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# Performance evaluation of methane separation from coal mine gas by gas hydrate formation in a stirred reactor and in a fixed bed of silica sand

Qi Dong-Liang Zhong<sup>a,b</sup>, Yi-Yu Lu<sup>a,\*</sup>, Dong-Jun Sun<sup>b</sup>, Wei-Long Zhao<sup>b</sup>, Zheng Li<sup>b</sup>

<sup>a</sup>State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China

<sup>b</sup>College of Power Engineering, Chongqing University, Chongqing 400044, China

## HIGHLIGHTS

- CH<sub>4</sub> separation from the coal mine gas was carried out by gas hydrate formation.
- Stirred reactor performed better than the silica sand bed for CH<sub>4</sub> recovery.
- CH<sub>4</sub> recovery was greatly promoted by adding SDS in THF solutions.

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## ABSTRACT

Coal mine methane (CMM) gas is a sort of unconventional natural gas that can be used as a clean supplementary energy resource when methane is purified. In this work, methane separation from a low-concentration CMM gas (30 mol% CH<sub>4</sub>, 60 mol% N<sub>2</sub>, and 10 mol% O<sub>2</sub>) was investigated using gas hydrate formation in a stirred reactor and in a fixed bed of silica sand with the presence of tetrahydrofuran (THF) and sodium dodecyl sulfate (SDS). The concentration of THF and SDS was fixed at 1.0 mol% and 500 ppm, respectively. The experiments were carried out in batch operation with the initial pressure fixed at 3.6 MPa, and the temperature was set at 277.15 K. The results indicated that gas hydrate formation in the stirred reactor and in the fixed bed of silica sand were both promoted by adding SDS in THF solutions. It was found that the hydrate-based separation process for CH<sub>4</sub> recovery from the CMM gas mixture performed better in the stirred reactor as compared to the fixed bed of silica sand employed in this work. The CH<sub>4</sub> recovery obtained at 1.0 mol% THF and 500 ppm SDS in the stirred reactor was about 40.5%, which was much higher than those obtained in TBAB solutions (26.2%) and cyclopentane/SDS solutions (33.3%).

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## 1. Introduction

Gas hydrates are nonstoichiometric crystalline inclusion compounds formed by water and a number of small molecules (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, etc.) at suitable temperature and pressure conditions [1,2]. The mass of carbon stored in hydrate deposits is estimated to be twice as much as that in the conventional fossil fuels (coal, oil and natural gas), as a result the naturally occurring gas hydrates have been considered as a potential energy resource [3]. Besides, gas hydrate formation/decomposition has been found to be a promising method for natural gas transport [4,5], cold storage [6], desalination [7–9], and gas separation [10–15].

Coal mine methane (CMM) gas is one type of unconventional natural gas and is usually mixed with air during the process of coal mining. It can be recovered as a supplementary energy resource because it exists abundantly in coal mines [16–18]. However, it is hard to utilize the CMM gas when methane concentration is below 30 mol%. Methane purification is recognized as one possible way to use the low-concentration CMM gas mixture. This method can also mitigate global warming and climate change because CH<sub>4</sub> is a strong greenhouse gas that is not allowed to discharge to the atmosphere. Recently, gas hydrate formation has been employed for CH<sub>4</sub> recovery from the low-concentration CMM gas mixture on a laboratory scale [19,20]. The challenge that hinders the development of the hydrate-based separation process for CH<sub>4</sub> separation is the high hydrate formation pressures at low CH<sub>4</sub> concentrations. For instance, the phase equilibrium pressure for gas hydrates

\* Corresponding author. Tel.: +86 23 65112372; fax: +86 23 65106440.  
E-mail address: [luyiyu@cqu.edu.cn](mailto:luyiyu@cqu.edu.cn) (Y.-Y. Lu).

formed from the CMM gas (30 mol% CH<sub>4</sub>, 60 mol% N<sub>2</sub>, and 10 mol% O<sub>2</sub>) is 9.6 MPa at 277.15 K [21]. This will render high gas compression cost. From the perspective of industrial application, low gas compression costs are usually required and can be obtained by reducing the operation pressures.

The use of thermodynamic promoters such as tetrahydrofuran (THF) [22,23], tetra-*n*-butyl ammonium bromide (TBAB) [24,25], and cyclopentane (CP) [26,27] is one approach to reduce the phase equilibrium pressures of gas hydrates formed with the low-concentration CMM gas. However, it was found that the CH<sub>4</sub> recovery and rate of hydrate formation were compromised by the use of thermodynamic promoters. For example, methane recovery obtained in the presence of TBAB was 27% [20] and increased to 33.3% while CP was added to the system [28]. It was also found that although the rate of hydrate formation was accelerated by the surfactant sodium dodecyl sulfate (SDS), methane recovery obtained in the presence of SDS was not increased as compared to that obtained in the absence of SDS. Another attempt to enhance gas hydrate formation is to increase the gas/liquid contact area by the use of silica sands instead of using the stirred reactors [29,30]. Linga et al. [31] assessed the performance of gas hydrate formation in a fixed bed of silica sand and in a stirred reactor. They tested four kinds of gas mixtures (C1/C2, C1/C3, C1/C2/C3, and CO<sub>2</sub>/H<sub>2</sub>/C3) and found that the rate of hydrate formation was higher than that obtained in the stirred reactor due to the transport of gas inside the sand bed and the huge gas/liquid contact surfaces, and a higher water conversion to gas hydrates was obtained in the fixed bed of silica sand. To the best of our knowledge, no studies have been reported on methane separation from the CMM gas mixture using gas hydrate formation in the combination of silica sand and surfactants. In addition, a better understanding on the kinetics of hydrate formation with the CMM gas mixture in stirred reactors and in the presence of porous media is of great importance to develop the hydrate-based separation process for CH<sub>4</sub> recovery from the CMM gas mixture.

The objective of this work is to evaluate the kinetics of CH<sub>4</sub> separation from a simulated CMM gas mixture by hydrate formation in a stirred reactor and in a fixed bed of silica sand. The performance of the fixed bed of silica sand is compared with that of the stirred reactor. THF is used as a thermodynamic promoter to reduce the hydrate phase equilibrium conditions while SDS is used as a surfactant to enhance gas hydrate formation. The influence of SDS on the kinetics of hydrate formation is also investigated in the stirred reactor and in the fixed bed of silica sand.

## 2. Experimental section

### 2.1. Materials

The gas mixture containing 30 mol% CH<sub>4</sub>, 60 mol% N<sub>2</sub>, and 10 mol% O<sub>2</sub> was employed and supplied by Chongqing Rising Gas with a reported uncertainty of ±0.05 mol% in the gas composition. The gas composition was the same as those used in the literature [20,28] and was selected to simulate the typical low-concentration CMM gas recovered from underground coal mines. THF and SDS with a certified mass purity of 99% were purchased from Chongqing Oriental Chemical Co., Ltd. Silica sand particles were supplied by Nanjing Chemical Reagent Co. Ltd. The surface area of the pores in sand particles was 0.17 m<sup>2</sup>/g and the average pore diameter was 59.5 nm. These parameters were measured by the surface area and porosity analyzer (Micromeritics ASAP 2010, USA). The scanning electron microscope (SEM) images of silica sands were captured using the Phenom ProX SEM (FEI Company, USA). Deionized water was used in all experimental runs.

### 2.2. Apparatus

The schematic diagram of the experimental apparatus is shown in Fig. 1. It consists of a high-pressure stainless-steel vessel immersed in a water bath. The volume of the vessel was 600 cm<sup>3</sup>. The temperature of the water bath was controlled by an external cryostat (THD-1030, Ningbo Tianheng Instrumentation Corp., China). The maximum operation pressure of the vessel was 10 MPa. Two quartz windows were equipped in the front and rear sides of the vessel, allowing a visual access to hydrate formation inside the vessel. A speed-adjustable electromagnetic stirrer (0–1000 rpm) was inserted into the reactor and used for solution agitation. This stirrer can be dismantled for the purpose of gas hydrate formation in quiescent format or in a fixed bed of porous media. Two platinum resistance probes (Pt 100, Chongqing Chuanyi Automation Corporation, China) with an uncertainty of 0.1 K were used to measure the gas and liquid temperature. A pressure transducer (Yokogawa Electric Corp., Japan) with an uncertainty of 0.06% of the span 0–10 MPa was employed to measure the pressure of the gas phase. The temperature and pressure of the reactor were recorded by a data acquisition unit (Agilent 34970A, USA) and logged into a computer. A gas chromatograph (GC-2014, Shimadzu Corp., Japan) with an uncertainty of 0.1 mol% was used to determine the composition of the gas mixtures remaining in the reactor and decomposed from the gas hydrates at the end of the experiments.

### 2.3. Procedures

In this work, kinetic experiments of gas hydrate formation with the CMM gas mixture were carried out in a batch mode based on the reported incipient phase equilibrium conditions in the presence of 1.0 mol% THF [32]. The procedure for hydrate formation in the stirred reactor was given as follows. Prior to the experiments, the crystallizer was cleaned with deionized water and dried. Then 252 cm<sup>3</sup> of 1.0 mol% THF solution was filled in the crystallizer. For the experiments performed in the presence of SDS, 252 cm<sup>3</sup> of 1.0 mol% THF solution containing 500 ppm SDS was used instead of the 1.0 mol% THF solution. The crystallizer and the tubing were purged at least three times with the low-concentration CMM gas mixture so as to remove the air present in the system. Then the reactor was pressurized to 3.6 MPa with the low-concentration CMM gas mixture from the gas cylinder. Once the temperature and pressure in the reactor reached desired values (277.15 K and 3.6 MPa), the crystallizer was isolated from the gas cylinder by closing the inlet and outlet valves. Meantime, the electromagnetic stirrer was started at a constant speed of 150 rpm. This was considered to be time zero for the experiments. The temperatures and pressure were recorded by the data acquisition unit and logged into a computer every 10 s. Gas hydrates were observed through the viewing windows during the process of hydrate formation. Note that the pressure in the reactor would decrease and the temperature would increase during the progress of hydrate formation. When the temperature restored to ~277.15 K and the pressure stabilized at a constant value (~2.8 MPa) for at least 2 h, it was considered as the end of the experiments. Then the gas mixture remaining in the vessel was sampled and the composition was analyzed using the gas chromatograph (GC) at the end of the experiments.

This procedure was also adopted for hydrate formation in the fixed bed of silica sand. The same reactor was used with the absence of the electromagnetic stirrer. The amount of water required to saturate the silica sand was 0.256 cm<sup>3</sup>/g, which was determined using the method reported in the literature [33]. Saturation of the silica sands means that the void spaces such as the interstitial spaces or pore volumes of the sands was fully filled

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