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Influence of hydrate structure on continuous separation of coal bed methane gas: A thermodynamic simulation study

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ABSTRACT

Influence of hydrate crystallographic structures on continuous $CH_4 + N_2$ gas separation is studied using thermodynamic simulations. A continuous separation process with discharge of hydrate crystals only (not as hydrate slurry; without liquid phases) is modelled. 35 mol% CH_4/N_2 and 50 mol% CH_4/N_2 gas separation simulations are performed for simple sI system, and isobutane sII, methylcyclohexane sH and neohexane sH promoted systems at pressures 1.0 MPa, 4.0 MPa and 7.0 MPa depending on hydrate structures. At the steady state, under 7.0 MPa, CH_4 concentration in hydrate phase ($x_{j=CH_4,hyd}$) and percentage of CH_4 recovery (S. Fr.) were in the increasing order of isobutane sII < neohexane sH ≈ methylcyclohexane sH < simple sI systems. In the sII and sH system studied, $x_{j=CH_4,hyd}$ and S. Fr. at the steady state were lower during gas separation at higher pressures. The maximum CH_4 concentration that can be recovered in hydrate for continuous 35 mol% CH_4/N_2 and 50 mol% CH_4/N_2 gas separations are calculated to be approximately 64 mol% CH_4/N_2 and 77 mol% CH_4/N_2 respectively.

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1. Introduction

Natural gas resources play important role in diversification of energy sources and reduction of greenhouse gas emission (IEA, 2011). Exploration of unconventional natural gas resources is essential to meet the increasing demand for clean energy. Coal bed methane (CBM), or also known as coal seam gas, is one unconventional energy sources being focused.

CBM refers to CH_4 gas trapped in layers of coal as a byproduct of biochemical and geochemical processes during coalification. CBM can be divided to three different categories depending on when the CH_4 is recovered. Firstly, (virgin) coal bed methane (VCBM) which refers to pre-mining exploration and the word virgin is used only if the coal is not planned to be mined. Secondly, coal mine methane (CMM) which refers to CH_4 gas released during coal mining activities; recovery of CMM is also driven by other factors such as, safety and mitigation of CH_4 emission to atmosphere, rather than only as energy source. Thirdly, abandoned mine methane (AMM) which refers to CH_4 recovered from disused underground coal mines. Although explored through different methods, almost pure CH_4 gas existing in the coal layers is mostly recovered as a mixture of CH_4 and N_2. This mixture can be a resultant of exposure to air or injection of flue gas as an enhanced CBM recovery method (Li et al., 2015; Olajossy et al., 2003; Pini et al., 2011).

In order to use the recovered CBM gas mixture as energy source, it is important to purify the mixture to reach high compositions of CH_4. Clathrate hydrate based gas separation is one potential method of purification. Clathrate hydrate (abbreviated as hydrate hereafter) is a crystalline compound, where a group of water molecules (host) forms hydrogen-bonded cage enclosing a different molecule (guest). Hydrate's high selectivity towards guest molecule, enables it to capture CH_4 molecules from the feed gas. There are three main hydrate structures: structure I (sI), structure II (sII) and structure H (sH) (Sloan and Koh, 2007).

Structure of hydrate formed can be determined from the size of guest molecule. For example, in the case of $CH_4 + N_2$ mixed hydrate, sI hydrate is formed because CH_4 molecules occupy the cages mainly. Also known as simple hydrate, this type typically requires high pressure to form. Therefore it is a common practice in this field to add another guest compound to the system to lower the pressure required for hydrate formation. Such compound is known as large molecule guest compound (LMGC). LMGCs form sII or sH hydrate, by occupying the large cages of their respective hydrate structures and as mentioned above, structure formed can be determined from the size of LMGC molecule. Summary of characteristics of each hydrate structure is presented in Table 1.

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Table 1
Characteristics of hydrate structures.

Hydrate structure	sI	sII	sH
Cage types[a]	5^{12}, $5^{12}6^2$	5^{12}, $5^{12}6^4$	5^{12}, $4^35^66^3$, $5^{12}6^8$
Volumetric capacity[b]/(m^3/m^3)	172	121	149
Hydrate formation pressure[c]/MPa	12.0[d]	0.4[e]	5.6[f]

[a] 5^{12} cage refers to pentagonal dodecahedron cage, and so on.
[b] At STP; only small cages are occupied for sII, small and medium cages are occupied for sH.
[c] 46.3 mol% CH_4/N_2; at 281 K.
[d] Calculated using CSMGem (Sloan and Koh, 2007).
[e] Tetrahydrofuran as LMGC (Sun et al., 2012).
[f] Neohexane as LMGC; Calculated using CSMGem (Sloan and Koh, 2007).

First example of utilizing hydrate for separation of CH_4 and N_2 was reported by Happel and co-workers using a system without any additives (Happel et al., 1994). Since early 2000s, there have been several publications (Li et al., 2012; Sun et al., 2015b, 2014, 2012, 2011; Zhong and Englezos, 2012; Zhong et al., 2013) by several groups from China on hydrate based gas separations mostly pertaining to CMM gas mixtures (with low CH_4 concentrations). Similar to experiments involving purifications of CO_2 gas mixtures, most publications reported on separation of $CH_4 + N_2$ have utilized sII hydrates mainly due to their low required formation pressure. However, in order to use CH_4 from purified CBM gas, it has to be compressed to various high pressures (as high as 7 MPa) to be injected into natural gas pipelines (Simpson, 2008). Therefore, it is important to understand the effect of hydrate structures on gas separation of CBM gas mixture at high pressures too.

In a typical experimental analysis, it is difficult to assess ability of "hydrate crystals only". Study using "hydrate crystals only" is important to eliminate the influence of CH_4 absorption in the liquid phases. Here, as a preliminary analysis, we have performed thermodynamic simulations of continuous $CH_4 + N_2$ gas separation. Thermodynamic simulation was opted due to its ability to exclude CH_4 absorption by LMGC and water in the system. Consistency of the "serial equilibrium states" model used with experimental results has been confirmed in previous study (Tomita et al., 2015). We have compared the performance of all three hydrate structures sI, sII and sH at three isobaric conditions – namely, 1 MPa, 4 MPa, 7 MPa, depending on the hydrate structure. Two different feed gas CH_4 concentrations (35 mol% CH_4/N_2 and 50 mol% CH_4/N_2) were tested. Performance evaluation was done using percentage of CH_4 recovery, and CH_4 concentration in the gas and dissociated hydrate phases.

2. Thermodynamic modelling and continuous gas separation

Pioneering clathrate hydrate thermodynamic modelling works done by van der Waals-Platteuw (Waals and Platteeuw, 1958), Bishnoi (Englezos and Bishnoi, 1988; Trebble and Bishnoi, 1987; Tse and Bishnoi, 1994) and several other researchers have paved way for the present work. It is worthy to emphasize that these models are not only useful to determine hydrate-multiphase equilibrium conditions, but also to evaluate performance of clathrate hydrate based technologies. Hydrate research group at Keio University has published several articles on utilization of products from above models for technologies namely, natural gas storage in hydrates and clathrate hydrate based gas separation (Akatsu et al., 2013; Tomita et al., 2015; Tsuji et al., 2005). These simulations have also exhibited good agreement with experimentally determined results. Hence, in the present study, we have further utilized the methods from previous thermodynamic simulation studies to perform evaluation that is highly technical and work-extensive to be done experimentally. This highlights the advantages of the proposed simulation method.

In this paper, continuous hydrate based gas separation is defined as a process where feed gas supply, hydrate slurry discharge and residual gas discharge operations are simultaneously performed. Fig. 1 shows the conceptual diagram of continuous gas separation using clathrate hydrate. Firstly, CH_4 and N_2 feed gas is supplied to the hydrate forming reactor, which contains water and LMGC. Due to preferential uptake of CH_4 in hydrates, CH_4-rich hydrates will be formed. Upon hydrate formation, a constant amount of CH_4-rich hydrate slurry (hydrate + water + LMGC) is drained from the reactor to the decomposer. The remaining water and LMGC in the decomposer after hydrate dissociation is pumped back to the hydrate forming reactor. At the same time, a constant amount of residual CH_4-lean gas in the hydrate forming reactor is released to be purified in a different multistage hydrate forming reactor or by other means such as membrane or pressure swing adsorption (PSA). Finally, the amount of gas lost during hydrate formation and residual gas removal are replenished to the hydrate forming reactor by the feed gas keeping pressure in the reactor constant. The material "transaction" through these four-step operations is then continuously repeated. It should be noted here that the net inflow and outflow of total moles of feed-gas constituents is always zero. As time progresses, the mole fraction evolution of the gas constituents in all phases become steady when the net inflow and outflow of EACH gas constituents reaches zero.

Experimentally studying the influence of clathrate hydrate structure on steady state composition of decomposed hydrate phase is complicated especially for continuous-type gas separation process employed in the present paper. Solubility of CH_4 and N_2 in the aqueous and liquid hydrocarbon phases affects the composition of the decomposed hydrate slurry phase greatly and it is very labour extensive to separate the CH_4-rich hydrate crystals from the liquid phases when they are discharged. Furthermore, because data that includes the amount of CH_4 absorbed in the liquid phase, can be directly used for industrial applications, there has been no much movements among researchers in this field to study the influence of hydrate only. Using clathrate hydrate thermodynamic models, fortunately, performance of a "hydrate only" based gas separation system can be extracted. In the case of continuous separation as employed in the present paper, constant inflow and outflow of materials should be considered. Thus, there is a need for simulations that reiterate the thermodynamic modelling calculations for every material "transaction" operation to understand the effect of different hydrate structures on gas separation performance.

It is highly essential for the readers to remember that only thermodynamic models are employed to perform these simulations. In other words, the values determined in this study do not necessarily correspond with the experimental data that is affected by hydrate formation kinetics such as reduced penetration of gas molecules to the bulk water due to thick film growth at the water surface or even usage of kinetic promoters such as sodium dodecyl sulphate (SDS). If macroscopic model from both thermodynamic

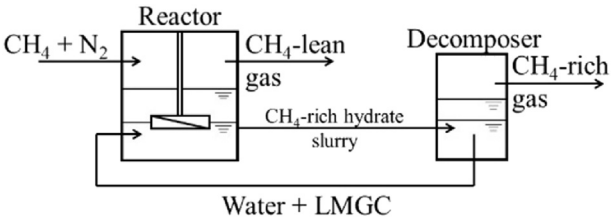

Fig. 1. Conceptual illustration of continuous hydrate based gas separation process. Two liquid phases represent aqueous and liquid hydrocarbon phases.

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