Recent advances in gas hydrate-based CO_2 capture

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Highlights

- A review study on hydrates based CO_2 capture
- Discussions of separation mechanisms, advantages and limitations
- Influence of various chemical additives and mechanical mixing methods
- Challenges for future research

Abstract

Hydrate-based CO_2 capture (HBCC) has received increasing attention, due to such advantages as the mild operating pressure and temperature, the ease of regeneration and its unique separation mechanism. This review paper is focused on the chemical additives and the mechanical methods that have been investigated to improve the CO_2 separation efficiency and energy consumption through HBCC technology. Detailed comparisons of the effects of various chemical additives and mechanical methods on gas consumption, operating conditions, hydrate induction time and CO_2 recovery are critically reviewed. The limitations and challenges of HBCC, in comparison with the conventional methods for CO_2 capture are discussed.

1. Introduction

Carbon dioxide (CO_2) capture is a continuous process which requires a significant amount of energy to operate. It contributes to around 70-90% of the total operating cost of the three-stage carbon capture and storage system that is commonly used for the reduction of CO_2 emissions (Herzog and Golomb, 2004). Current CO_2 capture employs adsorption, absorption and membrane technologies which are low in efficiency and usually require multiple stages. Continuous efforts have been made to search for alternative methods in the area of CO_2 capture so that the overall operating cost of the carbon capture can be reduced.

Generally, CO_2 is captured from the effluent of power plants through either post- or pre-combustion capture. Post-combustion capture refers to the treatment of flue gas before being released into the atmosphere. The flue gas consists of approximately 15-20% CO_2 and 5% O_2, with the balance being N_2, and it is emitted from a full combustion process. Pre-combustion capture refers to the capture of CO_2 from the fuel gas, which is the partially combusted fuel containing approximately 40% CO_2 and 60% H_2. The high CO_2 content in the fuel gas allows more efficient capture. However, it can only be employed in an integrated gasification combined cycle (IGCC) power plant where the fuel is pre-treated to produce CO_2/H_2 syngas. The CO_2 is then separated from the syngas while the H_2 is fed into the combustion process. Post-combustion CO_2 capture is less effective than the pre-combustion method. However, it can be retrofitted to any plant without much modification (Spigarelli and Kawatra, 2013). Regardless, the gas systems that are discussed in this paper are mostly CO_2, or CO_2/N_2, or CO_2/H_2.

Hydrate-based CO_2 capture (HBCC) technology is a novel process that has received enormous attention, both from the industry and academic researchers, during the last two decades. The technology operates at mild pressures and temperatures, through a unique separation mechanism that is easy to regenerate and capable of separating gas mixtures, which might not be achievable via conventional technologies (Englezos and Lee, 2005). A significant number of studies have reported on the potential application of gas hydrates technology in CO_2 capture. These include some early work that was mostly focused on phase equilibrium studies of pure CO_2 hydrates, and more recent work that has focused closely on investigations of various chemical additives and mechanical methods for enhancement of the efficiency of CO_2 capture and separation. This paper will review the recent developments and research activities conducted on HBCC with a focus on

chemical additives and mechanical approaches that are able to improve the selectivity, efficiency and kinetics of this technology. An introduction to the principles and significance of gas hydrates technology will be followed by detailed discussion of the current progress in technological improvements through the application of various chemical additives and mechanical methods. The key effects of the chemicals and mechanical methods, as well as the major outcomes of the research activities, will be summarised. In addition, the paper will give an account of the costs, limitations and challenges that are associated with HBCC, in comparison with the conventional technologies.

2. Hydrate-based CO_2 capture technology

2.1. Gas hydrates

Gas hydrates are solid clathrates made up of gas molecules (guests), such as methane (CH_4), CO_2, N_2 and H_2, that are caged within a cavity of hydrogen-bonded water molecules (host). They form under the favourable thermodynamic conditions of low temperature and high pressure, and they exhibit various structures depending on the size and chemical properties of the guest molecules (Sloan and Koh, 2008). Most small gas molecules, such as CO_2 and CH_4, form structure I (S_I). Structure II (S_{II}) hydrates form with larger gas molecules such as N_2 (Davidson et al., 1986) and propane. With the mixture of both small and large gas molecules, such as methane + cycloheptane, the structure H (S_H) may form (Sloan, 2003). This is due to the gas molecule repulsions which open various sizes of water cage. The crystal structures of these hydrates consist of different water cavities. The most common forms of water cavity include the irregular dodecahedron ($4^3 5^6 6^3$) and the pentagonal dodecahedron (5^{12}), as well as the tetrakaidecahedron ($5^{12} 6^2$), the hexakaidecahedron ($5^{12} 6^4$) and the icosahedron ($5^{12} 6^8$) that are often collectively described as $5^{12} 6^m$, with $m = 2, 4, 8$ (Sloan and Koh, 2008). The term "5^{12}" is used to indicate that a relatively smaller cavity contains 12 pentagonal faces, whereas the term "$5^{12} 6^m$" denotes a larger cavity with 12 pentagonal and m hexagonal faces, while "$4^3 5^6 6^3$" illustrates a medium cavity which contains 3 tetragonal, 6 pentagonal and 3 hexagonal faces. A combination of 5^{12} and $5^{12} 6^2$ is more commonly seen in S_I, while the combination of 5^{12} and $5^{12} 6^4$ is more commonly seen in S_{II}. In S_H, a combination of 5^{12}, $4^3 5^6 6^3$ and $5^{12} 6^8$ has been observed.

Formation of gas (in particular methane) hydrates has been a significant problem for the upstream oil and gas industry because they clog pipelines, valves, wellheads and processing

facilities, thus reducing production and causing safety problems. Extensive research activities have been undertaken in order to prevent or mitigate the formation of gas hydrates (Kelland, 2006). Research on the enhancement of gas hydrate formation began in the late 19th century after discovering the positive applications of gas hydrates for gas storage, separation, sequestration and desalination (Sloan and Koh, 2008).

2.2. Gas hydrate-based CO_2 capture

CO_2, as a small nonpolar hydrocarbon, forms S_I hydrates with a formula of $CO_2 \cdot n H_2O$ ($n = 5.75$) when coming into contact with water molecules below the equilibrium temperature and above the equilibrium pressure (Sloan and Koh, 2008). Upon dissociation, one volume of CO_2 hydrates can release 175 volumes of CO_2 gas at standard temperature and pressure conditions, which is potentially useful for the separation of the CO_2 from flue gas. The equilibrium phase diagram of CO_2 hydrates is presented in Fig. 1, which is constructed using an equation from experimental data reported by Kamath (1984). The figure also shows that other gases, such as N_2, H_2, O_2 and CH_4, form hydrates under slightly different equilibrium conditions. The equilibrium curve of H_2 was obtained from Dyadin et al. (1999).
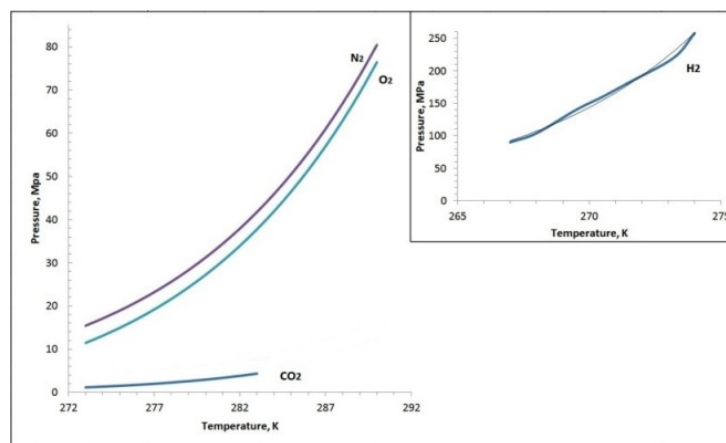

Fig. 1. The equilibrium phase diagrams of different hydrate formers.

As one can see from the equilibrium diagrams, CO_2 has the lowest hydrate-forming pressure in comparison with other components in flue gas. Separating CO_2 from the other gases can be achieved by first forming a solid hydrate phase that is enriched with CO_2. Dissociating the hydrates, after separating the hydrate phase from the gaseous phase, leads to the recovery of CO_2

that is much higher in concentration than the initial feed. Studies have shown that the concentration of CO_2 in the hydrate phase is at least four times greater than that in the gas phase (Duc et al., 2007). This hydrate-based CO_2 capture process is illustrated in a flow diagram displayed in Fig. 2. In brief, the gas mixture is sent to the hydrate formation reactor, in which CO_2 hydrates form as the pressure increases and temperature decreases. The hydrate slurry is separated from the CO_2-lean gas in the separator and sent to a hydrates dissociation reactor, from which purified CO_2 is collected, and the CO_2-rich gas is recycled for further processing.
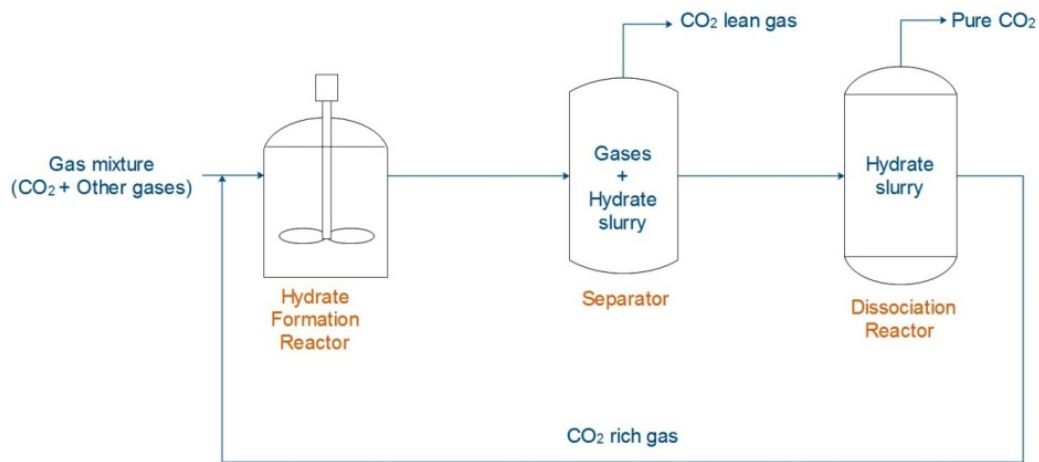
Fig. 2. Flow diagram of a HBCC processing unit.

2.3. Parameters describing the HBCC process

The efficiency of hydrate-based CO_2 separation is often described by such parameters as hydrate induction time, gas consumption, hydrate equilibrium pressure, CO_2 recovery or split fraction (S.Fr.) and separation factor (S.F.).

The hydrate *induction time* is the time taken for crystal nuclei to form that are not visible to macroscopic probes. In practice, the induction time is determined at the time the consumption of hydrate-forming gases becomes observable (Sloan and Koh, 2008). Total *gas consumption* is the maximum amount of gas enclathrated during the hydration process. It is measured in moles, which includes all compositions within the gas mixture. The amount of gas that has been consumed during hydrate formation can be calculated using Eq. (1) and Eq. (2) (Linga et al., 2007c):

$$\Delta \boldsymbol{n_g} = \boldsymbol{n_{g,0}} - \boldsymbol{n_{g,t}} = \frac{P_0 V}{Z_0 RT} - \frac{P_t V}{Z_t RT} \tag{1}$$

$$\Delta n_g^i = n_{g,0}^i - n_{g,t}^i = \frac{y_0^i P_0 V}{Z_0^i RT} - \frac{y_t^i P_t V}{Z_t^i RT} \tag{2}$$

where $n_{g,0}$ and $n_{g,t}$ are the total number of moles at time t = 0 and at any time t, respectively, Z is the compressibility factor calculated by the equation of the state, P is the pressure of the hydrate formation reactor, T is the temperature of the liquid phase, R is the ideal gas constant, i refers to component i of the gas mixture and y is the mole fraction in the gas phase. The volume of gas (V) is assumed to be constant throughout the hydrate formation process.

High gas consumption does not always mean high CO_2 consumption because the gas consumed might contain mostly gases other than CO_2. High separation efficiency is required for CO_2 capture, which is governed by two common factors: the *CO_2 recovery* or *split fraction* (S.Fr.) and the *separation factor* (S.F.). Split fraction refers to the percentage recovery of CO_2 and is determined using Eq. (3) (Linga et al., 2007c):

$$S.Fr. = n_{CO_2}^H / n_{CO_2}^{feed} \tag{3}$$

where $n_{CO_2}^H$ is the number of moles of CO_2 in the hydrate phase, and $n_{CO_2}^{feed}$ is the number of moles of CO_2 in the feed gas.

For a flue gas mixture containing CO_2 and another gas (A), the value of the *separation factor* is calculated using the following equation (Linga et al., 2007c):

$$S.F. = \frac{n_{CO_2}^H \times n_A^{gas}}{n_{CO_2}^{gas} \times n_A^H} \tag{4}$$

where $n_{CO_2}^H$ and n_A^H denote the number of moles of CO_2 and another gas (A) in the hydrate phase, respectively, $n_{CO_2}^{gas}$ is the number of moles of CO_2 in the residual gas phase and n_A^{gas} is the number of moles of A in the residual gas phase.

For CO_2 capture, a short induction time and high gas consumption, combined with high separation factor, are highly desirable. In practice, this is a challenging goal. Higher operating
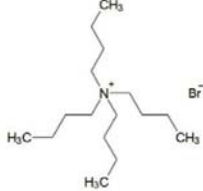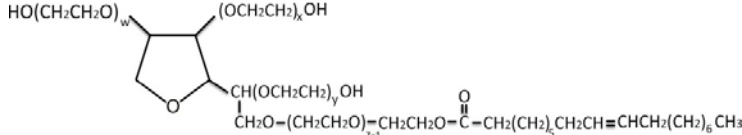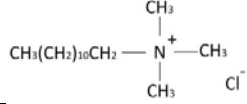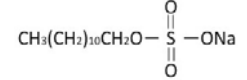
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pressure leads to fast/high gas consumption; however, it does not guarantee a high CO_2 recovery and separation factor, since gases other than CO_2 may also form hydrates at the same time. In addition, the required high pressure leads to an increase in compression costs due to the high energy consumption. Over the past two decades, research has been focused on the methods and processes that would lower the operating pressure, while increasing the hydrate formation rate and the selectivity to CO_2 gas. Various chemical additives have been extensively studied to improve the CO_2 capture/separation efficiency. Mechanical methods also have been investigated to improve the contact area and mass transfer between gas and water so as to enhance gas consumption and reduce induction time. The following sections will discuss these chemical additives and mechanical methods, with the focus being on their thermodynamic and kinetic effects on the CO_2 hydrate formation process and the ultimate separation efficiency.

2.4. Chemical additives

Chemical additives act as hydrate promoters that may reduce the equilibrium hydrate formation pressure, shorten the induction time, increase the hydration rate, enhance gas uptake and improve the selectivity of CO_2 in hydrate cages. The chemical additives are generally divided into two classes: kinetic promoters and thermodynamic promoters. Kinetic promoters are mostly surfactants that increase the rate of hydrate formation without taking part in the hydrate formation itself. Commonly used surfactants in hydrate forming systems include sodium dodecyl sulphate (SDS), Tween-80 (T-80) and dodecyl-trimethyl-ammonium chloride (DTAC). Thermodynamic promoters are small molecules that take part in hydrate formation by competing with gas molecules for hydrate cages. The most investigated thermodynamic promoters include tetrahydrofuran (THF), cyclopentane (CP), propane (C_3H_8) and tetra-n-butyl ammonium bromide (TBAB), among which THF, CP and C_3H_8 form hydrate crystals without changing the structure of the water cavity, while TBAB takes part in the process through the formation of a semi-clathrate structure by breaking the water cage (Eslamimanesh et al., 2012). The chemical structures of these promoters are presented in Table 1. The mechanisms, kinetics and thermodynamic effects of these chemical additives on the efficiency of CO_2 separation are discussed in the following sections.

Table 1

The chemical structures of various chemical additives and surfactants.

Chemical Additives		Chemical Structure
Thermodynamic Promoters	Tetrahydrofuran (THF)	
	Propane	H_3C CH_3
	Cyclopentane (CP)	
	Tetra-n-butyl ammonium bromide (TBAB)	
Kinetic Promoters (Surfactants)	Tween-80 (T-80)	$HO(CH_2CH_2O)_w$ $(OCH_2CH_2)_xOH$ $CH(OCH_2CH_2)_yOH$ $CH_2O-(CH_2CH_2O)_{z-1}-CH_2CH_2O-\overset{O}{\overset{\|}{C}}-CH_2(CH_2)_5CH_2CH=CHCH_2(CH_2)_6CH_3$ Sum of w+x+y+z=20
	Dodecyl-trimethyl-ammonium chloride (DTAC)	$CH_3(CH_2)_{10}CH_2 - \overset{CH_3}{\overset{\|}{\underset{CH_3}{N^+}}} - CH_3$ Cl^-
	Sodium dodecyl sulphate (SDS)	$CH_3(CH_2)_{10}CH_2O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-ONa$

2.4.1. Tetrahydrofuran

Tetrahydrofuran (THF) is one of the most commonly studied chemical additives in hydrate-based CO_2 capture technology. THF forms the S_{II} hydrate (Hawkins and Davidson, 1966) that contains 16 small cavities (5^{12}) and 8 large cavities ($5^{12}6^4$) per unit lattice at thermodynamic conditions of 0.1 MPa and 277.6 K (Strobel et al., 2009). Although CO_2 naturally forms the S_I hydrate with water, the presence of THF induces the formation of S_{II} hydrates for all gas components in flue gas (Park et al., 2013), in which CO_2 occupies both the small cages, competing with N_2 or H_2, and the large cages, while competing with THF (Kang and Lee, 2000).

The most significant impact of THF on hydrate-based CO_2 capture includes the drastic reduction of both hydration pressure and induction time. As a consequence, large amounts of hydrates form, which include CO_2 hydrates, along with H_2 or N_2 hydrates depending on the composition of the gas mixtures. The CO_2 recovery or splitting factor (*S.Fr.*) (Eq. (3)) may increasebut the separation factor (S.F.) (Eq. (4)) always reduces. Reduced rates of hydrate growth and initial gas uptake also have been reported (Adeyemo et al., 2010; Daraboina et al., 2013). As THF molecules occupy the large $5^{12}6^4$ cavities of S_{II} hydrates, high THF concentration also leads to reduced availability of cavities for CO_2 and other gases, therefore leading to reductions in both CO_2 recovery and separation factor. One percent mole (1 mol%) of THF has been reported to be optimal for CO_2 separation from CO_2/N_2 and CO_2/H_2 systems (Kang and Lee, 2000; Lee et al., 2010; Linga et al., 2007a). More details of THF-enhanced CO_2 separation reported by various research groups are summarised in Table 2.

2.4.2. Cyclopentane

Cyclopentane (CP) forms the S_{II} hydrate and occupies only large water cages at temperatures near 280 K and atmospheric pressure (Sloan and Koh, 2008; Sun et al., 2002). The presence of CP also reduces the equilibrium pressure and induction time. However, unlike THF, the formation of CO_2 hydrates in the presence of CP is independent of the concentration, which is likely due to the immiscibility of CP with water. Experimental results regarding CO_2 separation in the presence of CP are summarised in Table 3.

Table 2
The effects of THF on gas hydrate–based CO_2 capture.

Author(s)	Gas Systems*	Findings
Adeyemo et al. (2010)	$CO_2/N_2/THF$ $CO_2/H_2/THF$	• Pressure reduction: 9 MPa $\xrightarrow{\text{1 mol\% THF}}$ 5 MPa • CO_2 concentration for CO_2/N_2 system: 17 mol% $\xrightarrow{\text{Three stages, without THF}}$ 98.8 mol% • CO_2 concentration for CO_2/H_2 system: 40 mol% $\xrightarrow{\text{Three stages, without THF}}$ 92 mol%
Daraboina et al. (2013)	$CO_2/N_2/SO_2/THF$ $CO_2 = 17$ mol%, $N_2 = 82$ mol%, $SO_2 = 1$ mol%	• Gas Consumption: 0.164 mol $\xrightarrow{\text{1 mol\% THF}}$ 0.059 mol • Induction time: 10 min $\xrightarrow{\text{1 mol\% THF}}$ 6 min
Kang and Lee (2000)	$CO_2/N_2/THF$	• Pressure reduction: 14 MPa $\xrightarrow{\text{1 mol\% THF}}$ 1.65 MPa • CO_2 concentration: 17 mol% $\xrightarrow{\text{One stage, 1 mol\% THF}}$ 34.71 mol% 17 mol% $\xrightarrow{\text{Three stages, without THF}}$ 99.67 mol%
Kang et al. (2001)	$CO_2/N_2/THF$	• Pressure reduction: 8.35 MPa $\xrightarrow{\text{1 mol\% THF}}$ 0.48 MPa

		• CO_2 concentration: Two stages, without THF 17 mol% $\longrightarrow \longrightarrow$ 96 mol%
Lee et al. (2010)	$CO_2/H_2/THF$ CO_2 = 39.2 mol%, H_2 = 60.8 mol%	• Pressure reduction: 1 mol% THF 11 MPa $\longrightarrow$ 2.25 MPa • At 1.78 MPa: Gas consumption: 0.6 mol Induction time: 3.3 min • At 0.89 MPa: Gas consumption: 0.2 mol Induction time: 6.6 min
Linga et al. (2007a)	$CO_2/N_2/THF$ CO_2 = 16.9 mol%, N_2 = 83.1 mol%	• Pressure reduction: 1 mol% THF 7.7 MPa $\longrightarrow$ 2.5 MPa • CO_2 concentration: One stage, 1 mol% THF 17 mol% $\longrightarrow$ 36.9 mol% Three stages, 1 mol % THF 17 mol% $\longrightarrow \longrightarrow \longrightarrow$ 94 mol% • Induction time decreased with increasing THF concentration
Linga et al. (2007c)	$CO_2/N_2/THF$ CO_2 = 16.9 mol%, N_2 = 83.1 mol%; $CO_2/H_2/THF$ CO_2 = 39.2 mol%, N_2 = 60.8 mol%	• The equilibrium hydrate formation conditions: $CO_2/N_2 \longrightarrow$ 7.7 MPa, 273.7 K $CO_2/H_2 \longrightarrow$ 5.1 MPa, 273.7 K • Pressure reduction in CO_2/N_2 mixture: 1 mol% THF 7.7 MPa $\longrightarrow$ 0.345 MPa • Hydrates from CO_2/H_2 mixture grew faster than those from the CO_2/N_2 mixture • Induction time for CO_2/N_2 mixture:

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		16.3 min $\xrightarrow{\text{1 mol\% THF}}$ < 1 min
Park et al. (2013)	$CO_2/H_2/THF$	5.6 mol% THF resulted in the maximum stabilization effect - Pressure reduction: 8 MPa $\xrightarrow{\text{5.6 mol\% THF}}$ 0.5 MPa
Tang et al. (2013)	$CO_2/N_2/THF$ $CO_2 = 59$ mol%, $N_2 = 41$ mol%	- Optimal THF concentration: 1 mol% CO_2 recovery: 59% CO_2 $\xrightarrow{\text{1 mol\% THF}}$ 75% CO_2

[*]Default composition unless specified: In CO_2/N_2, $CO_2 = 17$ mol% and $N_2 = 83$ mol%; In CO_2/H_2, $CO_2 = 40$ mol% and $H_2 = 60$ mol%.

Table 3

Hydrate-based CO_2 separation in the presence of CP.

Author(s)	Gas Systems*	Findings
Li et al. (2012a)	$CO_2/H_2/CP$	• CO_2 concentration: $40 \text{ mol\%} \xrightarrow{\text{5 vo l\% CP}} 84 \text{ mol\%}$ • Gas uptake : 0.022 mol • Induction time: 15 s
Zhang and Lee (2008a)	CO_2/CP	• CO_2 hydrates growth: independent of CP volume; dependent on initial water volume and pressure • Best growth rate: at 5 vol% CP and 3.06 MPa • Induction time: < 0.2 h • Complete hydrate growth time: < 2 h
Zhang and Lee (2008b)	CO_2/CP H_2/CP	• CO_2/CP hydrate showed slightly higher dissociation temperature and lower pressure than both CO_2/THF and $CO_2/TBAB$ at 0.89 - 3.51 MPa
Zhang et al. (2009)	$CO_2/H_2/CP$	• Pressure reduction: $5.3 \text{ MPa} \xrightarrow{\text{1.5 vol\% CP}} 1.3 \text{ MPa}$ • CO_2 concentration: $40 \text{ mol\%} \xrightarrow{\text{Two stages, 1.5 vol\% CP}} 98 \text{ mol\%}$

*Default composition unless specified: In CO_2/N_2, CO_2 = 17 mol% and N_2 = 83 mol%; In CO_2/H_2, CO_2 = 40 mol% and H_2 = 60 mol%.

2.4.3. Propane

Like CP, propane (C_3H_8) also promotes hydrate formation at reduced equilibrium pressure (Babu et al., 2013b; Kumar et al., 2006). Propane alone forms S_{II} hydrates at 275 K and between 0.36 MPa and 0.48 MPa (Giavarini et al., 2003; Hendriks et al., 1996). It induces the formation of S_{II} hydrates when it competes with CO_2 for occupancy of large cages (Adisasmito and Sloan, 1992; Kumar et al., 2009a). A study has shown that 57% of large cages are occupied by CO_2 when 2.5 mol% C_3H_8 was added to the system (Kumar et al., 2009a). In most studies, the S_{II} hydrate form of CO_2 hydrates was observed. The formation of S_I hydrates also was observed when a gas mixture of 80.0% CO_2, 18.8 mol% H_2 and 1.2% C_3H_8 was used, reportedly due to the low propane concentration (Babu et al., 2013b). A pressure reduction of 49% was obtained when 2.5 mol% C_3H_8 was added to the hydrate system (Kumar et al., 2009a). This is less effective than THF. Reductions in induction time and hydrate formation rate also were reported by the same group. The lower growth rate caused less CO_2 gas to be enclathrated within a given period. Therefore, gas consumption was reduced from 0.101 to 0.078 moles within 2 hours. As for the CO_2 recovery and separation factor, the presence of C_3H_8 produced little effect on the former and a slight decreasing effect on the latter (Kumar et al., 2009a; Linga et al., 2007b).

2.4.4. Tetra-n-butyl ammonium bromide

Tetra-n-butyl ammonium bromide (TBAB) is a widely proposed gas hydrate promoter, which consists mainly of environmentally friendly TBA^+ ionic liquid. TBAB forms semi-clathrate (SC) hydrates, which is different from the action of other promoters (Davidson and Franks, 1973; Fowler et al., 1940). In the SC hydrate structure, bromide anions are bonded to water molecules and form water + bromide hosts, with the cages being occupied by cations as guests (Jeffrey and McMullan, 1967). Due to this feature, SC hydrates allow greater gas capacity in water cages and better stability at atmospheric pressure (Wataru et al., 2003). The phase boundaries of CO_2 hydrates in the presence of TBAB form at temperatures from 273.15 K to 291.15 K and pressures from 0.25 MPa to 4.09 MPa, which are much lower pressure values than for pure CO_2 hydrate formation, specifically at lower temperatures (1.15 MPa to 4.33 MPa) (Fig. 4).
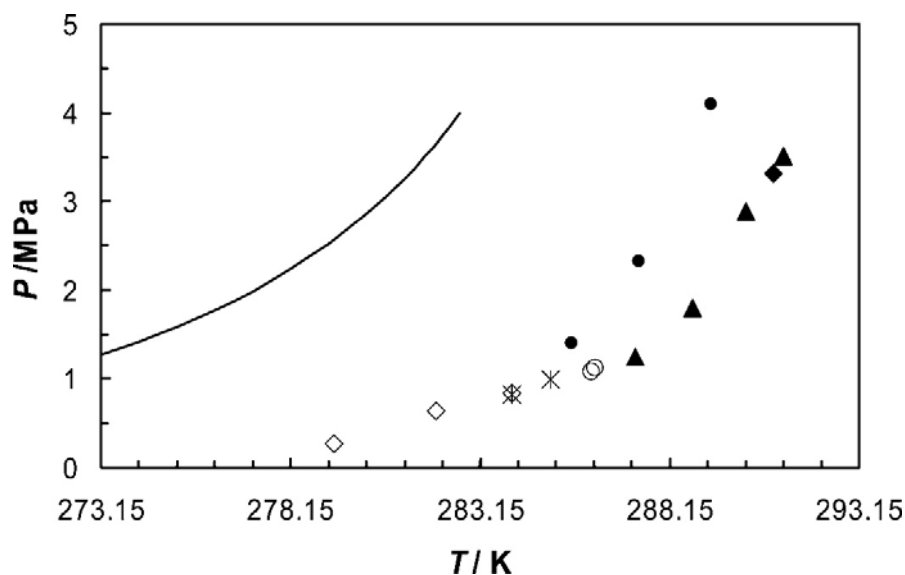
Fig. 4. CO_2/TBAB phase equilibrium data (Arjmandi et al., 2007): ●, TBAB, $w = 0.10$ and ▲, TBAB, $w = 0.427$; ✿, TBAB, $w = 0.05$ ○, TBAB, $w = 0.10$ and ✦, TBAB, $w = 0.40$; *, TBAB, $w = 0.65$; solid line, CO_2 hydrate phase boundary predicted by an in-house (HWHYD) model.

Studies on TBAB SC hydrates have demonstrated that there are two types, namely Type A and Type B, which grow simultaneously when in aqueous solution (Oyama et al., 2005). Type A has a cylindrical shape and a hydration number of 26. Type B has an irregular shape composed of thin crystals and shows a hydration number of 38. For the pure TBAB hydrate systems, when TBAB concentration is 0.014 mol%, type B is more stable than type A. Above 0.014 mol%, type A becomes more stable (Oyama et al., 2005; Wataru et al., 2003). The change of TBAB structure between these two different types in different TBAB concentrations makes the phase behaviour of SC hydrates difficult to study and complicated to analyse. Nevertheless, due to the high stability of TBAB's SC structure at low pressure, TBAB has the potential to reduce the formation pressure of CO_2 hydrate by up to over 90% at a concentration as low as 0.29 mol% (Li et al., 2010b). Increasing TBAB concentration not only reduces the equilibrium hydrate formation pressure but also increases the equilibrium hydrate forming temperature, which advances other clathrate hydrate promoters such as THF and CP (Meysel et al., 2011; Mohammadi et al., 2012). TBAB also has been found to reduce the induction time and increase the hydrate formation rate for the CO_2/N_2 mixture (Fan et al., 2009; Li et al., 2012b).

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Other types of TBA$^+$ salts, which are able to form SC hydrates, also have been reported. Some examples of these additives are tetra n-butyl ammonium fluoride (TBAF), tetra n-butylphosphonium bromide (TBPB), and tetra n-butyl ammonium nitrate (TBANO$_3$). TBANO$_3$ was found to be approximately 1.5 times more effective than TBAB in reducing the pressure of the CO$_2$/N$_2$ hydrate system (Li et al., 2012b). It also was found to instigate much higher gas uptake compared to TBAB at pressures between 2.5 and 4 MPa. Among the three TBA$^+$ salts investigated, it yielded the highest CO$_2$ recovery rate, 67%, and a separation factor of 15.54. The authors claimed that TBANO$_3$ and TBPB have high potential for replacing TBAB in the near future. The experimental studies of CO$_2$ capture by hydrates in the presence of TBAB are summarized in Table 4.

2.4.5. Surfactants and mixed chemical additives

Surfactants are a type of kinetic promoter that enhances the hydration kinetics by promoting gas solubility in water without modifying the thermodynamic equilibrium of the system. These compounds are composed of molecules that contain both a hydrophilic end and a hydrophobic end. Gas molecules form surfactant-gas associates with surfactants through strong hydrophobic interactions. Migration of the formed surfactant-gas associates to water molecules and/or structured water molecules is much easier than for pure gas molecules, due to the stronger affinity between water molecules and the hydrophilic end of the surfactant molecules. This ensures a faster formation of gas hydrates and, therefore, reduced induction time (Zhang et al., 2007). Fig. 5 is an illustration of the gas hydration process in the presence of sodium dodecyl sulphate (SDS). Surfactants have no effect on hydrate formation pressure. They can effectively improve the hydration kinetics by reducing the water surface tension.

Many surfactants have been investigated for hydrate-based CO$_2$ separation. Tween-80 (T-80), dodecyl-trimethyl-ammonium chloride (DTAC) and SDS are the most widely used. Among these three surfactants, SDS shows the greatest effect on hydrate promotion. This is mainly because SDS is an anionic surfactant, which is superior to both non-ionic and cationic surfactants for the same purpose (Okutani et al., 2008; Yoslim et al., 2010). Since surfactants do not partake in the enclathration process, unlike thermodynamic promoters, they do not sacrifice CO$_2$ recovery, separation factor or gas consumption for their enhancement of hydrate formation kinetics. Higher

CO_2 recovery, reportedly, has been associated with higher SDS concentrations. However, when the

Table 4

The effects of TBAB on hydrate-based CO_2 capture (weight percentage is presented as %).

| Author(s)	Gas Systems*	Findings
Babu et al. (2014a)	CO_2/H_2/TBAB TBAB = 0.3, 1.0, 1.5, 2.0, 3.0 mol%	• At TBAB = 0.3 mol%: highest gas consumption and longer induction time • At TBAB = 0.1 mol%: highest hydrate growth rate
Belandria et al. (2012a)	CO_2/N_2/TBAB CO_2 = 15.1, 39.9, 74.9 mol%, N_2 = 84.9, 60.1, 25.1 mol%, TBAB = 5, 30%	• Equilibrium hydrate formation: $\qquad\qquad\xrightarrow{\text{30\% TBAB}}$ 275.2 K, 10.1 MPa $\quad\longrightarrow\quad$ 285.7 K, 1.57 MPa • Increasing TBAB concentration: the dissociation pressure decreased and temperature increased • Increasing the N_2 concentration resulted in increasing hydrate formation pressure
Belandria et al. (2012b)	CO_2/N_2/TBAB CO_2 = 15.1, 39.9, 74.9 mol%, N_2 = 84.9, 60.1, 25.1 mol%, TBAB = 5, 30%	• Equilibrium pressure decreased with increasing TBAB concentration
Duc et al. (2007)	CO_2/TBAB N_2/TBAB CO_2 /N_2 /TBAB	• Pressure reduction at 284 K: $\qquad\qquad\xrightarrow{\text{0.29 mol\% TBAB}}$ CO_2: 14.36 MPa $\quad\longrightarrow\quad$ 0.84 MPa $\qquad\qquad\xrightarrow{\text{0.29 mol\% TBAB}}$ N_2: 50 MPa $\quad\longrightarrow\quad$ 29 MPa • Equilibrium pressure: $\qquad\qquad\xrightarrow{\text{0.29 mol\% TBAB}}$ CO_2 = 23.4 mol% , N_2 = 76.6 mol% $\quad\longrightarrow\quad$ 0.5 MPa $\qquad\qquad\xrightarrow{\text{0.29 mol\% TBAB}}$ CO_2 = 48.2 mol%, N_2 = 51.8 mol% $\quad\longrightarrow\quad$ 9 MPa
Gholinezhad et al. (2011)	CO_2/H_2/TBAB CO_2 = 40.2 mol%, H_2 = 59.8 mol%	• Gas consumption: 0.0502 mol at 5% TBAB; 0.086 mol at 10% TBAB

		• CO_2 recovery: 42% at 0% TBAB; 41% at 5% TBAB; 47% at 10% TBAB • Separation factor: 15.7 at 5% TBAB; 28 at 10% TBAB • CO_2 concentration at 10% TBAB: $\quad\quad\quad\quad\quad$ Two stages 40 mol% $\longrightarrow \longrightarrow$ 96 mol%
Kim et al. (2011)	$CO_2/H_2/TBAB$	• Optimal TBAB concentration: 1 mol% • Gas consumption: 0.031 mol • CO_2 recovery: 24% • Separation factor: 26 • Induction time: 10.2 min
Li et al. (2009)	$CO_2/N_2/TBAB$ CO_2 = 19.9 mol%, N_2 = 80.1 mol%, TBAB = 5%	• Induction time: 5 min • CO_2 recovery: 45% • Separation factor at 4.3 MPa: 7.3
Li et al. (2010b)	$CO_2/H_2/TBAB$ CO_2 = 39.2 mol%, H_2 = 60.8 mol%, TBAB = 0.14 to 2.67 mol%	• Pressure reduction $\quad\quad\quad\quad$ 0.29 mol% TBAB 9.84 MPa $\longrightarrow$ 0.4 MPa • Higher TBAB concentration resulted in further pressure reduction
Li et al. (2010c)	$CO_2/H_2/TBAB$	• Optimal conditions: 2.5 MPa and 0.29 mol% TBAB • Gas Consumption: at 2.5 MPa $\longrightarrow$ 0.12 mol at 4.5 MPa $\longrightarrow$ 0.16 mol • CO_2 in residual gas: at 2.5 MPa $\longrightarrow$ 18.5 mol% at 4.5 MPa $\longrightarrow$ 22 mol%
Li et al. (2010d)	$CO_2/N_2/TBAB/DTAC$	• CO_2 concentration at 1.66 MPa: $\quad\quad$ Two stages, 0.29 mol% TBAB and 0.028 mol% DTAC 17 mol% $\longrightarrow \longrightarrow$ 99.2 mol%

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		• CO_2 recovery: 54% • Induction time: 1 min • Optimal concentration of DTAC: 0.028 mol%
Li et al. (2011b)	$CO_2/H_2/TBAB$ $CO_2 = 39.2$ mol%, $H_2 = 60.8$ mol%	• Optimal TBAB conditions: 0.29 mol% concentration and 2.5 MPa • CO_2 concentration: 39.2 mol% $\xrightarrow{\text{0.29 mol\% TBAB}}$ 97 mol% • CO_2 recovery: 67.16% • Separation factor: 136.08
Li et al. (2012b)	$CO_2/N_2/TBAB$ $CO_2/N_2/TBANO_3$	• $TBANO_3 = 1$ mol%: ➢ Highest gas uptake ➢ Gas consumption: 0.088 mol ➢ CO_2 recovery and separation factor at 3.26 MPa: 67%, 15.5 ➢ Induction time: 4.2 min ➢ CO_2 concentration: 17% $\xrightarrow{\text{1 mol\% TBANO}_3}$ 7% • TBAB = 0.65 mol%: ➢ Gas consumption: 0.056 mol ➢ CO_2 recovery and separation factor at 3.26 MPa: 46%, 12.8 ➢ Induction time: 0.1 min • TBPB = 1 mol%: • CO_2 recovery and separation factor at 3.26 MPa: 61% and 14 • Induction time: 2.7 min
Li et al. (2012a)	$CO_2/H_2/TBAB/CP$	• CO_2, H_2, TBAB = 0.29 mol%: ➢ Gas consumption: 0.126 mol ➢ Induction time: 2.7 min • CO_2, H_2, TBAB = 0.29 mol%, CP = 5 vol%: ➢ Gas consumption: 0.214 mol

|		• Induction time: 0.32 min
Meysel et al. (2011)	CO_2/H_2/TBAB CO_2 = 20, 50, 75 mol%, H_2 = 80, 50, 25 mol%, TBAB = 5, 10, 2%	• Increasing TBAB concentration resulted in decreasing pressure • SC formed at a higher temperature than gas hydrates

Mohammadi et al. (2012)	CO_2/N_2/TBAB
	
	CO_2 = 15.1, 39.9 mol%, N_2=84.9, 60.1 mol%
		• Equilibrium hydrate formation condition for CO_2 = 39.9 mol%, N_2 = 60.1 mol%:
		   ➢ 5% TBAB: 285.6 K, 5.93 MPa
		   ➢ 15% TBAB: 286.6 K, 2.89 MPa
		   ➢ 30% TBAB: 286.4 K, 1.71 MPa

Mohammadi et al. (2013)	CO_2/H_2/TBAB
	
	CO_2 = 14.81, 39.52, 75.01 mol%, H_2 = 85.19, 60.48, 24.99 mol%
		• Equilibrium hydrate formation condition for CO_2 = 39.52 mol%, H_2 = 60.48 mol%:
		
		                5% TBAB
		278.4 K, 10.5 MPa ——————→ 288.6 K, 12.17 MPa
		
		               30% TBAB
		278.4 K, 10.5 MPa ——————→ 288.6 K, 4.07 MPa

[*]Default composition unless specified: In CO_2/N_2, CO_2 = 17 mol% and N_2 = 83 mol%; In CO_2/H_2, CO_2 = 40 mol% and H_2 = 60 mol%.

SDS concentration is too high, SDS micelles may form, resulting in reduced gas and liquid contact surfaces and, therefore, lower CO_2 recovery (Tang et al., 2013).
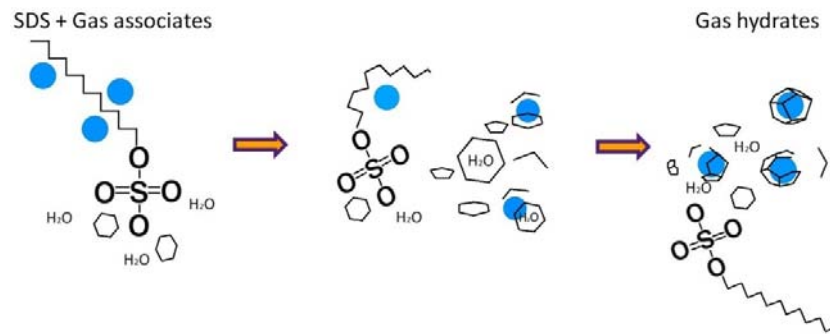
Fig. 5. Illustration of the migration of surfactants-gas associates to water molecules and/or cages.

Surfactants have been used together with THF or TBAB in order to achieve better separation of CO_2. For example, the SDS/THF additive mixture has been proven to double the gas uptake, compared with the case of using THF alone (Table 5). Addition of surfactants or light mineral oils into the hydration systems containing CP also has been found to increase the hydrate formation rate. This is due to the formation of a CP/water emulsion and the consequent increase in the CP/water interfacial area in the presence of surfactants. The presence of surfactants improves the gas diffusion through the gas/water and gas/hydrates interfaces, leading to enhanced inward and outward growth of hydrates (Fig. 6), therefore improving the hydrate formation rate. Other reported mixed chemical additives include CP/TBAB and DTAC/TBAB. The purpose of using mixed chemical additives is to reach higher CO_2 separation efficiency through the synergistic effects of the two chemical promoters. Table 5 summarises the findings by different research groups on the synergistic effects of chemical additives.
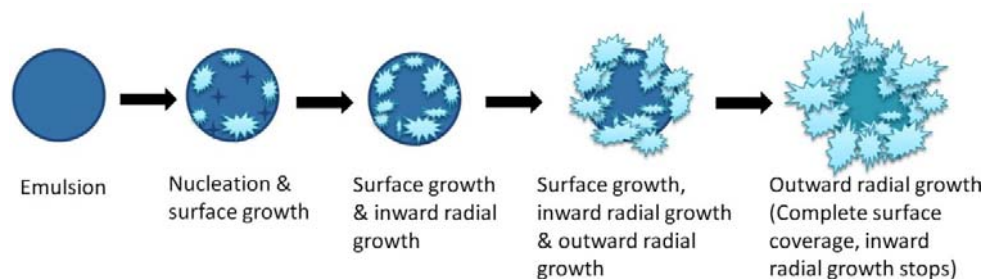
Fig. 6. Illustration of hydrate formation in an emulsion (Rework of Karanjkar et al., 2012).

Author(s)	System*	Findings
Herslund et al. (2014)	CO_2/THF/SDS SDS = 0.054 mol%	• Addition of 5 mol% THF decreased hydrate equilibrium pressure by up to 20%

Li et al. (2010)	CO_2/N_2/CP
	
	CO_2 = 16.6 mol%, N_2 = 83.4 mol%;
	
	CO_2/N_2/CP/H_2O emulsion
	
	CO_2 = 16.6 mol%, N_2 = 83.4 mol%
		• Higher hydrate formation rate in presence of CP/H_2O emulsion
		• CO_2 concentration in the presence of:
		  ➢ CP at 2.9 MPa $\longrightarrow$ 44 mol%
		  ➢ CP/H_2O emulsion at 3.29 MPa $\longrightarrow$ 35.29 mol%

Li et al. (2010d)	CO_2/N_2/TBAB/DTAC	• Higher pressure and induction time reduction, with addition of DTAC
		• CO_2 concentration:
		
		                 0.028 mol% DTAC, 0.29 mol% TBAB
		17 mol% $\xrightarrow{\hspace{4cm}}$ 67 mol%
		
		              Two stages, 0.028 mol% DTAC, 0.29 mol% TBAB
		17 mol% $\longrightarrow$ $\longrightarrow$ 99.4 mol%

Li et al. (2011c)	CO_2/H_2/TBAB/CP CO_2 = 38.6 mol%, H_2 = 61.4 mol%	• Optimal CP and TBAB concentrations: 5 vol% and 0.29 mol% • The addition of CP: sped up the nucleation rate and CO_2 separation • CO_2 separation: 5 vol% ratio CP/0.29 mol% TBAB 40 mol% $\xrightarrow{\hspace{3cm}}$ 93 mol% • Gas consumption: 0.22 mol • CO_2 recovery: 58% • Separation factor: 31 • Decreasing induction time with increasing CP/TBAB ratio

Li et al. (2012a)	$CO_2/H_2/TBAB/CP$ CO_2 = 38.6 mol%, H_2 = 61.4 mol%	• CO_2 concentration: 5 vol% CP, 29 mol% TBAB 38.6 mol% $\xrightarrow{\hspace{3cm}}$ 91.3 mol% • Gas uptake : 0.214 mol • Both S_{II} and SC hydrate observed at 4 MPa and 274.65 K • The formation of S_{II} hydrate by CP reduced the SC hydrate induction time from over 150 s to 19 s
Lirio et al. (2013)	$CO_2/THF/SDS$	• High reduction in reduction time in the presence of THF • Under 3 MPa, 500 ppm SDS/5 mol% THF: ➢ 91.9% yield ➢ 25 min induction time
Liu et al. (2014)	$CO_2/H_2/CP/TBAB$ CO_2 = 46.8, 15.6 mol%, H_2 = 53.2, 84.8 mol%, CP = 30, 50 vol%	• The optimal TBAB concentration: 0.29 mol% • Separation factor increased from 37 to 99 at 0.29 mol% TBAB • TBAB is an anti-agglomerant which can improve the flow behaviour of hydrate slurry
Torré et al. (2011)	$CO_2/$ THF/SDS	• Optimal concentrations: SDS > 1500 ppm 1% < THF < 4%
Torré et al. (2012)	$CO_2/$ THF/SDS	• Optimal concentrations: 0.3% SDS 4% THF • The combination of THF and SDS showed significant gas uptake • THF increased the hydrate temperature and decreased the hydrate pressure • SDS had no influence on equilibrium conditions
Yang et al. (2013b)	$CO_2/THF/SDS$	• Shortest induction time in presence of 1 000 mg/L SDS and 3 mol% THF

		• Hydrate equilibrium temperature decreased with increasing SDS concentration
Zhang et al. (2014)	THF/SDS/CO_2/N_2	• Increasing THF concentration resulted in lower reduction in equilibrium pressure • Optimal THF concentration: 3 mol%

[*]Default composition unless specified: In CO_2/N_2, CO_2 = 17 mol% and N_2 = 83 mol%; In CO_2/H_2, CO_2 = 40 mol% and H_2 = 60 mol%.

2.5. Mechanical methods

In addition to the chemical additives, investigations of various reactors and/or reaction conditions also have been carried out in order to improve the CO_2 formation efficiencies and to reduce energy consumption. In this paper, the term 'mechanical methods' is used because of its convenience. It should be noted that the discussions in previous sections were mostly of research activities that were based on laboratory experiments using a stirred tank reactor. In stirred tank reactors, the agglomeration of hydrate crystals becomes an obstacle to reducing the gas/water interface area and, consequently, the rate of hydrate formation and conversion of water. The fixed bed crystalliser with porous silica gel has been widely studied in an effort to overcome this problem. The porous nature of the silica used in the fixed bed can significantly enhance the contact area between gas and water, allowing more gas to be enclathrated in a shorter time, therefore, improving the total gas uptake and induction. A study reported by Seo and Kang (2010) showed that over 93% of small cages and 100% of large cages were occupied by CO_2 when porous silica gels were used. Improved CO_2 selectivity and hydrate formation rate also have been achieved using the silica bed (Kang et al., 2013). In fact, the dispersed water in silica pores reacts readily with gas mixtures, which in turn eliminates the need for energy intensive mechanical agitation and excess water. This remains a strong economic advantage that keeps the need for research going (Adeyemo et al., 2010; Seo et al., 2005).

The silica bed can be further classified into silica gel bed and silica sand bed. Silica is very cheap and more economically desirable for large scale CO_2 separation. Babu et al. (2013a) claimed that water conversion reached up to 36% in the silica sand bed but only 13% in the silica gel bed. They also reported that the silica sand bed gave better performance for hydrate-based CO_2 capture due to higher gas uptake. A study by the same group also demonstrated that the silica sand bed provided a higher rate of hydrate formation and total gas uptake, when compared with a stirred crystalliser (Linga et al., 2012). Changing the physical properties, such as the particle and pore sizes of the porous silica gel, can further improve the kinetics of hydrate formation. Kang et al. (2008) found that pores which are too small lead to inhibition of their effect on hydrate formation due to the decreased water activity in the pores. Hydrate blockage of the pores may reduce the contact of gas and liquid, leading to incomplete migration of the solution through the hydrates (Yang et al., 2013a). Increasing pore size can overcome this problem. Larger pores and

particle sizes tend to improve gas consumption, CO_2 recovery, separation factor and water conversion to hydrate, thus reducing the operating pressure (Adeyemo et al., 2010; Park et al., 2013). This is due to the lower flow resistance across a larger pore than a smaller pore. In other words, the larger exposed surface area of the silica gel significantly reduces induction time due to the better contact between gas and water within the gel (Kumar et al., 2013). A summary of the above-mentioned studies is given in Table 6.

The bubble method also has been attempted for gas hydrate-based CO_2 separation. Bubbles any larger or smaller do not have any effect on the separation process. The findings indicate that the hydrate shell formation around the bubble may hinder the further formation of hydrate within the bubble, due to isolation of the liquid from the gas (Luo et al., 2007). However, this can be improved by using a smaller bubble size. It was reported that an ideal size of gas bubbles for CO_2 separation is 50 μm (Xu et al., 2012b). Unlike stirring and the packed bed crystalliser, the bubble method requires a large bubbling column, which is not easily built and run on an experimental scale. This makes the method limited for further investigation.

More recent studies have shown that temperature fluctuation (via vibration) can be used to improve CO_2 hydrate formation (Li et al., 2011a; Liu et al., 2011; Xu et al., 2012a). This method is based on the fact that, when the temperature decreases, the solubility of CO_2 decreases in the hydrate-forming region while increasing in the non-hydrate-forming region (Kojima R et al., 2002). The authors reported that, in the experiments using temperature fluctuation, the pressure drop was increased by 30%. A 30-35% increase in total gas consumption also was observed. The positive effect of the temperature fluctuation was mostly observed during the early period of hydrate growth. The method was demonstrated to be effective when the reaction scale was increased by 100-fold (Xu et al., 2012a).

Table 6
CO_2 capture in fixed bed crystallisers.

Author(s)	Gas Systems*	Findings
Adeyemo et al. (2010)	CO_2/N_2 CO_2/H_2	• The rate of hydrate formation and hydrate yield were higher than in a stirred crystalliser • Total gas consumption, CO_2 recovery and water-to-hydrate conversion increased with larger pores and particle sizes

Babu et al. (2013a)	CO_2/H_2	• Sand bed:
		  ➢ Water conversion: 36%
		  ➢ Induction time: 18 min
		• Gel bed:
		  ➢ Water conversion: 13%
		  ➢ Induction time: 14 min
		• The performance of the sand bed was sensitive to the pressure driving force, while the gel bed was not
		• The sand bed is claimed to be a better porous medium

Babu et al. (2014b)	$CO_2/H_2/TBAB/THF$ TBAB = 0.3, 1, 3 mol%, THF = 1, 5.53 mol%	• In the presence of THF, higher gas consumption and shorter induction time in the silica sand bed crystalliser • By increasing THF concentration, higher gas consumption was achieved but induction time did not change significantly • Increasing TBAB concentration resulted in lower gas consumption and significant change in induction time
Kang et al. (2008)	CO_2	• Hydrate growth was inhibited in small pores • S_I hydrate was formed in silica gel pores, similar to that in bulk water
Kang et al. (2013)	CO_2/H_2	• With 100 nm silica gel, 98.7% CO_2 in hydrate phase was achieved under 9.2 MPa • Hydrate dissociation pressure decreased with increasing CO_2 concentration in the feed
Kumar et al. (2013)	CO_2	• Larger surface area enhanced water-to-hydrate conversion and

		shortened induction time
Linga et al. (2012)	CO_2 $CO_2/H_2/C_3H_8$ CO_2 = 38.1 mol%, H_2 = 59.4 mol%, C_3H_8 = 2.5 mol%	• Silica sand bed crystalliser showed higher rate of hydrate formation and higher gas uptake than in a stirred vessel

Park et al. (2013)	CO_2/H_2	• 100 nm gel:
		   ➤ Showed lowest equilibrium pressure
		   ➤ Increased gas uptake significantly

Seo and Kang (2010)	CO_2/H_2 CO_2 = 41 mol%, H_2 = 59 mol%	• CO_2 occupied 93% of small cages and 100% of large cages of S_I hydrate formed in silica gel pores • 98.7 mol% CO_2 in hydrate phase was achieved with 100 nm silica gel

[*]Default composition unless specified: In CO_2/N_2, CO_2 = 17 mol% and N_2 = 83 mol%; In CO_2/H_2, CO_2 = 40 mol% and H_2 = 60 mol%.

3. Advantages and limitations of current HBCC technology

The cost of HBCC technology in an integrated gasification combined cycle (IGCC) plant was reported in 1999 by the US Department of Energy to be US$ 8.75 per ton of CO_2 captured, which is comparable to the cost of US$ 59 per ton of CO_2 captured using conventional amine-based absorption and US$ 64 per ton of CO_2 for adsorption by zeolite (Ho et al., 2008; Reiner et al., 1994; Tam et al., 2001). It is this remarkable value that has drawn significant attention from CO_2 capture-related industries and has resulted in the increasing number of research projects involving HBCC technology over the past decade. Other advantages of HBCC technology include: 1) its moderate operational temperature range (273-283 K), 2) its relatively low energy consumption in hydrate dissociation/regeneration and the ease of recycling of aqueous solution containing additives, and 3) its capability for continuous operation, which allows large scale treatment (with the potential to achieve 8 000 ton/day CO_2) (Kang and Lee, 2000).

However, the practical application of HBCC technology is limited due to its high pressure operating condition and large footprint. A case study using HBCC technology was completed by Tajima et al., based on a 100 MW thermal power plant where the energy penalty for CO_2 capture was found to be 15.8% and the required reactor volume was 7 000 m^3 (Tajima et al., 2004). This shows that HBCC is still incomparable with conventional technologies, such as amine absorption, which has a much lower energy penalty (7-10%) (Tajima et al., 2004). A comparison of different CO_2 separation technologies is summarised in Table 7.

Table 7
A comparison of different CO_2 separation technologies.

Methods	Energy consumption (MJ/kg CO_2)	Cost (USD/ton CO_2)	Advantages	Drawbacks
Absorption	4 - 6 (Favre, 2007)	30 - 60 (Yang et al., 2011)	- Well established process - Up to 95% CO_2 recovery (Olajire, 2010) - Easily incorporated into existing plant	- Energy intensive regeneration (Aaron and Tsouris, 2005) - Degradation of solvent - Sensitive to SO_x and NO_x - Corrosion issue
Adsorption	2 - 3 (Mondal et al., 2012)	40 - 63 (Yang et al., 2011)	- Simultaneous dehydration (Olajire, 2010) - Lower regeneration energy - Adsorbents are commercially available	- Low selectivity - Low capacity - Slow adsorption rate - Only suitable for CO_2 concentration between 0.04% and 1.5% (Audus, 1997)
Membrane	0.5 - 1 (Bounaceur et al., 2006)	50 - 78 (Yang et al., 2011)	- No regeneration required - Simple system - No waste streams - Membranes are commercially available	- Only suitable for $CO_2 > 20\%$ (Bounaceur et al., 2006; Favre, 2007) - Sensitive to high temperature (Spigarelli and Kawatra, 2013) - Plugged by impurities (Olajire, 2010) - Low removal efficiency, multiple stages required - Sensitive to sulphur compounds - Membrane ageing (Brunetti et al., 2010)
Hydrate-Based	3 (Tajima et al., 2004)	8.75 (Tam et al., 2001)	- Moderate operational temperature range (273-283 K) - Relatively low energy consumption - Easy recycling of aqueous solution - Continuous operation allows large scale treatment (Kang and Lee, 2000)	- Immature technology - High pressure operating condition and large footprint (Tajima et al., 2004) - Large energy penalty (Tajima et al., 2004)

4. Conclusions

In summary, we have reviewed the available methods of improving the hydrate-based CO_2 separation technology in CO_2 separation efficiency, gas consumption and rate of hydrate formation, which includes chemical and mechanical approaches. The paper has focused on scholarly published research activities between 2000 and 2014. The studies performed to date show a more diverse field of research in chemical approaches, which include thermodynamic promoters (THF, TBAB, C_3H_8, CP) and kinetic promoters (surfactants). The research into mechanical methods is, however, receiving less attention. This is probably because people are comfortable with the default stirred reactor that is easier to build and run on a laboratory scale. The risk of building a different reactor for experimental purposes is not willingly undertaken, probably due to the large investment and unknown performance. However, the outcome from the review suggests that both chemical and mechanical approaches should be used, in parallel, to achieve the ultimate performance of hydrate-based technology. Also, a method should be established to ensure direct comparison of experimental results cross-batch and/or cross-laboratory. Moreover, the hydrate-based CO_2 separation method is known to be a novel technology with high potential. In order to outshine the conventional technologies, the economic aspect is a significant factor compared to performance. However, a detailed economic study on hydrate-based CO_2 separation is still unavailable in open literature. More studies on the feasibility and economic cost must be performed in order to convince the industry with a quantitative argument and to draw more investment into hydrate-based CO_2 separation technology in the near future.

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