus. A schematic diagram of the experimental apparatus employed for gas separation was shown in Figure 1. The stainless-steel reactor (7.5 cm in diameter, with an effective volume of 1000 cm³) equipped with a magnetic stirrer (Haian Scientific Research Apparatus Co., China) was designed to be operated below 20 MPa. The temperature of the reactor was controlled by circulating the coolant from a thermostat (Huber CC1-K20B) with a stability of ±0.01 K. The temperature of the reactor was monitored using two Pt100 resistance thermometers (Westzh WZ-PT100) within 0.1 K accuracy, which are placed in the middle and bottom of the reactor, respectively. A pressure transducer (Westzh CyB-20S) within 0.01 MPa in accuracy measured the pressure of the reactor. The solution of TBAB was introduced into the reactor by a high-pressure metering pump (Alipu JX/12.5) and a transducer (Westzh CyB-20S) within 0.01 MPa in accuracy measured the pressure of the reactor. A gas chromatography (GC, with a KeChuang GC9800TCD detector and Porapak Q packed column) was employed for gas separation was shown in Figure 1. The stainless-steel reactor (7.5 cm in diameter, with an effective volume of 1000 cm³) equipped with a magnetic stirrer (Haian Scientific Research Apparatus Co., China) was designed to be operated below 20 MPa.

2.3. Procedure. All hydrate separation experiments were carried out in the cell at 281.3 K and different initial pressures.

In the pressure recovery experiments (abbreviated as PR), the reactor was cleaned and evacuated and the vessel was purged with the 67 mol % CH₄/CO₂ gas mixture 5 times to ensure no air in the system. The magnetic stirrer stirred with 600 rpm. Then, the cell filled with TBAB solution of a certain concentration (400 or 600 mL) and gas mixture to the desired pressure. The cell cools to 281.3 K, during which time was set as zero for the experiments. During hydrate formation, a continuous supply of TBAB solution was provided. When the pressure decrease rate obviously slows (pressure drop less than 0.5 MPa), TBAB solution is supplied of TBAB solution was provided. When the pressure decrease rate obviously slows (pressure drop less than 0.5 MPa), TBAB solution is supplied.

2.4. Calculation Methods. 2.4.1. Number of Moles of Gas Consumed. The mole number of the gas mixture that formed hydrates (gas uptake, Δn) during the experimental process was calculated by the following equation:

\[
\Delta n = n_0 - n_f = \left( \frac{PV}{RT} \right)_{0} - \left( \frac{PV}{RT} \right)_{f}
\]

where P is the system pressure, T is the absolute temperature, V is the volume of the gas phase, and R is the gas constant. 2.4.2. CH₄ Recovery and CO₂ Separation Factor. The separation factor of CO₂ is calculated as follows:

\[
S = \frac{n_{CO_2}^H}{n_{CO_2}^G} + \frac{n_{CO_2}^H}{n_{CO_2}^G}
\]

where \( n_{CO_2}^G \) and \( n_{CO_2}^H \) are the mole numbers of CO₂ in the gas and hydrate phases at the end of the experiment, respectively, and \( n_{CO_2}^G \) and \( n_{CO_2}^H \) are the mole numbers of CH₄ in the gas and hydrate phases at the end of the experiment, respectively.

To evaluate the separation and recovery effects of CH₄ we defined the separation and recovery factor of CH₄ and calculated as follows:

\[
SR = \frac{x_{CH_4}^G}{x_{CH_4}^H}
\]

where \( x_{CH_4}^G \) is the mole fraction of CH₄ in the gas phase at the end of the experiment and measured by GC, \( x_{CH_4}^H \) is the mole fraction of CH₄ in the hydrate phase at the end of the experiment, and \( R_H \) is the hydration ratio of the mixture gas at the end of the experiment. \( x_{CH_4}^G \) and \( R_H \) are calculated as follows:

\[
x_{CH_4}^H = \frac{n_{CH_4}^H}{n_{CH_4}^G + n_{CO_2}^H}
\]

\[
R_H = \frac{\Delta n}{n_0}
\]

3. RESULTS AND DISCUSSION

3.1. Effects of the Pressure Recovery Method. Table 1 lists the experimental conditions and the results for the hydrate

<table>
<thead>
<tr>
<th>Experiment</th>
<th>P₀ (MPa)</th>
<th>Final gas uptake (mol)</th>
<th>CH₄ fraction in the gas phase (mol %)</th>
<th>CH₄ fraction in the hydrate phase (mol %)</th>
<th>SF CO₂</th>
</tr>
</thead>
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<tr>
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<td>90.38</td>
<td>29.49</td>
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</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.189</td>
<td>87.28</td>
<td>24.67</td>
<td>18.28</td>
</tr>
<tr>
<td>no</td>
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<td>0.072</td>
<td>86.90</td>
<td>15.19</td>
<td>37.04</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.136</td>
<td>80.89</td>
<td>21.89</td>
<td>15.10</td>
</tr>
</tbody>
</table>

formed from the 67 mol % CH₄/CO₂ gas mixture by PR and UPR modes with 0.1 mol % TBAB solution. The feed pressures are 1.14 and 3 MPa, and the initial gas liquid ratio (R₀) is 21.48, which is defined as.
where \( n_0 \) is the number of moles of feed mixed gas and \( V_L \) is the volume of the liquid phase.

As the results of Table 1 show, under the same initial pressure, the final gas uptake and CH\(_4\) fraction in the gas phase at the end of PR experiments are all higher than those of UPR experiments. The separation factor increases from 22.15 for the PR experiment to 37.04 for the UPR experiment at 1.14 MPa. This might due to more CH\(_4\) being captured in the solution for the PR experiment than the UPR experiment. At the initial pressure of 3 MPa, the amount of CH\(_4\) captured by hydrate for the PR experiment than the UPR experiment is similar, and much more CO\(_2\) was captured by hydrate because of CO\(_2\) hydrate selective formation; therefore, the separation factor is lower for UPR compared to PR at 3 MPa but higher at 1.14 MPa.

Figure 2 shows the gas uptake during the PR and UPR experiments at 1.14 and 3.00 MPa. During the pressure unrecovered test, the pressure reduced rapidly at the start, then slowed, and was kept constant after 50 min. The operation of PR can lengthen the hydrate formation period from 50 to 100 min, and the final pressure of PR is higher than that of other pressures. The slope variation of the gas uptake curve is opposite the variation of the pressure and can be divided into three stages. The first stage is the hydrate rapid formation period (0–25 min). The second stage is the period of hydrate formation rate reduction (approximately 50–100 min). The third stage is the period of equilibrium of gas and hydrate phases. The gas uptake and pressure curve is nearly kept horizontal at the third stage, indicating the termination of the hydrate formation. The final gas uptake of pressure recovery experiments improved significantly compared to the reducing pressure experiment, increasing 0.063 mol at 3 MPa. It was worth noting that hydrate cannot form with 0.1 mol % TBAB solution at 1.14 MPa. The results indicated that the pressure recovery method made more gas be captured by hydrate crystals.

Figure 3 shows CH\(_4\) and CO\(_2\) concentrations in the gas phase with time. During the separation process, the CH\(_4\) concentration increased and the CO\(_2\) concentration decreased. The maximum concentration of CH\(_4\) reached 90.38 mol % in 1.14 MPa with PR. In contrast, the maximum CH\(_4\) concentration of UPR is 86.90 mol % at the same pressure. In 3 MPa, the CH\(_4\) concentration increased to 87.28 mol % with PR. The results also demonstrate that more CO\(_2\) was enriched in the hydrate phase and a higher purity of CH\(_4\) was obtained with PR.

3.2. Effects of the TBAB Solution Concentration. TBAB is a structure promoter for gas hydrates. With the help of TBAB, gas and water formed semi-clathrate hydrate. Therefore, the TBAB concentration in the solution will greatly affect the hydrate formation quantity. The results of gas separation with various TBAB concentrations of PR were listed in Table 2. The feed pressures are 1.14 and 3 MPa, and the initial gas liquid ratio is 21.48.

At the same feed pressure, the experiment with 0.293 mol % TBAB obtained the best separation results among the tested TBAB concentrations, including the maximum final gas uptake, increased and the CO\(_2\) concentration decreased. The maximum concentration of CH\(_4\) reached 90.38 mol % in 1.14 MPa with PR. In contrast, the maximum CH\(_4\) concentration of UPR is 86.90 mol % at the same pressure. In 3 MPa, the CH\(_4\) concentration increased to 87.28 mol % with PR. The results also demonstrate that more CO\(_2\) was enriched in the hydrate phase and a higher purity of CH\(_4\) was obtained with PR.

\[
R_V = \frac{22400n_0}{V_L}
\]
CH₄ fraction in the residual gas phase, CO₂ separation factor, and CH₄ separation and recovery factor. The concentration of CH₄ in the gas phase was increased with time (Figure 4) and reached the maximum value at gas and hydrate phase equilibrium. Nonetheless, the CH₄ concentration in the hydrate phase did not increase with time but increased first and then dropped again. The phenomenon was more obvious in 0.293 mol % TBAB. The reason might be that hydrate formation reached thermodynamic equilibrium, while the CO₂ hydrate formation is easier than CH₄ hydrate, and CH₄ will be replaced in the cage.31,32

The maximum CH₄ concentration in the residual gas phase reaches 93.52 mol % in PR at 1.14 MPa and 0.293 mol % TBAB. The results indicated that TBAB solution with a concentration of 0.293 mol % is more suitable than 0.1 and 0.9 mol % for gas separation. TBAB of 0.293 mol % is considered as the optimum concentration for HBCC, because TBAB occupies the big cavities in the semi-clathrate hydrates and TBAB of more than 0.293 mol % makes no more contribution to CO₂ capture.10,33,34 Li et al.35 found that 0.293 mol % TBAB is the optimum concentration to obtain a high gas storage capacity based on the experiments of HBCC from the fuel gas mixture. The mole numbers of gas consumed and the mole numbers of CO₂ transferred into the hydrate phase decrease with the increase of the TBAB concentration when the TBAB concentration is higher than 0.293 mol %. Xu et al.36 reported that CO₂ occupied the large cages of semi-clathrate at 0.293 mol % TBAB concentration. The reason may be that, with a lower cage occupancy in small cages with a higher TBAB concentration, guest gas only occupied the small cages when the concentration of TBAB solution is above 0.293 mol %. A further investigation of the cage occupancy of different gas molecules in semi-clathrate cages at the molecular level was needed.24,37

### 3.3. Effects of the Pressure

Figure 5 presents the hydration ratio curve during the PR experiments of 0.293 mol % TBAB for the 67 mol % CH₄/CO₂ mixture gas with the feed pressures of 1.14 and 3 MPa, in which the initial gas liquid ratio is 21.48. The driving force is often defined as the difference in the experimental temperature or pressure from the equilibrium pressure or temperature. In this work, we refer to the driving force (ΔP) as the difference between the experimental pressure and equilibrium pressure at a given experimental temperature. For the different pressures at 0.293 mol % TBAB, the driving forces (ΔP) were 0.5 and 2.36 MPa for the experimental condition of 1.14 and 3 MPa at 281.3 K (extrapolated from Li et al.38).

As seen in Figure 5, the hydration ratio rises with time as a result of more gas captured by the hydrate cage and is finally kept steady after about 200 min because of equilibrium of gas and water.
hydrate phases. The final hydration ratios are 0.382 and 0.273 for 1.14 and 3 MPa, respectively, which indicated that the hydration ratio is higher in low pressure. It is well-known that the driving force (ΔP) decreases gradually with the increase of the CH4 concentration in the gas phase and the decrease of the experimental pressure. The final test pressure is approximately equal to the initial pressure with the help of the PR method. At this work, the driving force (ΔP) decreases mainly with the increase of the CH4 concentration in the gas phase. For the feed pressure of 1.14 MPa, the final CH4 concentration in the gas phase was 93.52 mol %, resulting in the driving force (ΔP) decrease to almost zero,39 and the mixture gas in the gas phase can no longer be captured by hydrate. For the feed pressure of 3 MPa, it is worth noticing that pressure kept reducing at stage three. The phenomenon could be attributed to CO2 dissolved in solution at a high experimental pressure, and a second semi-clathrate hydrate crystal might form after enough time.

Table 2 shows that, at the same concentration of TBAB solution, the final gas uptake increased, ranging from 0.113 to 0.193 mol for the tested TBAB solutions. The obtained CH4 concentrations in the gas and hydrate phase composition and separation factor were all higher at 1.14 MPa compared to the data obtained at 3 MPa, except in 0.9 mol % TBAB solution. The reason might be that the mixture gas hydrate formation is easier at a high experimental pressure and more CH4 was captured by hydrate at a high pressure. For 0.9 mol % TBAB solution, gas uptake was lower than in 0.293 mol % TBAB solution at 3 MPa and CH4 might be replaced by CO2 in the cage.35,32 The results indicated that HBCC from biogas carried out at a low pressure is more suitable.

3.4. Effect of the Initial Gas Liquid Ratio. Table 3 shows the CH4 concentration in the residual gas phase for the PR separation experiment. The initial gas/liquid ratio ranged from 7.52 to 48.32.

As Table 3 and Figure 6 show, the maximum CH4 concentration in the residual gas phase was 93.52 mol % and obtained at the initial gas liquid ratio of 7.59. The results shows that, at the same feed pressure and TBAB concentration, the higher CH4 concentration was achieved at a lower initial gas liquid ratio. Shimada et al.21 proposed that, in the hydrate structure of TBAB-3H2O, CH4 and CO2 molecules competed with each other to occupy 512 small cages in TBAB hydrate. Water is absolutely enough to form TBAB semi-clathrate hydrate when the concentration of TBAB solutions was lower than 0.9 mol %. At a lower initial gas liquid ratio, more 512 small cages were provided for the unit amount of gas. Golombok et al.41 demonstrated that CO2 hydrates form much faster than methane hydrate in some particular pressure regimes. At the same pressure, CO2 molecules could be more easily captured by cages in TBAB hydrate than CH4. More TBAB hydrate cages would tend to catch more CO2, indicating that a lower initial gas liquid ratio was more suitable for HBCC from biogas. These results of separation were advanced much than those reported in our previous literature.25 in which the CH4 concentration improved from 67.00 to 84.00 mol % in 0.293 mol % TBAB solution with 1200 ppm of [BMIm]BF4 at 278 K and 3 MPa.

3.5. Recovery and Separation Factor. Table 3 summarizes the CO2 separation factor and CH4 separation and recovery factor for the experiments of HBCC from the 67 mol % CH4/CO2 gas mixture through TBAB hydrate formation with the pressure recovery method. The CO2 separation factor is calculated using eq 2. The CH4 separation and recovery factor is calculated using eqs 3–5. As seen in Table 3, the CO2 separation factor ranges from 16.83 to 52.87 at a low operating pressure (1.14 MPa) and ranges from 9.20 to 37.39 at a high pressure recovery method. The CO2 separation factor is

<table>
<thead>
<tr>
<th>experiment number</th>
<th>V_solution (mL)</th>
<th>initial gas/liquid ratio (mol/mol)</th>
<th>TBAB (mol %)</th>
<th>P_int (MPa)</th>
<th>CH4 fraction in the gas phase (mol %)</th>
<th>CH4 fraction in the hydrate phase (mol %)</th>
<th>SF_CO2</th>
<th>SR_CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400–600</td>
<td>17.11</td>
<td>0.1</td>
<td>1.14</td>
<td>86.84</td>
<td>11.10</td>
<td>52.87</td>
<td>2.050</td>
</tr>
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<td>7.52</td>
<td>0.1</td>
<td>3.00</td>
<td>84.57</td>
<td>12.78</td>
<td>37.59</td>
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<tr>
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</tr>
<tr>
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<td>16.13</td>
<td>33.18</td>
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</tr>
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<td>6</td>
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<td>0.9</td>
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<td>13.39</td>
<td>28.24</td>
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<td>0.9</td>
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<td>23.00</td>
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<td>1.110</td>
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<tr>
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<td>23.00</td>
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<tr>
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<td>21.48</td>
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<td>44.01</td>
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<tr>
<td>12</td>
<td>400–600</td>
<td>17.11</td>
<td>0.9</td>
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<td>91.20</td>
<td>23.00</td>
<td>18.37</td>
<td>1.110</td>
</tr>
</tbody>
</table>

*Amount of solution refers to the solution volume in the crystallizer; e.g., 400–600 refers to the pressure recovery operation, in which the initial solution volume is 400 mL, and after the pressure recovery operation, in which the final solution volume is 600 mL.6 Mole ratio of initial gas and liquid.
operating pressure (3 MPa). The CH₄ separation and recovery factor ranges from 0.949 to 2.050 at a low operating pressure and ranges from 1.071 to 1.430 at a high operating pressure. The maximum CO₂ separation factor and CH₄ separation and recovery factor are obtained at 1.14 MPa, 0.293 mol % TBAB, and initial gas—liquid ratio of 7.59 with pressure recovery. It is worth noting that, with pressure recovery operation at 1.14 MPa, 0.293 mol % TBAB, and initial gas—liquid ratio of 7.59, the CO₂ separation factor increased to 42.17 and the CH₄ separation and recovery factor was 2.050, obtained at 1.14 MPa and 0.293 mol % TBAB with pressure recovery operation. It is likely that pressure recovery operation played a positive role in HBCC and could promote hydrate formation and gas separation.

4. CONCLUSION

The pressure recovery operation introduced into TBAB semi-clathrate hydrate to capture CO₂ from CH₄ (67.00 mol %)/CO₂ mixed gas is presented in this work. The influence of the TBAB concentration and the effects of the operating conditions on the hydrate formation were studied. The use of 0.293 mol % TBAB solution is preferred over the use of 0.10 and 0.90 mol % TBAB solutions at a high operation pressure, and the best operation condition is a low operation pressure (1.14 MPa). Pressure recovery operation is more effective than reducing pressure operation for HBCC. The highest CH₄ concentration in the residual gas phase was 93.52 mol %, which was obtained at 1.14 MPa and 0.293 mol % TBAB with pressure recovery operation. The maximum CO₂ separation factor was 52.87, and CH₄ separation and recovery factor was 2.050, obtained at 1.14 MPa and 0.10 mol % TBAB with pressure recovery operation. It is likely that pressure recovery operation played a positive role in HBCC and could promote hydrate formation and gas separation.

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The authors declare no competing financial interest.

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