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## Methane Production from Natural Gas Hydrates via Carbon Dioxide Fixation

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### Abstract

Natural gas hydrate (NGH) is an ice like solid compound containing hydrocarbon that is present in marine and permafrost environments. Thermal stimulation, depressurization or a combination of both these methods are the approaches to recover natural gas. One innovative and promising solution to secure the future energy needs and mitigate carbon dioxide emissions simultaneously is to replace CH<sub>4</sub> trapped in the gas hydrate deposits with carbon dioxide. In this short review, the state of the art experimental work in the CH<sub>4</sub> production from natural gas hydrates via carbon dioxide fixation is summarized and future directions and challenges are highlighted.

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### 1. Introduction

Natural gas hydrates (NGH) are ice-like solid compounds containing hydrocarbons and are present in marine and permafrost environments. It has been estimated that a mean of 20,000 TCM of natural gas (94%-99% CH<sub>4</sub>) exist – an amount significantly larger, possibly twice, that of all other fossil fuels present. At the current natural gas (NG) consumption, we have about 6000+ years of natural gas supply

Several methods such as thermal stimulation, depressurization and inhibitor injection have been considered/tested for the recovery of CH<sub>4</sub> from NGH deposits. It is widely believed that there are no technology stoppers for recovering NG from NGH but challenges do exist that are specific to NGH reservoirs. Another promising approach for recovering CH<sub>4</sub> trapped in natural gas hydrates is the exchange of CH<sub>4</sub> in the stable hydrate deposits with carbon dioxide. If this approach can be successful, then there is a huge potential sink for storing carbon dioxide in hydrate deposits at the same time producing CH<sub>4</sub> from these hydrates. This method will also have the added advantage of maintaining the hydrate structure in the geological formation after CH<sub>4</sub> recovery.

### 2. Approach

There are three structures which most gas hydrates form - cubic structure I (sI), cubic structure II (sII) and the hexagonal structure (sH). Both CH<sub>4</sub> and CO<sub>2</sub> typically form sI hydrates [1]. The proposed approach is based on the difference in the phase equilibria of CH<sub>4</sub> and CO<sub>2</sub> hydrates. At lower temperatures (>283 K), CO<sub>2</sub> hydrate is

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more stable than CH<sub>4</sub> hydrate. Ohgaki et al. [2] obtained phase equilibria for a mixed CH<sub>4</sub>-CO<sub>2</sub> hydrate system and observed a distribution coefficient of 2.5 between CH<sub>4</sub> in the gas phase and hydrate phase. This demonstrated the preference of CO<sub>2</sub> over CH<sub>4</sub> as a guest molecule of the sI hydrate.

### 2.1. Literature works in the CH<sub>4</sub>/CO<sub>2</sub> displacement process

Initial studies have been on hydrates in the bulk phase with pure water while it is only in recent studies that porous media and saline water have been introduced. Hirohama et al. [3] formed CH<sub>4</sub> hydrate in the bulk phase and attempted recovery with liquid CO<sub>2</sub> at the conditions within the hydrate stability region of both CO<sub>2</sub> and CH<sub>4</sub> hydrate. As the final conversion remained low, it was suggested that the conversion of the CH<sub>4</sub> hydrate at the interface with CO<sub>2</sub> inhibited mass transfer of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O. Lee et al. [4] demonstrated a limit to the degree of substitution expected at equilibrium conditions. In the same publication, CH<sub>4</sub> hydrate formed from finely powdered ice was exposed to CO<sub>2</sub> gas. In less than 5 hours, about half of the total CH<sub>4</sub> in the hydrate was able to be recovered. The kinetics of the reaction were observed to have no significant CO<sub>2</sub> pressure dependence while the particle size of hydrates was observed to have significant impact on the overall conversion achieved.

Ota et al. [5] investigated the CH<sub>4</sub>-CO<sub>2</sub> replacement reaction in a small cell using in situ laser Raman spectroscopy with pure water. It was proposed that future work determine the available surface area of the hydrate at various conditions and further improvements be made on the rate constant determination. Zhou et al. [6] examined surfactant and quartz sand effects on the kinetics of the CH<sub>4</sub>-CO<sub>2</sub> replacement reaction. It was concluded that using a CO<sub>2</sub>/H<sub>2</sub>O emulsion could increase the rate of reaction over the use of liquid CO<sub>2</sub>. In a separate publication [7], the most suitable conditions in which to replace CH<sub>4</sub> with CO<sub>2</sub> hydrate was found to be the area between 3 curves (L<sub>CO2</sub>-V<sub>CO2</sub>), (H-L<sub>w</sub>-L<sub>CO2</sub>) and (H-L<sub>w</sub>-V-CH<sub>4</sub>). As CH<sub>4</sub> hydrate is not stable in this zone, it was suggested that the most effective method to recover CH<sub>4</sub> was to depressurize the resource followed by CO<sub>2</sub> emulsion injection.

Yuan et al. [8] compared the replacement efficiency in three different types of hydrate samples: high gas saturation, high water saturation and high CH<sub>4</sub> hydrate saturation. It was concluded that a reservoir with underlying free gas, high gas saturation and low water saturation is most suitable for recovering CH<sub>4</sub> with CO<sub>2</sub>. In a separate work [9], a maximum CH<sub>4</sub> recovery of 35% was reported by running at conditions where pure CH<sub>4</sub> hydrate is unstable but CO<sub>2</sub> hydrate is stable. Deusner et al. [10] investigated production from CH<sub>4</sub> hydrates in quartz sand with pure ice by injecting hot supersaturated CO<sub>2</sub> at 95 °C in a flow-through apparatus instead of a typical batch fixed bed reactor. This unique method permitted a higher recovery of 40.7% in a relatively short duration of 44h but similar mass transfer limitations prevented further recovery.

It is noteworthy that the recent investigations using porous sediments and salt water have been unable to observe high CH<sub>4</sub> replacement rates observed by Lee et al. [4] and Kvanme et al. [11]. Lee et al. were able to avoid mass transfer effects by using fine pure ice particles of 50 μm and Kvanme et al. used Bentheim sandstone as a porous medium as well as brine of low salinity (0.1 wt% NaCl). It is likely that the porous unconsolidated quartz/silica sand media as well as the higher salinity of the water used have an impact on the reaction and thus further study has to be made into CH<sub>4</sub> and CO<sub>2</sub> hydrate formation in porous media replicating marine environments in order to develop effective recovery techniques.

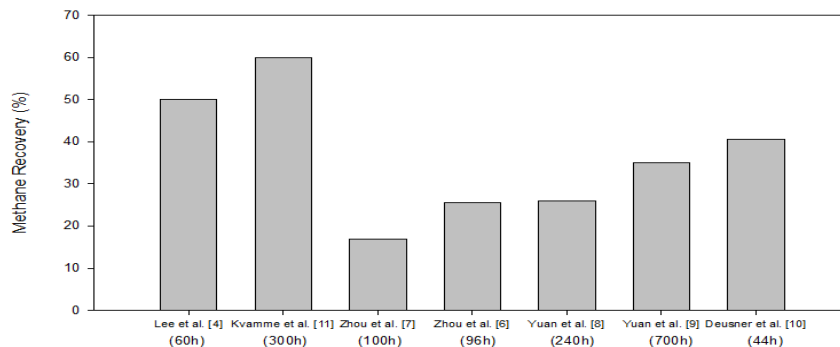


Figure 1: Comparison of CH<sub>4</sub> recovery obtained reported in the literature.

### 2.2. Effect of natural gas composition

The stability and structure of NGHs change significantly with composition. As proportion of larger hydrocarbons (e.g. C<sub>3</sub>H<sub>8</sub>) increases, the stability of the corresponding hydrate increases. Also, in the presence of

propane, even at low concentrations of 1.0%, the resultant hydrate is of the sII structure (CSMGEM, [1]). These hydrates are of much greater stability than that of pure CH<sub>4</sub> hydrate. CO<sub>2</sub> hydrate is only slightly more stable than 99% CH<sub>4</sub>, 1% propane hydrate and above temperatures of 273 K, the hydrocarbon hydrate is of greater stability.

Schicks et al. [12] investigated the exchange reaction with mixed hydrates containing CH<sub>4</sub> and propane. A swapping process between sI CO<sub>2</sub> hydrates and sII CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> hydrates was observed with the direction of reaction depending on the composition of the surrounding gas phase. This indicated that the driving force for hydrate conversion is not only the difference in thermodynamic stabilities but also due to a chemical disequilibrium between the gas phase and hydrate phase composition. This reflects an increased feasibility for natural gas recovery from NGHs through CO<sub>2</sub> fixation as it is possible to recover methane from hydrates more stable thermodynamically than CO<sub>2</sub> hydrate.

### 2.3. Impact of porous media on the kinetics

The amount of NGHs in the ocean is greater than that in permafrost by two orders of magnitude [1]. In natural submarine environments, CH<sub>4</sub> hydrate is subject to the effects of porosity and salinity. The effects of porosity and salinity on the thermodynamic stability of gas hydrates have been widely studied and are typically inhibitory. Literature studies have shown that pore diameter effect on thermodynamic stability becomes significant only at diameters (d<sub>p</sub>) smaller than 30 nm [13, 14]. The morphology of CH<sub>4</sub> hydrate formation was found to depend on particle size and pore space [15].

Methane hydrate formation and recovery in pure water was investigated in a variable volume bed of silica sand. It was concluded that bed size affects both formation and recovery rate. Dissociation behavior was observed to have two distinct periods and bed size only affected the rate of recovery during the initial period [16-18]. Recently, Mekala et al. [19] reported that in porous media, the presence of salts could act as kinetic inhibitors as well as alter the dissociation behavior of CH<sub>4</sub> hydrates from that in pure water. Kinetic results obtained by Linga et al. [20] investigating the formation kinetics of both CH<sub>4</sub> and CO<sub>2</sub> hydrates in 100% water saturated silica sand show that while gas uptake of CO<sub>2</sub> was faster during the initial period of 2-3h, total CH<sub>4</sub> gas uptake was significantly higher, nearly double that of CO<sub>2</sub> uptake. This could raise issues concerning the effectiveness of storing CO<sub>2</sub> within marine sediments as its hydrate formation rate is very slow in porous sediments compared to CH<sub>4</sub> hydrate formation. Another possible important aspect is the effect of salinity and the presence of higher hydrocarbons like ethane and propane on the hydrate formation/dissociation of the displacement process.

### 2.4. Recent Field Tests

ConocoPhillips and researchers from the University of Bergen have collaborated on laboratory studies on hydrate production through CH<sub>4</sub>-CO<sub>2</sub> exchange. Attempts to simulate naturally occurring hydrates include the use of Bentheim sandstone cores as a porous medium. The first field trial of CH<sub>4</sub> hydrate production using CO<sub>2</sub> has been completed successfully in the Ignik Sikumi Gas Hydrate Field in Alaska. Test data have indicated that solid state CH<sub>4</sub>-CO<sub>2</sub> exchange did take place [21]. JOGMEC has been involved in active development of the Eastern Nankai Trough where the first offshore production through depressurization flow test has ended and data analysis is underway [22].

## 3. Conclusions

Current understanding of natural gas hydrate formation and dissociation in the marine environment needs to be further investigated. Recent attempts at investigating the replacement reaction in porous media with saline water have not been successful at achieving high CH<sub>4</sub> recovery rates, with mass transfer limitations being the main hindrance. For further development of this method, the kinetics of formation and dissociation of natural gas hydrates (CH<sub>4</sub>, CO<sub>2</sub> and possibly mixtures with higher order hydrocarbons) in unconsolidated porous media and saline water simulating actual marine sediments need to be investigated. Furthermore, understanding the mechanism of the displacement process at the molecular level is needed. Recent field studies in the Ignik Sikumi gas hydrate field in Alaska are a promising development.

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## References

- [1] E.D. Sloan, Jr., C.A. Koh, *Clathrate Hydrates of the Natural Gases*, 3<sup>rd</sup> ed., CRC Press, Boca Raton, FL, 2008.
- [2] K. Ohgaki, K. Takano, H. Sangawa, T. Matsubara, S. Nakano, Methane exploitation by carbon dioxide from gas hydrates - Phase equilibria for CO<sub>2</sub>-CH<sub>4</sub> mixed hydrate system, *Journal of Chemical Engineering of Japan*, 29 (1996) 478-483.
- [3] S. Hirohama, Y. Shimoyama, A. Wakabayashi, S. Tatsuta, N. Nishida, Conversion of CH<sub>4</sub>-hydrate to CO<sub>2</sub>-hydrate in liquid CO<sub>2</sub>, *Journal of Chemical Engineering of Japan*, 29 (1996) 1014-1020.
- [4] H. Lee, Y. Seo, Y.T. Seo, I.L. Moudrakovski, J.A. Ripmeester, Recovering Methane from Solid Methane Hydrate with Carbon Dioxide, *Angewandte Chemie - International Edition*, 42 (2003) 5048-5051.
- [5] M. Ota, Y. Abe, M. Watanabe, R.L. Smith Jr, H. Inomata, Methane recovery from methane hydrate using pressurized CO<sub>2</sub>, *Fluid Phase Equilibria*, 228-229 (2005) 553-559.
- [6] X. Zhou, S. Fan, D. Liang, J. Du, Replacement of methane from quartz sand-bearing hydrate with carbon dioxide-in-water emulsion, *Energy and Fuels*, 22 (2008) 1759-1764.
- [7] X. Zhou, S. Fan, D. Liang, J. Du, Determination of appropriate condition on replacing methane from hydrate with carbon dioxide, *Energy Conversion and Management*, 49 (2008) 2124-2129.
- [8] Q. Yuan, C.Y. Sun, X. Yang, P.C. Ma, Z.W. Ma, B. Liu, Q.L. Ma, L.Y. Yang, G.J. Chen, Recovery of methane from hydrate reservoir with gaseous carbon dioxide using a three-dimensional middle-size reactor, *Energy*, 40 (2012) 47-58.
- [9] Q. Yuan, C.Y. Sun, B. Liu, X. Wang, Z.W. Ma, Q.L. Ma, L.Y. Yang, G.J. Chen, Q.P. Li, S. Li, K. Zhang, Methane recovery from natural gas hydrate in porous sediment using pressurized liquid CO<sub>2</sub>, *Energy Conversion and Management*, 67 (2013) 257-264.
- [10] C. Deusner, N. Bigalke, E. Kossel, M. Haeckel, Methane production from gas hydrate deposits through injection of supercritical CO<sub>2</sub>, *Energies*, 5 (2012) 2112-2140.
- [11] B. Kvamme, A. Graue, T. Buanes, T. Kuznetsova, G. Ersland, Storage of CO<sub>2</sub> in natural gas hydrate reservoirs and the effect of hydrate as an extra sealing in cold aquifers, *International Journal of Greenhouse Gas Control*, 1 (2007) 236-246.
- [12] J.M. Schicks, E. Spangenberg, R. Giese, B. Steinhauer, J. Klump, M. Luzi, New approaches for the production of hydrocarbons from hydrate bearing sediments, *Energies*, 4 (2011) 151-172.
- [13] S.P. Kang, J.W. Lee, H.J. Ryu, Phase behavior of methane and carbon dioxide hydrates in meso- and macro-sized porous media, *Fluid Phase Equilibria*, 274 (2008) 68-72.
- [14] T. Uchida, T. Ebinuma, S. Takeya, J. Nagao, H. Narita, Effects of pore sizes on dissociation temperatures and pressures of methane, carbon dioxide, and propane hydrates in porous media, *Journal of Physical Chemistry B*, 106 (2002) 820-826.
- [15] P. Babu, D. Yee, P. Linga, A. Palmer, B.C. Khoo, T.S. Tan, P. Rangsunvigit, Morphology of Methane Hydrate Formation in Porous Media, *Energy & Fuels*, 27 (2013) 3364-3372.
- [16] P. Linga, C. Haligva, S.C. Nam, J.A. Ripmeester, P. Englezos, Gas hydrate formation in a variable volume bed of silica sand particles, *Energy and Fuels*, 23 (2009) 5496-5507.
- [17] C. Haligva, P. Linga, J.A. Ripmeester, P. Englezos, Recovery of Methane from a Variable-Volume Bed of Silica Sand/Hydrate by Depressurization, *Energy Fuels*, 24 (2010) 2947-2955.
- [18] P. Linga, C. Haligva, S.C. Nam, J.A. Ripmeester, P. Englezos, Recovery of Methane from Hydrate Formed in a Variable Volume Bed of Silica Sand Particles, *Energy Fuels*, 23 (2009) 5508-5516.
- [19] P. Mekala, P. Babu, J.S. Sangwai, P. Linga, Formation and Dissociation Kinetics of Methane Hydrates in Seawater and Silica Sand, *Energy & Fuels*, 28(4) (2014) 2708-2716.
- [20] P. Linga, N. Daraboina, J.A. Ripmeester, P. Englezos, Enhanced rate of gas hydrate formation in a fixed bed column filled with sand compared to a stirred vessel, *Chemical Engineering Science*, 68 (2012) 617-623.
- [21] D. Schoderbek, H. Farrell, K. Hester, J. Howard, K. Raterman, S. Silpnarmert, K.L. Martin, B. Smith, P. Klein, ConocoPhillips Gas Hydrate Production Test Final Technical Report, in, United States Department of Energy, 2013.
- [22] M.H.R.D. Division, Flow Test from Methane Hydrate Layers Ends, in, Japan Oil Gas and Metals National Corporation, 2013.



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