

# SEPARATION OF METHANE FROM LOW CONCENTRATION COAL MINE METHANE BY HYDRATE-BASED PROCESS

Qiunan Lv<sup>1,2,3,4</sup>, Xiaosen Li<sup>1,2,3,4,\*</sup>

1 Key Laboratory of Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China

2 Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, PR China

3 University of Chinese Academy of Sciences, Beijing 100049, PR China

4 Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, PR China

## ABSTRACT

In order to avoid wasting resources, environmental pollution and prevent gas explosion in mine, purifying methane from low concentration coal bed methane by hydrate formation has been studied. For increasing the hydrate formation rate and methane recovery, 5.8 mol% tetrahydrofuran (THF) -300 ppm sodium dodecyl sulfate (SDS) solution were introduced. The key factors that influenced the gas consumption, reaction rate, methane concentration in the hydrate, methane recovery and separation factor were investigated. Experimental results indicated that the higher pressure, lower temperature, longer reaction time facilitated gas consumption, methane recovery and separation factor. The temperature was the key factor affecting the methane separation factor, and the increase of temperature is propitious to the improve selectivity of methane hydrate. Since the hydrate separation technology can substantially avoid the explosion problem caused by methane and on the basis of the results obtained in this work, we may say that this technology is quite suitable for the separation of coal bed methane mixed with air and has broad prospects for industrial applications.

**Keywords:** hydrate, low concentration coal bed methane, methane, separate, tetrahydrofuran, sodium dodecyl sulfat

Corresponding author. Tel: +86 20 87057037. Fax: +86 20 87057037.  
E-mail address: lixs@ms.giec.ac.cn.

## 1. INTRODUCTION

The total amount of coal mine methane (CMM) in the world is up to  $2.6 \times 10^{14} \text{ m}^3$ . The reserves of CBM are huge in China, with the amount of about  $(3\sim 3.5) \times 10^{13} \text{ m}^3$ , roughly equivalent to the proven reserves of natural gas[1]. And most of the low-concentration CMM (less than 30%) is directly discharged into the atmosphere. However, emission of methane to the atmosphere has a global warming potential that is 21 times greater than that of  $\text{CO}_2$  [2]. In order to use the low concentration CMM as energy source, researchers have carried out a lot of research on methane separation from CMM. Compared with the traditional separation method, gas hydrate crystallization has the advantages of small pressure loss, low cost, mild reaction conditions, simple technology and safety, etc. But the equilibrium pressure for gas hydrate formed from such a gas mixture is much higher than pure methane at a given temperature. Some additives such as tetrahydrofuran (THF), tetra-nbutyl ammonium bromide (TBAB), and cyclopentane (CP) are thermodynamic promoters, which can shift the equilibrium hydrate formation conditions to lower pressures and higher temperatures [3-5]. Some additives such as sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) [6] are kinetic promoters, which do not change the phase equilibrium, but change the gas solubility in the liquid and the

gas/liquid interfacial tension so as to increase hydrate formation rates [7]. Zhong et al. [2, 8-14] used TBAB, CP, SDS and water-in-oil (W/O) emulsion for the enhancement of gas hydrate formation. The concentration of CH<sub>4</sub> from 30% increased at least 13%, methane recovery rate is about 17~34%. Sun et al. [1,15] studied the separation of CH<sub>4</sub> from coal bed gas in TBAB and tetrahydrofuran (THF) solution. The recovery rate of methane is over 34.06%, and the gas storage in hydrates is 19-21 m<sup>3</sup>/m<sup>3</sup>. Zhang et al. [16-17] found 1 mol/L THF solution was the optimal condition. And SDS can increase the rate of hydrate formation [18]. The sponge can not only increase the hydrate formation rate, but also increase the gas storage capacity of the hydrate, but it does not play a role in improving the methane concentration. Li et al. [19] used THF and SDS as promoters for the separation of methane from CMM. The concentration of methane can be increased from 50% to 69.93%, and the recovery rate of methane can be up to 86.44%. Zhao et al. [20] had conducted separation experiments by adding promoters (THF and SDS). THF performed better than SDS for CH<sub>4</sub> separation from the CH<sub>4</sub>/N<sub>2</sub>/O<sub>2</sub> gas mixture. Tang et al. [21] found that SDS could increase the hydrate formation rate by promoting the dissolution of gas molecules in the solution. In recent years, separation of methane from CMM through forming hydrates have been studied by many researchers. However, most of them are CMM with methane concentration higher than 30% and the operation pressure is large during the separation process. The few studies on separation of methane from low concentration CMM have been conducted.

The objective of this work is to study the characteristics of CH<sub>4</sub> separation from the low concentration CMM gas mixture through hydrate formation in the mixed solution of THF and SDS. The effect of pressure, temperature, reaction time on gas consumption, concentration of CH<sub>4</sub> is investigated. The kinetic data reported in this work may prove useful in the development of hydrate-based technology for CH<sub>4</sub> separation from low concentration CMM gas.

## 2. RESULTS AND DISCUSSION

The CMM gas was simulated by 13.11 mol% CH<sub>4</sub>/N<sub>2</sub> gas mixture and all experiments were carried out in the 5.8 mol%THF-300 ppm SDS solution. The experimental apparatus and procedure were reported in our previous works [19].

### 2.1 Effect of pressure

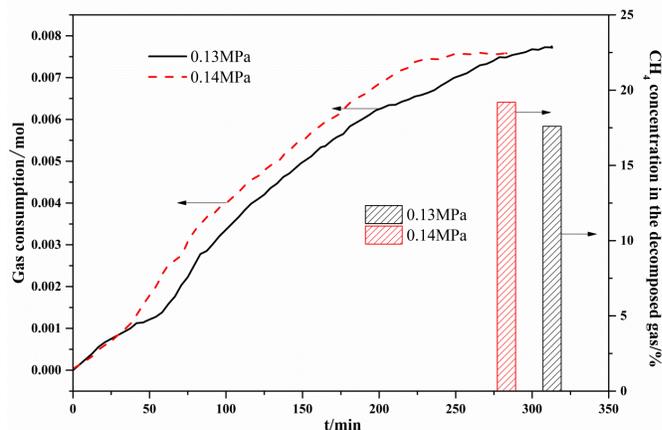


Fig 1 Effect of pressure on gas consumption and CH<sub>4</sub> concentration in the decomposed gas

Fig. 1 gave the mole of accumulative gas consumed by the hydrate formation process after nucleation in 5.8 mol%THF-300 ppm SDS solution at 273.15 K with different pressure driving forces. Therefore, time-zero in the figure corresponds to the induction time. As shown in Fig. 1, the gas consumption curve indicated that gas hydrate grows quickly once hydrate nucleation occurred. Because the mixture was at the explosive limit, the pressure was not too high. When pressure raised from 0.13 MPa to 0.14 MPa, and the pressure increased little. Therefore, it had little effect on gas consumption. However, as the pressure increased, the reaction time was shortened, and the rate of hydrate formation accelerated. The concentration of CH<sub>4</sub> in the decomposed gas increased from 17.6% to 19.19%. The increase of pressure resulted in more CH<sub>4</sub> hydrates forming

### 2.2 Effect of temperature

The effect of temperature on the gas consumption and the mole fraction of CH<sub>4</sub> in the decomposed gas at 0.13 MPa is shown in Fig. 2. As the temperature rised, the gas consumption decreased. Lowering temperature was beneficial to increase hydrate formation rate. When the temperature decreased, the concentration of CH<sub>4</sub> in the decomposed gas decreased. As the temperature rised, the molecular motion accelerated and the surface tension of the solution reduced. The

selectivity of CH<sub>4</sub> molecules entered into the hydrate lattice raised. So the concentration of CH<sub>4</sub> in the

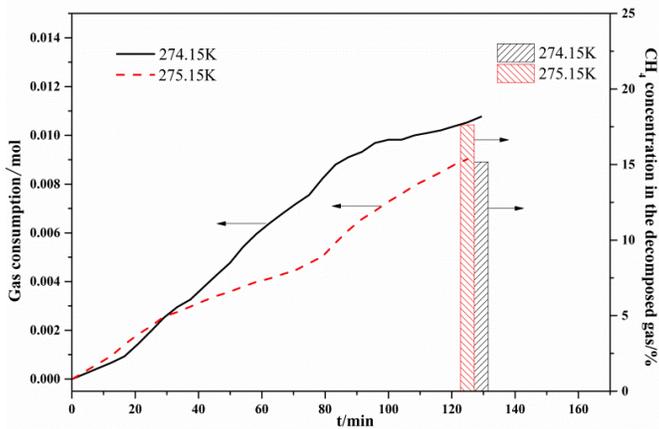


Fig 2 Effect of temperature on gas consumption and CH<sub>4</sub> concentration in the decomposed gas

decomposed gas increased.

### 2.3 Effect of reaction time

Fig. 3 shows the effect of reaction time on gas consumption during hydrate formation and the CH<sub>4</sub> molar fraction in the decomposed gas at 0.13 MPa and 275.15 K. With the increase of reaction time, the consumption of gas increased and the concentration of CH<sub>4</sub> in decomposed gas increased. This indicated that CH<sub>4</sub> and N<sub>2</sub> molecules continuously entered the hydrate lattice with the reaction, but the amount of CH<sub>4</sub> entering the hydrate was more than that of N<sub>2</sub> in the latter stage reaction.

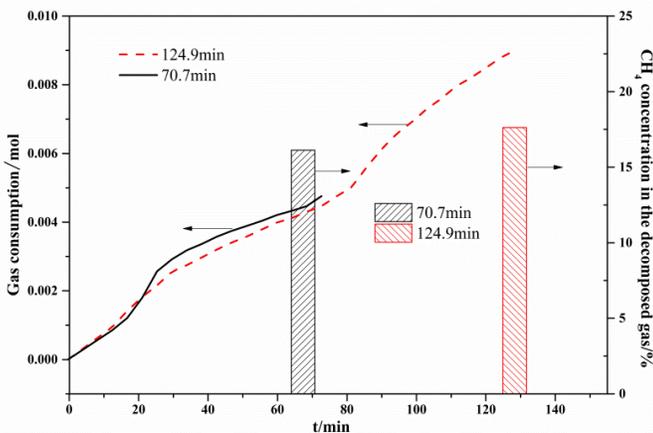


Fig 3 Effect of reaction time on gas consumption and CH<sub>4</sub> concentration in the decomposed gas

## 3. CONCLUSIONS

In this paper, the separation and purification of CH<sub>4</sub> gas in 13.11 %CH<sub>4</sub>+86.89 %N<sub>2</sub> mixture was studied in a 5.8 mol% THF-300 ppm SDS composite solution system. The effects of pressure, temperature and reaction time on gas consumption, hydrate formation rate, CH<sub>4</sub> concentration in hydrate phase, CH<sub>4</sub> separation factor and separation efficiency were investigated experimentally. The following conclusions were obtained.

1) increasing the pressure was beneficial to increase the gas consumption and formation rate, which was beneficial to hydrate formation and the enrichment of CH<sub>4</sub> in the hydrate phase.

2) reducing temperature was conducive to increasing gas consumption and generation rate. Increasing the temperature improved the selectivity of hydrate to CH<sub>4</sub>.

3) increasing the reaction time had no effect on the reaction rate, but it could increase the gas consumption, which was conducive to the enrichment of CH<sub>4</sub> in the hydrate phase.

## ACKNOWLEDGEMENT

This work is supported by National Natural Science Foundation of China (51506203, 51676196), Key Program of National Science Foundation of China (51736009), Key Research Program of Frontier Sciences, CAS (QYZDB-SSW-JSC028), and National Key R&D Program of China (2017YFC0307306), which are gratefully acknowledged.

## REFERENCE

- [1] Sun Q, Guo XQ, Liu A.X, et al. Experimental study on the separation of CH<sub>4</sub> and N<sub>2</sub> via hydrate formation in TBAB solution. *Industrial & Engineering Chemistry Research* 2011;50:2284–2288.
- [2] Zhong DL, Englezos P. Methane separation from coal mine methane gas by tetra-n-butyl ammonium bromide semiclathrate hydrate formation. *Energy Fuels* 2012;26:2098-2106.
- [3] Sun CY, Chen GJ, Zhang LW. Hydrate phase equilibrium and structure for (methane plus ethane plus tetrahydrofuran plus water) system. *J. Chem. Thermodyn.* 2010; 42:1173-1179.

- [4] Mohammadi AH, Richon D. Phase equilibria of binary clathrate hydrates of nitrogen+cyclopentane/cyclohexane/methyl cyclohexane and ethane+cyclopentane/cyclohexane/methyl cyclohexane. *Chem. Eng. Sci.* 2011;66:4936-4940.
- [5] Meysel P, Oellrich L, Raj BP, et al. Experimental investigation of incipient equilibrium conditions for the formation of semi-clathrate hydrates from quaternary mixtures of (CO<sub>2</sub>+N<sub>2</sub>+TBAB+H<sub>2</sub>O). *J. Chem. Thermodyn.* 2011; 43:1475-1479.
- [6] Wang F, Jia ZZ, Luo SJ, et al. Effects of different anionic surfactants on methane hydrate formation. *Chem. Eng. Sci.* 2015;137:896-903.
- [7] Wang TW, Deng Y, Guo XQ, et al. Experimental and modeling investigation on separation of methane from coal seam gas (CSG) using hydrate formation. *Energy* 2018;150: 377-395.
- [8] Zhong DL, Ye Y, Yang C. Equilibrium conditions for semiclathrate hydrates formed in the CH<sub>4</sub> + N<sub>2</sub> +O<sub>2</sub> +tetra-n-butylammonium bromide systems. *Journal of Chemical and Engineering Data* 2011;56:2899-2903.
- [9] Zhong DL, Ye Y, Yang C, et al. Experimental investigation of methane separation from low-concentration coal mine gas (CH<sub>4</sub>/N<sub>2</sub>/O<sub>2</sub>) by tetra-n-butyl ammonium bromide semiclathrate hydrate crystallization. *Ind. Eng. Chem. Res.* 2012;51:14806-14813.
- [10] Zhong DL, Ding K, Yan J, et al. Influence of cyclopentane and SDS on methane separation from coal mine gas by hydrate crystallization. *Energy Fuels* 2013;27:7252-7258.
- [11] Zhong DL, Ding K, Lu YY, et al. Methane recovery from coal mine gas using hydrate formation in water-in-oil emulsions. *Applied Energy* 2016;162:1619-1626.
- [12] Zhong DL, Daraboina N, Englezos P. Coal mine methane gas recovery by hydrate formation in a fixed bed of silica sand particles. *Energy Fuels* 2013;27:4581-4588.
- [13] Zhong DL, Sun DJ, Lu YY, et al. Adsorption-hydrate hybrid process for methane separation from a CH<sub>4</sub>/N<sub>2</sub>/O<sub>2</sub> gas mixture using pulverized coal particles. *Ind. Eng. Chem. Res.* 2014;53:15738-15746.
- [14] Zhong DL, Lu YY, Sun DJ, et al. Performance evaluation of methane separation from coal mine gas by gas hydrate formation in a stirred reactor and in a fixed bed of silica sand. *Fuel* 2015;143:586-594.
- [15] Sun Q, Guo XQ, Liu AX, et al. Experiment on the separation of air-mixed coal bed methane in THF solution by hydrate formation. *Energy Fuels* 2012;26:4507-4513.
- [16] Zhang BY, Wu Q. Thermodynamic promotion of tetrahydrofuran on methane separation from low-concentration coal mine methane based on hydrate. *Energy Fuels* 2010;24:2530-2535.
- [17] Zhang BY, Chen YP, Wu Q. et al. Sponge effect on coal mine methane separation based on clathrate hydrate method. *Chinese J. Chem. Eng.* 2011;19:610-614.
- [18] Wu Q, Gao X, Zhang BY. SDS effect on CH<sub>4</sub>/N<sub>2</sub>/O<sub>2</sub> hydrate formation rate for CMM separation and storage. *Adv. Mater. Res.* 2011;201-203:471-475.
- [19] Li XS, Cai J, Chen ZY, et al. Hydrate-based methane separation from the drainage coal-bed methane with tetrahydrofuran solution in the presence of sodium dodecyl sulfate. *Energy Fuels* 2012;26:1144-1151.
- [22] Zhao JZ, Zhao YS, Liang WG. CH<sub>4</sub> separation from coal bed methane by hydrate in the SDS and THF solution. *J. Chem.* 2016;1-6.
- [23] Tang JF, Zeng DL, Wang CL. et al. Study on the influence of SDS and THF on hydrate-based gas separation performance. *Chem. Eng. Res. Des.* 2013;91: 1777-1782.