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Methane hydrate formation in excess water simulating marine locations and the impact of thermal stimulation on energy recovery

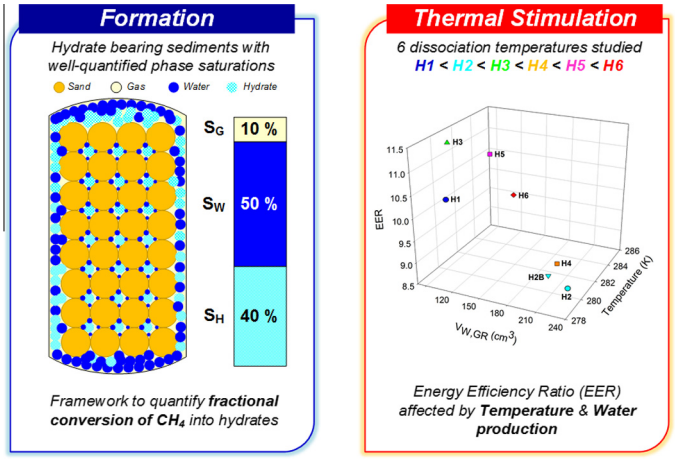
Zheng Rong Chong [a], Girish Anand Pujar [a], Mingjun Yang [a,b,*], Praveen Linga [a,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore
[b] Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, China

HIGHLIGHTS

- Formation of quantitatively similar hydrate sediments simulating marine sediments.
- Gas and water production simultaneously acquired under 6 temperatures.
- Water production severely affects gas production behavior.
- A temperature driving force of 2.1 K is needed for reasonable gas production rates.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we investigated the gas and water production profiles from methane hydrates formed in an excess water environment that mimic marine locations. Instead of pressurization by the addition of gas, water was injected into the sediment to create the high pressure environment of the reservoir, thereby creating a hydrate bearing sediment of high water saturation similar to those in marine locations. A framework is introduced to determine fractions of methane converted into hydrates during hydrate formation stage taking into account the effect of density changes, solubility and the in-situ pressure and temperature conditions. As opposed to 100% conversion assumed in the previous excess water works, our quantification shows that on average, the fractional conversion of methane is around 81.5% at comparable or larger experimental time scales (76–408 h). Upon the formation of quantitatively similar hydrate bearing sediments, the dissociation of methane hydrate was done under a constant pressure of 4.5 MPa subjecting to different thermal stimulation extents from 278.7 K to 285.2 K. It was found that low temperature driving force would result in an extremely low dissociation rate, and a minimum temperature of 280.7 K (corresponding to 2.1 K temperature driving force) is required to achieve a 90% dissociation within 10 h. In addition, through a simplified estimation of energy efficiency ratio (EER) and analysis of water production profile, we demonstrated the importance of water management in developing methods to effectively recover energy from hydrate bearing sediments.

* Corresponding author at: Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585, Singapore.
E-mail addresses: yangmj@dlut.edu.cn (M. Yang), Praveen.Linga@nus.edu.sg (P. Linga).

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1. Introduction

Clathrate hydrates are solid, crystalline inclusion compounds formed by guest molecules and water molecules, where the water molecules (host) form cages enclathrating the guest molecules [1–4]. In nature, an abundant amount of natural gas is available as natural gas hydrates (NGHs) in permafrost and the continental margin [5–9], which in turn represents a huge potential resource of fossil fuel. A vast majority of NGH is composed of methane (CH_4), and other minor components includes ethane (C_2H_6), propane (C_3H_8), and carbon dioxide (CO_2), etc. according to the origin of natural gas. NGHs deposits can be classified into different classes according to the layers present around [10–12]. Class 1 deposit contains a hydrate-bearing layer and an underlying two-phase zone comprised of gas and water, and it was found in the North Slope of Alaska [13]. Class 2 deposit contains a hydrate bearing layer with an underlying water saturated zone, which was found in Nankai Trough, Japan [14,15]. Class 3 NGH is composed of an isolated hydrate layer with no overlying and underlying fluid zones [10]. It is important to develop NGH exploration technologies suitable for different classes of NGH reservoirs to recover natural gas. The gas recovery is a complex event affected by various characteristics of the targeted NGH sediments, such as the hydrate saturation, permeability, pressure, temperature and heat and mass transfer [16–24].

In order to clarify the dissociation characteristics for different kinds of NGH deposits, it is necessary to obtain hydrate samples representative of those in the nature. Due to the high cost of NGH coring and inevitable perturbation to the naturally occurring hydrates, it is essential to form synthetic NGH or methane hydrates (MH) in the laboratories. The most common method to form MH in a laboratory setting is by '*excess gas*' approach, whereby water was first introduced to saturate the porous media, followed by gas injection to pressurize the vessel to the desired overpressure at a low temperature to initiate hydrate formation [25–30]. Under excess gas condition, it was reported that hydrate formation is more rapid at a lower initial water saturation [31] and a smaller scale [32]. Through microscopic analysis employing Raman spectroscopy and in situ X-ray diffraction, it was found that during MH formation, CH_4 is first incorporated into pentagonal dodecahedron (5^{12}) cage [33]. Recently, Ruffine studied the influence of methane injection rate on MH formation kinetics in silica sand and reported that high injection rate may induce the trapping of gas bubbles within the hydrate phase [34]. In a research elucidating the morphology of MH in porous media, it was found that MH formed from 'excess gas' method exhibited a cementing behavior to the porous media, as MH were favourably formed at water-wetted grain contact [35]. In nature, cementing hydrates are likely to be found around the base of gas hydrate stability (BGHS) with an underlying formation of high dissolved methane concentration or free gas [36].

Another approach to form MH in laboratory scale is through '*excess water*' approach, which was introduced in recent years [35,37–40]. The motivation for excess water approach was to mimic a condition similar to the nature whereby NGH is formed in pore filling or load bearing manner within the water saturated sediments [41–43]. Under an excess water approach, a fixed amount of gas is first introduced to the porous media, followed by the injection of water in excess [35]. In contrast with 'excess gas' approach, hydrates were not restricted to form at inter-granular contact. Therefore the cementing of hydrate deposit formed via excess water was found to be negligible below a hydrate saturation of 20% [35,37]. Prior to the introduction of excess water approach, research to form hydrates from dissolved methane had been conducted, as it is the major source of gas producing hydrates in nature [44]. It was reported that the hydrates formed from dissolved gas were typically pore filling hydrates with low hydrate saturation in coarse-grained sediments [45,46]. Although it was assumed that hydrates formed from dissolved methane would be more similar to the scenario in nature, such approach requires a long formation time (more than a few weeks) and sophisticated equipment [36,47,48]. Best et al. reported that the seismic wave attenuations are vastly different for hydrate deposit formed from excess-gas and excess-water conditions [49]. Li et al. validated a new kinetic model for hydrate formation based on the assumption that hydrates were formed from gas bubbles dispersed in liquid within the porous media when excess water approach was employed [32]. In that study, formations of hydrate were carried out with initial water saturation ranged from 53.3% to 69.9%. However, the phase saturations after hydrate formation were not reported in that study.

Hydrate dissociation kinetics have also been studied extensively to elucidate the production response from NGH employing different production techniques, including thermal stimulation [25,50–52], depressurization [26,53–55], inhibitor injection [56–58] or a combination of the abovementioned methods [17,55,59]. Among these production strategies, thermal stimulation is one of the most widely studied approach. In a laboratory setting, thermal stimulation of hydrates have been done via direct injection [50,60], immersion method [25,27,51] and electromagnetic heating [61,62]. It has also been employed in the first hydrate field production test in Mallik site, Canada [63]. However, numerical simulation has indicated that thermal stimulation on its own is not energy efficient [64,65]. Nonetheless, well bore heating is required to improve the rate of gas production, especially since hydrate dissociation is an endothermic process [65,66]. On top of that, it is also of interest to elucidate how temperature as an independent parameter will affect the stability of naturally occurring hydrates as a result of global warming [67–69].

It is clear that the essential pathway to study gas production behavior from MH is based on MH samples synthesized in the laboratory. Therefore, it is essential to elucidate the formation behavior of MH, particularly in the porous media, to synthesize artificial hydrates representative of that in nature. A majority of the MH research employed excess gas approach, which has little control over the quantification of hydrate saturation and formed cementing hydrates that is different from hydrates formed from dissolved methane [25,27,30,31,52,70–73]. On the other hand, excess water approach has been proposed and employed in recent years more in the context of understanding the physical properties. Among the few studies that deals with methane production from excess water environments, a precise quantification of the fractional conversion of methane is lacking as most of the studies presented on excess water approach assume that all the gas were converted into hydrates, which may not be true at the time scales in which the data has been reported [35,38,39,74]. In addition, the exact quantification of the phase (solid hydrate, liquid water and gas) distribution within the porous media in excess water approach is not available in the literature works.

In this study, we present an experimental method to produce synthetic hydrates of well quantified gas, water and hydrate saturation employing excess water approach that simulate hydrate sample in marine locations. Upon the formation of quantitatively comparable hydrate samples, we employed thermal stimulation method to different extents to elucidate the gas and water production behavior in response to a small temperature perturbation.

2. Experimental section

2.1. Materials

The gas applied in this study is CH_4 (99.9% purity) supplied by Singapore Oxygen Air Liquide Pte Ltd. Silica sand with particle size