

INVESTIGATION OF KINETICS OF MIXED NATURAL GAS HYDRATE FORMATION FOR ENERGY STORAGE APPLICATIONS

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ABSTRACT

SNG (solidified natural gas) technology is a promising and potential technology for long-term and large-scale storage of methane in hydrates due to the plethora of benefits it offers in comparison to conventional methods of storage. In this study, we aim to investigate the kinetics of mixed hydrate formation using a ternary C1(93%)-C2 (5%)-C3 (2%) gas mixture representing the natural gas. The main objective is to study the effect of presence of higher hydrocarbons (ethane and propane) in influencing the mixed hydrate formation kinetics with the additional presence of thermodynamic promoter, tetrahydrofuran.

Experiments to study the effect of temperature and pressure on the mixed hydrate formation kinetics in an unstirred reactor configuration were performed. Results from this study will provide salient information in order to advance the SNG technology towards commercial implementation.

Keywords: Natural gas; clathrate hydrates; energy storage; kinetics; promoter

NONMENCLATURE

Abbreviations

SNG	Solidified natural gas
CNG	Compressed natural gas
LNG	Liquefied natural gas
THF	Tetrahydrofuran

1. INTRODUCTION

Natural gas offers significant environmental benefits resulting in about 50% CO₂ reduction in comparison to coal when employed for power generation. Further

about 25% reduction in green-house gas emission when used as transportation fuel. There is a growing global demand for natural gas as a vital source of energy for its numerous applications. Natural gas currently supplies approximately 22% of the world's energy and is projected to increase from 120 trillion cubic feet (Tcf) in 2012 to 203 Tcf in 2040 [1]. In order to cope up with the rising demand in natural gas, efficient transportation and storage of NG are crucial. Storing natural gas in the form of clathrate hydrates (SNG), has many advantages as compared to the conventional NG storage in the form of CNG (Compressed NG) and LNG (Liquified NG). SNG offers a compact mode of storage with high volumetric storage capacity (up to 164 m³ of methane gas can be stored in just 1 m³ of hydrate) [2]. Further, it is the safest to handle due to its non-explosive nature. Also, it is environmentally benign and requires only moderate formation/storage conditions (temperature & pressure).

Recently, the rapid hydrate formation kinetics in presence of methane and 5.6 mol% tetrahydrofuran (THF) in a simple unstirred reactor configuration at moderate pressures and near ambient temperature conditions was demonstrated [3,4]. The feasibility of scale-up potential of this approach was also documented in the study. Molecular level characterization studies have revealed the characteristic two-step mixed hydrate formation process and a plausible mechanism for the rapid hydrate growth was formulated [5]. However, all these experiments employed pure methane gas only.

In this study, we aim to investigate the kinetics of mixed hydrate formation using a ternary C1(93%)-C2 (5%)-C3 (2%) gas mixture representing the natural gas. The main objective is to study the effect of presence of higher hydrocarbons (ethane and propane) in influencing the mixed hydrate formation kinetics with the additional presence of thermodynamic promoter, tetrahydrofuran

(THF). Hydrate formation experiments were conducted initially without THF followed by the conduction of experiments with stoichiometric THF (5.56 mol%). The advantage of employing the natural gas mixture is that the equilibrium conditions of hydrate formation will be milder than that envisaged for pure methane gas, thus resulting in more moderate temperature and pressure conditions of hydrate formation.

Hydrate phase equilibrium for experiments with THF will be determined at required experimental conditions to quantify the driving force available for experiments. Experiments to study the effect of temperature and pressure on the mixed hydrate formation kinetics in an unstirred reactor configuration were performed. Gas composition in hydrates were determined by Gas Chromatography. Results from this study will provide salient information in order to advance the SNG technology towards commercial implementation. Selected results are presented here.

2. EXPERIMENTAL SECTION

2.1 Material and methods

Methane-ethane-propane (92.88 mol% /5.08 mol% /2.04 mol%) mixed gas cylinder were procured from Singapore Oxygen Air Liquide Private Ltd (SOXAL). Analytical reagent grade tetrahydrofuran (THF) of 99.7% purity supplied by Fisher Chemicals was used. Ultra-pure distilled water obtained from a conventional apparatus was used in all experiments.

2.2 Experimental setup

The experimental set-up used is same as that employed by Veluswamy et al [6] with the schematic diagram (adapted) shown in Fig 1. Experiments were conducted in a customized reactor (CR) made of 316 stainless steel (SS-316). The reactor had an internal volume of 142 ml and was fitted with two marine-type acrylic viewing windows on the front and back of 30 mm diameter to allow for visual observations of the reactor contents. The reactor was fitted with a cooling jacket and maintained at the desired experimental temperature using Polyscience SD15R external refrigerator (ER). The 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 range of 0 – 20 MPa. This was coupled with the use of an analogue pressure gauge (PG) supplied by WIKA to identify pressure sensor drift if any. The reactor temperature was measured by a copper-constantan T type thermocouple supplied by Omega, with an

uncertainty of 0.1 K. The pressure transmitter and thermocouple were connected to a Data Acquisition (DAQ) system supplied by National Instruments, that was in turn connected to a computer (PC). Pressure and temperature data were recorded in 20 s time intervals, with the use of Lab-VIEW software provided by National Instruments. The setup was also equipped with a sample collection outlet operated by manual valve V4. Collected gas samples were analysed using Agilent Technologies 7890A gas chromatography system.

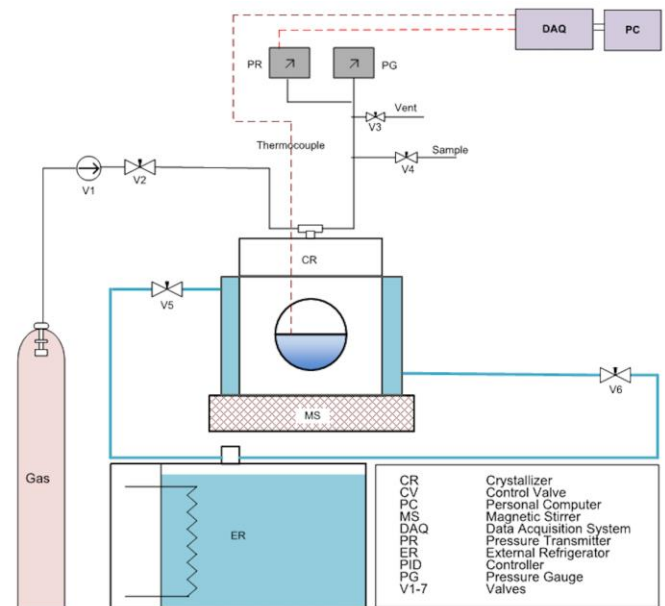


Fig 1. Schematic diagram of our experimental setup (adapted from Veluswamy et al.[6])

2.3 Hydrate formation procedure

All experiments conducted were of batch type and unstirred reactor configuration, which was achieved by shutting manual valves V2, V3 and V4 to isolate the reactor. In all experiments, 32.4 ml of aqueous solution was used. For experiments involving THF, the required volume of THF was measured using a pipette and added to ultra-pure distilled water in a beaker. The prepared solution was then charged to the reactor. The reactor contents were cooled to the desired experimental temperature using circulating water from the Polyscience chiller. Subsequently, 3 cycles of gas pressurization to about 0.1 MPa using the corresponding gas mixture followed by venting was done to purge the initial air present in the reactor. The reactor was then pressurized with the corresponding gas mixture to the required experimental pressure. After reactor pressure and temperature had stabilized, pressure and temperature data were recorded at 20 s time intervals

using the DAQ system. During hydrate formation, reactor pressure reduced as a result of gas molecules occupying the hydrate crystal cages. The reactor pressure drop along with the corresponding temperature profile, is correlated to the number of moles of gas consumed during hydrate formation. After the completion of gas hydrate formation, the reactor pressure stabilized and remained constant for an extended period indicating the end of the hydrate formation process

2.4 Hydrate dissociation procedure

After the completion of hydrate formation, gas samples were collected from the remaining gas phase of the reactor through valve V4, in order to determine the resultant gas composition using gas chromatography (GC). The remaining gas phase in the reactor was then vented off and the reactor pressure was reduced to almost zero. Thermal stimulation, in which the hydrates were heated beyond the hydrate stability region and maintained at 298.2 K, was then employed to perform hydrate dissociation in all experiments. Due to the release of captured gas molecules from the hydrate crystal cages, there was an increase in reactor pressure. Sufficient time was given for the reactor pressure to stabilize, which marked the completion of hydrate dissociation. Gas samples of the dissociated hydrate gas were then collected and analyzed using GC to determine the gas composition within the formed hydrates.

3. RESULTS AND DISCUSSION

3.1 Effect of pressure on mixed C1/C2/C3 hydrate formation kinetics

The all hydrate phase equilibrium conditions for the ternary gas system was determined by the CSMGem software to be 2.88 MPa at the set temperature of 283.2 K [7]. Two experimental pressures of 5 and 7.2 MPa were chosen to investigate the effect of varying driving force on the kinetics of ternary gas hydrate formation, with the respective pressure driving forces (2.12 and 4.32 MPa). At 5 MPa, the hydrate equilibrium temperature is 287.6 K, which translates to a thermal driving force of 4.4 K. With such low thermal driving force, no mixed C1/C2/C3 gas hydrates formed even after 15 h. When the experimental pressure was raised to 7.2 MPa, there was sufficient thermal driving force (9.8 K) for mixed C1/C2/C3 hydrate formation in experiment. Despite this driving force, the total gas uptake recorded was only 0.25 mmol of gas/mol H₂O achieved after 4h. The time taken for 90% completion was 202.33 min. Despite of the

pressure driving force of 4.32 MPa available, low uptake was achieved predominantly due to the quiescent reactor configuration employed, hydrate formed as thin film at gas-liquid interface offered resistance to further gas diffusion to the bulk and thus resulted in very low uptake and water to hydrate conversion.

3.2 Effect of pressure on mixed C1/C2/C3/THF hydrate formation kinetics

Three experimental pressures of 3, 4 and 5 MPa were chosen to determine the effect of varying pressure driving force on mixed C1/C2/C3/THF hydrate formation. The reactor was cooled to the set temperature of 283.2 K, and the gas uptake profiles at all three experimental pressures were plotted in Fig 2. The gas uptake profile recorded for mixed gas hydrate formation employing pure methane alone from previous work at 5 MPa and 283.2 K is also provided for comparison.

At the starting experimental pressure of 3 MPa, the rate of gas uptake was sluggish for about 160 min after induction time, subsequently increasing to reach a final gas uptake of 60 mmol/mol H₂O, with a time taken to 90% completion of 224.67 min. While the gas uptake potential was promising, the rate of mixed C1/C2/C3/THF hydrate formation at 3.0 MPa start pressure was too slow. This is understandable, as a lower pressure driving force was only available, and it might be insufficient to promote rapid formation of all mixed hydrate crystals. At the subsequent higher experimental pressures of 4 MPa and 5 MPa, higher gas uptakes of about 75 and 70 mmol gas/mol water respectively were observed. Moreover, the rate of gas uptake for the mixed C1/C2/C3/THF hydrates at both experimental pressures were very similar, except for a varied higher gas uptake rate between 90 to 110 min.

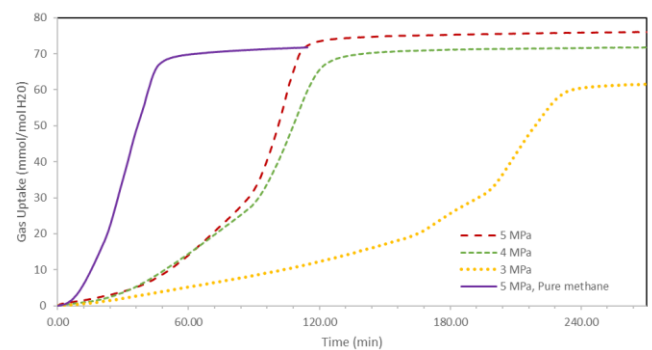


Fig 2. Gas uptake profiles during mixed hydrate formation at 283.2 K and different starting pressures (C1-C2-C3 gas mixture and pure methane)

Due to the higher rate for mixed natural gas hydrate formation, the time taken for 90% completion was about 120 and 110 min for 4 MPa and 5 MPa experiments respectively. Induction time of less than 3 min was observed for these experiments in comparison to about 20 min for 3 MPa experiment. Figure 2 also shows that the kinetics of mixed hydrate formation for the natural gas (in presence of ethane and propane) is lowered as the pure methane resulted in comparable gas uptake but in shorter time of about 60 min. Thus, it showcases the need for the addition of suitable kinetic promoters like surfactants or amino acids for improving the kinetics under the experimented conditions for the natural gas system. This will enable the improvement of kinetics of mixed hydrate formation to achieve like that observed for pure methane experiment.

Gas composition of mixed hydrates analyzed after dissociation shows methane composition of 93.1 ± 0.1 mol% which is same as that of the feed gas composition considered. Thus, there is no significant change in the gas composition during the mixed hydrate formation.

Experiments were performed with varying concentrations of tryptophan amino acid in the range of 100-500 ppm and the kinetics for the C1-C2-C3 mixed hydrate formation was observed at 5 MPa and 283.2 K. In presence of tryptophan (200 ppm), kinetics of hydrate formation had improved considerably proceeding to completion in about 80 min in comparison to about 110 min for experiments without the tryptophan promoter. Further investigations on other promoters that can further improve the kinetics of C1-C2-C3 mixed hydrate formation comparable to mixed methane hydrate formation is under progress in our laboratory

4. CONCLUSION

From the results obtained for experiments performed with C1-C2-C3 gas mixture, it can be concluded that gas uptake is comparable to that of pure methane along with similar gas composition in hydrates (obtained from GC analysis). However, the presence of higher hydrocarbons (ethane/propane) even at minor concentrations (<10%) caused a significant delay in kinetics of hydrate formation resulting in lower formation rates and longer time for completion under same experimental conditions (5 MPa and 283.2 K) studied. This necessitates the employment of suitable kinetic promoters for the investigation of kinetics of mixed hydrate formation to achieve faster hydrate formation rates like that observed for pure methane system in presence of stoichiometric tetrahydrofuran. In

this direction tryptophan amino acid was identified to be a promising promoter favoring the natural gas hydrate formation.

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