Feasibility of hydrate technology for natural gas storage and transportation*

Natural gas (environment-friendly fuel) plays a critical role in meeting the global energy demand. Thus, an urgent question arises about its efficient storage and transportation. The most common gas transportation method is through pipelines (PNG); this is not always practical due to distance and accessibility restrictions. Compressed natural gas (CNG) technology is another transportation and storage approach; yet safety problems and low capacity are the main disadvantages of this method. Although transportation of natural gas in liquefied form (LNG) is considered an acceptable approach for large-scale and long-distance applications, this technology requires cryo-temperature (–162°C). It faces the problem of constant gas boiling, imposing restrictions on storage time. Today, the storage and transportation of natural gas in gas hydrates (SNG) is a promising alternative. The inherent advantages are as follows: (i) the process of hydrate formation is environment-friendly since only water, gas and a small amount of the gas hydrate promoter are present in the system; (ii) gas molecules are recovered from a hydrate by reducing pressure or heating; (iii) moderate temperature and pressure are required for the formation and storage of the gas hydrate (in the presence of a promoter); (iv) relatively high energy content per unit volume, and (v) since gas hydrates are non-explosive, this method of gas storage is safe[1].

However, the hydrate promoters possess several undesirable properties such as toxicity, high foam formation during gas recovery and low storage stability. Thus, scientists are actively working on the targeted modification of substances to improve their properties to promote gas hydrate formation. In fact, systematic studies on the effect of structural modification of various substances on the formation and decomposition of gas hydrates are of great theoretical and practical importance[2].

In the absence of an extensive pipeline network, it is essential to adopt an alternative gas transportation method which is economical. Properly optimized SNG technology can cater to consumers in the power and fertilizer sectors, having larger gas re-

quirements. The city gas sector is relatively new, supplying gas for domestic usage through a local pipeline network.

The potential of gas hydrate-based technology (HBT) for transportation application is illustrated in the present study. Transportation of gas from an LNG storage location to a utilization point involves several steps: (a) hydrate formation, (b) dewatering, (c) pelletization and (d) transportation.

Natural gas, dominated by methane, converts into solid form in the presence of water at high pressure and low (below freezing) temperatures. It prominently occurs in cubic sI and sII structures. The sI (space group Pm3n) unit cell consists of

two 5^{12}-cages and six $5^{12}6^2$-cages, while the sII (space group Fd3m) unit cell has 16 5^{12}-cages and eight $5^{12}6^4$-cages. It is desirable to form hydrates at relatively low pressures in the present context. The ideal volumetric capacity of guest methane in sI and sII is 170 and 120 units respectively, assuming 100% occupancy. However, theoretically achievable capacity is 157 and 101 units respectively. In practice, it would be lesser and vary with experimental conditions. Acceptability of the HBT process demands simplicity as well as superior volumetric capacity. The present study demonstrates a rapid and efficient method of methane hydrate formation and assesses its stability in sI and sII structures. The
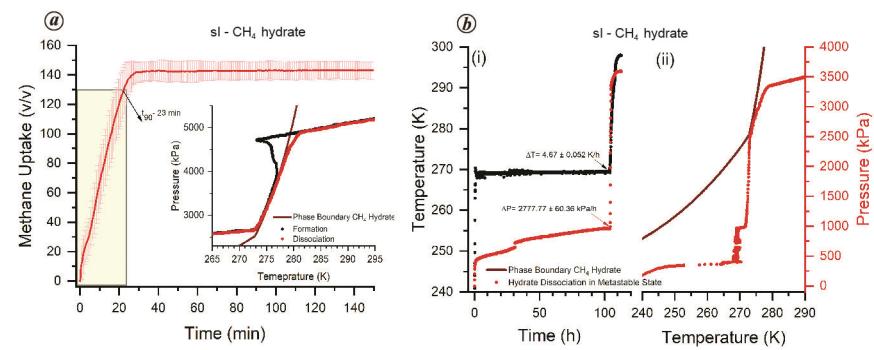

Figure 1. *a*, Methane uptake kinetics (red line) of sI hydrate (synthesized using 250 ml vessel). (inset) Pressure–temperature profile of formation (black dots) and dissociation (red dots) of the hydrate. Brown line denotes the phase equilibrium of sI methane hydrate. The shaded portion indicates the 90% reaction time. *b*, (i) Stability of methane hydrate versus time in the metastable window. Black and red dots denote temperature and pressure parameters respectively. Arrows indicate temperature and pressure increase rate. (ii) Hydrate dissociation behaviour outside the phase equilibrium conditions (brown line).
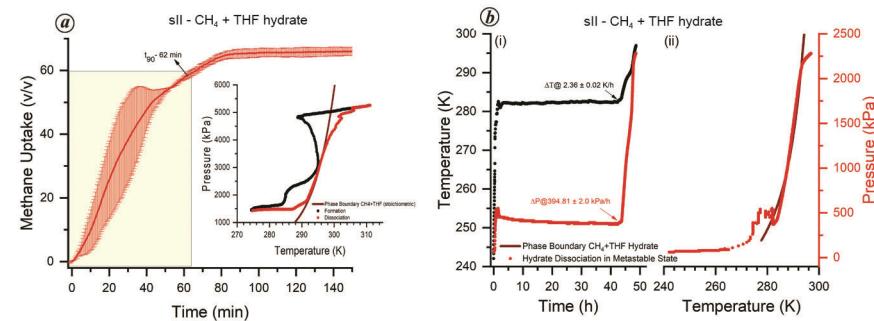

Figure 2. *a*, The sII methane hydrate uptake kinetics (in red line) (synthesized using 400 ml vessel). The inset shows the pressure–temperature profile of hydrate formation (black dots) and dissociation (red dots). The brown line represents the phase equilibrium line of sII methane hydrate. The shaded portion indicates the reaction time for 90% of hydrate conversion. *b*, (i) Stability of methane hydrate with time in the metastable window. Black and red dots denote temperature and pressure parameters respectively. The arrows indicate the temperature and pressure increase rate. (ii) The hydrate dissociation behavior outside the phase equilibrium conditions (brown line).

experiments were conducted in isochoric and unstirred conditions. They are user-friendly and easily adaptable for scale-up. Figures 1 *a* and 2 *a* show gas uptake during hydrate formation in sI and sII respectively. Insets in these figures depict the pressure–temperature (*p–T*) trajectory during freezing (black) and thawing (red) cycles, along with computed equilibrium (brown) curves. At ~5.0 MPa pressure, hydrate nucleation occurs around ~274.5 ± 1.9 and 287.8 ± 1.4 K in the sI and sII systems respectively. As shown in the shaded portion, the time taken for 90% of gas uptake in the hydrate is around ~23 ± 2.4 and 62 ± 8.1 min respectively. A small dose (0.5 wt%) of amino acid is added to water to accelerate hydrate formation in sI. Similarly, a stoichiometric amount of tetrahydrofuran is added to form sII hydrates.

The next step is to assess the stability near ambient pressures. Some hydrates are in the metastable state outside their thermodynamic stability limits. For example, methane hydrates retain their stability below the ice-melting point at lower pressures. This state is popularly known as the self-preservation window. The hydrates can be stable for a longer duration at near-ambient pressure and sub-zero temperature conditions[3,4]. The hydrate dissociation rate in this window is vital for designing the storage vessel and transportation distance. The stability of sI and sII hydrates was

monitored for 100 and 45 h at constant temperatures of ~270 and 283 K respectively, Figures 1 *b* and 2 *b* depict the results. The overall pressure increase (triggered by the hydrate dissociation) is about 950 kPa in sI hydrates, while it is significantly less in sII hydrates. Thus the gas in SNG form can easily be transferred for about 4000 km without measurable loss. Further, it can be stored in lighter insulated tanks as the required temperature is not very low.

Finally, gas is recovered by dissociating the hydrate at the dispensing location. The hydrates can be dissociated quickly by exposing the storage/crystallizer tank to ambient temperature. As shown in Figures 1 *b* and 2 *b*, typically, the temperature rises at 3°–5° per hour, and the hydrates dissociate rapidly.

The *p–T* trajectory of Figure 1 *b* (shown as (ii)) exemplifies the self-preservation of sI hydrates. A sudden surge in pressure is observed around the ice-melting temperature region. Although the precise reason for this phenomenon is unknown, a general view is that an ice layer around the hydrate grains prevents rapid dissociation. However, no such effect is seen in sII hydrates (Figure 2 *b*(ii)), and hydrate dissociation is along the thermodynamic phase boundary.

In summary, the present study demonstrates HBT for gas transport. Rapid and efficient hydrate conversion in sI offers a distinct alternative to conventional CNG or

PNG modes using low-dose amino acids. More extensive storage (~143 v/v) capacity in SNG has a clear advantage in the gas supply chain for the power or fertilizer industry. On the other hand, the requirement for city-gas supply can easily be fulfiled by adopting sII-type SNG.

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Fusarium verticillioides as an acaropathogenic fungus on two-spotted red spider mite (*Tetranychus urticae* Koch) from South Gujarat, India

Two-spotted red spider mite, *Tetranychus urticae* Koch, is an important polyphagous species of family Tetranychidae, attacking several agri-horticultural crops and causing economic loss. A moderate population of the spider mite may significantly affect crop production, while heavy infestation will result in the death of plants[1]. Spider mites puncture the epidermal layer and suck the oozing sap; they damage the internal tissues surrounding the area punctured using their chelicerae[2]. The two-spotted red spider mite remains active throughout the year under polyhouse as well as in open field conditions, causing 36.8–83.2% yield loss in okra[3]. It causes serious damage in various crops 10–15% in rice, 15–20% in tea, 10–25% in sugarcane, and 13–31%,

20–25% and 27–39% in brinjal, okra and chilli respectively[4].

Most species of *Fusarium* are saprophytic and relatively abundant as soil microbiota[5]. However, several *Fusarium* species are pathogenic on plants, insects and humans too[6]. More than 13 species are pathogenic to insects and their host range includes members of Coleoptera, Lepidoptera, Hymenoptera, Diptera and Hemiptera[7,8]. In South Gujarat, India, only a few farmers use biological methods for management of mites in different crops. Therefore, there is a need to identify native strains of new acaropathogenic organisms having the ability to control these mites. The aim of the present study was to identify effective means of biological control of

two-spotted red spider mite on okra crops in South Gujarat.

The mite-infested okra fields were visited frequently during June–July 2016 and the infested okra plants were examined to collect the diseased mites. The samples were taken immediately to the laboratory at N. M. College of Agriculture and ASPEE College of Horticulture and Forestry, Navsari Agricultural University, Navsari, Gujarat, where the infected mites with leaves were kept in sterile petri dish in a rearing room under controlled conditions (25° ± 2°C temperature and 70–80% relative humidity).

The infected mites were surface sterilized in 0.5% sodium hypochlorite solution for 10 sec, washed with sterile distilled