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Methane hydrate formation in the SiC foam ceramics packed reactor in presence of β -cyclodextrin

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Abstract. Cyclodextrins were used as environmental friendly additives in enhancing the kinetics of gas hydrate formation. Effects of β -Cyclodextrin (Beta-CD) on methane hydrate formation in the SiC foam ceramics packed reactor were evaluated in this paper. To investigate the roles of these additives played in the enhancement of hydrate formation kinetics, different concentrations of Beta-CD and sodium dodecyl sulfate (SDS) mixed solution were used in the gas hydrate formation system. The overall results demonstrated that the addition of Beta-CD promoted the formation of methane hydrate. Compared with the control experiments with only 200 ppm SDS and SFC packings, the induction time for methane hydrate formation was shortened by 97.6 % when 1000 ppm Beta-CD was added, while the maximum gas consumption rate and water conversion rate were increased by up to 284.2 % and 102.0 %, respectively. Results showed that simultaneous usage of Beta-CD, SDS and SFC packings enhanced the methane hydrate formation kinetics.

1. Introduction

Natural gas hydrate is ice-like crystalline compounds in which small molecules such as carbon dioxide, methane and ethane are trapped in a water cage formed by hydrogen bonds[1]. The special structure of gas hydrate provides a new and promising method for storing natural gas because approximately 160 standard volumes of natural gas can be stored in per unit volume hydrates[2]. Compared with conventional natural gas storage methods such as compressed natural gas (CNG) and absorbed natural gas (ANG), storing natural gas (methane) in the form of clathrate hydrates, called SNG (solidified natural gas), has several advantages, including higher controllability and considerable storage capacity. However, the slow kinetics of hydrate growth and random nature of hydrate nucleation are the main challenges that hinder the commercial application of SNG.

Therefore, different methods have been developed to improve the kinetics of hydrate formation, such as adding suitable kinetic-accelerating additives (generally surfactants), or altering the structure of reactors to increase the gas/ liquid contact area. Sodium dodecyl sulfate (SDS) is one of the most widely used surfactants that effectively fasten the formation of hydrates[3]. Although these chemicals are used at low concentrations, they still have some negative environmental impacts if used in large scale[4]. Therefore, eco-friendly promoter additives have been studied like amino acids, biosurfactants, and cyclodextrins[5]. Cyclodextrin is a series of cyclic oligosaccharides produced from starch which has a unique structure with hydrophilic outer surface and hydrophobic internal cavity. Studies have shown that cyclodextrin can increase the solubility of methane in water, thereby promoting hydrate



formation[6]. Ji et al.[7] recently reported that the methane hydrate formation kinetics was promoted in the presence of Beta-CD by molecular dynamic simulations. In this study, the effects of Beta-CD and SDS on methane hydrate formation kinetics were investigated respectively. Composite solution of different concentrations of the two additives was employed in the experiments.

Additionally, previously reported porous materials including silica sand, activated carbon, dry water, silica gel, nanotubes and foam packings have also been developed to accelerate the formation of hydrates[8]. In order to clearly observe the effect of Beta-CD and SDS on hydrate formation kinetics, a suitable amount of SiC foam ceramic (SFC) packings was used for assisting the hydrate to form[9].

2. Materials and methods

2.1. Materials

Methane (99.99% purity) used in this study was purchased from Shenzhen Huashidai Gas Co., Ltd. β -cyclodextrin (98 % purity) was obtained from Shanghai Aladdin biochemical technology Co., Ltd. Sodium dodecyl sulfate (analytical reagent grade, 99 % purity) was supplied by Beijing Bailingwei Chemical Technology Co., Ltd. The SFC packings were obtained from the Institute of Metal Research, Chinese Academy of Sciences. The packings was made in granular form (particle size: 3 mm; pore size: 1.0 mm).

2.2. Experiments

As shown in Fig. 1, a cylindrical stainless steel reactor (diameter: 50 mm, height: 50 mm, effective volume: 102 mL) with the maximum operation pressure of 20 MPa was used for the methane hydrate formation experiments. The temperature was controlled by immersing the reactor in a circulating coolant bath. The pressure and the temperature of gas and liquid phase inside the reactor were monitored using a pressure transducer (DC1300) with an uncertainty of $\pm 0.025\%$ and a temperature transducer (PT-100) with an accuracy of 0.1 K, respectively. The data acquired during the whole experimental process was recorded by the data acquisition system connected with a computer.

Before starting the experiments, the reactor was washed with deionized water for at least three times and then dried with compressed air. A certain amount of granular SFC packings (25 g) along with Beta-CD and SDS solution were added into the reactor after the gas tightness was tested fine. The concentration of Beta-CD ranged from zero to 1000 ppm, while that of SDS was set at 0, 100 ppm, 200 ppm and 300 ppm, respectively. Subsequently, the hydration reactor was purged with methane gas (0.5 - 1.0 MPa) for three times to flush out the residual air. Then the vessel was pressurized to the desired pressure. Meanwhile, the data acquisition system was started to collect the pressure and temperature information at a 10 s interval. The reactor was cooled down to the experimental temperature by being soaked in the water bath (temperature: ~ 274.65 K), and the pressure decreased with the temperature and reached stable around 7.3 MPa. The time when the pressure and temperature in the reactor reached the experimental conditions was defined as time zero. When the pressure drop ceased and maintained stable during the following 2 h, experiments were stopped. Each experiment was repeated for at least three times.

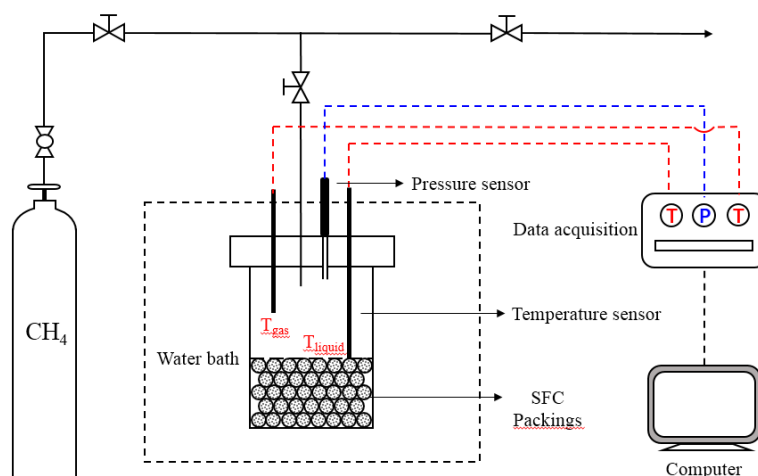


Figure 1. Schema of the experimental set-up.

2.3. Data analysis

The induction time (t_{ind}) was defined as the time from reaching the target temperature to the drastic increase in temperature. When the hydrate formed before reaching the pre-set temperature, the induction time was decided as zero. The gas uptake $(\Delta n_{H,\downarrow})_t$ was defined as the moles of gas consumed by hydrate formation at a given time, calculated using the equation as follows[10]:

$$(\Delta n_{H,\downarrow})_t = \frac{P_0 V_0}{z_0 R T_0} - \frac{P_t V_t}{z_t R T_t} \quad (1)$$

where P represents the pressure inside the reactor (Pa), V is the volume of gaseous phase (m^3) of the crystallizer, z is the compressibility factor calculated by the Pitzer correlation, T is the temperature in the reactor (K), R represents the universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$).

The normalized gas uptake (NG_t , mmol gas per mol water) was determined by dividing the number of moles of gas uptake by the number of moles of water in the reactor. To quantify the rate of hydrate formation, the maximum formation rate (F_{max} , $m^3 m^{-3} min^{-1}$) was calculated by the slope of the straight line fitting methane consumption with time (fast growth stage) using the least squares method. To figure out the amount of water taken by hydrate formation, the percentage of water conversion to hydrate (%) was determined by multiplying the normalized gas uptake by the hydration number. The hydration number is the number of water molecules required per guest methane molecule to form hydrate, which was set at 6.1 as suggested by Uchida et al.[11].

3. Results and discussion

3.1. Effect of the concentration of β -cyclodextrin on hydrate formation kinetics

In this section, the amount of SFC packings and the concentration of SDS in solution were set constant, while the concentration of β -cyclodextrin (Beta-CD) was set at 0, 500, and 1000 ppm, respectively. As is shown in Figure. 2(A), in the presence of 25g SFC packings and 200 ppm SDS solution, the normalized gas consumption (NG_t) was 48 mmol gas/ mol water after complete hydrate growth, which was just half of that in SDS and Beta-CD mixed solution (98 mmol gas/ mol water). Additionally, the higher the concentration of Beta-CD in liquid phase, the larger F_{max} could be reached during methane hydrate growth stage, which could also be suggested by the sharper slope of the gas consumption curve. When 25 g SFC packings was present and the concentration of SDS was increased to 300 ppm, the effects of different Beta-CD concentration on methane hydrate formation kinetics have been illustrated by Figure. 2 (B). It could be observed that the normalized gas consumption (NG_t) showed almost no change in 0ppm, 500ppm and 1000ppm Beta-CD solution. Such result suggested that SDS dominated in promoting hydrate formation process when the concentration of SDS was relatively higher (300 ppm).

However, obvious improvement in gas hydrate formation rate could still be observed as Beta-CD concentration increased.

The induction time, maximum gas consumption rate and water conversion rate was summarized in Table 1. Beta-CD increased the hydrate formation rate effectively when its concentration increased to 500 ppm and 1000 ppm. As Table 1 shows, in 200 ppm SDS and 1000 ppm Beta-CD mixed solution, F_{\max} was maximized ($14.6 \text{ m}^3 \text{ m}^{-3} \text{ min}^{-1}$), 284 % higher than that of control experiment with no Beta-CD. Moreover, the induction time was also reduced by up to 49.4 % - 97.6 %, which was mainly attributed to the fact that Beta-CD molecular could improve the heterogeneity of the solution. For example, the induction time was extremely shortened when 1000 ppm Beta-CD was present (0.1 h – 0.6 h), indicating that the hydrate nucleation was enhanced by high Beta-CD concentration solutions.

The overall results indicated that the addition of Beta-CD in solution facilitated the hydrate growth rate and increased the methane storage capacity. This could be explained by the fact that methane molecular might be trapped in the non-polar internal space of β -cyclodextrin molecular and therefore increased the solubility and dissolution rate of methane in water[6].

Table 1. Summary of experiments, induction time (t_{ind}), maximum growth rate (F_{\max}) and the percentage of water conversion to hydrate (274.6 K, 7.3 MPa).

System	SDS concentration (ppm)	β -CD concentration (ppm)	No.	t_{ind} (h)	F_{\max} ($\text{m}^3 \text{ m}^{-3} \text{ min}^{-1}$)	water conversion (%)
β -CD SDS SFC	200	0	1	6.2	3.4	17.6
			2	27.4	4.2	41.6
			3	-	-	-
			mean	16.8 (10.6)	3.8 (0.4)	29.6 (12.0)
		500	1	4.9	12.1	60.5
			2	9.8	9.5	59.9
			3	10.8	9.7	60.4
			mean	8.5 (2.6)	10.4 (1.2)	60.3 (0.3)
		1000	1	0.2	13.9	59.8
			2	0.1	15.2	59.1
			3	0.9	14.6	60.4
			mean	0.4 (0.4)	14.6 (0.6)	59.8 (0.6)
β -CD SDS SFC	300	0	1	0.8	6.7	61.1
			2	0	7.7	60.8
			3	0	7.8	61.8
			4	0.4	7.3	60.4
			mean	0.3 (0.3)	7.3 (0.5)	61.0 (0.5)
		500	1	0.0	12.1	53.5
			2	0.2	12.2	64.9
			3	4.5	12.3	67.1
			mean	1.6 (2.0)	12.2 (0.1)	61.8 (5.9)
		1000	1	0.1	14.4	60.0
			2	0.1	12.7	57.2
			3	0.1	12.6	58.7
			mean	0.1 (0.0)	13.2 (0.9)	58.6 (1.1)

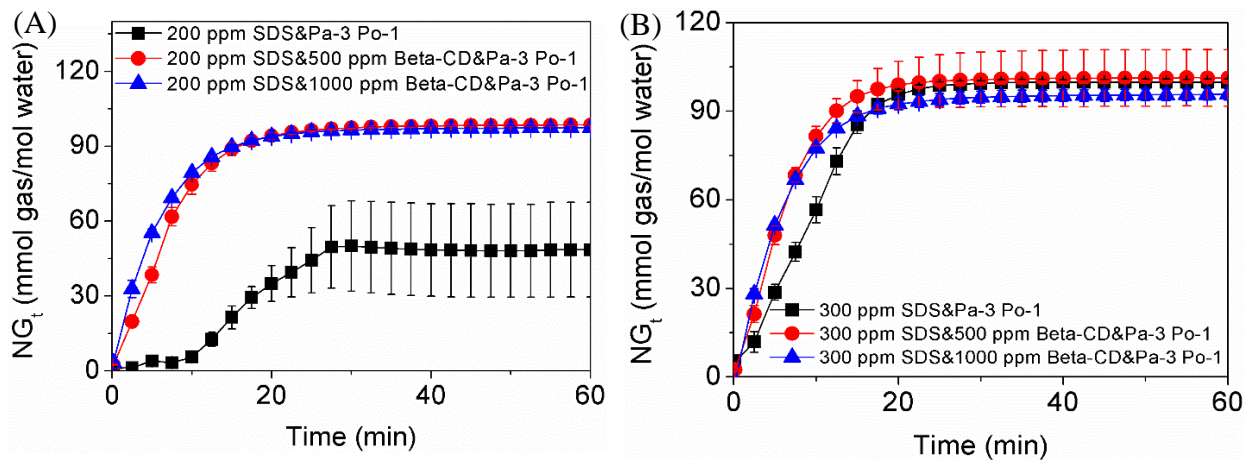


Figure 2. Normalized gas consumption during methane hydrate formation in presence of different concentrations of Beta-CD and SDS, as well as random SFC packings (Pa: particle size, mm; Po: pore size, mm)

3.2. Effect of the concentration of SDS on hydrate formation kinetics in the presence of β -cyclodextrin

As is shown in Fig. 3, when the concentration of Beta-CD was set at 500 ppm, there was little hydrate formed without SDS in the solution. When low concentration of SDS was added (100 ppm), the final methane consumption increased up to around 50 mmol gas/mol water. Furthermore, when the concentration of SDS was increased to 200 ppm and 300 ppm, the gas consumption almost doubled compared with that of 100 ppm SDS. Similar results could also be observed in Table. 1. For example, compared with 100 ppm SDS experiments, the maximum hydrate formation rate (F_{max}) and water conversion rate were increased by up to 89 % and 78 % when the SDS concentration increased to 200 ppm, respectively. Besides, the fluctuation of the results under the same conditions was reduced in the addition of higher concentration of SDS. Moreover, when the concentration of Beta-CD was constant, the induction time had a tendency to decrease as the concentration of SDS increased.

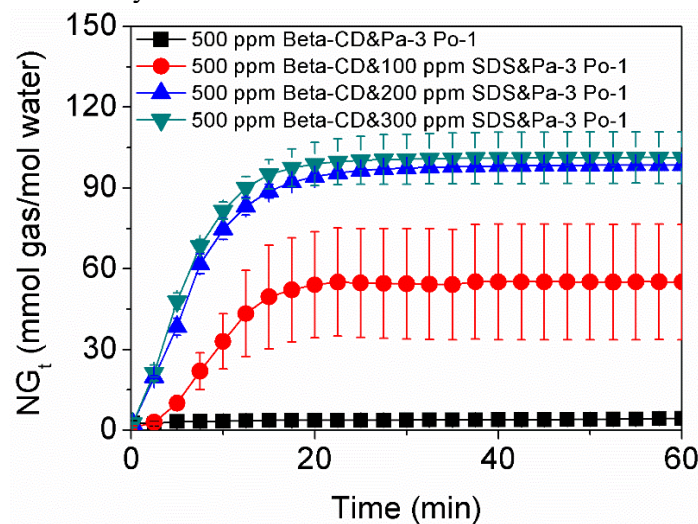


Figure 3. Normalized gas consumption during methane hydrate formation in presence of different concentrations of Beta-CD and SDS, as well as random SFC packings (Pa: particle size, mm; Po: pore size, mm)

4. Conclusions

The effects of the different concentrations of β -cyclodextrin (Beta-CD) and sodium dodecyl sulfate (SDS) on the methane hydrate formation kinetics were investigated in the presence of SiC foam ceramic (SFC) packings. Beta-CD, at concentrations of 500 and 1000 ppm, enhanced the methane hydrate formation rate effectively compared with control experiments with only low concentration of SDS and SFC packings. Induction time was decreased by the simultaneous usage of 1000 ppm Beta-CD, 200 or 300 ppm SDS and SFC packings in reactor. However, no pronounced promoting effect was observed when there were only Beta-CD and SFC packings in the system, which indicated that SDS also played an important role in the acceleration of hydrate formation kinetics. In conclusion, there might be synergistic effects between Beta-CD, SDS and SFC packings that make their performance more significant in facilitating hydrate growth. The future work should focus on investigating the specific roles that the Beta-CD, SDS and SFC packings played in enhancement of hydrate formation process.

References

- [1] Sloan Jr, E.D., Koh, C. (2007) Clathrate hydrates of natural gases. CRC press.
- [2] Yevi, G.Y., Rogers, R.E. (1996) Storage of Fuel in Hydrates for Natural Gas Vehicles (NGVs). *Journal of Energy Resources Technology*, 118(3):209-13.
- [3] Yoslim, J., Linga, P., Englezos, P. (2010) Enhanced growth of methane-propane clathrate hydrate crystals with sodium dodecyl sulfate, sodium tetradecyl sulfate, and sodium hexadecyl sulfate surfactants. *Journal of Crystal Growth*, 313(1):68-80.
- [4] Scott, M.J., Jones, M.N. (2000) The biodegradation of surfactants in the environment. *Biochimica et Biophysica Acta (BBA) - Biomembranes*, 1508(1):235-51.
- [5] Lin, Y., Veluswamy, H.P., Linga, P. (2018) Effect of Eco-Friendly Cyclodextrin on the Kinetics of Mixed Methane-Tetrahydrofuran Hydrate Formation. *Industrial & Engineering Chemistry Research*, 57(17):5944-50.
- [6] Mohammadi, A., Manteghian, M., Mirzaei, M. (2011) Effect of β -cyclodextrin on dissolution of methane in water. *Chemical Engineering Research and Design*, 89(4):421-7.
- [7] Ji H., Chen D., Wu G. (2017) Molecular Mechanisms for Cyclodextrin-Promoted Methane Hydrate Formation in Water. *The Journal of Physical Chemistry C*, 121(38):20967-75.
- [8] Linga, P., Clarke, M.A. (2017) A Review of Reactor Designs and Materials Employed for Increasing the Rate of Gas Hydrate Formation. *Energy & Fuels*, 31(1):1-13.
- [9] Wu, G., Liu, X., Chen, D. (2018) A kind of device enhancing gas hydrate formation: China, ZL 2018 2 0461489.6[P]. 2018-12-04.
- [10] Wang, F., Luo, S., Fu, S., Jia, Z., Dai, M., Wang, C. (2015) Methane hydrate formation with surfactants fixed on the surface of polystyrene nanospheres. *J Mater Chem A*, 3(16):8316-23.
- [11] Uchida, T., Hirano, T., Ebinuma, T., Narita, H., Gohara, K., Mae, S. (1999) Raman spectroscopic determination of hydration number of methane hydrates. *AIChE Journal*, 45(12):2641-5.