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Rapid methane hydrate formation to develop a cost effective large scale energy storage system

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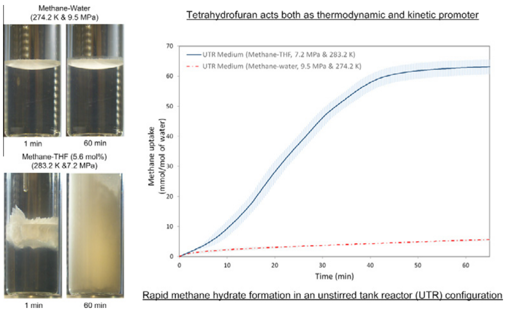
HIGHLIGHTS

- A new method for producing methane hydrates rapidly is presented.
- Tetrahydrofuran acts both as a thermodynamic and kinetic promoter in an unstirred tank reactor.
- A cost effective, large scale solidified natural gas (SNG) storage system is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Natural gas (NG) is the cleanest burning fossil fuel and its usage can significantly reduce CO_2 emissions from power plants. With its widespread use, there is an ever increasing need to develop technologies to store NG on a large scale. NG storage via clathrate hydrates is the best option for a large scale storage system because of its non-explosive nature, mild storage conditions, high volumetric capacity and being an environmentally benign process. In this work, we demonstrate a new method to achieve rapid methane hydrate formation in an unstirred tank reactor configuration (UTR) at moderate temperature and pressure conditions employing tetrahydrofuran (THF) as a promoter. For the first time, THF is reported to act both as a thermodynamic and an excellent kinetic promoter for methane hydrate formation. We demonstrate a multi-scale experimental validation of our method to a volumetric sample scale-up factor of 120 and internal reactor diameter scale-up factor of 10. Further, new insights on the dissociation behavior of the hydrates are reported. There is a competitive edge for storing NG via clathrate hydrates compared to compressed natural gas storage both in terms of cost and safety.

1. Introduction

NG is the cleanest burning fossil fuel and can meet stringent environmental norms, including reduced CO_2 emissions. This century is the golden age for natural gas (NG) according to International Energy Agency (IEA) [1]. With the inevitable global shift to a NG based economy, there is an ever increasing need to develop

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technologies to store NG on a large scale. Storage options for NG include LNG (Liquefied NG), CNG (Compressed NG), SNG (Solidified NG) via clathrate hydrates or as ANG (Adsorbed NG) via sorbents. LNG has a volumetric capacity of about 600 v/v and is a very effective mode to transport NG from source to market [2] but not suitable for storage due to the continuous gas boil-off issues. CNG (∼200 v/v at 200 atm) as mode of storage requires high pressure for both production and storage. The inherent flammable/explosive nature of natural gas, practically makes CNG hazardous for large scale NG storage. ANG requires adsorbing NG onto sorbents like activated carbon, carbon nanotubes (CNTs), graphene, metal organic frameworks (MOFs) etc. [3–6] Given the history of the development of CNTs for NG storage and known scale-up issues, there is a need to demonstrate process development for these materials.

Storage of natural gas as SNG via clathrate hydrates offers an excellent opportunity to store NG on a large scale. The term SNG (solidified natural gas) is coined similar to LNG, CNG or ANG and is defined as natural gas locked in the solid cages formed by water molecules. There are several advantages of SNG technology: high volumetric storage capacity, being environmentally benign, non-explosive nature, extremely safe to handle and cost effective [7,8]. Another highlight of SNG technology is that it is not sensitive to the presence of higher hydrocarbons like traces of ethane, propane etc. This is due to the fact that trace hydrocarbons can also be captured in the water cages if present and essentially they can result in a milder operating and storage conditions for SNG technology. At 283.2 K, presence of 5% propane (remaining methane) in natural gas results in hydrate formation pressure of just 2.17 MPa in comparison to 7.25 MPa pressure for pure methane gas. 'Self-preservation' is another phenomenon that is a characteristic advantage to SNG technology [9,10]. Maintaining subzero storage conditions at atmospheric pressure ensures extremely slow hydrate dissociation rates and thus offers kinetic stability due to self-preservation effect. Mimachi et al. [11] had recently demonstrated successful storage of NGH pellets for about 3 months under atmospheric pressure at 253 K without any considerable change in hydrate mass fraction and the stored gas composition. Moreover, energy recovery from SNG is relatively simple just like melting ice that can be achieved using low waste heat or seawater. Research on SNG has seen a progressive development in the past decade with demonstration plants in Japan and South Korea. Apart from NG storage, gas hydrates are promising candidates in storing hydrogen [12–14], to develop an environmentally benign technology for carbon dioxide capture and sequestration [15–18], desalination of seawater [19,20], cold storage [21,22] and gas separation applications [23,24]. Gas hydrates are also considered as a huge energy resource of the future due their presence in nature as either permafrost or marine deposits distributed across the world [25–27].

Despite several advantages highlighted for the SNG technology, there are a few challenges that impede the commercial deployment of this technology. There are four steps involved in SNG technology: hydrate formation step, dewatering step, pelletizing step, and storage step (involves depressurization to reach the storage condition of 1 atm). Major research challenges for the SNG technology are in the formation step (slow kinetics of hydrate formation and severe operating process conditions) and the storage step (cost of refrigeration during the storage of SNG at 248 K). Generally, the kinetics of hydrate formation in traditional stirred tank reactors is affected by mass transfer limitation at the gas/liquid interface due to the inability to continuously mix the gas/liquid/solid system for sustaining the hydrate growth. Also, due to high process costs involved, stirred tank reactors are energy intensive for a large scale deployment of SNG technology. On the other hand, in a quiescent unstirred system, methane hydrates are observed to form a hydrate film commonly referred to as "skin" at the gas–liquid interface offering resistance to further hydrate growth [28]. Two possible approaches to overcome the slow kinetics are: to employ an effective and innovative reactor configuration to enhance the kinetics but at the same time, the configuration should not be energy intensive for large scale deployment. The second approach is to choose promoters that can enhance the kinetics without compromising the storage capacity and operate at moderate experimental conditions.

Recent literature studies highlight the advantage of using fixed bed reactor configuration for achieving improved kinetics of methane hydrate formation. Materials like silica gel, aluminium foam, activated carbon, carbon tubes and hollow nano-silica were studied as fixed bed supports for improving the methane hydrate formation kinetics [29–32]. Further, novel materials like dry water [33] (free flowing hydrophobic silica powder with dispersed water), hollow silica [34,35] (very low bulk density) and dry gels [36] (gelling agent along with dry water for improving recyclability) were experimented for studying the methane hydrate formation kinetics. While recent literature works have shown enhanced kinetics in the presence of porous materials, in the overall SNG production and storage process chain, the use of porous material is less practical due to the challenges involved in pelletizing the hydrates along with the porous materials for effective storage and transport application. Another challenge is the increase in the volume of storage due to the presence of porous materials along with hydrates. Other reactor configurations [37] for providing improved gas/liquid contact for methane hydrate formation include bubble column [38], spray reactors [39–42] and eject type loop reactor [43]. Though it has been demonstrated that it is feasible to employ spray type configuration for methane hydrate production on a large scale, it will be cost intensive compared to the classic unstirred reactor configuration employed in the current study.

Apart from different reactor configurations, different thermodynamic and kinetic promoters are being evaluated for improving the hydrate formation conditions and the kinetics respectively [44–48]. Thermodynamic promoters are chemicals that facilitate hydrate formation at moderate temperature and pressure conditions but at the cost of storage capacity. This happens due to the fact that promoter molecules occupy the hydrate cages along with guest methane/natural gas. Methane forms a standard sI hydrate structure on its own. However, in the presence of thermodynamic promoter it is possible for methane to be present in other caged structures like sII or sH depending on the guest molecules [48–50]. With the assumption of complete occupancy of methane in small and large cages of sI hydrate structure, the theoretical methane storage capacity is 172 v/v (based on the gas release at STP). For sII and sH hydrate structures, large cages are occupied by added promoters (large guest molecules) and methane occupies small cages of sII and both small and medium cages of sH structure. With the assumption of complete occupancy of methane in aforesaid cages of sII and sH, the volumetric storage capacities are computed to be 115 and 143 v/v respectively [49]. Despite the 33% and 17% reduction in storage capacity considering sII and sH hydrate structures, the flexibility of hydrate formation at much moderate pressures and high temperatures than pure sI hydrates will offer higher incentives in the reduction of compression and refrigeration costs which will offer greater benefit for commercial scale SNG production. Several studies have been reported in the literature on sH methane hydrate formation with the presence of large molecules like neohexane, tert-butyl methyl ether (TBME), methylcyclohexane, etc. as guest. Lee et al. [48] investigated the kinetics of sH hydrate for different sH hydrate formers and methane in a stirred tank reactor and reported a highest methane uptake of 0.0261 mol/mol of water using TBME promoter. Later, several