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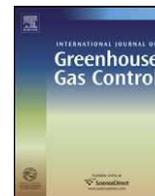
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A new apparatus to enhance the rate of gas hydrate formation: Application to capture of carbon dioxide

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ABSTRACT

A new apparatus employing a modular, mechanically agitated gas-inducing crystallizer is used to demonstrate the capture of CO₂ via hydrate crystallization. The crystallizer enhances the contact of hydrate forming gases with water and thus the rate of hydrate crystallization increases. Flue gas (CO₂/N₂) and fuel gas (CO₂/H₂) mixtures were used to represent post- and precombustion capture. A comparison between the rates of hydrate formation in different crystallizers is presented by defining a metric called the normalized rate of hydrate formation. The gas uptake and the separation efficiency for the fuel and flue gas mixtures were found to be greater compared to the results obtained in a smaller scale stirred tank reactor (Kumar et al., 2009c; Linga et al., 2008). The gas uptake and CO₂ recovery for flue gas mixture in the presence of THF obtained in this work was higher than that reported in the literature with tetra-*n*-butyl ammonium bromide and tetra-*n*-butyl ammonium fluoride (Fan et al., 2009; Li et al., 2009). Although hydrate crystallization is able to capture CO₂, the power required for mechanical agitation was found to be very significant. If the hydrate process is to be used industrially then hydrate crystallization must be carried out without mechanical agitation.

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1. Introduction

Clathrate hydrate crystallization has been regarded as a potential unit operation for seawater desalination, gas fractionation, gas storage and other applications (Chatti et al., 2005; Davidson, 1973; Englezos, 1993; Makogon, 1981). During the past 15 years the emphasis has been on natural gas storage and transportation (Gudmundsson et al., 2000; Matsuda et al., 2006; Thomas and Dawe, 2003) and on carbon dioxide capture from flue and fuel gases (Aaron and Tsouris, 2005; Kang and Lee, 2000; Klara and Srivastava, 2002; Linga et al., 2007a; Seo et al., 2005). Hydrate formation is also a factor when considering injection of CO₂ into the ocean (Lee et al., 2003; Tsouris et al., 2004, 2007). If hydrate is to be formed from liquid water then the efficient contacting of the gas with water plays a key role in the above applications. This is because agglomeration of the hydrate crystals creates a barrier to increased conversion in stirred tank reactors (Englezos, 1996). A schematic illustrating how agglomeration of floating crystals creates a barrier to efficient gas/water contacting which in turn limits the conversion in a stirred tank reactor is provided by Linga (2009). Therefore, the search for efficient gas hydrate formation vessels or reactors is ongoing.

Although there are several configurations and patents available in the literature for production of gas hydrates, the choice of the best multi phase reactor is still unknown (Heinemann et al., 2001; Iwasaki et al., 2002; Mori, 2003; Waycuilis and York, 2002; Yamasaki et al., 2003). Mori (2003) reviewed the subject and concluded that there is a need to focus on developing hydrate reactors with much improved hydrate forming efficiencies. One of the new approaches underway to enhance the kinetics of hydrate formation is to employ a fixed bed column with silica gel as a medium to capture CO₂ from flue and fuel gases via hydrate crystallization (Adeyemo et al., in press; Seo et al., 2005) or to employ a slurry bubble column (fluidized bed) arrangement to enhance the rate of hydrate formation (Hashemi, 2009) or use a non-stirred batch reactor with cyclopentane as a promoter (Zhang and Lee, 2009).

A small size (volume = 323 cm³) stirred vessel was used in our laboratory to demonstrate how hydrate crystallization can be employed to capture CO₂ from flue and fuel gases (Kumar et al., 2009c; Linga et al., 2007a,b, 2008). It has also been used to assess the storage potential of natural gas in structure H hydrate systems (Lee et al., 2005). The kinetics of gas hydrate formation in this vessel is influenced by mass transfer in a short period of time due to agglomeration of hydrates at gas/liquid interface (Linga, 2009). The need for the enhancement of the rate of gas hydrate formation is more acute when additives are used. For the CO₂ capture applications additives such as tetrahydrofuran (THF) or propane

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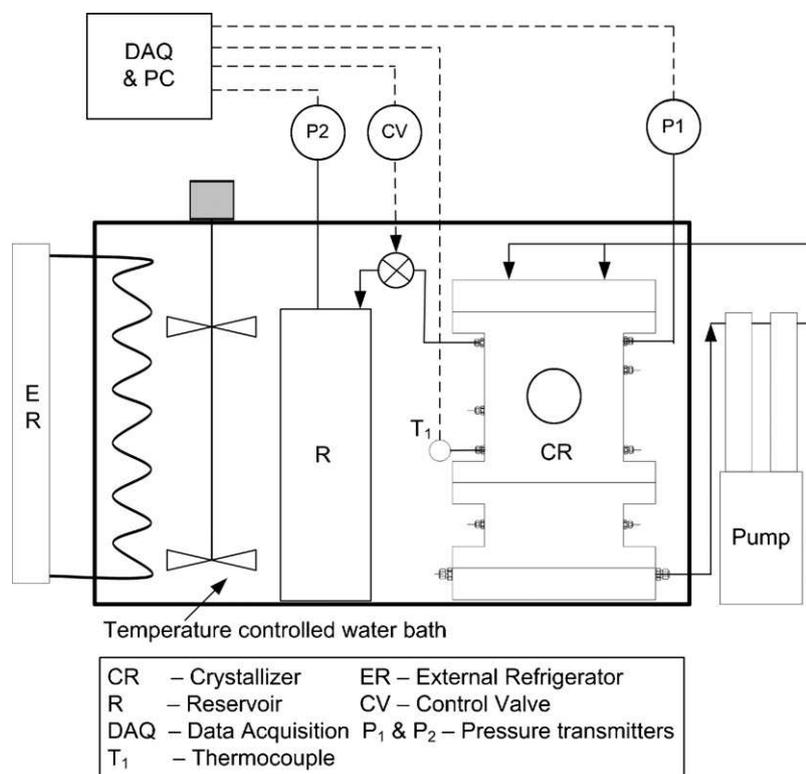


Fig. 1. Schematic of the apparatus.

are required to reduce the operating pressure and thus improve the process economics. The additives, however, reduce the rate of hydrate formation (Kumar et al., 2009c; Linga et al., 2007b, 2008). Linga et al. (2007b, 2008) reported that the rate of hydrate formation and the total gas consumption in the presence of THF (1.0 mol%) as an additive is less than the system without the presence of additive in water. Similar observations were reported by Kumar et al. (2009c) for pre-combustion capture via hydrate crystallization in the presence of propane (2.5 mol%) as an additive. In this work, we present a new larger scale mechanically agitated gas-inducing crystallizer (volume of reactor = 1892.7 cm³) with different gas/water contact modes to enhance the rate of hydrate formation. The crystallizer is equipped with a gas-inducing impeller that enables efficient recycling of gas from the headspace (gas phase of crystallizer) into the liquid and along with an added blade to constantly renew the gas-liquid interface. The apparatus is used to assess the hydrate-based separation process of CO₂ capture from a flue gas and fuel gas mixture.

2. Experimental

2.1. Materials

The gas used for the postcombustion capture experiments is a CO₂/N₂ (16.9/83.1 mol%) mixture used by Linga et al. (2008). THF was added to the water to reduce the required pressure to form hydrate (Kang and Lee, 2000; Linga et al., 2008). THF with 99% purity used in the experimental work was supplied by Fisher Scientific. A mixture of CO₂ (40%) and H₂ (60%) represents a fuel gas mixture (Klara and Srivastava, 2002). It was found that addition of a 3.2 mol% of C₃H₈ reduces the required hydrate formation pressure by 50% (Kumar et al., 2006) and thus facilitates a process that is economically attractive (Kumar et al., 2009a,c). Thus, a ternary CO₂/H₂/C₃H₈ (38.1/59.4/2.5 mol%) gas mixture used by Kumar et al. (2009c) is used in this study. The gas was ultra high

purity (UHP) grade and was supplied by Praxair Technology Inc. The water used was distilled and deionised.

2.2. Apparatus

Fig. 1 shows a schematic of the new apparatus. The crystallizer (CR) is supplied with hydrate forming gas from the supply vessel (SV) to support the crystal formation. Both CR and SV are immersed in a water bath whose temperature is regulated by an external refrigerator (VWR Scientific). Two Rosemount smart pressure transmitters, model 3051 (Norpac controls, Vancouver, BC) are employed for pressure measurement with a maximum uncertainty of 0.075% of the span (0–15,000 kPa), i.e. 11 kPa. The temperatures of the hydrate phase and the gas phase in the crystallizer are measured using Omega copper-constantan thermocouples with an uncertainty of 0.1 K. A control valve (Fisher Bauman) coupled with a PID controller enables carrying out the formation experiment at constant pressure. The data acquisition system (National Instruments) is coupled with a computer to record the data as well as to communicate with the control valve during the experiment and the software used for this purpose is LabView 7.0 (National Instruments). The apparatus is also equipped with a safety pressure valve.

Fig. 2 shows the cross section of the crystallizer which has a total volume of 1892.7 cm³. The crystallizer has two removable sections connected together with top and bottom flanges. Mechanical stirring and the stirring geometry is important in order to increase gas/water contact and enhance water conversion to hydrate (Ngan and Englezos, 1996). This crystallizer improves contact through a mechanical stirrer, the shaft of which has a special arrangement with the propeller. This type of impeller is known as gas-inducing impellers. This arrangement is such that when the experiment is run under pressure it allows the flow of gas through the shaft from the head space (gas phase of the crystallizer) to the liquid through the propeller blades. A detailed review of gas-inducing reactors is available in the literature

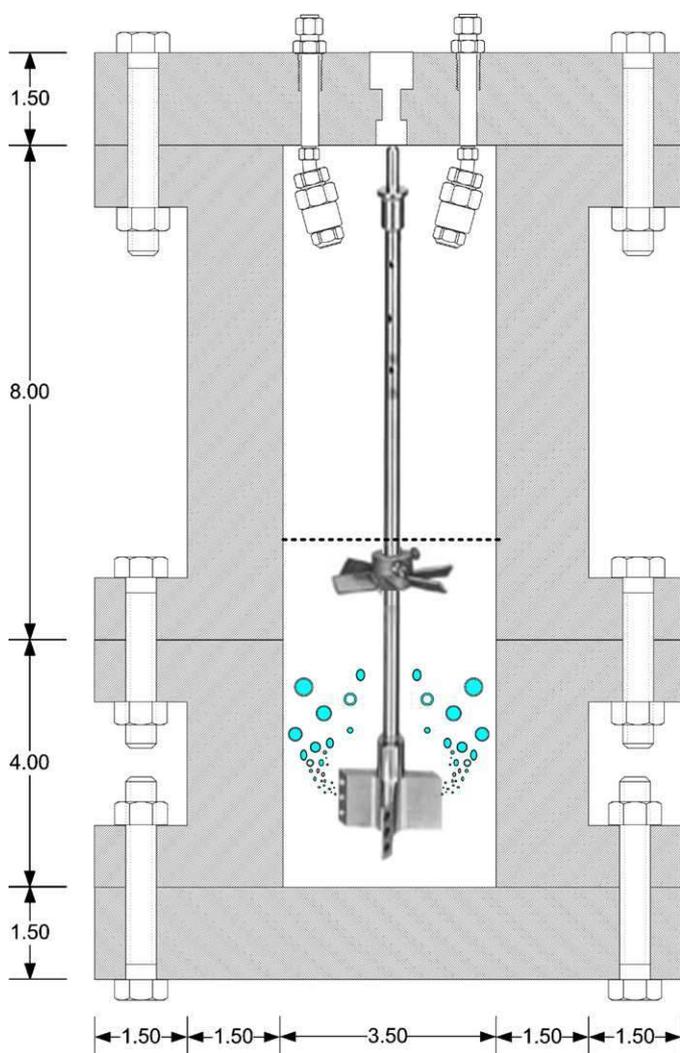


Fig. 2. Cross section of the crystallizer with the stirrer and nozzle arrangement.

(Patwardhan and Joshi, 1999). In addition there is an impeller connected just below the gas/liquid interface which will constantly renew the gas/liquid interface. This enables the crystallizer to operate in a manner that prevents accumulation of agglomerated crystals at the interface. It is noted that as the mass of the hydrate particles increases with time the system will tend towards that state. The impeller in this crystallizer extends the onset of this state quite considerably compared to a simple stirred vessel that does not have the capability to constantly “scrape” the hydrates from the neighborhood of the gas/liquid interface. Hence, it enables proper mixing as well as internal circulation of gas into the liquid. Thus, the mixing arrangement allows the crystallizer to operate in a manner that the hydrate particles remain in suspension over an extended period of time compared to conventional stirred vessel arrangements.

2.3. Experimental procedure

All hydrate crystal formation experiments were carried out in a semi-batch manner with a fixed amount of water and a continuous supply of gas at constant temperature and pressure (semi-batch operation). It is customary to denote the difference between the experimental pressure at the start of the experiment and the equilibrium hydrate formation pressure (L_W-H-V) at the experimental temperature as the *driving force*. It is noted that the driving force changes during the kinetic experiment since the composition

of the gas phase in CR changes with time (Linga et al., 2007b). A volume of 700 mL of water was injected into the crystallizer for each experiment. In the experiments with aqueous solutions, 1.0 and 1.5 mol% THF concentrations were used. A mechanical agitation speed of 400 rpm was employed (Linga, 2009). The experimental procedure for the hydrate formation and separation experiment was similar to the procedure reported by Linga et al. (2008). The mass of gas being consumed in the crystallizer (gas uptake) versus time was calculated based on the temperature and pressure measurements. This is a standard technique to carry out macroscopic kinetic measurements (Bishnoi and Natarajan, 1996). In addition, gas phase composition in the hydrate vessel was also measured with a Varian CX-3400 gas chromatograph (GC) equipped with a thermal conductivity detector.

After the end of hydrate formation, the pressure in the crystallizer was quickly brought down to atmospheric and the hydrate crystals were allowed to dissociate completely. The gas which evolved from the decomposed hydrate and that released from the liquid water phase (dissolved amount) was collected in the crystallizer. The composition of this gas was determined by gas chromatography and thus the hydrate composition (on a water free basis) was found.

Experiments with fresh water as well as with memory water were conducted. Memory water refers to water that has experienced hydrate formation and then is used for hydrate formation again. In this work memory water was obtained by decomposing hydrates and using it to form new hydrate 3 h after the hydrate decomposition.

2.4. Conversion of water to hydrate

Conversion of water to hydrate is calculated as follows

conversion of water to hydrates (mol%)

$$= \frac{\Delta n_{H_2O} \times \text{hydration number}}{n_{H_2O}} \times 100 \quad (1)$$

where Δn_{H_2O} is the number of moles of gas consumed for hydrate formation at the end of the experiment and n_{H_2O} is the total number of moles of water in the system. The hydration number is the number of water molecules per guest molecule. It can be determined experimentally by simultaneously using powder X-ray diffraction and Raman spectroscopy on solid hydrate phase (Kumar et al., 2008, 2009a; Sum et al., 1997; Susilo et al., 2007; Uchida et al., 1999; Udachin et al., 2001) or by solid state NMR spectroscopy (Davidson et al., 1983; Ripmeester and Ratcliffe, 1988).

In the presence of THF, the next equation is employed

conversion of water to hydrates (mol%)

$$= \frac{(\Delta n_{H_2O} + \Delta n_{THF}) \times \text{hydration number}}{n_{H_2O}} \times 100 \quad (2)$$

where Δn_{THF} is the number of moles of THF consumed for hydrate formation at the end of the experiment. Δn_{THF} is calculated as follows

$$\Delta n_{THF} = \text{hydration number} \times \frac{(\text{number of large cages}/\text{number of small cages})}{\text{hydration number for full occupancy}} \quad (3)$$

The hydration number of 5.71 (Kang et al., 2001b) was used for the CO_2/N_2 gas mixture and 10.05 (Kumar et al., 2009a) was used for the $CO_2/H_2/C_3H_8/H_2O$ gas mixture.

Table 1

Experimental conditions along with measured induction times and hydrate formation rates for CO₂/N₂/THF/H₂O system at 273.7 K. The CO₂/N₂ composition of the mixture was 16.9 mol% CO₂ and balance N₂.

System	Exp. no.	Sample state	Driving force ^a (MPa)	P _{exp} (MPa)	Induction time (min)	Final gas consumed (mol of gas/mol of H ₂ O)	Water conversion to hydrate ^b (%)
(CO ₂ /N ₂ /THF/H ₂ O) 1.0 mol% THF	1	Fresh	1.2	1.5	70.3	0.0098	8.4
	2	Memory	1.2	1.5	1.7	0.0089	7.6
	3	Fresh	2.2	2.5	52.0	0.0178	15.2
	4	Memory	2.2	2.5	0.7	0.0174	14.9
	5	Fresh	2.2	2.5	10.7	0.0181	15.4
	6	Memory	2.2	2.5	0.7	0.0180	15.3
	7	Fresh	1.2	1.5	60.3	0.0092	7.8
	8	Memory	1.2	1.5	2.7	0.0090	7.6
(CO ₂ /N ₂ /THF/H ₂ O) 1.5 mol% THF ^c	9	Fresh	2.2	2.3	4.0	0.0163	13.9
	10	Memory	2.2	2.3	0.3	0.0164	14.1

^a Driving force = P_{exp} - P_{eq} (P_{exp} = experimental pressure, P_{eq} = equilibrium pressure) at the beginning of the experiment.

^b Hydration number of 5.71 (Kang et al., 2001b) was used for the calculation.

^c Experiments carried out at 274.25 K.

3. Results and discussion

Table 1 summarizes the relevant experimental conditions, the induction time for crystallization, the moles of gas consumed and the water conversion to hydrate. It is noted that for both the THF concentrations used, the 17% CO₂/N₂ gas mixture forms structure II hydrate (Kang and Lee, 2000; Kang et al., 2001a). However, in the absence of THF this mixture forms structure I (Seo and Lee, 2004). Experiments with 1.0 mol% were carried out for two driving forces of 2.2 and 1.2 MPa at 273.75 K. The equilibrium formation pressure for the 1.0 and 1.5 mol% THF for 16.9% CO₂/N₂ gas mixture is 0.345 at 273.75 K and 0.130 MPa at 274.25 K, respectively (Linga et al., 2008).

As seen in Table 1 the memory water experiments have shorter induction times as compared to the fresh water experiments. The induction times for experiments conducted with fresh water range from 10.7 to 70.3 min. However, for the memory water, the induction times were less than 2 min. It is generally accepted that induction times are shorter for experiments conducted in memory water (Lee et al., 2005; Linga et al., 2007b; Uchida et al., 2000). In a practical application the vessel will be larger and since water will be re-used it will have memory. As a result the induction times for crystallization are expected to be in the order of a few minutes.

The final gas consumption at the end of the experiment is approximately the same for both fresh and memory solutions. It can also be seen in Table 1 that the total number of moles consumed at the end of the experiment was found to be higher in the case of 1.0 mol% (compared at the same driving force of 2.2 MPa). This concentration dependency was also observed for the fresh experiments at the same corresponding driving force. Linga et al. (2008) reported the same behavior for several experiments carried out at different driving forces for experiments using solutions of 0.5, 1.0 and 1.5 mol% THF in the small stirred vessel (323 cm³). The water conversion to hydrate indicates the extent of hydrate formation which is greater when 1 mol% of THF is used under the same driving force (2.2 MPa). Recently, Lee et al. (in press) reported a similar concentration dependency of THF for kinetic experiments on a semi-batch stirred tank reactor for the fuel gas mixture and concluded that 1.0 mol% is the optimal amount. This is similar to that for flue gas separation reported by Linga et al. (2008).

Fig. 3 shows the effect of driving force (difference between the experimental pressure and the equilibrium pressure at the start of the experiment) on the rate of hydrate formation for 1.0 mol% THF solution. As expected the total number of moles consumed increases with the increase in operating pressure (and hence driving force) at a given temperature. The same trend was also observed for the fresh water experiments. Water conversion to

hydrates for all of the experiments carried out is given in Table 1. As seen in table, the water conversion to hydrate is also higher (double) for the higher driving force experiments (15%) compared to the lower driving force experiments (8.0%). Thus, a driving force of 2.2 MPa is preferable.

The CO₂ composition of the residual gas phase in the crystallizer at the end of the experiment is given in Table 2. As seen, the CO₂ content in the gas phase decreases indicating enrichment of the hydrate phase with this gas. The increased CO₂ content of the hydrate is also shown as the hydrate composition on a water free basis in the same table. This composition was obtained by decomposing the hydrate. This information aids the calculation of the separation factor and the split fraction or CO₂ recovery. These two metrics (split fraction or CO₂ recovery and separation factor) were introduced by Linga et al. (2007a) to evaluate the separation efficiency of the hydrate process. The CO₂ recovery or split fraction (S.Fr.) of CO₂ is calculated as follows

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2}^{\text{Feed}}} \quad (4)$$

where $n_{\text{CO}_2}^{\text{Feed}}$ is the number of moles of CO₂ in feed gas and $n_{\text{CO}_2}^{\text{H}}$ is the number of moles of CO₂ in hydrate phase at the end of the experiment. The separation factor (S.F) is determined from the following equation

$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} \times n_{\text{N}_2}^{\text{gas}}}{n_{\text{N}_2}^{\text{H}} \times n_{\text{CO}_2}^{\text{gas}}} \quad (5)$$

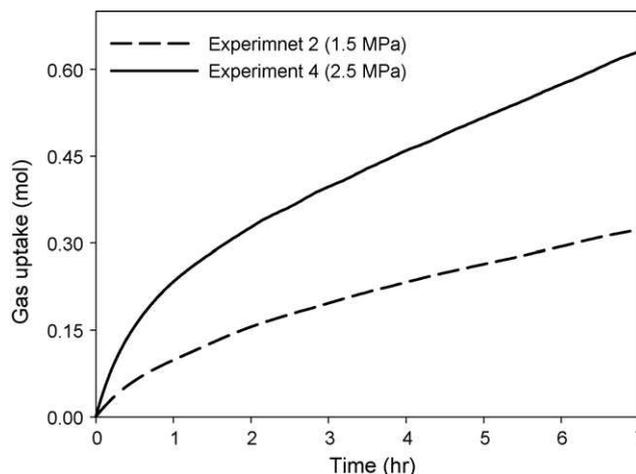


Fig. 3. Gas uptake curves for 1.0 mol% THF concentration solutions with memory at 273.7 K and different pressures (driving forces).

Table 2CO₂ composition at start and end of the experiment as analyzed by gas chromatography along with the calculated split fraction or CO₂ recovery and separation factor.

Parameter	Experiment 1	Experiment 3	Experiment 4	Experiment 9
THF concentration (mol%)	1.0	1.0	1.0	1.5
Feed gas composition (start), mol fr	0.169	0.169	0.169	0.169
Gas phase composition (end), mol fr	0.100	0.092	0.095	0.105
Hydrate phase composition, mol fr	0.351	0.383	0.372	0.321
Gas consumption (end), mole	0.36	0.66	0.65	0.59
Split fraction or CO ₂ recovery, mol fr	0.60	0.61	0.63	0.58
Separation factor	4.12	4.31	4.52	3.88

where $n_{\text{CO}_2}^{\text{gas}}$ is the number of moles of CO₂ in the gas phase at the end of the experiment, $n_{\text{N}_2}^{\text{gas}}$ is the number of moles of N₂ in the gas phase at the end of the experiment and $n_{\text{N}_2}^{\text{H}}$ is the number of moles of N₂ in the hydrate phase.

As seen in Table 2 the split fraction ranges from 0.58 to 0.63 indicating that approximately 60% of the CO₂ in the feed gas is separated in one stage of hydrate formation. For example, the CO₂ recovery or split fraction for experiment 4 (273.7 K and 2.5 MPa) is $0.216/0.345 = 0.63$ and for experiment 1 (273.7 K and 1.5 MPa) is $0.122/0.203 = 0.60$. One can then conclude that it would be prudent to have the first stage of hydrate formation for CO₂ capture from a flue gas operating at the lowest pressure of 1.5 MPa since the CO₂ recovery is practically the same with that of the experiments studied at 2.5 MPa. However when we compare the CO₂ recovery (Table 2) and the gas uptake (Fig. 3) in tandem, we can see that for the experiment at 2.5 MPa the final gas consumption is almost 2 times greater than for the experiment at 1.5 MPa. From a practical point one must have the best possible CO₂ recovery and gas uptake too.

Alternative additives like tetra-*n*-butyl ammonium bromide (TBAB) and tetra-*n*-butyl ammonium fluoride (TBAF) have been proposed for the separation of CO₂ from flue gas using the hydrate process (Fan et al., 2009; Li et al., 2009). Hence it is of our interest to evaluate the performance of THF obtained in this work with that of TBAB and TBAF available in the literature (Fan et al., 2009; Li et al., 2009). Li et al. (2009) reported a minimum operating pressure of 4.3 MPa required for the hydrate based separation process in the presence of 5 wt% (0.293 mol%) TBAB at 277.65 K. The presence of TBAB (5.0 MPa) would require high operating pressure compared to THF (2.5 MPa) as an additive which would result in higher compression costs for the hydrate process. Additionally, the presence of THF results in a better CO₂ recovery from the flue gas mixture. Fig. 4 summarizes the CO₂ recovery obtained in this work and the data available in the literature (Fan et al., 2009; Li

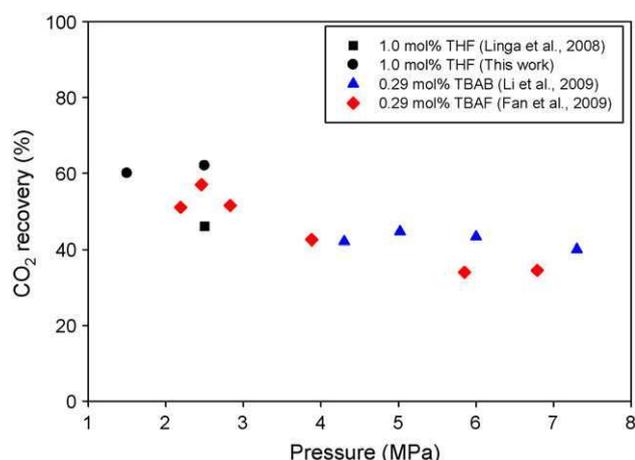


Fig. 4. Comparison of CO₂ recovery obtained for 1.0 mol% THF in the new large scale reactor to that of the laboratory scale reactor (Linga et al., 2008) and to the data available in the literature for TBAB and TBAF (Fan et al., 2009; Li et al., 2009).

et al., 2009; Linga et al., 2008). As seen in the figure, the CO₂ recovery is higher in the new apparatus compared to the laboratory scale apparatus and also higher than experiments conducted with TBAB and TBAF (Fan et al., 2009; Li et al., 2009).

Fan et al. (2009) reported a final gas consumption (calculated based on pressure drop data) of 0.14–0.32 moles for experimental pressures between 3.4 and 7.3 MPa in the presence of TBAB and 0.063–0.191 moles for experimental pressures between 2.2 and 6.8 MPa in the presence of TBAF. Taking into account the amount of water (Fan et al. (2009) report 600 cm³ of liquid contents) taken for experiments, gas consumption on a water free basis is 0.004–0.010 mol of gas per mol of water for experimental pressures between 3.4 and 7.3 MPa for TBAB containing system and 0.002–0.006 mol of gas per mol of water for experimental pressures between 2.2 and 6.8 MPa for TBAF containing system. This gas consumption is significantly lower than the gas consumption obtained in our work which is 0.0092 mol of gas per mol of water at 1.5 MPa (average of four experiments given in Table 1) and 0.0178 mol of gas per mol of water at 2.5 MPa (average of four experiments given in Table 1), respectively. Hence the use of THF for CO₂ capture from flue gas using the hydrate process is better for the economics of the process (requires lower operating pressure) and also the performance (gas consumption on a water free basis and CO₂ recovery) is better compared to TBAB and TBAF.

Table 3 summarizes the experimental conditions and the results for the experiments conducted on the fuel gas mixture in the presence of propane as an additive. Experiments were conducted at 3.8 MPa and 273.7 K since Kumar et al. (2009a,c) reported that a (38.1/59.4/2.5 mol%) CO₂/H₂/C₃H₈ mixture forms structure II hydrate and that the presence of propane does not affect the separation efficiency. This gas mixture required a minimum pressure of 2.1 MPa to form hydrate at 273.7 K. As expected the induction times given in Table 3 are shorter for the experiments conducted with the memory solutions.

Fig. 5 shows the comparison of gas uptake obtained from experiments 1, 3 and 5 (see Table 3). As can be seen, hydrate formation slows down after 1 h and reaches a plateau. In spite of the improved mechanical agitation, sufficient hydrate mass is formed which decreases gas/liquid contact and slows hydrate growth and reaches a plateau. A similar behavior was observed for the memory experiments. The maximum conversion of water to hydrate obtained for the (38.1/59.4/2.5 mol%) CO₂/H₂/C₃H₈ system was 10.4 mol% at 273.7 K and 3.8 MPa. The hydrate was found to contain 83.1% CO₂, 6.9% C₃H₈ and rest H₂.

Overall, the gas uptake in the new apparatus for both the systems has improved compared to that obtained in the small vessel. This is evident if one compares the moles of gas consumed (gas uptake) per mole of water in the two apparatus. Fig. 6 shows the results for two such experiments performed under same pressure and temperature. During the first 2 h, the rates are similar with that in the new large mechanically agitated gas-inducing crystallizer. During this phase, the hydrate particles are well suspended in the liquid (based on visual observation). After 2 h of hydrate growth, particle agglomeration and growth results in accumulation of gas hydrate crystals at the gas/liquid interface in

Table 3Experimental conditions along with measured induction times and hydrate formation rates for CO₂/H₂/C₃H₈/H₂O system at 273.7 K.

System	Exp. no.	Sample state	Driving force ^a (MPa)	P _{exp} (MPa)	Induction time (min)	Final gas consumed (mol of gas/mol of H ₂ O)	Water conversion to hydrate ^b (%)
(CO ₂ /H ₂ /C ₃ H ₈ /H ₂ O)	1	Fresh	1.7	3.8	8.7	0.0101	10.1
	2	Memory	1.7	3.8	3.3	0.0093	9.3
	3	Fresh	1.7	3.8	13.0	0.0103	10.4
	4	Memory	1.7	3.8	4.7	0.0094	9.4
	5	Fresh	1.7	3.8	8.7	0.0104	10.4
	6	Memory	1.7	3.8	3.3	0.0097	9.8

^a Driving force = P_{exp} - P_{eq} (P_{exp} = experimental pressure, P_{eq} = equilibrium pressure) at the beginning of the experiment.^b Hydration number of 10.05 (Kumar et al., 2009a) was used for the calculation.

the laboratory apparatus. This state prevents any further gas uptake and hence reaches a plateau (Linga, 2009). On the other hand, in the new large scale mechanically agitated gas-inducing crystallizer, the presence of the second impeller just below the gas/liquid interface prevents the accumulation of crystals at the interface there by constantly renewing the gas/liquid contact. Hence the gas uptake obtained in this work is substantially higher (72.6%) than that in the small vessel due to a better contacting of gas and liquid. This is achieved by mechanical agitation and with the circulation of gas through the liquid phase by the gas-inducing impeller. A similar comparison between two experiments conducted for the fuel gas mixture is shown in Fig. 7. As seen, the gas uptake is significantly higher in the new apparatus.

It is interesting to compare the CO₂ recovery or split fraction obtained in this work with the values obtained using the small scale stirred vessel and reported by Linga et al. (2008). The experimental conditions and the results for the two experiments shown in Figs. 6 and 7 are given in Table 4. The CO₂ recovery is 36.9% higher in the new apparatus indicating a better capture of CO₂ in the crystals. Also, the CO₂ recovery was calculated for an experiment (experiment 5) conducted with the fuel gas mixture. The CO₂ recovery or split fraction for experiment 5 in this work (273.7 K and 3.8 MPa) is 0.441/0.927 = 0.48. This value is compared with the one reported by Kumar et al. (2009c) for experiment 6 (273.7 K and 3.8 MPa). The CO₂ recovery for that experiment is 0.065/0.138 = 0.47 and is also shown in Table 4. In this case the CO₂ recovery is not improved even though gas uptake improves as in the case with the CO₂/N₂/THF system. In this system, however, there is propane in the gas mixture which is also taken up by the hydrate. Hence, the higher gas consumption due to better gas/water contact achieves a CO₂ recovery of 0.48. The large cages of

the hydrate are occupied by CO₂ and C₃H₈ whereas the small ones are occupied by CO₂ and H₂ (Kumar et al., 2009a,b).

Mori (2003) compared the rate of hydrate formation between different reactors available in the literature by defining a metric called “rate of guest-gas fixation” by hydrate formation per unit volume inside the reactor. It is noted that the above metric does not take into account the amount of water used in the hydrate formation experiment. As one can see from the water conversion to hydrate results (Tables 1 and 3), there is a significant amount of unreacted water at the end of the formation experiment. The normalized rate of hydrate formation taking into account the amount of water used in the experiment is represented as follows,

$$\text{normalized rate of hydrate formation} \left(\frac{\text{mol/mol}}{\text{h}} \right) = \left[\frac{(\Delta n_{H_2O})_t / n_{H_2O}}{t} \right] \quad (6)$$

Fig. 8 represents the calculated normalized rate of gas supply with respect to the amount of water for small stirred vessel (Linga et al., 2008), the new apparatus (this work) and data available in the literature (Fan et al., 2009). As seen in the figure, the calculated normalized rate of gas supply is more than ~1.4 times higher for the new large scale apparatus compared to the lab-scale apparatus for the experiment carried out at a lower driving force and ~1.8 times higher at higher driving force. The normalized rate of hydrate formation in the presence of THF is also higher compared to the presence of TBAF at any given pressure as seen in the figure. For instance, the normalized rates obtained for TBAF at 2.16 MPa are lower than the normalized rate obtained with THF at 1.5 MPa for both the small scale stirred tank crystallizer (Linga et al., 2008) and

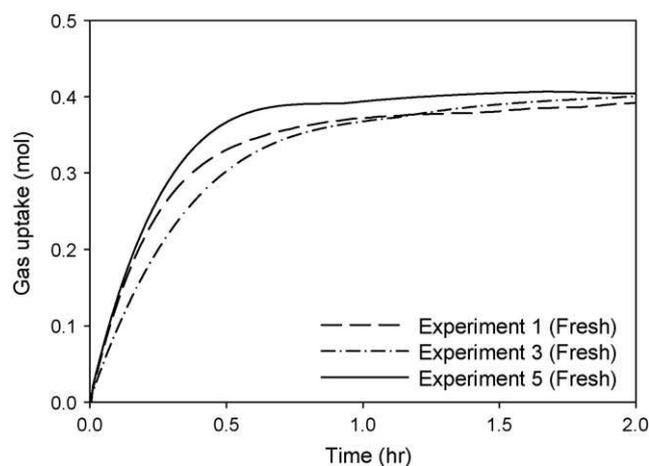


Fig. 5. Gas uptake measurements for three experiments conducted at 3.8 MPa and 273.7 K in fresh water for CO₂(38.1%)/H₂(59.4%)/C₃H₈(2.5%)/H₂O system. The experiment number given in the figure corresponds to the experiments given in Table 3.

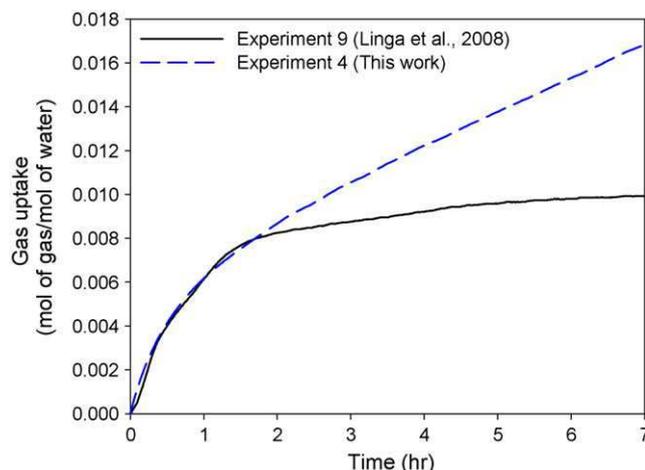


Fig. 6. Comparison of gas uptake (hydrate growth) for hydrate formation for 1.0 mol% THF (pressure = 2.5 MPa, temperature = 273.7 K) on a water free basis. Time zero corresponds to the induction time for the experiment.

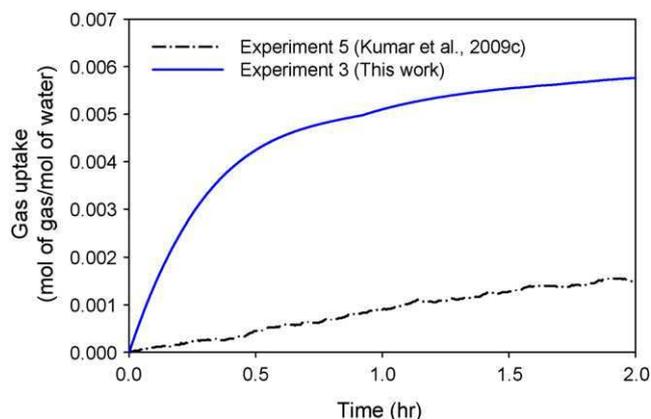


Fig. 7. Comparison of gas uptake (hydrate growth) obtained for CO₂(38.1%)/H₂(59.4%)/C₃H₈ (2.5%)/H₂O system (pressure = 3.8 MPa, temperature = 273.7 K) on a water free basis. Time zero in this graph corresponds to induction time for the experiment.

the new large scale mechanically agitated gas-inducing crystallizer (this work). The rate with TBAB is also expected to be lower if one extrapolates to lower pressures. Recall that the CO₂ recovery and gas consumption were also higher for the system with THF compared to TBAF and TBAB. The normalized rate of hydrate formation for the fuel gas mixture was calculated and found to be 0.00485 mol/(h mol of water) for the experiments given in Table 3 (the reported normalized rate is the average of six experiments). The normalized rate of hydrate formation for the experiments reported by Kumar et al. (2009c) was calculated and found to be 0.00433 mol/(h mol of water).

Conceptual process flow sheets have been proposed in the literature for the postcombustion capture and pre-combustion capture of CO₂ based on the hydrate process (Kumar et al., 2009c; Linga et al., 2007a, 2008). It was reported that in order to obtain a 98% rich CO₂ stream from flue gas mixture, three hydrate formation/decomposition stages are required. Two hydrate formation/decomposition stages are required to obtain a 98% rich CO₂ stream from a fuel gas mixture. Our results on the flue gas mixture in this work on a large scale indicate that the CO₂ rich stream coming out of the first stage would contain approximately 38% CO₂ (Table 2) when operated at 2.5 MPa and 273.7 K in the presence of 1.0 mol% THF. It is noted that Linga et al. (2008) reported a hydrate composition of 37% CO₂ for the same operating conditions in the small vessel. It is reasonable to assume that three stages of hydrate formation/decomposition will be required in order to obtain a highly (>94%) concentrated CO₂ stream. Kumar et al. (2009b) proposed a two stage hybrid hydrate/membrane process to obtain a 98% rich CO₂ stream for a (38.1/59.4/2.5 mol%) CO₂/H₂/C₃H₈ gas mixture. The authors reported that the first stage of hydrate formation produces a CO₂ composition of 83.7% (Kumar et al., 2009c) which is similar to the results obtained at a larger scale in this work (83.1% CO₂). Again, it is reasonable to assume that two stages of hydrate formation would be required to produce a high purity CO₂ (98%) stream from a fuel gas mixture.

Table 4

Comparison of CO₂ recovery or split fraction between small (lab scale) and the new large scale apparatus for the flue and fuel gas mixture.

Description	CO ₂ (16.9%)/N ₂ (83.1%)/1.0 mol% THF		CO ₂ (38.1%)/H ₂ (59.4%)/C ₃ H ₈ (2.5%)/H ₂ O	
	Exp. 4 (Table 1)	Exp. 9 Linga et al. (2008)	Exp. 5 (Table 3)	Exp. 6 Kumar et al. (2009c)
Volume of liquid (ml)	700	140	700	140
Temperature (K)	273.7	273.7	273.7	273.7
Pressure (MPa)	2.5	2.5	3.8	3.8
Split fraction or CO ₂ recovery	0.63	0.46	0.48	0.47
Water conversion to hydrate (%)	14.9	7.1	10.4	8.2

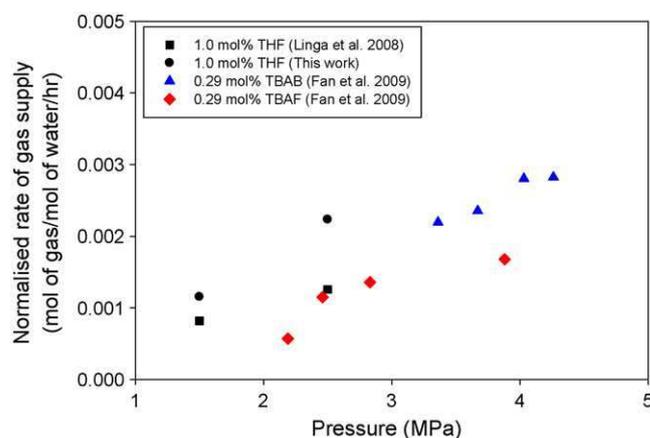


Fig. 8. The normalized rate of gas supply calculated by taking into account of the volume of water (Eq. (3)) for the experiments conducted in the presence of 1.0 mol% THF in the lab-scale apparatus (Linga et al., 2008) and the new large scale apparatus (this work) and data available in Fan et al. (2009).

It is noted that in order to compress a flue gas from atmospheric pressure to 2.5 MPa for a typical 500 MW power plant, the energy penalty is 53% of the power output (Linga et al., 2008). On the other hand, in order to compress a fuel gas mixture which is at 2–7 MPa (IPCC, 2005), the energy penalty for compression is only 2.9% of the power output (Kumar et al., 2009c). The drawback of the hydrate process employing a stirred vessel configuration is the power consumption associated with mechanical agitation. The estimated power consumption for the stirrer arrangement in our apparatus for a typical experiment is 0.541 kWh/mol of captured CO₂. A 500 MW typical pulverized coal fired power plant produces a pretreated flue gas of 80,372 kmol/h. Hence, the power consumption required to produce a hydrate stream consisting of 6354.6 kmol of CO₂/h (calculated based on CO₂ recovery and hydrate composition) would be 3437.8 MW. This would render deploying the hydrate process for CO₂ capture impossible. Thus, even though gas hydrate crystallization is able to capture CO₂ and enhanced gas/water contact improves the rate of crystallization the contact mode must be such that far less energy is consumed. Some of the potential contact modes are to employ a fixed column using silica sand or silica gel as a medium (Adeyemo et al., in press; Linga, 2009; Seo et al., 2005), a fluidized bed column (Hashemi, 2009) or a non-stirred batch reactor in the presence of cyclopentane as a promoter (Zhang and Lee, 2009). Recently, Adeyemo et al. (in press) reported water to hydrate conversions of up to 45% after 4 h of hydrate formation conducted in a fixed bed column with silica gel as a medium for both post- and precombustion capture of CO₂ via hydrate crystallization. It is noted that the last two contact modes, fluidized bed column and a non-stirred batch reactor looks promising but are yet to be proven for the CO₂ capture process via hydrate crystallization.

A new gas hydrate formation apparatus equipped with a modular, mechanically agitated gas-inducing crystallizer having a volume of 1892.7 cm³ is presented. The new apparatus improves

the gas/water contact and as a result the gas uptake during hydrate crystallization increases significantly compared to the previously used laboratory apparatus. The apparatus was used to demonstrate how CO₂ can be captured from flue and fuel gas mixtures. The CO₂ recovery was found to improve indicating a better separation of CO₂ from the feed gas. A new metric namely normalized rate of hydrate formation that takes into account the amount of water used for experiments was proposed and used to compare performance of different hydrate formation reactors. The power consumption associated with employing stirred tank vessel configuration was estimated and found to be very significant. Hence, if the hydrate process is to be scaled up and used industrially the crystallization must be carried without mechanical agitation.

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