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Kinetic study on mixed cyclopentane-CO_2 hydrates in the presence of sodium chloride

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ABSTRACT

Hydrate-based technologies are the new topics in the hydrate community with many industrial applications. Recently, gas hydrate-based desalination (HBD) is considered as a novel and potential solution for water treatment. The gas hydrate-based desalination process will be promoted with higher hydrate formation rate and lower operating pressure in the presence of promoters.

In this work, Cyclopentane (CP) is used as a hydrate promoter for CO_2 hydrate-based desalination process. The main purpose of this research is to obtain the kinetic data of mixed CP−CO_2 hydrates in the presence of sodium chloride with 3.5 wt.%. The experimental data for mixed CP−CO_2 hydrates in the presence of sodium chloride are obtained in a batch reactor system with a temperature range of 2.3÷10.7 °C and a pressure range of 23÷33 bars. The effects of temperature, pressure, agitation speed and amount of CP on kinetics of mixed CP−CO_2 hydrate formation are also reported. This research would provide the new data to progress the hydrate-based desalination and water treatment.

Introduction

Water is the basic need for human life. The shortage of clean or drinking water makes seawater desalination is becoming essential. The present methods for desalination as: thermal distillation, cold freezing, reverse osmosis (RO), ion exchange, etc. [1] have limits with a high energy consumed and greenhouse gas emissions [2-3].

Recently, hydrate based desalination (HBD) is being widely investigated [4-5]. By this way, the water forms a framework around the gas or/and liquid molecules creating the hydrate solids. These hydrate particles are separated from concentrated salty solution and dissociated, producing clean water and hydrate formers as gas or/and liquid molecules which are recycled to desalination process [6]. The main advantages of HBD process are (1) low energy cost; (2) applicable to high salty solutions; (3) high capacity and efficiency.

Cyclopentane (CP) is a promising candidate as a hydrate former for desalination [7]. In addition, the combination of CP with CO_2 can help the crystallization of CP-CO_2 binary hydrates in softer conditions [8-12].

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In this way, CP can be hydrate former and additive. The fact that Cyclopentane is being received much attention because: (1) high desalination efficiency; (2) CP can be separated from fresh water after desalination (CP is insoluble in water) [13-14].

This work will address the kinetics of hydrate-based desalination (HBD) process using CP-CO_2 binary hydrate engineering in the presence of sodium chloride with a salt concentration of 3.5 wt.%. The fact that the effects of temperatures, pressures, stirring speeds and CP amount on the CP-CO_2 hydrate formation will be investigated. Furthermore, the optimal conditions of HBD process are being performed. Finally, hydrate washing and dissociation data to produce fresh water will be reported.

Experimental

Experimental chemicals and apparatus

Chemicals

Cyclopentane is from Aladdin (96% in purity). Sodium chloride used is provided from Fisher Chemical (99.5% in purity). The water used for the experiments is distilled water (produced by a distiller) from laboratory.

Apparatus

The reactor is manufactured by PARR equipment with an internal volume of 1.35 L and with a jacket cooling system. Two stirrers are used for mixing the gas and liquid phases. There are two PT100 temperature sensors for measuring the temperatures of gas and liquid phases. The pressure is measured by a sensor and controlled by several valves. The experimental temperature and pressure data are recorded by the Labview software on the computer. More details are in Fig 1 or [15].

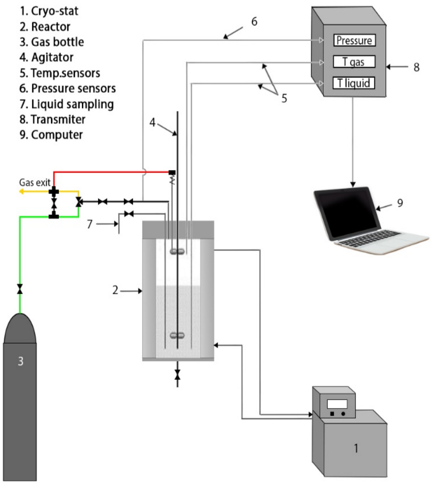

Fig 1: High pressure gas hydrate reactor system [15]

Experimental procedure

The 400 mL of prepared solution (3.5 wt.% of NaCl) and amount of cyclopentane (depending on the experimental conditions) are introduced to the reactor. Set the cryostat (chiller) to 25°C, waiting for the gas and liquid temperatures are stable. Start opening the valves to inject the CO_2 and waiting for pressure is stable. The cryostat is then set from 1°C-10°C to decrease the reactor temperature to the reaction points. The batch is agitated from 250-450 rpm on both the upper gas and lower liquid parts. A temperature increase and pressure drop at the same time are noticed as gas hydrate formation. Stop the crystallization process once the for hydrate formation reaches the equilibrium point (almost no change in pressure and temperature is stable). Decrease the pressure to ambient one and stop the chiller. Open the reactor to take the gas hydrate solid samples. They are served for hydrate washing and dissociation to produce and analyze the fresh water.

Initial experimental conditions

In this research, the experimental tests are conducted at different conditions. The initial conditions of each experiment are presented in Table 1. These conditions are based on the thermodynamic results on CP-CO_2 hydrate in the presence of NaCl [14]. The salt concentration (3.5 wt.%) is selected as it in the seawater.

Table 1: Initial conditions of each experiment

No	NaCl (wt.%)	T (°C)	P (bar)	Speed (rpm)	V_{cp} (ml)
1	3.5	2.3	28	350	44.50
2	3.5	5.2	28	350	44.50
3	3.5	10.7	28	350	44.50
4	3.5	2.3	28	350	0.0
5	3.5	8.1	28	350	22.25
6	3.5	2.3	28	350	22.25
7	3.5	2.3	28	350	11.13
8	3.5	2.3	33	350	44.50
9	3.5	2.3	28	450	44.50
10	3.5	2.3	33	350	0.0
11	3.5	2.3	28	250	44.50
12	3.5	2.3	23	350	44.50

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Measurement and calculation

The gas and liquid temperature and pressure in the reactor during hydrate crystallization are recorded by the Labview on the computer.

The gas (CO_2) consumption is calculated by the pressure drop during the hydrate formation using the following equation: PV=znRT, where P is pressure, V is gas volume, z is the gas compressibility factor, n is number of mole of CO_2, R is gas constant and T is temperature.

The water samples after hydrate washing and dissociation are analyzed (the salt concentration) by the potentiometric titration method and to calculate the salt removal efficiency (SRE).

Results and discussion

The typical experiment for CP-CO_2 hydrate formation and kinetic results

The pressure dropped during the nucleation stage of hydrate formation, followed by a rapid increase in temperature (Fig 2). It is evident that there are two peaks of temperature after hydrate formation (for almost all experiments). This can be two hydrate structures (sI for CO_2 hydrate and sII for CP-CO_2 and/or CP hydrates) formed.

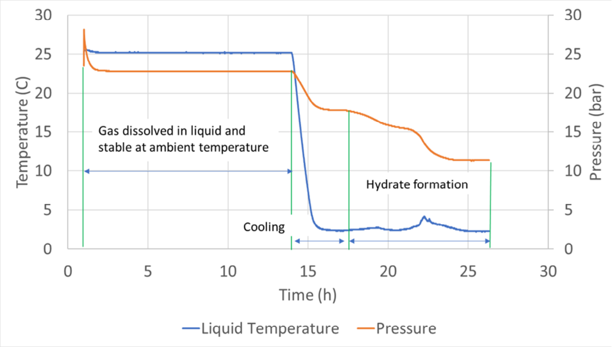

Fig 2: Temperature and pressure evolution of cyclopentane-CO_2 binary hydrate formation experiment with 3.5 wt.% of NaCl, T =2.3 °C, P= 28 bar, stirring speed at 350 rpm, CP=44.5 ml (Exp.1)

Table 2 shows the kinetic results (induction time and average kinetic rate) of all experiments performed. The induction time in each experiment is defined as the difference one between the time that system starts entering the formation hydrate zone to the time that system begins forming hydrate. The average kinetic rate (AKR) of is the ratio of total CO_2 consumption (mol) to the total time (h) from the beginning of gas hydrate formation to the end of experiment (almost no change in pressure and temperature, it is attributed to the kinetic equilibrium point). It is noted that no hydrate formed in the exp4-5-7-10.

Table 2: Kinetic results of all experiments

No	T (°C)	P (bar)	Speed (rpm)	V_{cp} (ml)	Induction time (h)	Average kinetic rate (AKR) (mol/h)
1	2.3	28	350	44.50	2.8	0.047
2	5.0	28	350	44.50	2.0	0.057
3	10.7	28	350	44.50	3.6	0.017
4	2.3	28	350	0.0	-	-
5	8.1	28	350	22.25	-	-
6	2.3	28	350	22.25	3.1	0.028
7	2.3	28	350	11.13	-	-
8	2.3	33	350	44.50	1.8	0.061
9	2.3	28	450	44.50	2.5	0.064
10	2.3	33	350	0.0	-	-
11	2.3	28	250	44.50	5.5	0.044
12	2.3	23	350	44.50	2.5	0.049

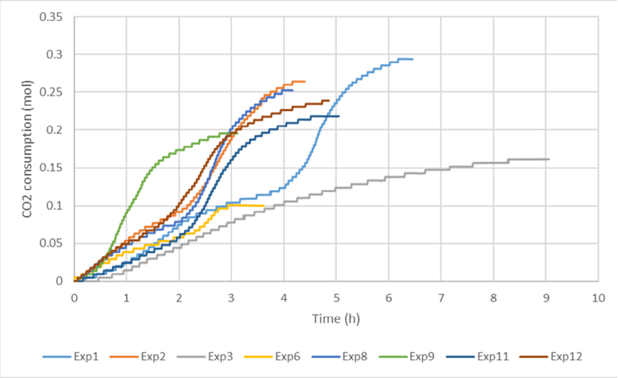

Fig 3: CO_2 consumption during gas hydrate formation

Fig 3 shows CO_2 consumption during gas hydrate formation for all experiments that forming hydrates (several experiments not formed hydrates because of hard conditions). The slope of these curves shows the kinetic rate of hydrate formation by the time through CO_2 consumption during crystallization process. It is observed that generally the kinetic rates increase after a certain period of time and decrease at the end of experiments (equilibrium points). The exp9 (experiment 9) shows very high kinetic rate at the beginning of hydrate formation after a half an hour. The other experiments presents the sharp increase of kinetic rate after about 2 hours.

Effects of temperature on CP-CO_2 hydrate formation

From the Table 2, the temperature increase may decrease the kinetic rate and increase the induction time (compare exp1 and exp3; exp2 and exp3; exp5 and exp6). This is explained by the higher temperature resulted in the lower driving force (the difference between the experimental and thermodynamic equilibrium temperatures) for hydrate formation. As a result, the lower kinetic rate and the longer induction time are observed.

Interestingly, it is observed a shorter induction time and higher kinetic rate when temperature increases (compare exp1 and exp2). This can be the homogenous phase in the reactor after hydrate formation led to a better gas (CO_2 consumption) and heat transfer during hydrate crystallization.

Effects of pressure on CP-CO_2 hydrate formation

The increase of pressure led to an increase of kinetic rate and a decrease in induction time (compare exp1 and exp8; exp8 and exp12). This is explained by the higher pressure resulted in the higher driving force (the difference between the experimental and thermodynamic equilibrium pressures) for hydrate formation. As a result, a higher kinetic rate and a shorter induction time are observed.
In contrast, compare exp1 and exp12, we saw the slight increase of induction time and decrease of kinetic rate when the pressure increases. This may due to a homogenous phase presented in the reactor led to better gas and heat transfer during hydrate crystallization.

Effects of rotational speed on CP-CO_2 hydrate formation

The increase of rotational speed led to the increase of kinetic rate and decrease the induction time (compare exp1, exp9 and exp11). This is attributed to the higher stirring speed caused the better mixing and contacting between the gas and liquid phases (better mass transfer in the system). As a result, hydrate may form at shorter time and higher kinetic rate observed.

Effects of CP/H_2O ratio on CP-CO_2 hydrate formation

The increase of CP/H_2O ratio led to the increase of kinetic rate and decrease the induction time (compare exp1, exp4, exp6 and exp7; compare exp8 and exp10). This may be explained that the lower CP/H_2O ratio led to not enough CP (stoichiometric coefficient as volumetric ratio between the aqueous solution and cyclopentane is 9:1) for CP-CO_2 hydrate formation. As a result, a lower hydrate formation rate and longer induction time are observed.

Optimal conditions for kinetics of CP-CO_2 hydrate based desalination

Based on the kinetic results, it is evident that the exp2 results show the optimal conditions for kinetics of CP-CO_2 hydrate based desalination. These are due to the short induction time, high temperature, low pressure, medium stirring speed and high kinetic rate.

Hydrate washing and dissociation to produce fresh water

In this work, the pure water is used in order to wash the hydrate solid samples at three and five times (20ml pure water each time over 100 ml gas hydrate solids). The salt removal efficiency (SRE) for desalination reaches up to 97.7% (see in Table 3).

Table 3: The water analysis result after hydrate washing

STT	Washing (times)	NaCl in solution before (wt.%)	NaCl after dissociation and washing (wt.%)	Salt removal efficiency (SRE) (%)
1	0	3.5	3.43	2.0
2	3	3.5	0.13	96.3
3	5	3.5	0.08	97.7

Conclusion

Generally, temperature increases, the kinetic rate decreases and induction time increases. It is general that the higher the pressure, the higher kinetic rate and the shorter induction time are observed. The higher the rotational speed, the higher the hydrate formation kinetics and shorter induction time are obtained. Decreasing of CP/H_2O ratio led to the lower hydrate formation rate and longer induction time. The optimal conditions for CP-CO_2 HBD are the short induction time, high temperature, low pressure, medium stirring speed and high kinetic rate. By hydrate washing process, it is confirmed that the salt is not inside the hydrate solids but on the hydrate surface and the SRE reaches up to 97.7%.

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