Experimental Study of the Enhancement of CO₂/C₃H₈ Hydrate Kinetics With Cyclopentane for Desalination

Jibao Zhang[1], Xialian Xing[1], Tianbiao He[1, 2, 3*]

1 Department of Gas Engineering, College of Pipeline and Civil Engineering, China University of Petroleum (East China), Qingdao 266580, China

2 Shandong Provincial Key Laboratory of Oil & Gas Storage and Transportation Safety, Qingdao 266580, China

3 Qingdao Engineering Research Center of Efficient and Clean Utilization of Fossil Energy, Qingdao 266580, China

ABSTRACT

The kinetics of CO_2/C_3H_8 hydrate at the temperature of 275.6K-277.6K and pressure of 2MPa-3MPa was investigated. To improve the rate of hydrate formation and water conversion, cyclopentane (CP) with a volume ratio of 0.05-0.25 was employed as a promotor. The results demonstrated that higher pressure leads to more hydrate formation due to higher driving force. Moreover, the addition of CP can significantly accelerate the hydrate formation under a low pressure of 2MPa. The highest gas uptake with a CP/liquid phase ratio of 0.25 was 4.5 times higher than without CP. The findings in this study could provide insights on selecting appropriate conditions which improve the kinetics of hydrate formation to achieve the purpose of hydrate-based desalination.

Keywords: Hydrate-based technology, desalination, kinetics, cyclopentane

1. INTRODUCTION

Freshwater plays an essential role in human activities and is one of the crucial resources for sustainable development. Due to severe water pollution, the rapid development of the economy, and population growth, freshwater quality has deteriorated and faces a serious shortage trend [1, 2]. Therefore, various desalination technologies have been proposed to get fresh water from seawater [3]. Recently, distillation, multi-stage flash (MSF), and reverse osmosis (RO) have been widely used all over the world [4]. However, these technologies to obtain fresh water still have high energy consumption and equipment costs. Hence, researchers pay more attention to a novel desalination technology named hydrate-based desalination with low energy-intensive and cost-saving. Currently, the hydrate-based desalination (HBD) technology is relatively mature and with the advantage of being low energy-intensive [5].

Hydrate crystal is a non-stoichiometric clathrate, mainly formed by hydrogen bonds of water molecules to form a cage to enclose guest molecules [6]. In order to promote hydrate formation kinetics and conversion, various hydrate guests have been proposed. Gas is often used as guest molecules to form hydrates, such as carbon dioxide (CO_2), methane (CH_4), and propane (C_3H_8) [7-9]. CO_2 is more suitable as a hydrate former because it has a lower pressure for hydrate formation and an even higher salt rejection rate than methane [10]. It is found that the kinetics of CO_2 hydrate formation was not affected by salt in porous media [11]. Propane is not only a promising hydrate former because of its mild conditions but also a hydrate promoter that can reduce the phase equilibrium pressure for hydrate formation [12]. In addition, cyclopentane is a promising promoter that can form hydrate crystals at atmospheric. It was found that cyclopentane as an additive improved the kinetics of methane hydrate formation [13].

At present, there are many pieces of research on CO_2/C_3H_8 double gas hydrate, mainly focusing on the exploration of CO_2/C_3H_8 hydrate phase equilibrium, and few kinds of research on the kinetics of CO_2/C_3H_8 hydrate formation. The low hydrate formation rate and water conversion to hydrate need to be improved further. In addition, the kinetics of hydrate formation with CO_2/C_3H_8 gas mixture as hydrate former and combined with cyclopentane as a promoter to study the kinetics of hydrate formation are rarely discussed.

In this work, we adopted a mixture gas of 10% CO_2 and 90% C_3H_8 as hydrate former and cyclopentane as a

kinetic promoter to improve the kinetics of hydrate. Experiments were conducted in 3.4wt% NaCl solution to evaluate the kinetics of hydrate formation. The effect of experimental pressure from 2.0MPa to 3MPa on hydrate formation was also studied. Finally, different CP/liquid phase volume ratio experiments from 0.05 to 0.25 were analyzed. Furthermore, compared with previous studies that employ the CO_2/ C_3H_8 mixture gas as hydrate formers and cyclopentane as the promoter, our experimental condition can accelerate the hydrate formation rate and increase water conversion hydrate and obtain more hydrates, which will make HBD more favorable.

2. EXPERIMENTAL SECTION

2.1 Materials

The gas/gas mixtures employed was CO_2 (10mol%) and C_3H_8 (90mol%), which were purchased from Yantai Deyi Gas Co., Ltd. Cyclopentane with a purity of 96% was purchased from Shanghai Macklin Biochemical Co., Ltd. NaCl with a purity of 99.9% was obtained from Sinopharm Chemical Reagent Co., Ltd. The deionized water was produced by a water deionization system in the laboratory. 3.4wt% NaCl solution was prepared using a precision balance with a minimum reading of 1 mg.

2.2 Apparatus

The experimental apparatus used in this work is shown in Fig. 1. The stainless-steel crystallizer with a sufficient volume of 180 mL is immersed in a constant temperature water bath. The experiment pressure of the crystallizer is controlled by the pressure transducer (range of 0-16MPa) with the accuracy of ± 0.25%. The gas and liquid phase temperature in the crystallizer is measured using a Pt1000 thermoprobe with the uncertainty of ±0.05 K. The booster pump is used to increase the outlet pressure of the gas cylinder to reach the required pressure the experiment. The mechanical agitator is controlled by an external controller with a speed range from 0 to 1500 pm. The signals of temperature and pressure are collected by the data acquisition system recorded in the computer.
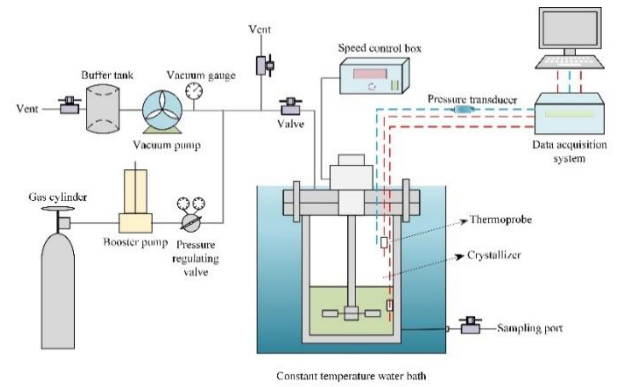

Fig. 1. Schematic of the experimental apparatus.

2.3 Experimental procedure

In this study, NaCl aqueous solution with a concentration ratio of 3.4wt% was used to simulate seawater. The experimental procedures were shown as follows:

(1) The crystallizer was cleaned with deionized water 2-3 times before the experiment.

(2) The NaCl aqueous solution and CP liquid were poured into the crystallizer. Then the air in the crystallizer was evacuated by a vacuum pump.

(3) The temperature of the crystallizer was cooled by the water bath to the experiment temperature. Once the gas-phase temperature reached the desired value (approximately 30 mins), the gas mixture was introduced into the crystallizer with stirring at a rate of 400 rpm. It is assumed as time zero for the experiment.

(4) The data acquisition system recorded pressure and temperature data and shown on the computer every 10 s. When hydrates began to form, there was a noticeable rise in temperature and a decrease in pressure.

(5) When there was no pressure change, it was regarded as the end of hydrate formation.

2.4 Performance index

The moles of gas consumed for hydrate formation was calculated using Eq. (1):

$$\Delta n = V\left[\left(\frac{P}{zRT}\right)_0 - \left(\frac{P}{zRT}\right)_t\right] \qquad (1)$$

Where V represents the volume of the gas phase in the reactor; P, T represents the pressure and gas-phase temperature of the reactor; R is the universal gas constant, and z is the compression factor calculated by the Peng-Robinson equation of state.

The conversion of water to hydrate was defined in Eq. (2):

$$\beta(\%) = \frac{\Delta n}{n_{H_2o}} \times hydrate\ number \times 100 \qquad (2)$$

Where Δn is the consumed gas moles calculated at the end of hydrate formation; n_{H2O} is the moles of 40mL water in the reactor; the hydration number is the number of water molecules required to form a hydrate per gas molecule. For the case of 10% C_3H_8/90% CO_2 used in this study, the hydration number is 8.21, which is obtained from Nambiar et al [14].

The rate of gas uptake for hydrate formation at the end of the experiment was calculated using Eq. (3):

$$r = \frac{\Delta n_{t+\Delta t} - \Delta n_t}{\Delta t} \qquad (3)$$

where r is the rate of gas uptake, which represents the rate of hydrate formation; Δn_t is the moles of gas consumed for hydrate formation at a particular moment, and Δt is the interval time for the data acquisition system to record data. The rate of gas uptake is averaged every 30 minutes.

3. RESULTS AND DISCUSSION

The kinetic of CO_2/C_3H_8 hydrate formation with cyclopentane as additive in the 3.4wt% salt solution were experimentally investigated. A total of 16 experiments were conducted at 2.0-3.0MPa and 275.6K-277.6K with CP/liquid phase ratios from 0.05 to 0.25. Tables 1 and 2 showed the experimental conditions, induction time, gas consumption, and percent conversion of water to hydrate. To assess the uncertainty, each experiment was repeated twice.

Table 1. Experiment results at different pressures and temperatures.

Exp. no	Pressure (MPa)	Temperature (K)	Induction Time (min)	End of experiment		β(%)
				Time (h)	Gas uptake (mol of gas/mol of water)	
1	3	275.6	8.35	21.5	0.0435	35.69
2	3	275.6	14.68	21.7	0.0459	37.69
3	3	276.6	26.17	24.8	0.0377	30.96
4	3	276.6	30.52	21.1	0.0378	30.97
5	3	277.6	50.10	22.9	0.0343	28.15
6	3	277.6	55.73	21.4	0.0338	27.73
7	2.5	275.6	35.20	21.6	0.0294	24.13
8	2.5	275.6	49.35	23.8	0.0296	24.17
9	2	275.6	8.35	22.2	0.0173	14.24
10	2	275.6	14.68	20.6	0.0223	18.28

Table 2. Summary of experimental conditions, induction times, gas consumption, and final conversion of water to hydrate at 2MPa with different CP/liquid phase volume ratios.

Exp. no	CP/liquid phase volume ratio	Induction Time (min)	Time (h)	Gas uptake (mol of gas/mol of water)	β(%)
11	0.05	32.78	22.2	0.0217	17.86
12	0.05	15.67	46.8	0.0293	24.11
13	0.15	18.30	16.7	0.0292	24.08
14	0.15	26.30	22.4	0.0342	28.09
15	0.25	6.76	46.5	0.0414	34.01
16	0.25	3.18	21.0	0.0403	33.09

3.1 Effect of pressure on hydrate formation in NaCl solution

Fig. 2 shows the gas uptake curve of hydrate formation experiment at 3MPa and 275.6K (experiment 2 in Table 1) along with temperature variation in a gas phase in 3.4wt% NaCl solution. The hydrate formation process is mainly that the introduced gas comes into contact with the surface of the NaCl solution, then the hydrate nucleates and growth can be observed. Since hydrate formation is an exothermic reaction, the sudden rise of temperature at 0.41h is defined as the induction time. Due to progressive nucleation, it can be seen that the temperature suddenly rises again at 1.3h. Subsequently, the temperature gradually restored to 275.6K because the water bath absorbs the reaction heat. The gas uptake increases to 0.0438 after 3.1h and reaches a plateau, which indicates that the rate of hydrate formation slows down, and there is no more gas consumption.
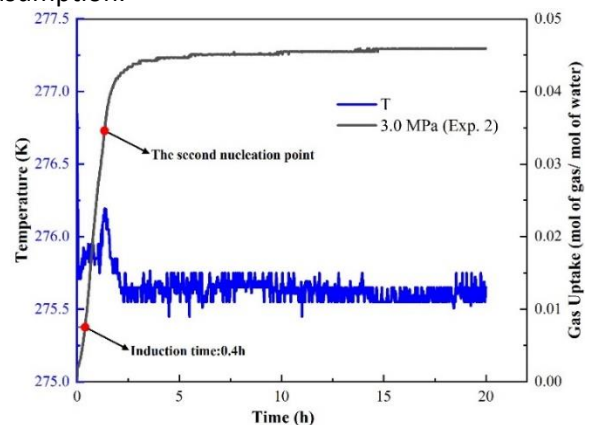

Fig. 2. Gas uptake measurement curve with temperature profile at 3MPa and 275.6K without stirring

Fig. 3 illustrates the effect of experimental pressure on the hydrate formation at the different pressures

experimented at 275.6K in the salt solution. The water conversion to hydrate is equivalent to the gas uptake, which is presented by the secondary y-axis at the right-hand side in the figure. As shown in Fig. 3, the gas uptake increases first and then reaches a stable state. It is because hydrates are continuously formed after nucleation and accumulate at the gas-liquid interface, which enlarges the mass transfer resistance. Significantly for further gas-liquid contact and thereby results in low water conversion to hydrate. The gas uptake of the experiment at 3.0MPa reaches a platform at 3.1 h, while that at 2.5MPa and 2.0Mpa takes 3.4h and 6.1h, respectively. Moreover, the final gas consumption value conducted at 3MPa is 0.0459 mol/mol, which is 56.2% and 107.8% higher than the gas uptake conducted at 2.5 MPa and 2.0MPa, respectively. It indicates that the gas consumption increases dramatically as the experiment pressure increases. Similarly, the water conversion to hydrate for the experiment at 3MPa is higher than that of the other two pressures. The increase in experimental pressure leads to a higher driving force for hydrate formation. The larger the driving force is, the more hydrate is formed, and the faster the hydrate formation rate is.
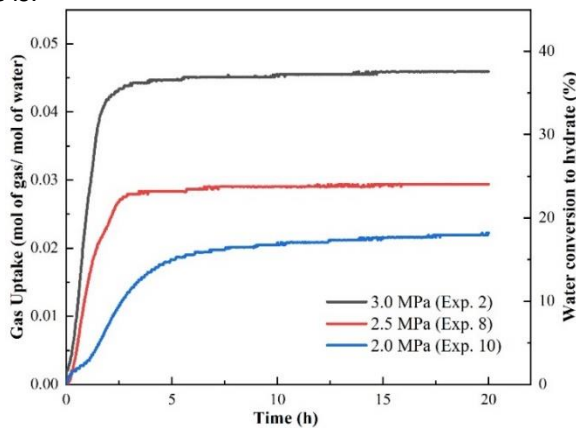

Fig. 3. Effect of driving force (pressure) on the gas uptake curve in 3.4wt% NaCl solution without stirring.

Fig. 4 shows the average rate of hydrate formation at 275.6K with different experimental pressures. It can be seen that the average rate of hydrate formation in the first 1.5h is in the following orders: 3 MPa > 2.5 MPa> 2 MPa. Afterward, the average rate of hydrate formation gradually decreases and reaches to zero which means no further hydrate formation. The peak value under the experimental pressure of 3.0 MPa is 1.6 and 7.4 times higher than that of experiment at 2.5 MPa and 2.0 MPa, respectively, which indicates that the maximum rate of hydrate formation increases with the increase of experimental pressure. Moreover, it should be noted

that the driving force at 2MPa is not large enough, which leads to a lower rate of hydrate formation and a lower final water conversion to hydrate. Thus, it is vital to choose suitable pressure to promote hydrate formation.
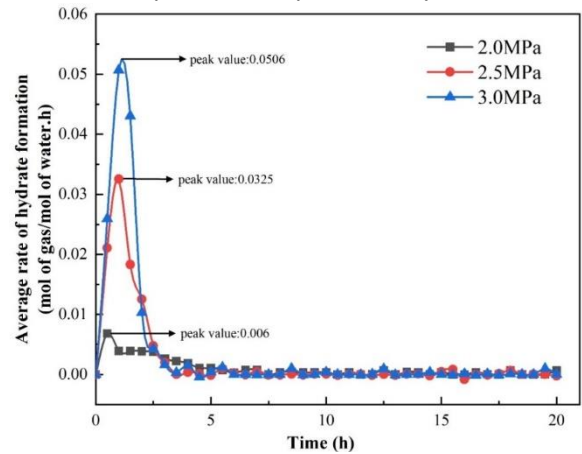

Fig. 4. Comparison of the average rate of hydrate formation at three different experimental pressures from 2MPa to 3MPa and 275.6K without stirring

3.2 Effect of CP/liquid phase ratios on hydrate formation in NaCl solution

According to Fig. 3, the final gas consumption is only 0.02 for the experiment at 2MPa, which can be further improved by adding promoter CP. Table 2 summarizes the experimental conditions and results with different CP/liquid phase ratios at 2MPa. The gas uptake changes at 275.6K and 2MPa with different CP/liquid phase ratios are shown in Fig. 5. It can be seen that the gas uptake increases rapidly and then reach a stable value. This is because hydrate quickly nucleates when the stirring starts, resulting in large amounts of hydrate formation. However, the accumulation of hydrate crystals at the gas-liquid interface hinders further hydrate formation. Moreover, CP as a promoter is vital to increase the gas uptake and accelerate the formation of hydrates. The value of gas uptake is only 0.018 after 5h without CP, while the gas consumption increases to 0.0367 with a CP/liquid phase ratio of 0.25. With the increase of CP/liquid phase ratio, the CO_2/C_3H_8 gas uptake value increases with reaction time. What should be noted here is that when CP/liquid phase ratio is 0.15, the gas consumption tends to be stable about 1.5h. However, the gas absorption that CP/liquid phase ratio is 0.325 is still rising. Gas absorption values between the two are equal at 3.06h. However, the reaction time exceeds 3.06h, the gas consumption value with CP/liquid phase ratio of 0.25 is much higher than that with CP/liquid phase ratio of 0.15. When the CP/liquid phase ratio

increases from 0.05 to 0.25, the gas consumption increases, which leads to more hydrate forming. The value of gas consumption with a CP/liquid phase ratio of 0.25 is 1.1 and 1.7 times higher than that with CP/liquid phase ratio of 0.15 and 0.05, respectively. The increase of CP/liquid phase ratio corresponds to the more volume of CP in solution for hydrate growth, which results in a faster hydrate formation rate and higher water conversion to hydrate. This similar phenomenon is also reported by Lv et al. [14].
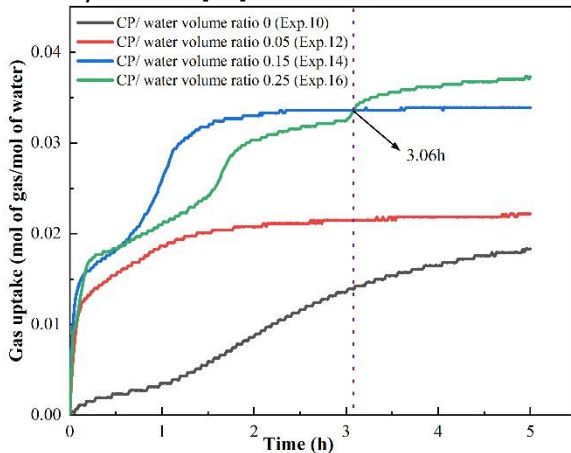

Fig. 5. Effect of CP/liquid phase ratio on the gas uptake curve at 275.6K and 2MPa with stirring at the speed of 400 rpm.

Due to the exothermic characteristic of hydrate formation, the energy consumption of the hydrate-based desalination is determined by the reaction temperature. With a lower reaction temperature, a larger refrigeration capacity is required and thereby consuming more energy. Thus, it is crucial to choose the appropriate reaction temperature. Fig. 6 demonstrates the effect of different temperatures on the water conversion to hydrate with CP/liquid phase volume ratio of 0.25. When the CP/liquid phase ratio is specified, the final water conversion to hydrate decreases with the increase of experiment temperature. Moreover, the final conversion of water to hydrate conducted at 275.6K is 5.1% higher than water conversion to hydrate conducted at 276.6K and 20.2% higher than that conducted at 277.6K respectively. However, when the temperature difference is 1K, the final water to conversion to hydrate only decreases or increases by 12.6% at most. Suggesting the little effect on the water conversion to hydrate and rate of hydrate formation with the smaller temperature difference.
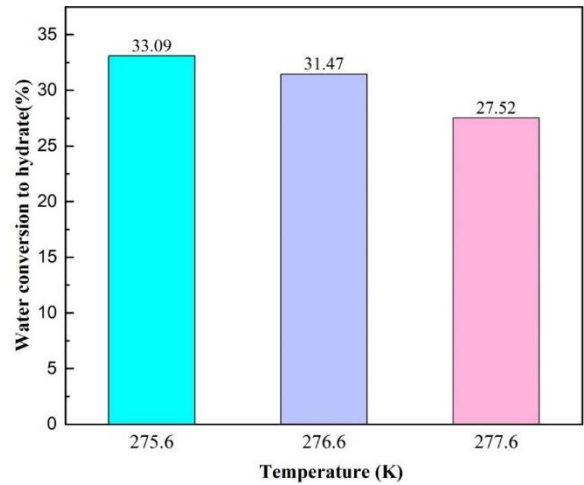

Fig. 6. Water conversion to hydrate change versus different CP/water volume ratios at 2.0MPa and 275.6K

4. CONCLUSION

In this study, CO_2/C_3H_8 hydrate formation experiments at pressure from 2MPa to 3MPa and temperature from 275.6K to 277.6K with different CP/liquid phase ratios from 0.05 to 0.25 were investigated. The results showed that the value of CO_2/C_3H_8 gas uptake for an experiment conducted at 3MPa was the highest, up to 0.0459, which indicated that the experimenting pressure had an effect on hydrate formation. Due to low gas uptake under the 2MPa experiment, CP as a promoter was added to improve the gas consumption and CO_2/C_3H_8 water conversion to hydrate with different CP/liquid phase ratios. The highest gas uptake was obtained when CP/liquid phase ratio was 0.25 at 2MPa and 275.6K. Moreover, the temperature had an significant impact on the kinetic of hydrate formation. Finally, it can be concluded that the CP/liquid phase ratio of 0.25 was the most superior, which can accelerate the hydrate formation rate and get more hydrates at the experiment of 2.0MPa and 275.6K.

ACKNOWLEDGEMENT

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