Fuel xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Enhanced clathrate hydrate formation kinetics at near ambient temperatures and moderate pressures: Application to natural gas storage

Hari Prakash Veluswamy [a], Sharad Kumar [a], Rajnish Kumar [b], Pramoch Rangsunvigit [c], Praveen Linga [a,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117 585, Singapore
[b] Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Pune, India
[c] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand

HIGHLIGHTS

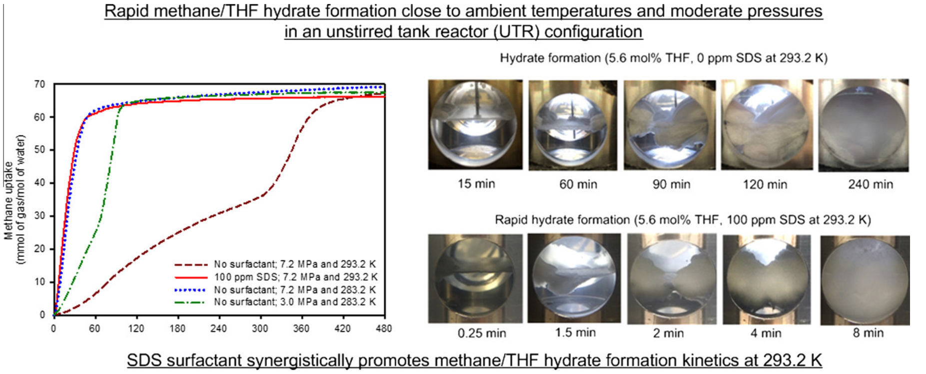
- Rapid production of methane/THF hydrates closer to ambient temperatures is presented.
- Substantial methane uptake observed in methane/THF hydrates even at moderate pressures.
- Synergistic effect of tetrahydrofuran (THF) and sodium dodecyl sulfate (SDS) is presented.
- 100 ppm SDS surfactant facilitates rapid methane/THF hydrate formation at 293.2 K.

ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form 13 May 2016
Accepted 15 May 2016
Available online xxxx

Keywords:
Natural gas storage
Methane hydrates
Unstirred reactor
Rapid kinetics
Surfactant
Tetrahydrofuran

GRAPHICAL ABSTRACT



ABSTRACT

SNG (solidified natural gas) technology via clathrate hydrates is a potential method for large scale stationary storage of natural gas. Clathrate hydrate formation kinetics in presence of methane and 5.6 mol% tetrahydrofuran (THF) was investigated in an unstirred reactor configuration at moderate pressure and temperature conditions. It is well known that the presence of THF generally improves the thermodynamic stability of the resulting hydrate. In order to study the scale-up potential of this approach, kinetics of hydrate growth at temperatures close to ambient conditions and moderate pressures is required. Hydrate formation experiments were performed at three different temperatures – 283.2 K, 288.2 K and 293.2 K and at experimental pressures of 7.2 MPa, 5.0 and 3.0 MPa. Further, we report a synergistic effect of kinetic promotion of mixed methane hydrate formation by coupling THF and sodium dodecyl sulfate (SDS) at 293.2 K. For the first time, we observe rapid mixed methane/THF hydrate formation kinetics at 293.2 K in presence of just 100 ppm sodium dodecyl sulfate surfactant with methane gas uptake of 3.45 (±0.17) kmol/m^3 of water in 1 h. This is also the first study to demonstrate such rapid hydrate formation kinetics with significant methane storage capacity at temperature of 293.2 K (closer to the ambient temperature). Further, substantial methane gas uptake of 3.52 (±0.13) kmol/m^3 of water is possible even at reduced experimental pressure of 3.0 MPa and 283.2 K in 2 h. Minimal energy requirement in an unstirred reactor for mixed methane/THF hydrate formation/storage can propel the SNG

---

* Corresponding author.
E-mail address: Praveen.Linga@nus.edu.sg (P. Linga).

http://dx.doi.org/10.1016/j.fuel.2016.05.068

Please cite this article in press as: Veluswamy HP et al. Enhanced clathrate hydrate formation kinetics at near ambient temperatures and moderate pressures: Application to natural gas storage. Fuel (2016), http://dx.doi.org/10.1016/j.fuel.2016.05.068

technology for large scale commercial deployment. Further improvement in the process can be achieved by optimizing the cooling requirement through innovative reactor design and operating the process in a semi-batch or continuous mode.

1. Introduction

Share of natural gas in the global primary energy will be increasing steadily till 2040 based on the forecast by International Energy Agency (IEA). Storage and transport of natural gas effectively and efficiently, is highly important in the current golden era of natural gas [1]. Storing natural gas in the form of clathrate hydrates or gas hydrates, known as SNG (Solidified Natural Gas) [2] or NGH (Natural Gas Hydrate) [3], has numerous advantages – it offers a compact mode of storage with high volumetric storage capacity (up to 164 m^3 of methane gas can be stored in just 1 m^3 of hydrate [4]), being non-explosive it is very safe to handle, environmentally benign mode of storage and it is highly cost effective compared to the conventional methods of NG storage in the form of CNG (Compressed NG) and LNG (Liquefied Natural Gas) [2,5,6]. Despite several benefits offered by SNG technology for natural gas storage, till date there has been no commercial plant for the production, transport and storage of SNG except a couple of pilot demonstration plants in Japan and South Korea [7,8]. Few of the key existing challenges include the need for severe operating conditions (low temperature and high pressure requirement for hydrate formation) and the slow kinetics of hydrate formation. In addition, the storage temperature of 253 K at atmospheric pressure is based on the anomalous 'self-preservation' effect [9–13]. Further, high costs incurred due to the potential gas pre-compression and agitation (required during hydrate formation) along with cooling costs (both during hydrate formation and storage step) hinder the large scale deployment of SNG technology.

To overcome the slow kinetics, continuous research efforts have been put forth in improving the kinetics of methane hydrate formation either by innovative reactor designs [14–20] including the use of different porous media [21–29] or the use of kinetic promoters (predominantly surfactants) in order to enhance the rate of hydrate formation [30–35]. Though the kinetics of hydrate formation is improved by a choice of suitable reactor or kinetic promoter, there is no reduction of the high energy requirement due to low temperature and high pressure conditions of hydrate formation. Added to this, there is no mitigation of conditions required for storage (about 253 K at 0.1 MPa). Thus, a holistic approach is required to address all the major challenges of the SNG technology process chain wherein the improvement in kinetics of hydrate formation along with milder hydrate storage conditions is necessary.

Moderate conditions of hydrate formation (at higher temperatures and low/moderate pressures) can be achieved only with the addition of a 'thermodynamic promoter'. These promoters (typically large size guest molecules) predominantly occupy and stabilize the large sized hydrate cages at moderate conditions of temperature/pressure thereby lowering the methane storage capacity in comparison to pure methane hydrates. Thus, the choice of a thermodynamic promoter must provide significant impact on the operating and storage conditions albeit a penalty on the storage capacity of methane is inevitable. Many thermodynamic promoters have been reported and studied for methane hydrate formation [2,14,19,36–44]. Though exhaustive literature is available on the hydrate phase equilibrium conditions for these different thermodynamic promoters, kinetic investigation studies using these promoters are relatively scarce. sH mixed methane hydrate formation in presence of large guest molecules had been investigated in detail by Susilo et al. [37,43]. Other notable kinetic studies for mixed methane hydrate formation with use of thermodynamic promoters include the formation of mixed methane hydrates in presence of cyclopentane [19,41] and tetrahydrofuran (THF) [2,40,44]. All kinetic studies available on mixed methane hydrate formation at higher temperatures (with and without thermodynamic promoters) have been performed only in stirred tank reactor configuration [45,46].

Recently, we reported a new approach to form hydrates rapidly, in presence of methane and THF in an unstirred reactor configuration at 283.2 K with very fast gas uptake rates [2]. In this work, by synergistically combining small concentrations of sodium dodecyl sulfate (SDS) kinetic promoter, we report rapid mixed methane/THF hydrate formation at 293.2 K. Further, we evaluate the effect of SDS up to its critical micelle concentration and identify that there is a concentration dependent kinetic promotion or inhibition of mixed methane hydrates in the presence of THF. This study reports rapid mixed methane/THF hydrate formation kinetics at near room temperature and at low pressures in a simple quiescent unstirred reactor configuration with the simultaneous employment of THF and SDS.

2. Experimental section

2.1. Materials

Gas cylinder containing methane gas of 99.9% purity purchased from SOXAL Pte Ltd, analytical reagent grade tetrahydrofuran (THF) of 99.7% purity obtained from Fisher Chemicals, and 99% pure biotechnology grade sodium dodecyl sulfate (SDS) from AMRESCO were used for experiments. Water obtained from Elga micromeg deionizaton apparatus was used in all experiments.

2.2. Experimental apparatus

The experimental setup was the same apparatus used by Veluswamy et al. [47]. All experiments were of batch type and conducted in a customized reactor (CR) made of SS316 and designed for a maximum working pressure of 10 MPa. The reactor had an internal volume of 142 ml and was fitted with two marine type viewing windows (at the front and back) of 30 mm diameter to allow the visual observation of reactor contents. The reactor was submerged in a water bath and Polyscience SD15R external refrigerator (ER) was employed to maintain the reactor contents at experimental temperature. Reactor pressure was measured using a Rosemount 3051 Pressure Transmitter (PT) supplied by Emerson Process Management, with a maximum uncertainty of 0.1% within the pressure range of 0–20 MPa. An analog pressure gauge (PG) supplied by WIKA was also coupled to monitor the reactor pressure. The reactor temperature was measured by a copper-constantan T type thermocouple supplied by Omega (uncertainty of 0.1 K). Both the pressure transmitter and thermocouple were connected to a Data Acquisition (DAQ) system supplied by National Instruments, that was connected to a computer (PC). Temperature and pressure data were recorded every 20 s, with the use of LabVIEW software provided by National Instruments.

Please cite this article in press as: Veluswamy HP et al. Enhanced clathrate hydrate formation kinetics at near ambient temperatures and moderate pressures: Application to natural gas storage. Fuel (2016), http://dx.doi.org/10.1016/j.fuel.2016.05.068