

An innovative approach to enhance methane hydrate formation kinetics with leucine for energy storage application



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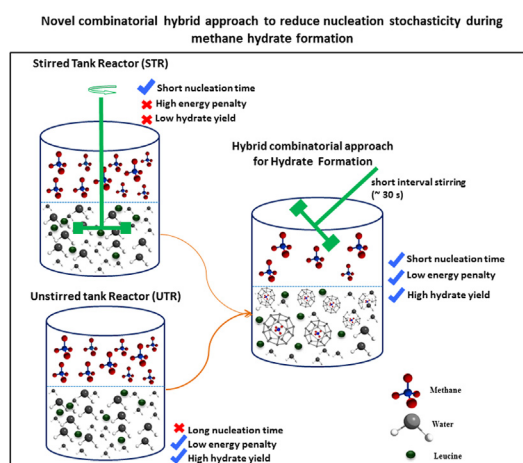
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HIGHLIGHTS

- Innovative combinatorial hybrid approach to reduce nucleation stochasticity and enhance hydrate growth.
- Methane hydrate growth curves are similar in UTR and STR configurations in presence of leucine.
- Amalgamation of stirred (STR) and unstirred (UTR) configuration is demonstrated.
- Reliable method for scale up and commercial production of Solidified Natural Gas (SNG).

GRAPHICAL ABSTRACT



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ABSTRACT

Natural gas storage in clathrate hydrates or solidified natural gas (SNG) offers the safest, cleanest and the most compact mode of storage aided by the relative ease in natural gas (NG) recovery with minimal cost compared to known conventional methods of NG storage. The stochastic nature of hydrate nucleation and the slow kinetics of hydrate growth are major challenges that needs to be addressed on the SNG production side. A deterministic and fast nucleation coupled with rapid crystallization kinetics would empower this beneficial technology for commercial application. We propose a hybrid combinatorial approach of methane hydrate formation utilizing the beneficial aspect of environmentally benign amino acid (leucine) as a kinetic promoter by combining stirred and unstirred reactor operation. This hybrid approach is simple, can easily be implemented and scaled-up to develop an economical SNG technology for efficient storage of natural gas on a large scale. Added benefits include the minimal energy requirement during hydrate growth resulting in overall cost reduction for SNG technology.

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1. Introduction

Increasing global demand for natural gas (NG), the cleanest burning fossil fuel, necessitates the development of large scale stationary storage systems for NG to cater to widespread applications. Gas hydrate is a promising candidate for large scale storage

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of natural gas (NG) in a cost effective, extremely safe/non-explosive and environmental friendly manner. High storage capacity (about 173 v/v) aided by the relative ease in gas recovery with minimal energy requirement carves a niche for hydrates to store NG compared to known methods of conventional NG storage. Huge reserves of natural gas hydrates exist across the globe and ongoing research efforts focus on recovering natural gas from these hydrate reserves by different methods/measures [1–3]. Energy storage in clathrate materials has been proposed in the past two decades [4–9]. Slow kinetics and stochastic induction times during hydrate formation deter the imminent usage of hydrates for energy storage in large scale applications. These challenges have to be addressed in order to propel the clathrate hydrate technology for energy storage suited for commercial applications [10–14].

Surfactants have been employed since early 1990s to enhance the kinetics of methane hydrate formation [15–20]. Another class of compounds that can enhance the kinetics of hydrate formation is amino acids. Termed as the ‘building blocks of proteins’, amino acids are organic compounds consisting of an amine ($-\text{NH}_2$) and carboxylic ($-\text{COOH}$) functional group along with a characteristic side chain. Amino acids have been recently reported to promote methane hydrate formation significantly inferring their potential for storing methane in hydrates [21,22]. Recent morphological investigations on methane hydrate formation in presence of amino acid under quiescent condition, revealed a characteristic ‘breathing effect’ along with occurrence of methane bubble in the bulk solution [22]. Methane hydrates formed showed remarkable flexibility that enabled the methane bubble to expand deep inside the aqueous solution thereby promoting the hydrate growth in simple quiescent configuration. Added advantage of amino acid is the absence of foam formation during gas recovery (by depressurization/thermal stimulation) unlike the surfactant based kinetic promoters [21]. It is known that stirred tank reactors result in low hydrate yield (water to hydrate conversion) despite high initial hydrate formation rates due to the inadvertent mass transfer resistance offered by the forming hydrates [23]. Also, quiescent water system without any kinetic promoter results in ‘methane hydrate skin’ with the least hydrate yield [24,25]. Banking on the earlier stated advantageous aspect of flexible and porous methane hydrate formation in presence of amino acid, it is inquisitive to investigate kinetics of methane hydrate formation in a well-mixed system using amino acids.

We hypothesize that in presence of leucine (amino acid), if we employ a stirred/agitated system; we can possibly overcome the crystal agglomeration at the gas/liquid interface and it would result in a higher methane uptake compared to systems without the presence of leucine under the same operation. We compare this performance with that of kinetics in a quiescent (unstirred) configuration and report interesting observations. Based on these results, we later propose an innovative hybrid approach suited for large scale methane hydrate production coupling the advantageous aspects of both stirred and unstirred reactor configurations.

2. Experimental section

2.1. Materials

Methane gas cylinder of 99.9% purity purchased from SOXAL Pte Ltd and L-leucine amino acid of 98% purity purchased from Sigma Aldrich were used for experiments. Ultra-pure distilled water obtained from a conventional apparatus was used in all experiments.

2.2. Experimental apparatus

The setup used for conduction of experiments is shown in Fig. 1. Batch type experiments were performed in a customized stainless

steel reactor (CR) of 142 ml internal volume. The reactor was fitted with marine type viewing windows of 30 mm diameter at the front and back to allow observation of the reactor contents during the experiment. The reactor was fabricated with a cooling jacket to allow the flow of coolant (water) to maintain the reactor contents at experimental temperature. The external refrigerator used was Polyscience 9102 of 6 L capacity. Pressure Transmitter Rosemount 3051 (PT) supplied by Emerson Process Management was used to measure the reactor pressure and has an uncertainty of 0.1% within the pressure range of 0–20 MPa. An analogue pressure gauge (PG) supplied by WIKA was also used to monitor reactor pressure. The reactor temperature was measured by a copper-constantan T type thermocouple supplied by Omega that has an uncertainty of 0.1 K. Both the pressure transmitter (PT) and thermocouple (T1) were connected to a Data Acquisition (DAQ) system supplied by National Instruments, and connected to a computer (PC). For stirred experiments, a magnetic stirrer bar was placed inside the reactor and was controlled by ‘2mag MIXdrive1’ submersible magnetic stirrer in order to mix the reactor contents at 500 rpm (optimized speed for hydrate formation). For unstirred experiments, no stirrer bar was placed inside the reactor and the stirrer was kept switched off. Temperature and pressure data of the reactor were recorded every 20 s in the PC, with the use of LabVIEW software provided by National Instruments.

2.3. Experimental procedure

Amino acid solution of required concentration was prepared by weighing appropriate amount of the amino acid in a Mettler Toledo balance ME204 (uncertainty of 0.0001 g) and dissolving the same in 53 ml of water. This quantity of water was chosen so that the gas/liquid interface occurs at the centre of the viewing window. The amino acid solution was then transferred to the reactor and then sealed tight with the reactor lid to ensure no leakage. Reactor was then connected to the Polyscience chiller to cool the reactor contents at experimental temperature of 275.2 K. Afterwards, the reactor was purged with methane gas to remove the initial air present in the reactor following which it was pressurized to the experimental pressure. After the pressure and temperature readings stabilized (about 2–3 min after pressurization), the pressure and temperature values were recorded employing the DAQ system. For stirred experiments, stirrer was started immediately after temperature/pressure stabilization. Period of time between this starting point and the formation of the very first hydrate crystal is referred as the ‘induction time’. This induction time could also be inferred from the temperature spike observed in the reactor due to the exothermicity of hydrate formation process. In tandem, the pressure of the reactor drops continuously due to the enclathration of methane gas into the hydrate cages. Hydrate formation is considered complete when the pressure of the reactor system stabilizes with no further drop. When hydrates start forming, the pressure in the reactor reduces and this pressure reduction can be correlated to the gas uptake in the hydrates as shown in Eq. (1).

$$\text{Gas uptake in hydrates at time } t, \Delta n_t = V_{\text{CR}} \left(\frac{P}{zRT} \right)_0 - V_{\text{CR}} \left(\frac{P}{zRT} \right)_t \quad (\text{mmol}) \quad (1)$$

where V_{CR} is the volume of the gas phase in the crystallizer, R is the universal gas constant, T and P are the measured temperature and pressure at time 0 (initial condition; start of the experiment) and time t in the crystallizer respectively. The compressibility factor, z , can be obtained from the Pitzer’s correlation. We report normalized gas uptake on the basis of water taken for each experiment computed from Eq. (2) as shown:

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