Contents lists available at ScienceDirect

Fuel

Controllable methane hydrate formation through trace carbon dioxide charging

Yuanmei Song [a,b], Fei Wang [a], Guoqiang Liu [c], Shengjun Luo [a,*], Rongbo Guo [a,*]

[a] Shandong Industrial Engineering Laboratory of Biogas Production & Utilization, Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess, Qingdao 266101, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] College of Chemical Engineering, Qingdao University of Science & Technology, Qingdao 266042, China

HIGHLIGHTS

- Methane hydrate formation was accelerated by increasing CO_2 content.
- The easier formed CO_2 nuclei triggered faster hydrate nucleation.
- Addition of a certain amount of CO_2 in induction period triggered fast methane hydrate growth stage.

GRAPHICAL ABSTRACT
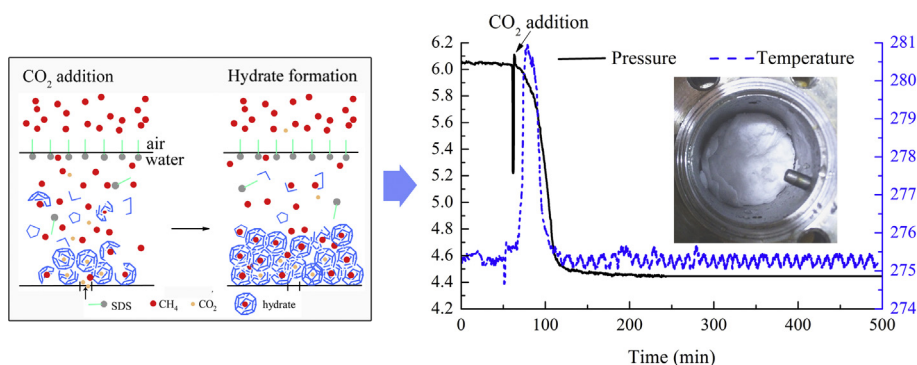
ARTICLE INFO

ABSTRACT

An initial method to efficiently control methane hydrate formation process was investigated in this work. This method included an in-situ injection of a small amount of CO_2 into the reactor during the nucleation stage to explore hydrate formation in 0.5 mmol/L sodium dodecyl sulfate (SDS) solutions. Results showed that charging CO_2 higher than 2% in the mixed gases could induce immediate methane hydrate growth stage. Furthermore, when 3% CO_2 was injected into the reaction system at different time points, the times required for hydrate formation were all shortened significantly. Especially at the injection points of more than 30 min, the subsequent crystals growth began immediately after CO_2 injection. Besides, the formed hydrates tended to aggregate in the vicinity of CO_2 injection zones. Such promotion effect was possibly caused by the triggering effect of preferentially formed CO_2 hydrates in the reaction system. This work provides a novel and simple method to control hydrate formation process, which is of great significance to the transportation and storage of natural gas.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Gas hydrates are categorized as clathrates, which are nonstoichiometric crystalline compounds composed of external cages formed by hydrogen-bonded water molecules and enclosed guest gases such as CH_4, C_2H_6, CO_2 etc. [1]. Attracted by the high gas storage of the hydrate as well as the high safety and economy in the methane formation process, many researchers have regarded the

hydrate-based technology for storage and transportation of natural gas as a promising method [2–4]. However, the long induction time and low growth rate during the hydrate formation restricted the wide applications of hydrate-based technologies in industries [5]. Searching for efficient ways to overcome those obstacles has stimulated increasing interest of researchers who contributed a lot to kinetics and thermodynamics studies for promoting the hydrate formation process. Both physical [6–8] and chemical methods [9] were verified as effective ways to improve the methane hydrate formation, among which sodium dodecyl sulfate (SDS) was the most efficient and economical accelerant for hydrate growth rate [10]. Nevertheless, the physical ways are economically infeasible as they require higher energy input and extra production cost. Chemical promoters are difficult to recover as well as cause serious contaminations. Besides, the application of methane hydrate is limited by large amounts of foam produced during hydrate dissociation with high-concentrated SDS. Therefore, it is urgent to develop more efficient and economical ways to improve the hydrate formation.

As natural gas is a gaseous mixture composed of primary gas of methane and a small number of other gases such as carbon dioxide, propane, ethane etc., each component may affect the kinetic and thermodynamic properties of natural gas hydrate [11]. Thus, it is a possible and potential way to apply other gaseous hydrate formers to accelerate methane hydrate formation. For example, C_3H_8 molecules tend to occupy large cavities to stabilize the hydrate structure and the as-formed C_3H_8 hydrates could be the accelerants to help faster nucleation of other crystals [12,13]. Some researches on the CH_4/CO_2 mixture were mainly aimed at the separation technology to purify biogas or the extraction of CH_4 accompanied by sequestration of CO_2 simultaneously. Decreased equilibrium pressure with the increasing CO_2 concentration at a specific temperature was beneficial to hydrate formation in view of thermodynamics [14–16]. The work by Yan Sun et al. [17] showed that CO_2 hydrates could formed firstly, followed by methane hydrates formation when the partial pressure of methane reached the formation pressure. From the point of dynamic point, studies on the mechanism of CH_4/CO_2 mixed gas hydrate indicated that the growth rate of hydrate was enhanced by high CO_2 concentration and the induction time decreased linearly with concentration [16,18,19]. Theoretically, the solubility of CO_2 is about 10 times greater than that of CH_4 in the gas-liquid-hydrate ternary system, which also make it easier for CO_2 to form hydrate if the binary gas of CO_2 and CH_4 coexist in the liquid phase [20]. Structurally, CO_2 tend to occupy large cages $4^3 5^6 6^3$ while CH_4 molecule occupy small cages 5^{12} in the hydrates which determined the stable structure in spite of the same structure of sI for both carbon dioxide and methane [18]. Moreover, the hydrates containing an amount of CO_2 would be denser than pure methane hydrate and the mixed gas hydrate presented best stability than pure methane hydrate or carbon dioxide hydrate [21].

On the premise that the existing CO_2 hydrate crystal in the reaction system can initiate the nucleation of methane hydrate, it was suggested that the methane hydrate formation process can be controlled by injecting an amount of CO_2. In view of practical use of natural gas hydrate, the CO_2 content was usually controlled within 5%. Thus, in this work, the effect of trace of CO_2 addition on the methane hydrate formation was investigated. In addition, the controlling role of the CO_2 during the hydrate formation process through charging CO_2 into the reactor at different time points was also explored.

2. Experimental

2.1. Materials

Methane (purity > 99.99%) and mixed gas (1/3 carbon dioxide and 2/3 methane) were provided by Heli Gas Company; sodium

dodecyl sulfate (SDS, A.R.) (purity > 99.8%) was provided by Xiya Reagent Company; The deionized water used in this experiment was laboratory-made with conductivity of $1.1 \pm 0.1\ \mu s/cm$ at 298.15 K.

2.2. Hydrate formation process

The established set-up applied in this experiment is described in Fig. 1. The main components include two piston containers with the volume of 1 L and one reactor made of 316 L stainless steel (roughness $\leqq 0.2\ \mu m$) with volume capacity of 200 mL. The internal pressure and temperature variations were monitored and recorded by the computer through a thermocouple and a pressure transducer. The containers and reactor were immersed in a temperature–controlled liquid bath made of glycol and water (volume ratio of 1:2). The reaction temperature was controlled at 275.15 K with the accuracy of 0.01 K.

The reactor was firstly washed and rinsed with deionized water for three times in order to remove residual hydrates. Methane was pressurized into piston containers in advance to reach the reaction temperature in case pressure changes during the cooling process. Then 30-mL SDS solution (0.5 mmol/L) was injected into the reactor and the reactor was flushed with methane to evacuate air from the cell. Pure methane of 6 MPa was charged into reactor after the temperature inside the reactor reached the required temperature of 275.15 K. When CO_2 was required during the reaction process, the methane in the reactor was released slowly to a certain value. Subsequently, the mixed gases of CO_2/CH_4 was charged also to 6 MPa through the channel connected to the reactor, by which way the total pressure for hydrate reaction could maintain constant. When reaction was completed, the reactor was depressurized quickly while the temperature was decreased to reduce hydrate dissociation. Then the reactor was opened and the hydrates morphology was observed by taking photos.

3. Results and discussion

3.1. Pure methane hydrate formation process

As a common hydrate promoter for both carbon dioxide and methane hydrate, the SDS with a low concentration of 0.5 mmol/L was chosen in this work to get rapid formation process. Taking the stochastic nucleation into consideration, every experiment was repeated for three times. The pressure and temperature evolutions in the pure methane hydrate formation process in the SDS solutions or water were shown in Fig. 2. When the hydrate started to form and grow, the pressure decreased with time owing to the gas consumption which was called the hydrate growth stage (noted on the blue line in Fig. 2). Clearly, more than 300 min of stagnation period always preceded the hydrate growth stage, during which almost no gas was consumed. This stage was named as induction period related to the hydrate nucleation process (as marked on the blue curve in Fig. 2) [22]. Compared with deionized water where no pressure drop was observed within 10 h, the hydrate formations in the SDS solutions were all completed in 400 min. Thus, using 0.5 mmol/L SDS solution improved hydrate formation greatly. Moreover, the rapid hydrate growth led to the sharp temperature increase due to the exothermal reaction. However, the long induction times ranging from 300 to 400 min were still unfavorable in the practical utilization of methane hydrate.

The hydrates morphology and growth pattern in the reactor in the SDS solution was shown in Fig. 2(B). The mushy methane hydrates showed upward growth pattern and almost covered the whole sidewall of the reactor, which was possibly caused by the capillary effect of porous hydrate crystals [23,24]. However, the