




Effect of pressure on methane recovery from natural gas hydrates by methane-carbon dioxide replacement



Chun-Gang Xu^{a,b,c,d}, Jing Cai^{a,b,c,d,e}, Yi-Song Yu^{a,b,c,d,e}, Ke-Feng Yan^{a,b,c,d}, Xiao-Sen Li^{a,b,c,d} 

^a Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510641, PR China

^b CAS Key Laboratory of Gas Hydrate, Guangzhou 510640, PR China

^c Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, PR China

^d Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, PR China

^e University of Chinese Academy of Sciences, Beijing 100083, PR China

HIGHLIGHTS

- Pressure condition of CH₄-CO₂ replacement is systematically investigated.
- Pressure must be between CH₄ and CO₂ hydrate formation equilibrium pressures.
- Replacement rate and efficiency are related to pressure and CH₄ partial pressure.
- Replacement in large cavities determines the rate and efficiency.

ARTICLE INFO

Keywords:

CH₄ hydrate

Replacement

CO₂

In-situ Raman

ABSTRACT

Methane recovery from natural gas hydrates via CH₄-CO₂ replacement is promising for its advantage in methane recovery and CO₂ capture in the form of CO₂ hydrates. However, up to date, it is still unclear what influence the CH₄-CO₂ replacement rate and CH₄ recovery efficiency. In this work, the effects of the pressure on the dynamic of the replacement are systematically investigated by in situ Raman. The results indicate the CH₄-CO₂ replacement rate and CH₄ recovery efficiency are related to the total operating pressure and the CH₄ partial pressure in a CH₄-CO₂ binary system. On the one hand, the CH₄-CO₂ replacement can only occur under such operating pressures that the CH₄ partial pressure is lower than the pure CH₄ hydrate formation equilibrium pressure and the CO₂ partial pressure is higher than the pure CO₂ hydrate formation equilibrium pressure. On the other hand, under a certain pressure, the lower CH₄ partial pressure leads to the higher replacement rate. Due to that the condition of temperature and pressure changes continuously in the process of the replacement, the research results are of significance for guiding the successful CH₄-CO₂ replacement.

1. Introduction

Natural gas hydrates (NGHs) are ice-like compounds that formed by water molecules and gas molecules under low temperature or/and high pressure, and water molecules constructs different cavities by hydrogen bonds and gas molecules stably reside in the cavities by van der Waals' force [1]. NGHs intensively exist in sea floor or permafrost in the mainly forms of three structures, including structure I (sI), structure II (sII) and structure H (sH). An sI hydrate cell generally contains six 5¹²6² cages and two 5¹² cages, and an sII hydrate cell consists of eight 5¹²6⁴ cages and sixteen 5¹² cages, and an sH hydrate cell includes one 5¹²6⁸, two 4³5⁶6³ and three 5¹² cages [1–3]. It is estimated that the total

amount of carbon resource contained in the NGHs is about twice as much as that in the proven fossil fuel reserves. Consequently, the NGHs are considered as potentially alternative energy resource for the future [4–9]. CH₄ recovery from NGHs reservoirs, thereby, become a research hotspot. Presently, the main recovery methods include thermal stimulation, depressurization, chemical inhibitor injection, but the issues such as enormous energy consumption, risks of the probably catastrophic landslide and serious environmental pollution restrict the commercial application of the methods [10]. Therefore, it appeals to newly effective and environmental friendly production technologies. One new technology is CH₄-CO₂ replacement. By the method, CH₄ can be replaced out from NGHs cavities by CO₂, and CO₂ can be

* Corresponding author at: CAS Key Laboratory of Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China.
E-mail address: lixs@ms.giec.ac.cn (X.-S. Li).

sequestered in the form of CO₂ hydrates simultaneously [11–14]. Thus the CH₄-CO₂ replacement technology from NGHs is also considered as a promising technology in both CH₄ recovery from NGHs and carbon emission reduction (CCS).

The CH₄-CO₂ replacement in NGHs was firstly proposed by Ohgaki et al. [15–17]. In a sealed reactor, CH₄ composition was found continuously increased in gas phase after injecting CO₂ into the simulated NGHs, and meanwhile, CO₂ composition decreased accordingly. Ohgaki et al. thought that the result was attributed to the replacement between CH₄ and CO₂ in the hydrates. After then, CH₄-CO₂ replacement in NGHs was extensively studied from the thermodynamics, kinetics, process and mechanism for its potential on producing CH₄ from NGHs and capturing CO₂ simultaneously [14,18–20]. On the aspect of thermodynamics, the CH₄-CO₂ replacement reaction was proven to be spontaneous under the condition of 275.2 K and 3.25 MPa because the Gibbs free energy (ΔG) of -3.49 kJ/mol was obtained by Ote et al. [21] And the thermodynamic feasibility of CH₄-CO₂ replacement in NGHs was demonstrated through molecular dynamics (MD) simulation by Yezdimer et al. [22] and Geng et al. [23], respectively. On the aspect of kinetics, Ors and Sinayuc [24] proved that the CH₄-CO₂ replacement mostly took place in the surface of the simulated hydrates in porous media under 277.15 K and 3.7 MPa. Ota et al. [25,26] used liquid CO₂ to replace CH₄ from the simulated NGHs and found the replacement was the process in which CH₄ hydrates firstly decomposed and then CO₂ hydrates formed. In their experiments, CH₄ recovery efficiency was about 53.0% after 307 h, and it was found the replacement mainly happened in the large 5¹²⁶² cavities. Based on the experimental phenomenon and results, they thought the replacement was dominated by gas diffusion in the hydrates. Lee et al. [27] also proved that the replacement mainly occurred in large cavities by nuclear magnetic resonance (NMR) analysis, and they confirmed that no hydrate structure transition happened during the replacement. Schicks et al. [28] investigated the conversion of the primary CH₄ hydrate into a CO₂-rich hydrate by in situ Raman and powder X-ray diffraction (PXRD), and they considered the conversion process was induced by the gradient of the chemical potential between the hydrate phase and the environmental gas phase. Furthermore, they considered the conversion process could be described as a process of CH₄ hydrate decomposition and CO₂ hydrate formation process, and the conversion rate depended on the surface area of the hydrate phase and the concentration gradient of one component between the hydrate phase and the gas phase. On the aspect of process, many studies were systematically carried out to the enhancing CH₄ recovery efficiency by CH₄-CO₂ replacement. For instance, Kvamme [29] compared the CH₄ recovery efficiency using pure CO₂ and CO₂/N₂ gas mixture, and they found the adding of N₂ was advantage of gas diffusion in NGHs and finally promoted the CH₄-CO₂ replacement. Lee et al. [30] carried out CH₄-CO₂ replacement experiments with pure CO₂ and CO₂/N₂ gas mixture to investigate the hydrate structure transition between sI and sII, and the experimental results showed the efficiency obtained from the replacement with CO₂/N₂ gas mixture was about 20% higher than that with pure CO₂. And interestingly, they also found the hydrate structure transitioned from sII to sI and the replacement happened in both large and small cavities. The similar results were also found in our previous experiments of CH₄ recovery from NGHs with CH₄-CO₂ replacement [31]. In the experiments, CH₄ hydrate and CO₂ hydrate were found to coexist in the form of sI hydrates and no any structure transition from sI to sII happened.

Adding small gas (e.g., N₂ or H₂) into CO₂ was proven to be effective to promote CH₄-CO₂ replacement and even enhance CH₄ recovery efficiency [13,32,33]. Besides, the conditions of thermodynamics and kinetics have great influence on the replacement and CH₄ recovery efficiency, including operating conditions, the compositions of the displacement gas, hydrate structure and gas injection ways, etc. However, up to date, few studies were reported on investigating the effect of the replacement process on the CH₄ recovery efficiency. For example, it is still unclear whether the CH₄ recovery efficiency is influenced by the

operating pressure and the CH₄ fraction pressure in the gas phase. Does it be better to replace CH₄ with CO₂ under higher pressure? And what kind of influence on the CH₄-CO₂ replacement would be brought about by the change of the system pressure? What more, there are few reported evidences that whether the replacement occurs in the large cavities or not.

In this work, the effect of the operating pressure on the CH₄-CO₂ replacement is specially investigated. The replacements are carried out under different pressures with integrated gasification combined cycle (IGCC) syngas. On the one hand, IGCC technology is considered as one kind of clean coal technology that is quite important for those countries with coal as their main energy resource, such as China, India and Russia [34]. On the other hand, CO₂ and H₂ are the main two components of the IGCC syngas [34,35]. Therefore, it needs to effectively capture CO₂ from IGCC power plants to avoid the greenhouse effect getting worse caused by a large number of CO₂ emissions. Using CO₂/H₂ gas mixture to replace CH₄ out from NGHs is expected to capture and sequester CO₂ in the form of forming CO₂ hydrates and simultaneously obtain CH₄/H₂ gas mixture with higher energy density. In the work, IGCC syngas is simulated with CO₂/H₂ (40.0%/60.0%) gas mixture. The replacement mechanism and the replacement kinetic process are systematically investigated through a lots of experiments in which the gas hydrate structures and hydrate compositions are determined by powder X-ray diffraction (PXRD) and in situ Raman spectra.

2. Experimental section

2.1. Apparatus and materials

As shown in Fig. 1, the experimental apparatus mainly consists of the gas supply system, the stainless steel high-pressure reactor with inner volume of 100 mL, the temperature control system, the operating panel and the temperature-pressure detector and data acquisition system. There are two visual quartz windows mounted on front and back sides of the reactor for viewing and Raman measurement. The ethylene glycol solution (25 wt%) are used as coolant, and the water-bath temperature can be auto-adjusted from 263 to 353 K. The thermocouples (Pt100, JM6081) with uncertainties of ± 0.1 K and Setra smarte pressure transducers (model 552, Boxborough, MA, USA) are employed to measure the temperature.

CH₄ with a purity of 99.9%, simulated IGCC syngas of 39.9% CO₂ + 60.1% H₂, and CO₂/CH₄ with different compositions are supplied by Foshan Huate Gas Co., Ltd. The deionized water with the resistivity of 18.25 m Ω cm⁻¹ is produced with an ultra-pure water machine from Nanjing Ultrapure Water Technology Co., Ltd. The gas component is determined by a gas chromatograph (GC) typed Agilent 7890A.

2.2. Procedure

Firstly, using deionized water to wash the reactor 3–4 times. Then, injecting 30 mL deionized water the reactor, and then, evacuating the reactor to air free. Then, starting the temperature controlling system to cool the system temperature to 276.15 K. After then, slowly injecting the CH₄ gas into the reactor from the bottom of reactor to the set operating pressure. Then, pure CH₄ hydrates would gradually form. With the hydrate formation, the pressure in the reactor would gradually decrease. Therefore, CH₄ gas is need to supplied into the reactor to maintain the operating pressure. Several days after, once no CH₄ gas is supplied into the reactor, it is considered that the CH₄ hydrate formation complete. Hereafter, the simulated IGCC syngas of 39.9% CO₂ + 60.1% H₂ is injected into the reactor from bottom of reactor, and by adjusting the inlet/outlet valves, the residue CH₄ gas is discharged at the same time but the pressure is kept at 4.50 MPa or 6.00 MPa. After the CH₄ in the gas phase is lower than 2.0%, the inlet/outlet valves are shut off. And then the CH₄-CO₂ replacement gradually begins in the

Download English Version:

<https://daneshyari.com/en/article/6680496>

Download Persian Version:

<https://daneshyari.com/article/6680496>

[Daneshyari.com](https://daneshyari.com)