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Clathrate Hydrate Capture of CO_2 from Simulated Flue Gas with Cyclopentane/Water Emulsion*

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Abstract Capture of CO_2 by hydrate is one of the attractive technologies for reducing greenhouse effect. The primary challenges are the large energy consumption, low hydrate formation rate and separation efficiency. This work presents a new method for capture of CO_2 from simulated flue gas [CO_2(16.60%, by mole)/N_2 binary mixture] by formation of cyclopentane (CP) hydrates at initial temperature of 8.1 °C with the feed pressures from 2.49 to 3.95 MPa. The effect of cyclopentane and cyclopentane/water emulsion on the hydrate formation rate and CO_2 separation efficiency was studied in a 1000 ml stirred reactor. The results showed the hydrate formation rate could be increased remarkably with cyclopentane/water emulsion. CO_2 could be enriched to 43.97% (by mole) and 35.29% (by mole) from simulated flue gas with cyclopentane and cyclopentane/water (O/W) emulsion, respectively, by one stage hydrate separation under low feed pressure. CO_2 separation factor with cyclopentane was 6.18, higher than that with cyclopentane/water emulsion (4.01), in the range of the feed pressure. The results demonstrated that cyclopentane/water emulsion is a good additive for efficient hydrate capture of CO_2.
Keywords cyclopentane, hydrate, CO_2 capture, emulsion, flue gas

1 INTRODUCTION

The emission of carbon dioxide (CO_2) from the combustion of fossil fuels has been identified as the major contributor to global warming and climate change. Between 1995 and 2001, the average global CO_2 emission grew at a rate of 1.4% per year. Electric-power generation remains the largest source of CO_2 emission, emitting as much CO_2 as that from the rest of the industries combined [1]. To reduce these environmental concerns, there is considerable international collaboration to establish coal-based technologies that minimize CO_2 emissions without significantly increasing costs. Carbon capture and storage (CCS) is currently considered to be technically feasible for emission reduction. Many ways can reduce CO_2 emissions, such as absorption, adsorption, and membrane separation [2−4]. Although these processes have proved successful for the selective removal of CO_2 from multicomponent gaseous stream, they still have some critical problems associated with large energy consumption, corrosion, foaminess, and low capacity [5−8]. Recently, one promising technology, hydrate separation has attracted more attention [9−11].

Gas hydrates are crystalline composed of water and gas under suitable conditions of low temperature and high pressure. There are three known hydrate structure (I, II, H) in which water molecules arrange themselves around guest molecules. Fully loaded sI methane hydrate contains about 170 volumes of methane (STP) per volume of hydrate [1]. When gas hydrates are formed from mixture of gases, the concentration of these gases in the hydrate phase and that in the gas phase is different. Consequently, the component that forms hydrate more easily might be enriched in the hydrate phase. Because hydrates have the capacity to store large amount of gas and to separate gas mixture, hydrate technology has attracted much attention as a potential means for capturing CO_2.

Kang *et al*. [12, 13] and Linga *et al*. [14, 15] have systematically studied the process of hydrate capture of CO_2 with tetrahydrofuran (THF) as an additive. The results show that the addition of THF reduces the operating pressure and enhances the corresponding kinetic rate. It is verified that the hydrate-based gas separation process makes it possible to recover more than 99% (by mole) of CO_2 from flue gas by three hydrate separation stages. Although these results are promising, the separation process with THF as an additive has some problems: for example, the temperature required in the separation process is very low (0.6 °C), THF is harmful to health/safety and contaminates environment, and the hydrate formation rate is slow. Recently, tetra-*n*-butyl ammonium salts as an attractive additive have received much attention, such as, tetra-*n*-butyl ammonium bromide (TBAB) and tetra-*n*-butyl ammonium fluoride (TBAF). We have studied extensively the kinetics and separation efficiency of CO_2 capture by formation of semi-clathrate hydrates with TBAB as an additive [16].

Recently, cyclopentane hydrate has been studied as thermal energy storage media [17]. It is known that cyclopentane forms a structure II hydrate at a

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temperature near 280 K at atmospheric pressure. Fan *et al*. [18] reported that the quadruple point, at which the above three phases plus a vapor phase coexist, was at 280.22 K and 19.8 kPa. Tohidi *et al*. [19] first reported hydrate dissociation data for cyclopentane in binaries and ternaries with methane or/and nitrogen. The comparison with other newly discovered hydrate forming compounds showed that cyclopentane was the strongest hydrate promoter with neopentane in the second place. The equilibrium data of methane, mixture gas (methane + ethane + propane), hydrogen, carbon dioxide + cyclopentane were measured [20, 21]. Zhang *et al*. [22] investigated the kinetics of CO

2.3 Preparation of cyclopentane/water (O/W) emulsion

Tween 80 [5% (by mass)] was dissolved in 200 ml of distilled water. Cyclopentane was then added to the aqueous solution at volume ratio of 1∶5, followed by 5 min of mixing with a homogenizer (FJ 200-S) at 5000 $r \cdot min^{-1}$ to generate the emulsion droplets. Fig. 2 shows a microscope photograph of prepared cyclopentane/water emulsion (ZEISS Observer. A1). The emulsion droplets are about 2−5 m in size (Fig. 2).

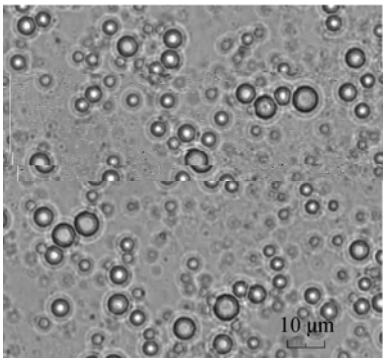

Figure 2 Microscope photograph of prepared cyclopentane/water emulsion

2.4 Hydrate capture procedure

There are two routes to form the cyclopentane hydrate for capturing CO_2 (Fig. 3). In route 1, the liquid phase is the mixture of cyclopentane and water. In route 2, it is the prepared cyclopentane/water emulsion that forms the cyclopentane hydrate.

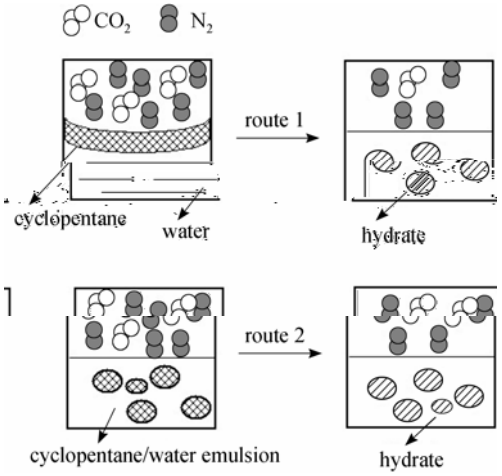

Figure 3 Two routes of cyclopentane clathrate hydrate formation

After 240 ml of the mixture solution or the prepared cyclopentane/water emulsion of volume ratio of 1∶5 (40 ml cyclopentane/200 ml distilled water) was introduced into the evacuated reactor, the reactor was cooled to the desired temperature. When the cell temperature was stabilized, the reactor was vacuumed and purged using gas mixture of CO_2 [16.60% (by mole)]/N_2 four to five times to ensure the absence of air, and then gas mixture was charged into the cell to the given pressure. Then the stirrer was started to initiate hydrate formation. During the experiment, the temperature and pressure were recorded. After hydrate formation finished (the system pressure was constant), the stirrer was stopped, and the residual gas was transferred and analyzed with GC. Then the vent valve was opened and the remaining gas was purged, the vessel was warmed to 25 °C to make the hydrate dissociate completely. The dissociated gas composition was also determined with GC.

3 CO_2 SEPARATION FACTOR

The CO_2 separation factor is calculated as follows:

$$S = \frac{x_1 / x_2}{y_1 / y_2} \tag{1}$$

where x_1 and y_1 are the concentration of CO_2 in the hydrate (or emulsion) phase and gas phase at the end of experiment, respectively, x_2 and y_2 are the concentration of N_2 in the hydrate (or emulsion) phase and gas phase at the end of experiment, respectively.

4 RESULTS AND DISCUSSION

4.1 Hydrate formation kinetics

Figures 4 and 5 show the typical pressure and temperature during hydrate formation process in the presence of cyclopentane and cyclopentane/water emulsion, respectively, at initial temperature of 8.1 °C for CO_2 [16.60% (by mole)]/N_2 binary mixture gas. The system pressure decreases gradually at first 0.5 h and then is constant, indicating that the hydrate formation is completed and the system reaches equilibrium.

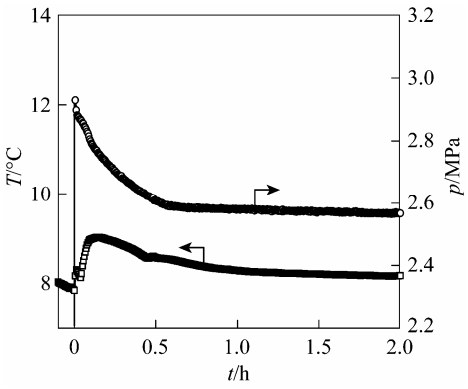

Figure 4 The trend of the feed pressure and temperature during hydrate formation process with cyclopentane

Figures 4 and 5 show remarkably pressure drop

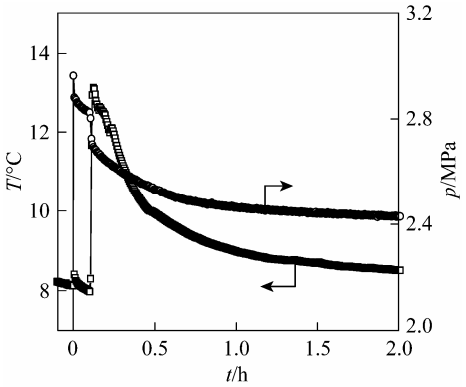

Figure 5 The pressure and temperature during hydrate formation process with cyclopentane/water emulsion

accompanying with sharp temperature increase, which is the exothermic effect found in formation of cyclopentane hydrate from cyclopentane/water emulsion [17]. The large temperature increase can be explained by the large cyclopentane-water-gas contact area in the presence of cyclopentane/water emulsion. The temperature changes in hydrate formation experiments are shown in Figs. 6 and 7 under different feed pressure.

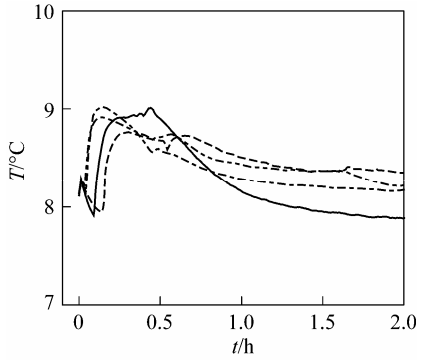

Figure 6 Temperature in hydrate formation experiments with cyclopentane
—— 2.49 MPa; - - - - 2.67 MPa; - · - · 3.25 MPa; - - - - 3.49 MPa

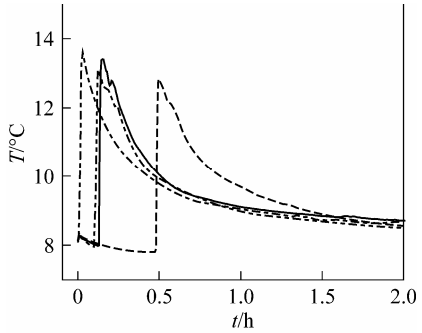

Figure 7 Temperature in hydrate formation experiments with cyclopentane/water emulsion
- - - - 3.66 MPa; —— 3.24 MPa; - · - · 2.97 MPa; - - - - 2.60 MPa

Compared the results in Figs. 6 and 7, it is found that the increase in temperature due to hydrate formation is about 1 °C with cyclopentane, and about 5 °C with the cyclopentane/water emulsion. A larger increase in temperature corresponds to a higher rate of hydrate formation, and vice versa [17]. Thus, the hydrate formation rate with the cyclopentane/water emulsion is higher than that with cyclopentane. From Fig. 3, it is clear that in the presence of cyclopentane/water emulsion, the contact area for gas and liquid in route 2 is larger than that in route 1, which may cause higher hydrate formation rate.

4.2 Compositions of vapor phase and hydrate (or emulsion) phase

The vapor and hydrate (or emulsion) equilibrium composition in the presence of cyclopentane and cyclopentane/water emulsion at initial temperature of 8.1 °C are shown in Tables 2 and 3, respectively. The influence of the feed gas pressure is investigated when the CO_2 content in the gaseous feed is 16.60% (by mole). z_1, x_1, and y_1 represent the concentration of CO_2 in feed gas, hydrate (or emulsion) phase and vapor, respectively. In Table 2, CO_2 concentration in the hydrate phase varies from 37.51% (by mole) to 43.97% (by mole) with the feed pressure range from 2.49 to 3.95 MPa, and shows a maximum at 2.90 MPa. The result demonstrates that CO_2 is enriched in the hydrate phase in the presence of cyclopentane. However, CO_2 concentration in the emulsion phase changes from 28.71% to 35.29% (by mole) with the feed pressure from 2.60 to 3.66 MPa with the cyclopentane/water emulsion. As shown by route 1 (Fig. 3), cyclopentane floats on the water because its density is lower than that of water. CO_2 may previously dissolve in cyclopentane layer because of its higher solubility in cyclopentane than that of N_2 and subsequently CO_2 is trapped in the cyclopentane hydrate. However, there is no selective dissolution of CO_2 in route 2, so the CO_2 concentration in the hydrate phase is lower than that in route 1.

Table 2 The vapor and hydrate equilibrium composition for CO_2(1)/N_2(2)-cyclopentane and water mixture

T/°C	p/MPa	z_1/%	x_1/%	y_1/%
8.1	2.49	16.60	38.74	11.49
	2.67		39.01	11.36
	2.90		43.97	11.27
	3.25		38.64	11.58
	3.49		38.12	11.60
	3.95		37.51	12.06

Table 3 The vapor and emulsion equilibrium composition for CO_2(1)/N_2(2)-cyclopentane/water emulsion

T/°C	p/MPa	z_1/%	x_1/%	y_1/%
8.1	2.60	16.60	32.22	12.49
	2.97		32.45	12.27
	3.24		35.29	11.97
	3.66		28.71	13.97

4.3 Separation factor

Figure 8 displays the CO_2 separation factor calculated by Eq. (1) under different conditions. The CO_2 separation factors with cyclopentane are higher than those with cyclopentane/water emulsion under the same feed pressure, which may be explained by the selective dissolution of CO_2. For example, at initial temperature of 8.1 °C, the optimum CO_2 separation factor with cyclopentane is 6.18, while it is 4.01 with the cyclopentane/water emulsion. It is also found that the increase in the feed pressure is disadvantageous to CO_2 separation, because N_2 competes with CO_2 for cage occupancy with higher driving force.

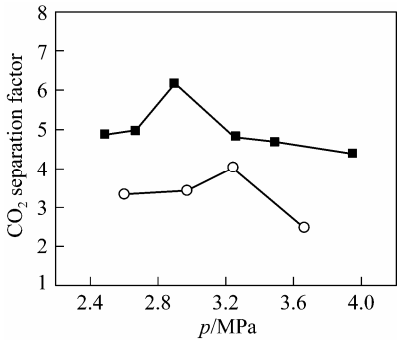

Figure 8 CO_2 separation factor *vs.* feed pressure with cyclopentane and cyclopentane/water emulsion
■ CP; ○ CP emulsion

5 CONCLUSIONS

The effect of cyclopentane and cyclopentane/water emulsion on hydrate formation rate and separation efficiency was investigated for capture of CO_2 from simulated flue gas [O_2(16.60%, by mole)/N_2 binary mixture] at initial temperature of 8.1 °C by formation of cyclopentane clathrate hydrates. The main conclusions are as follows.