Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Recovering methane from quartz sand-bearing hydrate with gaseous CO_2

Q1 Shuanshi Fan, Xi Wang, Yanhong Wang, Xuemei Lang*

Q2 *Key Lab of Enhanced Heat Transfer and Energy Conservation, Ministry Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640 Guangdong, China*

ARTICLE INFO

Article history:
Received 27 December 2016
Revised 1 April 2017
Accepted 1 April 2017
Available online xxx

Keywords:
Hydrate
Methane
CH_4 recovery
CO_2 sequestration

ABSTRACT

The replacement method by CO_2 is regarded as a new approach to natural gas hydrate (NGH) exploitation method, by which methane production and carbon dioxide sequestration might be obtained simultaneously. In this study, CO_2 was used to recover CH_4 from hydrate reservoirs at different temperatures and pressures. During the CO_2–CH_4 recovery process, the pressure was selected from 2.1 to 3.4 MPa, and the temperature ranged from 274.2 to 281.2 K. Calculating the fugacity differences between the gas phase and the hydrate phase for CO_2 and CH_4 at different conditions, it has found rising pressure was positive for hydrates formation process that was helpful for the improvement of CH_4 recovery rate. Rising temperature promoted the trend of CH_4 hydrate decomposition for the whole process of CO_2–CH_4 replacement. The highest recovery rate was 46.6 % at 3.4 MPa 281.2 K for CO_2–CH_4 replacement reaction in this work.

1. Introduction

As the demand of the clean energy increasing with global climate change, natural gas attracted more attention for its high enthalpy upon combustion and low carbon emission [1]. Natural gas hydrate (NGH) is an energy resource for methane which total reserves in the world is estimated to range between 0.82×10^{13} and 2.10×10^{15} m^3 CH_4 at standard temperature and pressure (STP) [2]. It have been found under the seabed or in the permafrost regions and expected to be a next-generation energy source [3,4]. The exploitation of NGH has very important social and economic effect, especially for shortage of energy nowadays. How to efficiently and safely exploit NGH remains a huge challenge. The simple exploiting methods include thermal stimulation, depressurization and inhibitors injection [5], which destroy the phase equilibrium of hydrate reservoir to cause hydrate decomposition. It would raise concerns about landslide and seabed ecosystem destruction.

The replacement method by use of CO_2 is regarded as a safe natural gas hydrate exploitation method, which injects CO_2 into the hydrate reservoir to recover CH_4 and sequesters CO_2 through storage in the deep sea. Compared to other exploiting methods, such as thermal stimulation, depressurization and inhibitors injection, replacement recovery method can maintain the ground mechanical stability and reduce water production by reformation of CO_2 hydrate [6]. Ebinuma [7] and Ohgaki et al. [8] proposed the idea of replacing CH_4 with CO_2 from hydrate deposits in sea floor and studied the equilibrium components. Smith et al. [9] researched the possibility of exchanging hydrate with CO_2. And the viability of replacement natural hydrate with CO_2 had been proved both in thermodynamics and kinetics [10,11]. Bai et al. [12] studied CO_2 replacing CH_4 hydrate by molecular dynamics simulations explaining the processes consist of the methane hydrate dissociation and the CO_2 hydrate formation. They thought CO_2 hydrate formation would reduce the replacement ratio as the CO_2 hydrate layer hindered the mass transfer of CH_4 and CO_2 molecules.

Many studies indicated that replacement ratio was closely related to temperature and initial pressure. Li et al. [13] examined the gaseous CO_2 replaced CH_4 in hydrate reservoirs with the experimental conditions at 271.2 to 276.0 K and 2.8 to 3.25 MPa. It showed that the CH_4 recovery ratio was increased with the temperature rising, and growing the initial pressure of CO_2 could also improve the CH_4 recovery ratio. Ota et al. [14] got the same result that CH_4 recovery ratio increased with the rise of initial pressure under CO_2 liquid pressure, while CH_4 recovery ratio did not change at higher pressures above the CO_2 liquid pressure. Ota thought the replacement ratio was dependent on pressure and phase conditions. Yuan et al. [15] showed using liquid CO_2 could obtain more CH_4 than using gaseous CO_2 for replacement process. They thought the fugacity of liquid CO_2 decreases slightly during the replacement reaction compared with gaseous CO_2. Zhou et al. [16] divided the phase equilibrium diagram into four parts on replacement of CH_4 in hydrate with CO_2, and considered Part A was an optimal area for CO_2–CH_4 replacement process, which is shown in

---

* Corresponding author.
E-mail address: cexmlang@scut.edu.cn (X. Lang).

http://dx.doi.org/10.1016/j.jechem.2017.04.014
2095-4956/

Please cite this article as: S. Fan et al., Recovering methane from quartz sand-bearing hydrate with gaseous CO2, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.04.014

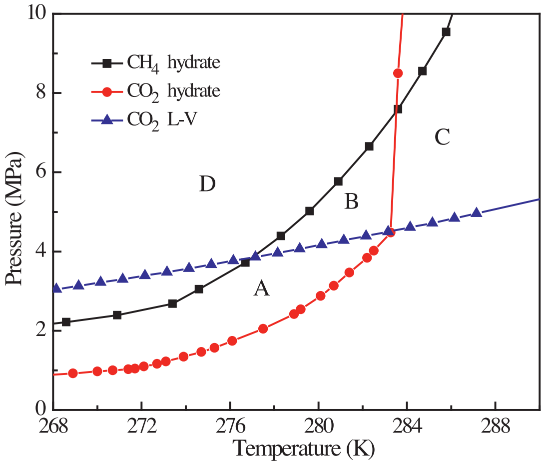

Fig. 1. Phase equilibrium diagram of replacement of CH_4 in hydrate with CO_2. Part A is CO_2 hydrate formation area with gaseous CO_2. Part B is CO_2 hydrate formation area with liquid CO_2. Part C is neither formation area of CH_4 hydrate and CO_2 hydrate. Part D is CH_4 hydrate and CO_2 hydrate simultaneous formation area.

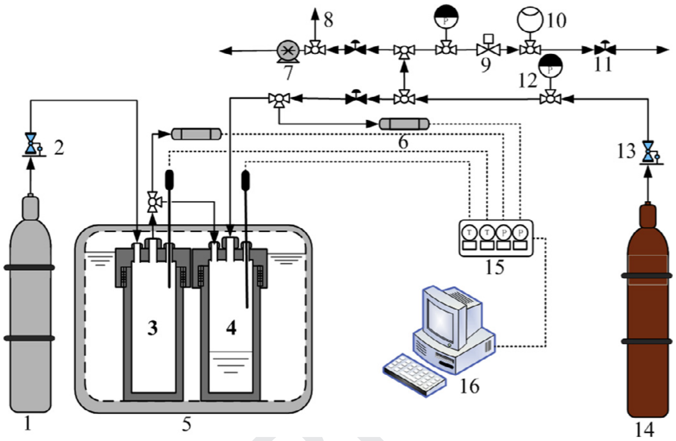

Fig. 2. Schematic of the experimental apparatus.
1–CO_2 cylinder, 2–relief valve; 3–buffer, 4–cell, 5–thermostatic bath, 6–pressure sensor, 7–vacum pump, 8–sample connection, 9–back pressure valve, 10–mass flow meter, 11–vent valve, 12–pressure gauge, 13–CH_4 relief valve, 14–CH_4 cylinder, 15–data collector, 16–PC.

Fig. 1. CH_4 recovery ratio relied on the initial replacement condition. However, the pressure and composition were changing during the relacement processes and the trend of CH_4–CO_2 exchanging decreased with reaction time.

In this work, we investigated how the pressure and the temperature affect the methane recovery ratio during the replacement processes, considering two steps, the methane hydrate decompose and the CO_2 hydrate formation. Furthermore, the whole process of the trend of CH_4–CO_2 exchange was quantified by calculating the fugacity differences between the gas phase and the hydrate phase for CO_2 and CH_4. The driving force was described by the fugacity differences between the gas phase and the hydrate. The quantification of the driving force was essential to evaluate the kinetics of CH_4 hydrate decomposition and CO_2 hydrate formation.

2. Experimental

2.1. Materials and apparatus description

Methane and carbon dioxide were supplied by the Guangzhou Zhuozheng Gas Industry Corporation, with a stated minimum purity of 99.9 mol%. The purity of SDS was 99%, purchased from Shanghai Biological Technology Co., Ltd. The quartz sand used in the experiment was from Zhengzhou Union Water Co. with a content of 95%. Distilled water was prepared in the laboratory.

A schematic diagram of the experimental apparatus is shown in Fig. 2. The experimental apparatus mainly consists of gas supply module, reaction module and data acquisition module. The gas supply module provides CH_4 and CO_2. The reaction module is used for CH_4 hydrate formation and CH_4–CO_2 exchange included a high pressure reactor ($\varphi 44 \times 200$ mm), a buffer tank and a thermostatic bath (THD-3015, Tianheng Device Co., Ningbo, China). The high pressure reactor and the buffer tank can withstand a maximum pressure of 25 MPa. The system temperature is maintained with an accuracy of 0.1 K using the thermostatic bath. The data acquisition module (Agilent 34970A, Agilent Tech., China) collects the pressure and temperature of the reactor tank and the buffer tank. The gas composition is analyzed by an in-line gas chromatograph (GC9800).

2.2. Procedure

2.2.1. Formation of CH_4 hydrate

A known amount of 0.03 wt% SDS solution and quartz sand were introduced into the high pressure reactor shown in Fig. 2. The temperature of thermostatic bath was stabilized at 274.2 K. The reactor was then sealed, vacuumed for about 30 min, and charged to CH_4 three to four times to ensure no air. CH_4 gas feed into the reactor to 15 MPa. The data acquisition module recorded the pressure and temperature. Hydrate formation could be considered completed when the experimental pressure was no change for 24 h.

2.2.2. Replacement of CH_4 with gaseous CO_2

After complete formation of the CH_4 hydrate, the temperature of the thermostatic bath adjusted to 271.2 K. The back pressure regulator was set to the desired experimental pressure, and then the free CH_4 in the reactor was released. The gaseous CO_2 was introduced into the reactor. Then, the temperature of thermostatic bath adjusted to the experimental temperature and kept constant. The replacement of CH_4 in the hydrate phase started. The gas composition in the reactor was analyzed by the gas chromatogram during the CO_2–CH_4 replacement reaction. The replacement of CH_4–CO_2 was considered completed when the composition of CH_4 in the gas phase keep stable in 24 h.

2.3. Data processing

The recovery ratio is a very important factor to evaluate CO_2–CH_4 process from the hydrate. The definitions of them as Eq. (1),

$$\eta_{Re} = \frac{n_{CH_4,Re}}{n^{i}_{CH_4,H}} \times 100\% \tag{1}$$

Where $n^i_{CH_4,H}$ and $n_{CH_4,Re}$ are the initial molar quantity of CH_4 in the hydrate phase and the moles of CH_4 displaced in its hydrate, respectively. These can be calculated by Eqs. (2) and (3),

$$n^{i}_{CH_4,H} = n^{i}_{CH_4,Total} - n^{i}_{CH_4,G} \tag{2}$$

$$n_{CH_4,Re} = x_{CH_4,Inter} n_{Mgas,Inter} \tag{3}$$

$n^i_{CH_4,Total}$ and $n^i_{CH_4,G}$ stand for the numbers of moles before and after the formation of CH_4 hydrate respectively. And they can be calculated on the basis of the equation of state (EoS), the temperature and pressure in vapor phase which were recorded in the process of CH_4 hydrate formation. $x_{CH_4,Inter}$ is the mole fraction of CH_4 in

Please cite this article as: S. Fan et al., Recovering methane from quartz sand-bearing hydrate with gaseous CO2, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.04.014