Speedy Hydration of Carbon Dioxide Hydration in an Immediate Coolant of Ice Granules

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ABSTRACT: Hydrate-based carbon capture (HBCC) has been considered as a promising technique in recent times. However, large exothermic heat of hydration and lower solubility of the gas in water cause a slower hydration rate and poor gas uptake during hydration. In the present work, a phase change heat removal method was applied, in which ice granules surrounded by normal alkanes were used as an immediate coolant and quick nucleation center to intensify the carbon dioxide capture through hydrate formation. Normal alkanes have great potential to enhance gas–water contact due to their high solubility with CO₂ and thus may enhance the hydration rate. The slurries of ice in normal alkanes from cooling three different W/O emulsions were prepared to perform all the hydration experiments in a batch autoclave at a constant temperature of 267.15 K and pressure range of 1.9–2.5 MPa with a stirring speed of 600 rpm. Kinetics of CO₂ hydrate formation such as induction time, hydration duration, molar gas uptake, and hydrate growth rate were determined using a mole balance (PVT) model. Compared to earlier investigations of hydrate formation, in present work, the hydrate growth rate increased by 7–39 times and enlarged to 352 times as compared to pure water while gas uptake per mole of water increased by 1.6–10 times.

1. INTRODUCTION

Increasing CO₂ emissions by fossil fuel consumption to fulfill the increasing energy demand has become a global challenge that must be controlled to reduce its global impact in the form of global warming, climate change, floods, and many other disadvantages.¹ Effective carbon capture and storage techniques need to be adopted to overcome given challenges. Many available conventional technologies including membrane separation, adsorption, and absorption have some restrictions such as low storage, higher cost, and complicated processing.²,³ Recently, hydrate-based carbon capture (HBCC) and hydrate-based CO₂ separation (HBCS) methods have been recognized for their great advantages such as environmental benignity and efficient and economical capture, storage, and separation of CO₂.⁴–⁹ A clathrate hydrate is defined as a stoichiometric compound in which gases like CO₂ and CH₄ are entrapped into the water molecule in moderate temperature and pressure conditions. Typically, 170 volume of gas can be stored per volume of methane, natural gas, and carbon dioxide hydrates in standard conditions,¹⁰ which is highly attractive for gas storage. Natural hydrates and kinetics of gas and water production from hydrate-based sediments are well explained in recent studies.⁹,¹⁰ Numerous articles have been published to highlight the potential applications of hydrate-based CO₂ capture.¹¹–¹⁷ However, there are still some barriers to utilize this promising technology such as slow hydrate formation, low gas uptake per mole of water, and lower induction time. Many researchers made efforts to intensify the carbon dioxide hydrate formation by using different approaches. For example, some researchers focused on kinetic promoters to enhance the hydration rate, while thermodynamic promoters have also been used by some investigators to shift the equilibrium pressure downward.¹⁷–²² However, problems of slower growth rates and lower gas uptakes during hydration still require sufficient improvements. Higher exothermic heat of hydration²³,²⁴ is one of the main reasons that reduce the hydrate formation rate and causes hydrate agglomeration, mass transfer resistance at the gas–water interface, and heat transfer resistance at the water hydrate interface. In past studies, many researchers also focused on removal of hydration heat by indirect methods, such as immersing a hydrator in the water bath, using a heat exchanger,²⁵ wrapping coiled copper tubes inside the hydrator,²⁶ and using aluminum foam,²⁶ although, in these indirect heat removal methods, the heat transfer coefficient was lower than those in the direct heat removal methods. It was reported by many researchers that low gas solubility in water also hindered hydrate formation and growth rate. For
example, Yu and co-workers\textsuperscript{14} significantly reduced the surface tension of aqueous solution by using a synergistic combination of graphite nanoparticles and specific concentration of SDBS. Although the storage capacity was improved as compared to pure water, lower gas solubility in water curbed the hydrate growth rate. Englezos et al.\textsuperscript{27} also developed a model for pure water hydration and reported that lower solubility of the gas in water limited the mass transfer driving force. Recently, some researchers have suggested that the water—oil emulsion system is useful to increase the contact area between gas and water molecules by increasing the solubility of gas in solution and thus enhance hydrate formation.\textsuperscript{28–30}

Nevertheless, removal of hydration heat is still a challenge that must be removed to improve the growth rate and the gas uptake during hydration. As phase change particles have larger heat storage capacity and surface-to-volume ratio,\textsuperscript{31,32} which may also be highly attractive to absorb hydration heat and enhance the hydrate formation kinetics, and as hydrate formation heat is almost equal to the latent heat of ice to water, most of the hydration heat can be immediately removed by melting the ice particles in oil. Furthermore, ice particles can provide quick nucleation centers to hydrate, which may also result in a shorter induction time. Thus, following the above approach in this work, a phase change heat removal method was used by making slurry of ice in oil. Normal alkanes including decane, heptane, and hexane were used as a continuous phase in three different W/O emulsions. An autoclave was used to form hydrates by using ice granules as an immediate refrigerant and nucleation center and the surrounded normal alkanes as an absorbent of high solubility. Their mergence has great potential to improve carbon dioxide hydrate formation. All the experiments were performed at a constant temperature of 267.15 K, impeller speed of 600 rpm, and pressure range of 1.9–2.5 MPa. An increment of 0.3 MPa was enough to determine the effect of pressure on hydrate growth speed.

2. EXPERIMENTAL FACILITY AND CHEMICALS

All the experiments were performed in a 316L SST hydrator having an effective volume and withstand pressure of 61.3 cm\textsuperscript{3} and 20 MPa, respectively. To monitor the gas pressure, a CYB-20S transmitter was installed at the gas side of the vessel. Two Pt 100 resistance thermometers were also fixed inside the upper and lower parts of the hydrator to measure the temperatures of CO\textsubscript{2} gas and emulsion, respectively. To attain the desired temperature, the hydration vessel was connected with a water bath containing a 50% solution of ethylene glycol and water. All inlet tubes including the hydrator were insulated by polyurethane foam to prevent heat losses. A pump with a maximum flow rate of 20 mL min\textsuperscript{-1} was also linked with the hydrator to insert the emulsion. A stirrer speed of 600 rpm was attained by adjusting a magnetic stirrer on top of the hydrator, having a maximum rotation capacity of 1200 rpm. The computer acquisition system was also associated with a hydrator to record the temperature and pressure with a 5 s interval. All the components of the apparatus are shown in Figure 1.

99.9% pure CO\textsubscript{2} was purchased from Lufang Inc., Company, Tianjin, China. Surfactants (S-80/T-80) were bought from Heowns Biochemical Technology Co., Ltd., Tianjin, China. Heptane, hexane, and decane with a concentration of ≥98 wt % were obtained from Tianjin Yuan Li Chemical Engineering Co., Ltd., Tianjin Fuyu Fine Chemicals Co., Ltd., and Shanghai Titan Scientific Co., Ltd., respectively.

2.1. Experimental Method. First, the hydrator was thoroughly washed with pure water and purged by inserting CO\textsubscript{2} gas pressure up to 1 MPa, and the same procedure was repeated five times alternatively. To ensure gas tightness, gas was discharged from the hydrator up to 2.5 MPa and all the inlet valves were closed; after 2 h, if the pressure drop was as low as 0.015 MPa, then the system was taken as gas-tight. Finally, at room temperature, 30 mL of prepared emulsion having 21 mL of \( n \)-alkane and 30 vol % water-cut was pumped into the hydrator and cooled down to experimental temperature by setting the water bath. To achieve the desired temperature of 267.15 K, a 50 vol % mixture of water and ethylene glycol was allowed to circulate from the water bath to the vessel’s surrounding walls. Once the emulsion cooled down to the experimental temperature, CO\textsubscript{2} gas was discharged from the cylinder to attain desired pressure in the hydrator. Once the temperature of the liquid phase became constant again, rotation of the agitator was adjusted to 600 rpm and the
alkanes, the freezing point of oil must be lower than water, and lower surface tension of oil. All these properties have potential to intensify the hydration process.

Surfactants Span-80 and Tween-80 were chosen based on appropriate hydrophilic–lipophilic balance (HLB = 9), as used by Fu et al. Emulsion formation was started by carefully balancing the desired amount of surfactants in a beaker. Then, desired amounts of oil and water were precisely measured through a graduated cylinder and mixed with surfactants. The ratios of water to oil and water to surfactants were listed in Table 1, including higher solubilities of CO2 in liquid water are listed in Table 2. A stirring speed of 10,000 rpm was used to attain a well dispersion of water in oil. To check the stability at different stirring rates, a prepared emulsion of water in decane was monitored for 30 h, and images were taken. The emulsion remained stable throughout the observing period as can be seen in Figure 2. Finally, the emulsion was inserted into the hydrator and cooled down to 267.15 K to freeze the water particles.

2.3. Hydrate Formation Mechanism and Experimental Data Analysis. After turning on the impeller, pressure in the gas phase started to decrease continuously, which confirmed the gas absorption in oil and formation of hydrate. Hydration was assumed to be complete when the change in pressure was almost negligible, i.e., 0.02 MPa h⁻¹. As the impeller was started, oil as the continuous phase in the W/O emulsion allowed CO₂ molecules to be absorbed at a faster rate. Once the gas became saturated in oil, the dissolution heat of CO₂ absorbed by the oil made the ice melt on the surface of ice granules, where the hydration started at the water layer. Exothermic heat of hydrate formation was quickly removed by ice granules and produced more free water, which, therefore, decreased hydrate agglomeration and heat transfer resistance and thus enhanced hydrate formation and its rate. The schematic steps of hydrate formation are explicitly demonstrated in Figure 3.

A mole balance equation based on the pressure volume and temperature method was developed to analyze the experimental data, and the mole number of CO₂ encapsulated during hydrate growth was obtained by the following general relation

$$\Delta n_G = \Delta n_{abs} + \Delta n_{hi}$$

(1)

where $\Delta n_G$, $\Delta n_{abs}$, and $\Delta n_{hi}$ are denoted as the changes in total molar CO₂ gas consumption in the liquid phase, absorption in oil, and consumption during hydration, respectively, and $\Delta n_G$ can be determined using eq 2.

$$\Delta n_G(t) = \frac{1}{R} \left( \frac{PV}{ZT - T} \right) = \frac{PV}{ZT}$$

(2)

Here, $P$, $T$, $V$, $R$, and $Z$ are the state equation parameters experimental pressure, temperature, volume of the gas phase, gas constant, and compressibility factor, respectively. Subscripts 1 and t are used for the beginning of hydrate formation and during hydration, respectively. The Peng–Robinson equation of state was used to calculate the compressibility factor against experimental temperature and pressure. Values of temperature and pressure were obtained using a software-associated recorder from the experimental setup. The change

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**Table 1. Properties Related to Phase Change and Solubilities of Substances Used in Present Work**

| chemical used to prepare W/O emulsions | fusion point (K) | surface tension (dynes/cm) | mole fraction of CO₂ in liquids | latent heat of phase change (kJ/kg) |
|---------------------------------------|-----------------|---------------------------|-------------------------------|-----------------------------------|
| n-C₁₀H₂₂ | 243 | 23.9 | 20.20 | 202 |
| n-C₁₆H₃₄ | 182.6 | 20.03 | 21.40 | 140 |
| n-C₁₀H₂₂ | 177.8 | 17.91 | 22.04 | 160 |
| H₂O | 0 | 8.1 × 10⁻⁶ | | 334 |

**Table 2. Properties of Emulsions and Droplet Sizes**

| emulsion type | surfactant (g) | stirring rate (rpm) | stirring time (min) | avg. droplet size (nm) |
|---------------|----------------|--------------------|---------------------|------------------------|
| (#1) S-80: 0.36; T-80: 0.282 | 10,000 | 10 | 1498 |
| (#2) S-80: 0.36; T-80: 0.282 | 10,000 | 10 | 1720 |
| (#3) S-80: 0.36; T-80: 0.282 | 10,000 | 10 | 1977 |

*S-80: 4 wt % water; mass ratio of Span-80 to Tween-80: 0.783.

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Figure 2. (a) Photo of the three 30 vol % water-in-decane emulsions prepared by using different stirring rates. (b) Photo of the separation layer in the three emulsions after 30 h.
in the molar amount of CO2 gas in the oil phase during hydrate formation can be calculated using eq 3.

\[
\Delta n_{\text{oil}}(t) = \left[ {x_1 \over 1-x_1} - {x_t \over 1-x_t} \right] n_o
\]

(3)

\[
x = {n_{\text{oil}} \over n_o + n_w}
\]

(4)

Here, \( x \) is the solubility mole fractions of CO2 gas in oil, which was calculated from the PR equation of state.\(^3\)\(^4\) The molar amount of normal alkane in the emulsion was determined against their experimental temperature and pressure data at the onset of hydration (\( x_t \)) and during hydration (\( x_t \)). Finally, molar consumption of CO2 gas during hydrate growth was calculated by rewriting eq 1 as follows

\[
\Delta n_{\text{hyd}}(t) = \frac{1}{R} \left[ \frac{P_{V_f}}{Z_t T_f} - \left( \frac{P_{V_1}}{Z_t T_f} \right) \right]
\]

\[
- \left[ {x_1 \over 1-x_1} - {x_t \over 1-x_t} \right] n_o
\]

(5)

where the volume of the gas phase at time \( t \) is denoted by \( V_g \) and it changed with hydrate growth because hydrate volume is 1.25 times higher than water volume \(^3\)\(^6\) and can be obtained by the following relation

\[
V_i = V_h - (V_L + 1.25 V_{H,0}(t) - V_{H,O}(t))
\]

(6)

\[
V_i = V_h - V_L
\]

(7)

Here, \( V_i \), \( V_h \), \( V_L \), and \( V_{H,0}(t) \) are the total volume of the reactor, the volume of the liquid phase, and the volume of used water at time \( t \), respectively.

\[
V_{H,O}(t) = {\Delta V_{\text{CO}_2}^{\text{hyd}}(t) N_{\text{hyd}} M_w \over D_w}
\]

(8)

By combining eqs 7 and 8, eq 6 can be rewritten as

\[
V_i = V_i - {0.25 \Delta n_{\text{hyd}}(t) N_{\text{hyd}} M_w \over D_w}
\]

(9)

where \( N_{\text{hyd}} M_w \) and \( D_w \) represent the hydration number, molar mass, and density of water, respectively. The hydration number was calculated by a method provided in the literature.\(^7\)

Molar gas usage during hydrate formation was finally determined by substituting the value of \( V_t \) in eq 5, which may be written as eq 10.

\[
\Delta n_{\text{hyd}}(t) = {1 \over R} \left[ \frac{P_{V_f}}{Z_t T_f} - \left( \frac{P_{V_1}}{Z_t T_f} \right) \right] - \left[ {x_1 \over 1-x_1} - {x_t \over 1-x_t} \right] n_o
\]

(10)

3. RESULTS AND DISCUSSION

3.1. Absorption-Hydration \( P-t \) Curves Obtained from Experimental Data. In this work, three different alkanes were used to prepare three W/O emulsions of 30 vol % water-cut to investigate the CO2 hydrate formation by the direct heat removal method through ice granules. All hydrate experiments were performed under isothermal and isochoric conditions at a temperature of 267.15 K. Typical absorption-hydration \( P-t \) (pressure vs time) curves were obtained in each experiment after starting the impeller. The resulting curves consisted of three stages, including (1) dissolution of CO2 in oil, (2) induction time, and (3) hydrate growth as demonstrated in Figure 4. First, a sharp decrease in pressure from \( P_0 \) to \( P_1 \) occurred due to CO2 gas absorption in oil. Second, a straight line depicted the saturation of gas in oil, and the length of this fixed period is also known as the induction time of hydrate. Finally, after the induction time, a second pressure drop from \( P_1 \) to \( P_{\text{end}} \) indicated the gas consumption due to hydrate growth. All three stages are illustrated in Figure 4, where \( P_0 \), \( P_1 \), and \( P_{\text{end}} \) stand for initial experimental pressure, onset pressure of hydrate growth, and pressure at the end of hydration, respectively.

The pressure variation curves are illustrated in Figure 5 as a function of time for three different W/O emulsions, namely, water in hexane, water in heptane, and water in decane. A difference of 0.3 MPa in experimental pressure was taken to determine the influence of pressure on hydrate formation. The effect of initial experimental pressure on the rate of pressure drop during hydration was clearly observed. For example, in the case of the (#1) emulsion, pressure reduction from \( P_1 \) to \( P_{\text{end}} \) completed in 3.3 min, which increased to 6.1 min by...
decreasing pressure up to 1.9 MPa. Similar trends were also attained in the case of the (#2) and (#3) emulsions as shown in Figure 5. It was also observed that alkane, i.e., hexane, having higher gas solubility and lower surface tension produced quick absorption and hydration as compared to the other two alkanes, i.e., heptane and decane. This is the reason why the maximum pressure reduction rate is achieved in the (#1) emulsion and the minimum rate is achieved in the (#3) emulsion. Thus, the time taken by the pressure drop from $P_1$ to $P_{\text{end}}$ in the former case was 3.6 min, which increased to 6.5 min in the latter.

3.2. Induction Time for Hydrate Formation. As mentioned before, a constant line that appears after gas absorption is known as the induction time, which is depicted in Figure 4. In this study, the nucleation time was shortened by using ice as a quick nucleation center. Furthermore, at constant temperature, a direct relation between initial pressure and induction time was also observed in each emulsion system. For instance, in the case of the (#1) emulsion, the nucleation time increased from 0.5 to 4.05 min by decreasing experimental pressure from 2.5 to 1.9 MPa. At difference of the same pressure range, the induction time decreased from 1.7 to 5.2 min in the case of the (#2) emulsion. Alike patterns were also obtained in the (#3) emulsion, and all trends of induction time as a function of experimental pressure are illustrated in Figure 6. Three trials have been made for each induction time’s experiment, and error bars are also provided in Figure 6. A comparison of the induction time in the current and previous investigations is also listed in Table 4, which shows that the induction time in the present work shortened sufficiently. In addition to the experimental pressure, the induction time was also dependent on surface tensions of alkanes. It was also noticed that the induction time increased in lower surface tension’s emulsion and vice versa. For example, decane has greater surface tension than heptane and hexane, and thus, a maximum induction time of 6.5 min was obtained in the (#3) emulsion at an experimental pressure of 1.9 MPa. Similarly, the lowest induction time of 0.5 min was achieved in the case of the (#1) emulsion.

3.3. Gas Uptake during Hydration. The molar amount of CO$_2$ gas used to form hydrates was calculated by the pressure volume temperature (PVT) method under isothermal and isochoric conditions as described in the preceding section, and the final mathematical expression is shown in eq 10. In this work, the influence of direct hydration heat removal by ice granules was clearly observed in the form of significant enhancement of gas uptake during hydrate formation in each emulsion system. It actually reduced the heat transfer resistance at the water hydrate interface and thus prevented hydrate dissociation. Figure 7 illustrates the trends of molar gas uptake as a function of time in three different W/O emulsions, where molar gas uptake is denoted by the slope of the curve, which increased from zero to maximum and finally approached zero again, which is considered as equilibrium. It was noticed that experimental pressure and the type of alkane influenced the amount of gas uptake in each emulsion system. As shown in Figure 7, when pressure increased from 1.9 to 2.2 MPa, molar gas uptakes also increased from 0.0198 to 0.0226 and similarly augmented to 0.026 at 2.5 MPa. Likewise, gas uptake
Present and Previous Studies

Gas uptake during hydration in the current study relative to previous studies was augmented remarkably. For example, in the case of the (#1) emulsion, 0.052 mol of CO2 gas per mole of water was used to form hydrates. In earlier studies done by Yu et al.,14 and Zhou et al.,37 graphite nanoparticles and two different surfactants, namely, SDBS and TBAB, were added in water to improve hydrate formation kinetics but the achieved CO2 gas uptake values were only 0.018 and 0.02 mol per mole of water, respectively. In the present work, meanwhile, molar consumption slightly reduced from 0.052 to 0.048 and to 0.045 in the case of the (#2) and (#3) emulsions, respectively, due to the difference of gas solubilities and surface tensions of alkanes. However, these uptakes were still much greater than those in earlier investigations. In an earlier work,15 pure water was also used to form hydrate and attained CO2 consumption as low as 0.005 mol per mole of water. A comparison with the previous studies shows that CO2 consumption per mole of water in the current work increased by 1.6–10 times as presented in Table 3.

As hydrate formation is an exothermic process, it is obvious that greater hydration heat will be released during higher hydrate formation and vice versa. Temperature variation curves during hydration of the water-in-hexane emulsion at different experimental pressures can be seen in Figure 8.

3.4. Rate of Hydration. The hydrate growth rate is one of the main parameters to evaluate the hydrate-based carbon capture process. It mainly depends upon molar gas consumption during hydrate growth, time taken by hydrate formation, and initial amount of water present in the emulsions, which are denoted as $\Delta H_{H2O}$, $\Delta H_{H}$ and $V_{H2O}$, respectively. The hydrate growth time is considered as the duration of hydrate growth starting from $P_1$ to the point where hydrate growth almost becomes zero, i.e., $P_{end}$, as shown in Figure 4. As seen in Figure 7, when 95% or more of hydration completes, the growth rate seems to move very slowly. The same fashion was also found in an earlier study,28 therefore, we calculated and compared the growth rate on the basis of 95% of hydration. The mathematical expression given in eq 11 was used to evaluate the average hydrate growth rate.

$$ (R_{avg})_{95\%} = \frac{1}{V_{H2O}(0)} \frac{d\mu}{dt} \approx \frac{1}{V_{H2O}(0)} \left( \frac{\Delta H_{H}}{\Delta H_{H2O}} \right)_{95\%} $$

The maximum hydration rate was achieved in the case of the (#1) emulsion because of the larger miscibility of CO2 in hexane, the lower surface tension of hexane, and, most importantly, the direct phase change heat removal by ice granules. It was obvious that higher solubility of CO2 in paraffins provided larger contact at the gas–water interface. As the solubility of carbon dioxide in hexane is greater than that in heptane and the latter’s is greater than decane’s, the hydration rate was the highest in the (#1) emulsion as 1568 mol m$^{-3}$ min$^{-1}$, which decreased to 1061 in the (#2) emulsion and similarly further reduced to 708 in the (#3) emulsion at the same experimental pressure of 2.5 MPa. In the same fashion, values of growth rate varied at other experimental pressures, and all the trends of growth rate are shown in Figure 9. The hydration formation rate was also reduced by decreasing the pressure, which is obviously due to less thermodynamic driving force. For example, when pressure was decreased from 2.5 to 2.2 MPa, the rate of hydration decreased from 1568 to 962, 1061 to 504, and 708 to 330 mol m$^{-3}$ min$^{-1}$ in the (#1), (#2), and (#3) emulsions, respectively, as illustrated in Figure 9.

The achieved results of hydrate formation kinetics, including induction time $T_{ind}$, average hydration rate, and hydrate growth time $\Delta H_{H}$, in the present and previous studies are listed in Table 4 against their experimental conditions and methodologies. In order to attain meaningful comparison, only those experimental data were included, having a thermodynamic

Table 3. Molar Gas Uptake during Hydrate Formation in Present and Previous Studies

| experimental conditions          | gas uptake per mole of water |
|---------------------------------|-----------------------------|
| (#1) W/O emulsion, 2.5 MPa, 267.15 K (this work) | 0.052                        |
| aqueous solution of TBAB and 0.08% graphite nanoparticles at 277 K, 4.5 MPa | 0.018                        |
| aqueous solution of 0.04% SDBS and graphite nanoparticles at 3.5 MPa, 277.15 K | 0.02                         |
| semibatch O/W emulsion, 2.3 MPa, 277.6 K | 0.032                        |
| 0.15 wt % Fe$_3$O$_4$ nanoparticles + magnetic field at 3 MPa, 274 K | 0.0198                       |
| pure water | 0.005                        |
driving force similar to or higher than that in present work. The average hydration rates of all studies enlisted in Table 4 were calculated on the basis of 95% of hydration. The results clearly indicated the significance of the phase change heat removal method by ice granules. As compared to pure water, the hydrate growth rate enlarged by 350 times in the present work. Furthermore, in comparison with earlier studies, other than pure water, the achieved highest growth rate increased by 7–39 times as shown in Table 4.

Gas storage capacity per volume hydrate is also a very important factor in hydrate base gas storage technology. The storage capacity of CO₂ gas in standard T and P conditions per volume of hydrate has been calculated and is shown in the table below. It was noticed that the storage capacity has a direct relation with the experimental pressure and a maximum value of 135 (v/v) was achieved in the case of the water-in-hexane emulsion. The data has also been compared against the previous studies as listed in Table 4. The method that was used to evaluate the storage capacity (SC) is given as follows

$$V_H = \frac{N_{hyd} \times \Delta n_h(t) \times V^MT}{V_H}$$

(13)

Here, $N_{hyd}$ is the hydration number, while $V^MT$ is the molar volume of the empty hydrate lattice, which can be calculated by the following relation,39 where the units of P and T are MPa and kelvin, respectively, while $N_A$ is Avogadro’s number.

$$V^MT = \left(11.835 + 2.217 \times 10^{-5}T + 2.242 \times 10^{-6} \times T^2\right) \times 10^{-30}N_A \times \frac{46}{8.006 \times 10^{-3}P + 5.448 \times 10^{-12}P}$$

(14)

3.5. Effect of Water Droplet Size on Hydrate Formation. TheNano Zetasizer designed by Britain Malvern Instruments was used to measure the average droplet sizes of the three prepared emulsions, and images of the peaks are shown in Figure 10. Although the same surfactant’s mass fractions were used to prepare all three emulsions, the water droplet size was not the same because of different paraffin’s surface tension as shown in Table 5. Alkanes having lower surface tension produced smaller water droplets than the higher one. As the surface tension of decane is higher than those of heptane and hexane, a maximum droplet size of 1977 nm is obtained in the (#3) emulsion and a minimum of 1498 nm is obtained in the (#1) emulsion due to the lowest surface tension of hexane. Different droplet sizes produced different surface areas of the water droplet, which affected the mass transfer driving force of gas on the water-oil interface and thus varied the amount of gas consumption during hydration. For instance, as listed in Table 5, moles of gas uptake during hydration increased from 0.024 to 0.0261 by decreasing the droplet diameter from 1977 to 1498 nm.

4. CONCLUSIONS

To intensify the carbon dioxide hydration, ice granules as an immediate coolant surrounded by paraffin were used to absorb the heat of hydration. Normal alkanes as the continuous phase increased the absorption rate of CO₂ in them, while ice particles as the distributed phase in phase change slurry quickly absorbed hydration heat and thus reduced heat transfer resistance during hydration. Experimental outcomes showed that the CO₂ hydrate growth rate significantly enhanced in the present study and a maximum growth rate of 1429 mol m⁻³ min⁻¹ was achieved. Achieved gas uptake per mole of water was increased by 1.6 to 10 times. The average hydration rate was 352 times larger than that of pure water and 7–39 times than those obtained with other methods. The induction time was directly dependent on two factors including experimental

Table 4. Comparison of the Results between This Work and Previous Works

| hydrate formation conditions | $T_{init}$ (min) | storage capacity (v/v) | $\Delta$hyd (min) | avg. hydration rate (mol m⁻³ min⁻¹) |
|-----------------------------|------------------|------------------------|-------------------|-----------------------------------|
| 2.5 MPa, 267.15 K, 600 rpm, (#1) W/O emulsion (this work) | 2 | 135.4 | 3.36 | 1429 |
| 2.5 MPa, 267.15 K, 600 rpm, (#2) W/O emulsion (this work) | 4 | 130.2 | 3.9 | 1061 |
| 2.5 MPa, 267.15 K, 600 rpm, (#3) W/O emulsion (this work) | 5 | 125.5 | 5.91 | 708 |
| 2.3 MPa, 277.6 K, 450 rpm, 45 wt % O/W PCS16 | ≤1 | 107.6 | 7.9 | 200 |
| 4.2 MPa, 273.15 K, 0.03% SDS solution + aluminum foam | 112.3 | 32 | 125 |
| 277.15 K, 3.5 MPa, 0.04% SDSBS solution14 | 14.5 | 91 | 55 | 18 |
| 1.7 MPa, 277.6 K, 360 rpm, 0.1 wt % TBPP solution | 0.6 | 86.2 | 15 | 46.2 |
| 3 MPa, 274 K, 0.15 wt % Fe₃O₄ nanoparticles + magnetic field15 | 15 | 93 | 75 | 14.7 |
| 3 MPa, 274 K, pure water15 | 45 | 97 | 61 | 4.05 |

“Types of emulsions: (#1): water in hexane; (#2): water in heptane; (#3): water in decane.
pressure and alkanes’ surface tension. A minimum induction time of 0.5 min at a pressure of 2.5 MPa was achieved in the water-in-hexane emulsion.

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Figure 10. Measured water droplet sizes in various emulsions.

| emulsion type | droplet size of water (nm) | molar gas uptake |
|---------------|----------------------------|------------------|
| (#1)          | 1498                       | 0.0261           |
| (#2)          | 1720                       | 0.025            |
| (#3)          | 1977                       | 0.024            |

Table 5. Molar Gas Uptake with Different Droplet Sizes at 2.5 MPa, 267.15 K, and 600 rpm

Notes
The authors declare no competing financial interest.

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■ NOTATIONS

\( D_w \): density of water \\
\( M_w \): molecular weight of water \\
\( \Delta n_{CO_2} \): CO\(_2\) in the gas side (mol) \\
\( \Delta n_{H_2O} \): CO\(_2\) used in hydration (mol) \\
\( \Delta n_{oil} \): carbon dioxide absorbed in oil (mol) \\
\( n_\text{paraffin} \): paraffin in emulsion (mol) \\
\( n_{H_2O}(t) \): water amount at time \( t \) (mol) \\
\( N_{\text{hydration}} \): hydration number \\
\( P \): pressure of the gas phase \\
\( P_0 \): initial experimental pressure \\
\( P_1 \): pressure at the beginning of hydration \\
\( P_{end} \): pressure at the end of hydration \\
\( R_{avg} \): average hydration rate \\
\( R \): gas constant \\
SST: stainless steel \\
\( T_{ind} \): induction time \\
\( T \): temperature of the liquid phase
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