Paper ID APEN-MIT-2022_9476
Applied Energy Symposium: MIT A+B
July 5-8, 2022 • Cambridge, USA

Investigation on synthetic natural gas storage in the form of gas hydrate

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Abstract—Natural gas has the potential to replace the conventional liquid-based fuel economy. The shale gas boom catalyzed the development of natural gas catering facilities and inventions worldwide. Natural gas has contributed to lowering pollutant emissions and efficient energy conversion in transportation. The significant challenge presents to transporting natural gas economically and more safely. It has been published that liquefied natural gas transportation is favorable for a longer range, while small-scale transportation can be taken using compressed natural gas. Medium-scale natural gas transportation may be tackled by using gas hydrate as a transporting medium for natural gas. The current study discusses storing synthetic natural gas in the form of gas hydrate. The extensive experimental approach was used in the presence of well-known kinetic hydrate promotors and thermodynamic hydrate promotors. The micro Differential Scanning Calorimetry study was also performed in order to understand the fundamentals of the formation and dissociation of natural gas hydrate. The study was also extended for the artificial neural network-based modelling to reduce the future experiments' dependency.

Keywords— Natural gas hydrate, Energy storage and transportation, hydrate promotors, Artificial neural network, modelling

I. INTRODUCTION

The world is moving toward gaseous fuels in order to decrease the pollution caused by the usage of liquid fuels. Liquefied natural gas (LNG) has a widespread chain for transporting natural gas across the continents [1-3]. The main challenge is to transport the natural gas over a shorter distance. Currently, compressed natural gas (CNG) is used to transport natural gas over short distances. It is also suffering from safety problems which can be known from the accidents that occurred in past decades. Natural gas may not be economical to transport for longer distances as CNG form compared to gas hydrate form of natural gas [1-4]. Past research shows that natural gas hydrates (NGH) are one of the better alternative approaches to transporting the gas hydrates [3,4]. Gas hydrates are the ice-like structure encapsulating gas in a cage made by water molecules [5,6]. These are formed when gas and water are brought together at low temperatures and moderate pressure.

The significant challenge for utilizing the gas hydrates technology is the mass transfer limitation pertains at the interface, as gas hydrates start forming from the gas-liquid interface [5,6]. To overcome mentioned limitations, various routes are encountered, including process intensification and the addition of chemical additives. Process intensification includes modifications in the various designs of the reactor setup that can enhance the mass transfer evenly throughout the experiment [7]. At the same time, chemical additives can enhance the gas hydrate formation rate by various means. Kinetic hydrate promoters (KHPs) are the chemical additives that can reduce the surface tension pertain at the gas-liquid interface to promote gas hydrate formation [5,6]. KHPs have the limitation of an excessive amount of foaming as a major class of KHPs are surfactant molecules, which can create troubles at the time of scale-up of the process. Another chemical class is known as thermodynamic hydrate promoters (THPs), which can shift the thermodynamic phase equilibria of the gas hydrate formation process [6,7]. However, THPs are taking part in the gas hydrate formation process, the separation of THPs from the solution is difficult. Little relaxed conditions compared to hydrate formation with pure water.

The current study focuses on the development of the gas hydrate-based study to store and transport synthetic natural gas. The fundamental approach to the in-depth thermodynamics of synthetic natural gas hydrate HP μ-DSC was also performed to get an insight into the formation and dissociation mechanism [11,12]. To understand the impact of the process design on the natural gas hydrate formation, two different types of mixing were used [11,12]. In the present study of synthetic natural gas hydrate, a systematic experimental approach was performed with additives which work as KHPs like sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) in a bottom stirred reactor. In another approach, THPs like 1-3 dioxolane and tetrahydrofuran (THF) were used in the top stirred reactor. In order to reduce the dependence of experimental work, an artificial intelligence-based artificial neural network (ANN) model was also developed in Matlab R21. Being a stochastic phenomenon, there was a need to use different neuron layers for developing the ANN model

[8,9]. ANN can predict the experimental data in future whenever we need data for analysis with good accuracy.

II. Materials and Methods

Species	w/w %
CO2	1.84
CH4	87.71
C2H6	5.21
C3H8	3.62
n-C4H10 + i-C4H10	1.62

Table 1 Natural gas composition

A. *Materials*

The chemical used in the study were LR grade. SDS was supplied by Himedia laboratories Pvt. Ltd, India. SDBS was supplied by Loba chemie Pvt. Ltd, India. THF was supplied by Avantor Performance Materials India Ltd, India and dioxolane was supplied by Sigma-Aldrich Co Ltd, India. The chemicals used have a purity of 99 % and are used without further treatment. Milli-Q water was used throughout the study; therefore, the pure water used in the study is the same. The natural gas with 99.5 % purity was supplied by the Indo Gas agency, India.

B. *Experimental method*

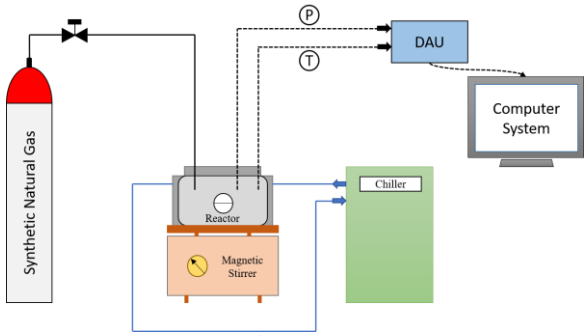

Figure 1 Experimental set-up for synthetic natural gas hydrate study

Reactors were rinsed and clean with Milli Q water before each experiment. To make the required amount of aqueous solution, additives were mixed with Milli Q water using a stirrer until the solution became homogeneous. The solution is added to the reactor with a magnetic pellet after drying it thoroughly. The reactor was closed tightly, and the required temperature of 274.15K was achieved by circulating coolant (ethylene glycol + water). Then natural gas was charged to the reactor. Once the exothermic temperature peak was achieved, stirring was started on 400 RPM. Temperature and Pressure data at every 5 seconds were collected by the data acquisition system and further processed for the amount of mole consumption and gas uptake. Experiments with KHPs and THPs were performed in different reactor setups.

C. *High-pressure μ-Differential Scanning Calorimetry (DSC)*

HP Micro-DSC (Microcalvet) supplied by setaram was used for confirming formation and dissociation kinetics. Analysis was performed in the three separate stages in the cyclic approach. In the 1st stage, which is also known as the cooling stage, the temperature decreased from 25 °C to - 40 °C at a rate of 0.3 °C/min, followed by the stabilization stage, in which the temperature was kept constant at -40°C for 45 min. The third and final stage is known as the heating stage, in which the temperature was raised to 25°C at a rate of 0.3 °C/min.

D. *Theory and calculations*

The gas hydrate formation process is categorized mainly into two parts: (1) Induction Period and (2) Growth Period. The induction time is the time taken for the nucleation of the first solid hydrate crystal. The nucleation has been followed by the hydrate growth, where the hydrate formation takes place very quickly and consistently, which results in a sharp pressure decline. The present study includes induction time as the time until a sudden pressure drop was observed with the simultaneous increase in the temperature. The gas trapped or the amount of gas enclathrated in the cages is calculated by taking the difference between moles of gas injected in the crystallizer and the moles of gas present in the gas phase. at any given time "t" by using the **equation 1** [10] .

$$\left(\Delta n_{h,\downarrow}\right)_t = \left(\frac{V_r P}{zRT}\right)_{t=0} - \left(\frac{V_r P}{zRT}\right)_{t=t} \quad (1)$$

where,
Vr = Volume of the gaseous phase in the reactor,
P = pressure in the reactor,
T = temperature in the reactor,
R = Universal gas constant
z = Compressibility factor, calculations based on Pitzer's correlation
The hydrate formation rate is calculated by the forward difference formula as given in **equation 2** [5,6].

$$\left(\frac{d\left(\Delta n_{h,\downarrow}\right)_t}{dt}\right) = \frac{\left(\Delta n_{h,\downarrow}\right)_{t=0} - \left(\Delta n_{h,\downarrow}\right)_{t=t}}{\Delta t} \quad (2)$$

III. Result and Discussion

A. *Natural gas mole consumption in the presence of KHPs:*

The mole consumption of synthetic natural gas is represented in Fig. 2. The comparative study in the presence of the most promising conventional surfactants was performed in order to understand their impact on the natural gas hydrate formation. As shown in Fig 2(a), the natural gas mole consumption in the presence of 0.01 mol % SDS and SDBS was significantly higher than the pure water, which suggests extensive hydrate growth. The primary natural gas to gas hydrate conversion occurs in the initial 20 minutes of the experiment. The lower concentration of surfactants assures the economics of the overall process. The presented study strengthens the approach of utilizing the SDS and SDBS for the natural gas-based gas hydrate research and provides the basis for the scale-up of the whole process.

B. *Natural gas mole consumption in the presence of THPs:*

Another approach to overcome the interfacial mass transfer limitation during the gas hydrate formation is to

apply THPs, which can enhance the hydrate growth by taking participation into it. It is required to explore this approach as it provides a better idea and comparison between KHPs and THPs to promote synthetic natural gas hydrate formation. The present study uses the well-known THPs, including THF and 1,3 dioxolane, in a top stirred reactor system for an impact assessment on the gas hydrate formation. The results are pretty promising for both the THPs system in comparison to the pure water system. The comparison of the gas hydrate formation with KHPs shows that THPs have lower mole consumption, which supports the fact that THPs are responsible for reducing gas storage capacity into gas hydrate.

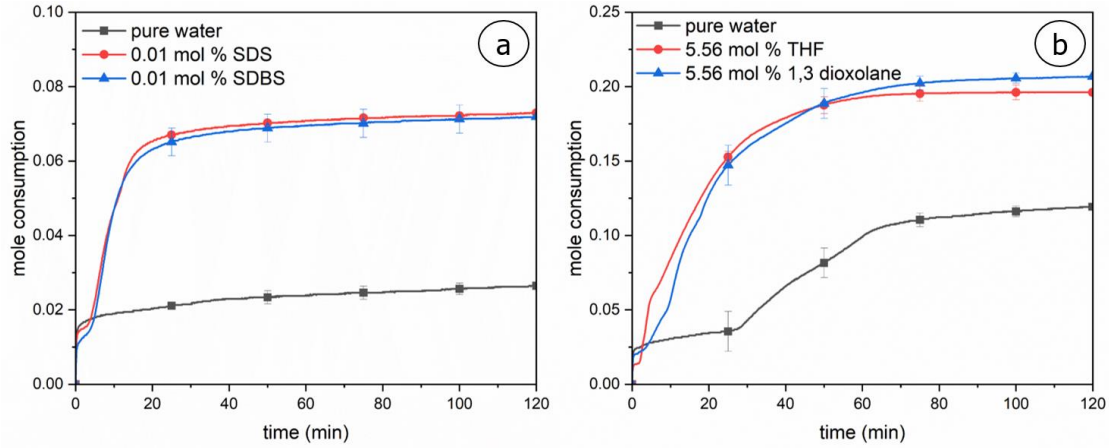

Figure 2 Synthetic natural gas mole consumption in natural gas hydrate (a) in the presence of pure water and 0.01 mol % kinetic hydrate promotors (SDS, SDBS) (b) in the presence of pure water and 0.01 mol % thermodynamic hydrate promotors (THF, 1,3 Dioxolane)

C. Thermodynamics study of synthetic gas hydrate in micro DSC:

The thermodynamic study is essential to quantify the gas hydrate formation as gas hydrate formation is a stochastic process. In the thermodynamic study, the usual ice crystallization (exothermic) and ice melting (endothermic) peaks with high intensity are represented in Fig.(a) The gas hydrate formation and gas hydrate dissociation peaks have significantly less intensity compared to the crystallization and ice melting peaks of pure water; therefore, Fig. (b) and (c) represented the magnified version of the gas hydrate related peaks in order to confirm the gas hydrate formation. The energy requirement for gas hydrate formation and dissociation must be helpful in order to scale up the process.

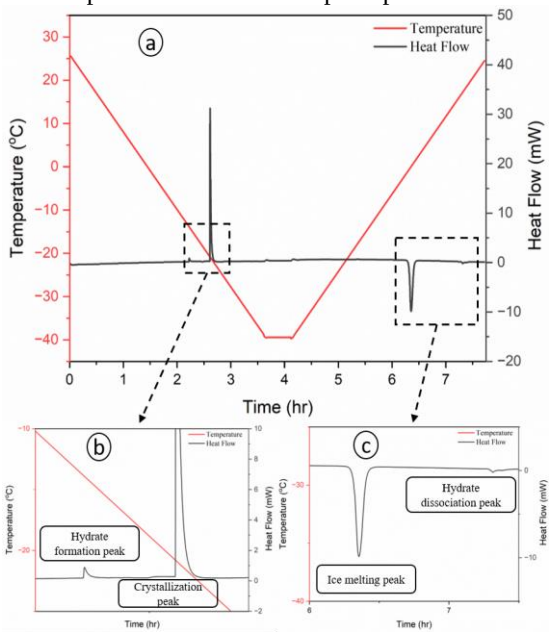

Figure 3 Micro DSC analysis for synthetic natural gas hydrate (a) Overall study for natural gas hydrate formation and dissociation in cyclic manner (b) natural gas hydrate formation (c) natural gas hydrate dissociation

D. Artificial neural network(ANN)

ANN has the same working approach as the biological neural network presented in human beings. The input data was analyzed in multiple hidden neuron layers in order to achieve every permutation and combination of the individual data. The prepared model was optimized to achieve the experimental results. The individual model predicted the results for natural gas hydrate formation with water. In the present model, a total of five hidden neuron layers were used to obtain an output which was close to the experimental results. The ANN model followed the experimental data in a very good manner. The linear regression of experimental and model data is 0.9182. ANN model will have application in the prediction behavior of various novel chemical additives with the less experimental requirement.

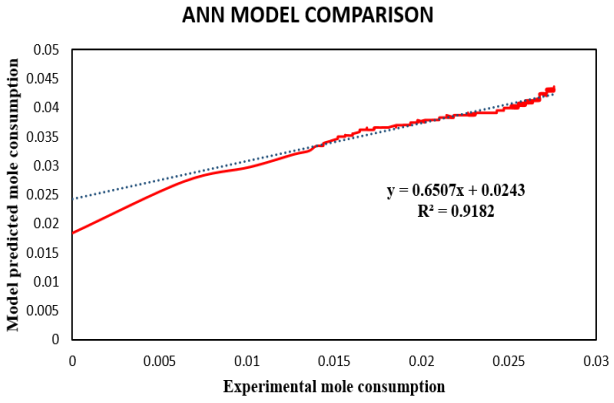

Figure 4 Mole consumption comparison of experimental results and ANN model predicted results

IV. Conclusion

Over the years, natural gas has become one of the prime sources of energy as having its safe and clean nature. The major challenge with the natural gas economy is to transport natural gas in an efficient and sustainable way. The storage of natural gas in the form of gas hydrate can be an optimistic and economical way for medium-scale natural gas transportation. The presented study demonstrated the synthetic natural gas storage in the form of gas hydrate in a stirred tank reactor setup. The gas hydrate promotors, including kinetic hydrate promotors such as SDS, SDBS and thermodynamic hydrate promotors like THF, 1,3 dioxolane, were used in order to understand their impact on gas hydrate formation and dissociation. The thermodynamics of the process was also studied using micro DSC. The experimental data were used to develop the ANN-based model, which can support the future findings in the current investigations. The model and experimental data are coordinated with each other very well, having R^2 value of 0.9182.

V. References

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