



# Investigation on the kinetics of carbon dioxide hydrate formation using flow loop testing

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## ABSTRACT

As a potential replacement for  $CH_4$  hydrates in the petroleum industry and as an environment-friendly secondary refrigerant in the chemical industry,  $CO_2$  hydrates are proven for several industrial applications. Most of the studies on  $CO_2$  hydrates are mainly conducted in bench top facilities with very limited research work in the flow loop. A newly built high-pressure flow loop was used to investigate the effect of four parameters (initial pressure, temperature, flow rate, and liquid loading) on  $CO_2$  hydrate formation. The process of hydrate formation and its morphological evolution in the flow loop were observed visually and analyzed. The experimental results revealed that the gas consumption increased as the initial pressure increased; however, it decreased with the increase of the temperature, flow rate, and liquid loading. The effect of the induction time on  $CO_2$  hydrate formation was also analyzed in detail.

## 1. Introduction

The transportation of unprocessed well streams has revealed critical issues with respect to flow assurance, such as wax deposition (Chi et al., 2016, 2017, Dubey et al.), hydrate formation, etc. Hydrate formation has been considered as a serious economic and safety issue in the oil and gas production ever since blockages were discovered in the pipeline (Byk and Fomina, 1968). The coexistence of natural gas and water under appropriate pressure and temperature conditions leads to the formation of crystalline solids, and thermodynamically, these compounds are solid solutions called as gas hydrates (Davy, 1811; Byk et al., 1968; Englezos, 1992). These are formed by the hydrogen bonded water molecules trapping the guest molecules (hydrocarbons and noble gases) within a cage like structure. The unique properties of gas hydrates such as high latent heat of melting ( $374 \text{ kJ kg}^{-1}$ ) and high gas storage along with the industrial concerns led to extensive research works on its development and handling (Jerbi et al., 2010). This problem becomes predominant in the offshore projects where the seabed has much lower temperature and higher pressure (Li et al., 2013; Gao et al. 2016a; Gao et al. 2016b; Gao and Gray, 2017). The oil and gas industry is mainly focusing on hydrate inhibition and prevention, while the chemical industry is showing its potential industrial applications as a two-phase secondary refrigerant to minimize the environmental

hazards (Fournaison et al., 2004; Marinha et al., 2006; Jerbi et al., 2010).

For an elaborative understanding of hydrates, it is required to characterize the hydrate forming elements and mechanisms on its formation and dissociation, with which appropriate models could later be developed. Sun et al. (2003) studied the kinetic behavior of refrigerant  $CCL_2F_2$  (R12) hydrates using a transparent flow loop. The pressure had little effect on the particle size, however it increased the rate of hydrate formation. Moreover, the hydrate particle concentration increased with the increase of the liquid flow rate. Sarshar et al. (2010) investigated the kinetics of hydrate formation for a propane mixture using a circulating flow reactor. A mathematical model was later developed for the process of hydrate formation based on the crystallization, mass transfer, and thermodynamic concepts. This model's prediction matched fairly well with the experimental gas consumption data. Talaghat (2013) measured the rate of hydrate formation with and without kinetic hydrate inhibitors in a circulating loop and concluded that the hydrate growth rate increased as the pressure increased. Lv et al. (2015) studied the hydrate induction time using a high-pressure flow loop. The results showed that the induction time of natural gas hydrate formation was affected by various factors such as supercooling, supersaturation degree, liquid loading, and anti-agglomerant dosage. It has to be noted that the induction time of hydrate formation has both microscopic and

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macroscopic definitions (Kashchiev et al., 1991; Natarajan et al., 1994; Bishnoi et al., 1996; Kashchiev, 2000; Kashchiev and Firoozabadi, 2003). The former refers to the period of time starting from the initial equilibrium state to the time of the nucleation being finished. The latter has been used in this work, which refers to the period of time starting from the initial equilibrium state to the time when the system temperature is about to rise suddenly due to massive hydrate formation.

As discussed before, the kinetics of hydrate formation are affected by several parameters, and elements forming hydrates have unique properties of their own. Among several guest molecules, carbon dioxide ( $CO_2$ ) is well-known to form gas hydrates with water under positive temperature and high pressure conditions (Sun et al., 2011). It has an interesting application in the oil and gas industry as a swapping molecule for natural gas ( $CH_4$ ) and in the chemical industry for its application as a secondary refrigerant (Fournaison et al., 2004) and  $CO_2$  sequestration (Servio and Englezos, 2001; Park et al., 2006). Moreover,  $CO_2$  hydrates are found to be more stable even under low pressure conditions (Fournaison et al., 2004), and they are easily formed by injecting into the cooled aqueous solution, thereby avoiding the usage of mechanical process for refrigeration (Marinhas et al., 2006; Jerbi et al., 2010).

Most of previous research works on  $CO_2$  hydrate formation were conducted in high-pressure reactor vessels (Lv et al., 2015), while very few studies have been reported using a flow loop. In fact, due to the geometry differences between the reaction vessel and flow loop, the results obtained from the reaction vessels were unable to be applied to the flowing system directly. Until now, only Jerbi et al. (2010) studied  $CO_2$  hydrate formation and dissociation kinetics using a flow loop and concluded that the increase in gas injection rate facilitates hydrate formation.

Since the kinetics of  $CO_2$  hydrate formation have not yet been clearly understood, it is of critical importance to conduct research on  $CO_2$  hydrate formation in the flow loop system. In this work, a high-pressure flow loop has been newly built to systematically and statistically study the effects of the initial pressure, temperature, flow rate, and liquid loading on the kinetics of  $CO_2$  hydrate and to understand its hydrate formation process. Hence, understanding the mechanism of gas hydrate formation and factors affecting the hydrate formation process in a flowing system is of great importance to help not only in the prevention of hydrate formation but also in its industrial applications as refrigerants.

## 2. Experimental program

### 2.1. Materials

The Changzhou City tap water was used as the liquid phase, which was distilled and deionized before use, and  $CO_2$  was used as the gas phase [certified purity of 99.8 vol% (Changzhou Jinghua Industrial Gases Co. Ltd.China)].

### 2.2. Experimental facility

The schematic experimental setup is shown in Fig. 1. The newly built flow loop is capable of conducting high-pressure (maximum of 15 MPa) and two-phase (gas-liquid) flow experiments with two viewports for visual observation of the process of hydrate formation. The total capacity of the flow loop is about 7.5 L. The test section consists of six different sections. Along the flowing direction, three straight sections of length 0.5, 1, and 2.5 m are followed by a semicircle section of radius 0.63 m. It is then connected to another two straight sections with the length of 3 and 1.5 m. In order to increase the contact surface between gas and liquid phases, a helical twisted stripe is installed inside the first two sections of the pipe. The test section is a pipe-in-pipe heat exchanger made of stainless steel based on ANSI Schedule 40 Type S. The ID and OD of inner pipe are 26.7 and 33.4 mm, respectively. The ID

and OD of outer pipe are 52.6 and 60.3 mm, respectively.

A magnetic centrifugal pump with a flow rate of  $3 \text{ m}^3/\text{h}$  is installed to circulate the mixture in the flow loop. The admission line is equipped with a gas booster pump which delivers a maximum outlet pressure of 42 MPa. This pump is used to pressurize the gas when the operating pressure goes above the gas cylinder pressure. In addition, the automatic control valve (TESCOM) is used to improve the accuracy of the gas pressure control. In order to maintain a constant wall temperature, a coolant with a capacity of 500 L is installed outside the pipe, and the temperature is controlled by a water chilling unit with an operating range of  $-15 \text{ }^\circ\text{C}$  to  $20 \text{ }^\circ\text{C}$ .

The flow rate and density of the mixed fluids are measured by a Coriolis mass flowmeter (YKLLK-S-025), which are obtained from Dalian Youke Instruments and Apparatus Development Center. The uncertainty in flow rate measurement is 0.15–0.25% and in density measurement is  $\pm 0.002 \text{ g/ml}$ . As shown in Fig. 1, two differential pressure transmitters (Honeywell STD720) are installed in upstream and downstream of the test section. The pressure transmitters (Rosemount 3051) and temperature transmitters (Rosemount Pt100) are installed in each segment of the test section. The data from all the equipment are collected and recorded in a Data Acquisition System.

1: gas cylinder; 2: gas booster pump; 3: buffer tank; 4: gas mass flow meter; 5: liquid storage tank; 6: turbine flowmeter; 7: liquid booster pump; 8: liquid mass flow meter; 9,10 – viewport; 11: circulating pump; 12: tank reactor; V1,V5: pressure regulating valve; V2-V4, V7, V9, V14-V16,V18: needle valve; V6, V8, V10-check valve; V11-13, V18: high-pressure ball valve; V17: safety valve; PR1-5: pressure transducer; TR1-5: temperature sensor; PDR1, PDR2: differential pressure transducer.

### 2.3. Experimental procedures

Firstly, the tightness of the flow loop system was carefully checked and cleaned three times thoroughly using distilled water. The flow loop was then filled with the desired amount of water followed by evacuation procedure using a vacuum pump until the pressure reaches  $-0.02 \text{ MPa}$   $CO_2$  was then injected gradually into the flow loop until the system pressure reaches the set value. In order to maintain fixed initial conditions in all the tests during the gas injection process, the temperature of the ambient ( $19 \text{ }^\circ\text{C}$ ) was maintained above the hydrate formation temperature. The fluids were then circulated at the desired flow rate for an hour to make sure that the gas gets saturated in the liquid at the ambient temperature. As the flow rate and system pressure become stable, the cold glycol with the desired temperature was introduced into the annular region, and the experiment was started. The hydrate formation process was monitored in a high-pressure visual observation window. The conditions such as differential pressure exceeding the maximum allowable range, pressure and temperature of the system getting stabilized, and test duration reaching the set value, indicate the completion of the experiment.

### 2.4. Test matrix

In this work, all the experiments were conducted at constant volume (the initial operating pressure was maintained constant) as shown in Table 1. Totally, four initial operating pressures (4.5, 5, 5.5, and 6.5 MPa), four coolant temperatures (274.2, 275.2, 276.2, and 277.2 K), four flow rates (16, 24, 30, 40 and 48 L/min), and three liquid loadings (66.7, 73.3, and 80 vol%) were conducted. All experiments were repeated and showed a reasonable consistency within 10% error. Appendix A shows an example of a repeated experiment.

### 2.5. Calculation of the amount of gas consumed during hydrate formation

Gas consumption is an important parameter in the process of  $CO_2$  hydrate formation. The moles of  $CO_2$  consumed is calculated from the molar balance as shown in Equation (1). In this work, the mole of  $CO_2$

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