



Enhancing methane hydrate formation in bulk water using vertical reciprocating impact



Peng Xiao^a, Xiao-Mei Yang^a, Chang-Yu Sun^{a,b,*}, Jin-Long Cui^a, Nan Li^a, Guang-Jin Chen^{a,*}

^a State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

^b Faculty of Engineering, China University of Petroleum, Karamay 834000, China

ARTICLE INFO

Keywords:

Gas hydrate
Methane storage
Kinetics
Reciprocating impact
Intensification method

ABSTRACT

A new method to improve the methane hydrate formation rate and gas uptake was developed through continuous impact on hydrate block with high interstitial water cut. Experimental investigations were conducted at temperature and pressure ranges of 273.3–279.2 K and 3.4–6.0 MPa, respectively, for different water loads and impact frequencies. Hydrate formation in quiescent sodium dodecyl sulfate (SDS) solution and pure water with rotational stirring was investigated for comparison. The reciprocating impact intensification method significantly improved the formation rate in both slurry and hydrate block stages as well as the final gas uptake. The fastest formation was observed at 274.7 K and 6.0 MPa, where 90% of hydrate formation was completed within 4 h. The largest gas uptake (150.3 V/V) in the hydrate was observed at 279.2 K and 6.0 MPa, which was slightly higher than that obtained from SDS. The advantage of the proposed method is that the final hydrate block is compacted in a significantly smaller bulk volume than that of the fluffy hydrate formed from SDS. Multi-growth was observed in hydrate formation when the reciprocating impact method was adopted. Temperature and pressure affected the formation kinetics but not methane uptake. The optimal conditions for hydrate formation in bulk water included a water/inner reactor space volume ratio of 0.18 and an impact frequency of 30 times/min. Additionally, the lowest power consumption for reciprocating impact was calculated as 3.77×10^{-3} kW/h/mol. These results indicate that it is feasible to store methane using clathrate hydrates without additives.

1. Introduction

Global warming is mainly caused by the increasing concentration of CO₂ in the atmosphere. To curb climate warming, a consensus for reducing CO₂ emissions has been reached. Natural gas produces less CO₂ during combustion and is regarded as a potential alternative fuel to oil and coal. Thus, because of its ever-increasing demand, the development of technologies to store and transport natural gas has become more significant. Natural gas is mainly transported in the form of liquefied natural gas (LNG), compressed natural gas (CNG), and via pipelines. It is estimated that ~70% of the total gas reserve is either too small to justify a liquefaction facility or too far from an existing pipeline [1]. In recent years, the potential of natural gas transportation using gas hydrate has been researched. Gas hydrate, non-stoichiometric crystalline compound formed from hydrogen-bonded water molecules and small guest molecules at specific temperatures and pressures, is widely recognized as a substantial unconventional source of energy as well as the severe risk of blockage in oil and gas pipelines. Moreover, the capacity (each volume of hydrate can store 180 volumes (STP) of gas [1]), less

necessity of low temperature compared to LNG (–162 °C) and the lower pressure than CNG (200–250 atm) [2] and nonexplosive character make it an excellent candidate for natural gas storage and transportation. However, its industrial application is deterred by stochastic induction time, low formation rate, and low gas uptake. Thus, these practical problems need to be addressed to drive gas hydrates into industrial natural gas transportation.

To solve the aforesaid problems, additives known as kinetic promoter have been introduced in during hydrate formation, of which surfactants account for a large proportion, and have been widely used to accelerate hydrate formation. These additives were found to remarkably improve the kinetics of hydrate formation without affecting the thermodynamic conditions [3]. Though some controversies over the mechanism exist [4–6], it is indisputable that surfactants are effective kinetic promoters for hydrate formation. Among these surfactants, sodium dodecyl sulfate (SDS) is the most commonly used promoter [7,8]. Link et al. [9] adopted different surfactants to promote methane hydrate formation. Their results suggested that the addition of SDS afforded a methane uptake value > 97% of the theoretical limit. Hence,

* Corresponding authors at: State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China (C.-Y. Sun).
E-mail addresses: cysun@cup.edu.cn (C.-Y. Sun), gjchen@cup.edu.cn (G.-J. Chen).

they concluded that SDS is the most appropriate additive for enhancing methane hydrate formation. Lin et al. [10] determined a maximum gas storage capacity of 170 V/V in 650-ppm SDS aqueous solutions. Although additives can significantly enhance the formation kinetics and gas uptake of the hydrate, the sole use of anionic surfactants, especially SDS, affords the most efficient promotion [11–13]. However, some disadvantages of using SDS in hydrate formation have restricted its potential for industrial hydrate application. First, SDS presents hydrate particles from agglomerating so that leads to the formation of a snow-like hydrate on the reactor wall [14] that decreases the storage density. Secondly, the hydrate formed from the SDS solution is less stable than that formed from pure water [10] and generates substantial foam during hydrate dissociation. Another class of kinetics additive is amino acid, which has been recently reported to significantly improve methane hydrate formation. Veluswamy et al. [15] proposed a simple approach to improve methane hydrate formation by combining stirred and unstirred operation in the presence of leucine. Similar hydrate formation kinetics in both stirred and unstirred reactor were observed and methane uptake > 130 mmol/mol was afforded by this novel method. Added advantage of using leucine is that the hydrate generates no foam during dissociation [16], which is superior to the use of SDS. In a morphology study of methane hydrate formation using Leucine, channel-like structures were observed during hydrate growth, which serve as a bridge and a contact mode, thereby resulting in further conversion of water to hydrate [17]. However, storage capacity of gas in hydrate can be decreased by the formation of porous hydrate from these structures.

Mechanical agitation is the most conventional physical method used to accelerate the batch reaction. When used in hydrate formation, most mechanical agitation methods are of the rotational stirring type and for the sake of seal, they are mostly magnetic [18–20]. Some studies suggested that stirring reduces induction time [18,20]. In addition, both of the formation rate [19,20] and storage capacity [20] increase with an increase of stirring rate. However, it also suggested a long time stirring can result in decomposition of formed hydrate [20]. The hydrates first appear at the gas/water interface and subsequently grow into a rigid hydrate film that hinders any further growth under static conditions. Rotational stirring can continuously renew the gas/water interfacial area and thus, shortens the induction time and accelerates the formation rate during the early stage of hydrate formation. Typical stages during hydrate formation in a batch reactor are the slurry and hydrate block stages. The rheological property of natural gas hydrate slurry directly measured with a high-pressure rheometer, suggests the presence of shear thinning behavior [21]. Namely, conventional (rotational) stirring will provide inadequate agitation for the hydrate slurry, thereby leading to inefficient gas transfer. Additionally, the most used magnetic stirrer would get stuck in the forming hydrate, resulting in a large amount of interstitial water and low gas uptake. Thus, even in a stirred reactor, slow kinetics and low gas uptake are inevitable. Moreover, during hydration processing, the power needed for stirring increases with increasing hydrate slurry viscosity. Consequently, the rotational stirring energy required for large scale application of gas storage via gas hydrate is intensive. Furthermore, some studies have suggested that stirring is unfavorable for scaling-up hydrate production [22,23]. Physical methods including a bubble column [24], spraying reactor [25–27], have also been introduced to enhance hydrate formation. Well-dispersed gas or water in these types of reactors afford faster hydrate formation and a higher gas uptake. However, these reactors pose several practical difficulties including fully filled foam-like hydrate shells in the gas space that are difficult to break [24] and the long time required for the conversion of high water to hydrate [28]. Another approach to improve hydrate formation is dispersing the water onto porous materials/structures or nanoparticles (fixed bed), including silica sand [29,30], silica gel [31,32], hydrophobic silica particles [33,34], etc. A latest detailed review summarized those relevant works [35], and in all of those studies presented in the review, the hydrate

formation rate was increased via the dispersed water. Although these materials can improve formation rate and gas uptake of hydrate, they increase the bed volume so that decrease the storage density.

The elimination of interstitial water is the most critical factor to improve the storage capacity of the gas hydrate that forms from pure water. In this work, we designed a new reactor comprising an impact system in which the interstitial water is extruded from the hydrate block with continuous impact to allow the reaction to proceed. Another expected advantage of the reciprocating impact system is that in the hydrate slurry, the impactor acts as a stirrer that also crushes the floating hydrate film at the gas/water interface to afford more satisfactory formation kinetics than those afforded by rotational stirring. Reciprocating stirring has been adopted in our previous works [36–39] to agitate water in oil emulsions and ZIF-8/glycol slurry systems. However, to the best of our knowledge, its use to improve formation kinetics and gas uptake of hydrates in bulk water, especially after hydrate particle agglomerated into a hydrate block, has not been tested to date. Thus, in this study, we systematically investigated the effects of reciprocating impact on methane hydrate formation in bulk water using our newly designed reactor. Moreover, hydrate formation in pure water with rotational stirring and in quiescent SDS solution was also studied for comparison.

2. Experimental section

2.1. Materials

Methane (99.99% purity) was supplied by Beijing AP BAIF Gases Industry Company Limited. Double distilled water with a conductivity < 10^{-4} S m⁻¹ was distilled in our laboratory. SDS (99.9% purity) was purchased from Aladdin Reagent (Shanghai) Company Limited.

2.2. Experimental apparatus

The setup used in this work is illustrated in Fig. 1, which consists of three main parts: a gas supply system including a CH₄ cylinder and a blind cell, a reaction system comprising a reactor and stirring/impact devices, and a data acquisition system. A batch type stainless steel reactor (diameter = 4.9 cm, height = 12.7 cm) was adopted to perform hydrate formation experiments. The effective internal volume of the reactor, including the volume of the pipelines connected to it, was 245 mL. A rotational stirrer was used to enhance hydrate formation in comparative trials, while a reciprocating impactor was used both as a stirrer in the hydrate slurry and to extrude interstitial water after hydrate block formation. The stirrer and impactor were controlled separately by two groups of magnets driven by two electric motors. One group of magnets rotated below the reactor while the other group maintained reciprocating motion beside the reactor. The magnets were lifted vertically upward to a height of 8.6 cm by an electromotor and subsequently allowed to free fall down to the bottom of the vessel. The maximum lifting weight of the magnets was 370 g. A stainless steel blind cell with an effective internal volume of 769 mL was used to pre-cool methane to the experimental temperature. Both the blind cell and the reactor were installed in an air bath. Needle valves (V1, V2, and V4) were used to control gas injection and discharge. A reducing valve (V3 in Fig. 1) was used to maintain the reactor pressure constant during hydrate formation (adjusting accuracy = ± 0.1 MPa deviation from the set value). To monitor pressure and temperature values, two pressure transmitters (uncertainty = 0.1%, pressure range = 0–20 MPa) were installed on the blind cell and reactor, while a Pt100 resistance temperature detector (uncertainty = 0.1 K) was installed on the reactor at the height of 1.9 cm from the bottom. This position was marked on Fig. 1 based on relative height of the probe and the reactor. Pressure and temperature data were acquired by means of a data logger and recorded every minute on a computer.

Download English Version:

<https://daneshyari.com/en/article/6580696>

Download Persian Version:

<https://daneshyari.com/article/6580696>

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