

Capturing Carbon Dioxide through a Gas Hydrate-Based Process

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Gas hydrate based technology is one of new promising methods for capturing carbon dioxide. The carbon dioxide hydrate is a green compound which does not have any impact on the environment and the process is assumed to be less energy intensive. However, the development of gas hydrate based technology is suffering from slow formation rate and long induction time and endothermic nature of gas hydrate formation. In this article, a process based on gas hydrate technology is introduced for capturing of carbon dioxide from gaseous stream. The heart of this process is a new gas hydrate crystallizer which is designed especially for enhancing the hydrate formation rate. A series of semi-batch process is performed to investigate the performance of this setup for capturing carbon dioxide from a high carbon dioxide content methane-carbon dioxide gas mixture. Results indicated that new crystallizer has the ability to significantly reduce the induction time, increase the formation rate and overcome to the generated heat problem. Furthermore, it shows that pressure has the highest influence on formation rate and separation efficiency of the process among the studied parameters.

1. Introduction

Capturing carbon dioxide (CO₂) is the first and most challenging step of carbon capture and sequestration (CCS) projects. Most of natural gas reservoirs have CO₂ and hydrogen sulphide and there are different capturing methods that have been used and improved for several years to capture these acid gases (Kohl and Nielsen, 1997). Among the methods are chemical absorption (amine), adsorption, membrane separation and cryogenic fractionation. The first industrial scale CCS project that is launched at Boundary Dam SaskPower, Saskatchewan province, Canada at October 2014, is using chemical absorption technology for capturing carbon dioxide. However, the absorption process is suffering from high capital expenditure and operational expenditure. Estimations showed that the deployment of this technology can reduce the thermal efficiency of a modern power plant from approximately 45 % to approximately 35 % (MacDowell et al., 2010). Besides absorption, other capturing methods are also facing the same problems. Capture technologies should open the way for large-scale production of low-carbon or carbon-free electricity and fuels for transportation, as well as for small-scale or distributed applications. The energy required to operate CO₂ capture systems reduces the overall efficiency of power generation or any other processes. Increasing the efficiency of power generation process is the key to solve the problem. However, less efficient, old plant are now in service and producing tones of CO₂ yearly. Furthermore, CCS projects cannot be limited to the power plants. In utilization of non-conventional resource of fuel gas, such as biogas, mainly landfill gas (Bove and Lunghi, 2006) or high CO₂ content natural gas (Burgers et al., 2011), capturing CO₂ is an essential stage of both gas treatment and CCS application (Lestinsky et al., 2014). In addition, capturing CO₂ from other sources of emission, such as international shipping or other long distance/international trade transportation, can play an important role in overall reduction of GHG emission (Zhou and Wang, 2014). Therefore, minimization of energy requirements for capture technology is one of the highest priorities for future technology development in order to minimize overall environmental

impacts and cost (Aaron and Tsouris, 2005) and thus, there is room for new and novel technologies for capturing CO₂.

Gas hydrate-based separation is one of these new technologies. Clathrate hydrates or gas hydrates are non-stoichiometric crystalline inclusion compounds formed by physically-stable interactions between water and gas molecules when subjected to appropriate temperature and pressure conditions. This crystalline structure consisted of some cages (cavities) where only suitable-sized molecules can fit in, based on this fact, the hydrate formation process is recommended for separation of gases with different molecular size (Sloan and Koh, 2008). Seo et al. (2000) reported a proof of concept to CO₂ separation from multicomponent gas stream by the formation of carbon dioxide hydrate. Since then, several researches are reported on utilization of gas hydrate as separation medium. Carbon dioxide was separated from nitrogen by using silica gel as platform by (Seo et al., 2005), while Linga et al. (2008) used tetrahydrofuran (THF) as promoter for this separation and Sun et al. (2014) showed that this separation can be performed via a continuous process. CO₂/H₂ separation is also reported by Linga et al. (2007) in the presence of THF. Seo and Kang (2010) claimed that presence of silica gel can enhance the CO₂/H₂ separation. Li et al. (2011) tried this separation by utilizing tetra-n-butyl ammonium bromide plus cyclopentane as promoter. For separation of carbon dioxide from methane (Seo et al., 2000) provide the concepts while Sun et al. (2014) performed the separation in a CSTR reactor. Later, Seo et al. (2014) studied the phase boundary and separation of CH₄/CO₂/N₂ in presence of acetone as promoter. However, the mentioned studies mostly focused on fundamentals. Most of the aforementioned reported processes are based on laboratory-scale equipment's, batch-type with low capacity process which may not be applied on an industrial scale project. Looking into this shortcoming, Xu et al. (2012) performed an experimental study on hydrate-based separation of CO₂ from H₂ by utilizing a bubble column reactor. Their results showed that the hydrodynamic properties such as gas flow rate and bubble size have important impact on the overall separation. However, as discussed by Mori (2003), the bubble column reactors are suffering from slow hydrate formation rate. Furthermore, providing tiny, uniform bubbles in the entire column cross section and length is not a simple task. Therefore, bubble columns cannot provide enough contact area for continuous production of gas hydrate. On the other hand, spray columns provide huge contact area which is result in higher gas hydrate formation. However, the heat of hydrate formation may not be removed throughout the reactor walls efficiently, as the continuous phase is gas with lower heat capacity/conductivity. In this work, a gas hydrate formation process for separation of CO₂ from CH₄, based on spray column technology as the reactor is investigated. The spray column is designed in a way that heat of gas hydrate formation remove more efficiently from the reactor. CO₂/CH₄ system is chosen for study the applicability of this process for high CO₂ content conditions such as biogas or CO₂-rich natural gas reservoirs.

2. Experiment apparatus, procedure and materials

The main lacking of information on gas hydrate formation process is the absence of quantitative study of hydrodynamic parameters' effect on kinetics of process. Therefore, a single stage gas hydrate formation process is designed to study the CO₂ separation from CH₄. These two gases show similar behaviour during gas hydrate formation process. Therefore, separation of them is the most challenging practice in utilization of gas hydrate-based process and separating CO₂ from N₂ or H₂ will be easier by proposed process.

2.1 Apparatus

Figure 1 shows the process flow diagram (PFD) of proposed process. Based on this PFD, a pilot plant is fabricated by a local company. The main part of process is gas hydrate reactor that is made by stainless steel 316 and total volume of 5,250 mL. As mentioned before, the reactor is based on spray tower concepts. In addition, to stabilize the reactor temperature during process, an extra quench line is added to the middle of reactor. This line is also spraying cold water in the middle of reactor, where the gas hydrate formation generates heat. This extra water is stabilizing the reactor temperature within the design value. The reactor is placed inside a thermo-stated glycol bath that its temperature can be adjusted from 263 K to 300 K. The process consisted of a continuous gas stream inlet which separated into one CO₂ lean stream that collects from the top of reactor and one CO₂ rich stream that collects from the top of separator. High pressure condition is supported by utilizing one gas compressor and water pump. The water is recycling from the separator, cooling down in the settler tank and returning back to the reactor. Other details of setup are shown in Figure 1. The setup is also equipped with pneumatic control valves (not shown in Figure 1). An Omron PLC along with a PC is used to control the process. A gas mixing station is used to mix CO₂ with CH₄ by using mass flow controllers. In addition, a ServoMax 4200 gas analyser is used to analyse the composition of outlet gases. All pressures, temperatures, reactor level, gas composition and gas/liquid flow rates are recording every second by HMI (Human Machine Interface) software is prepared

through Labview studio 7.0 platform. Pressure and temperature are measured by ± 0.1 bar and ± 0.01 K accuracy.

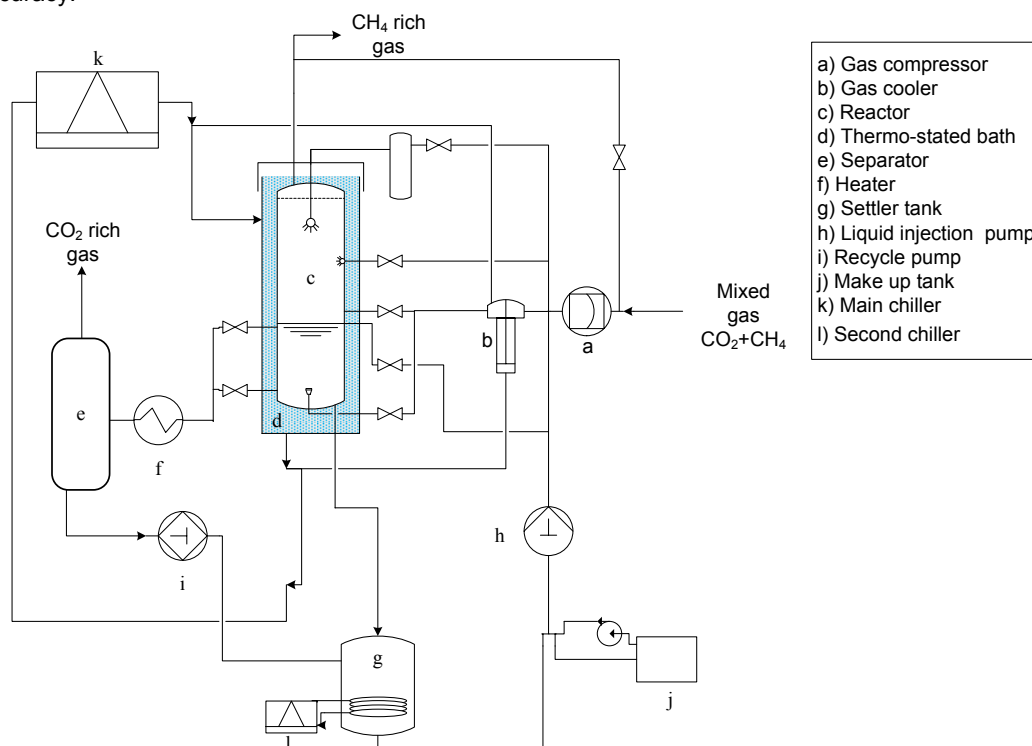


Figure 1: Process flow diagram of experimental setup

2.2 Experiment procedure and materials

As mentioned before, it is important to measure the impact of hydrodynamic parameters as well as statistics parameters such as pressure and temperature on the kinetics of process. The focus in this stage of experiments was on formation of gas hydrate.

Therefore, a series of semi-batch experiments is designed for this purpose. Four parameters are chosen for investigation: Initial reactor pressure, initial degree of subcooling, initial gas phase composition and liquid flow rate. Impacts of these parameters on the gas consumption rate and separation factor are studied. Respond Surface Method (RSM) is used to design experiments and data analyses. Total 18 experiments are designed for the model. Pressure range is from 30 to 50 bar, degree of subcooling is ranged from 3 to 7 K, water flow rate varies from 100 to 200 mL/min and CO₂ concentrations is set from 60 to 80 mol%. These values are chosen due to the limitation of equipment and gas hydrate phase boundary. The hydrate-liquid water-vapor equilibrium is calculated by CSMGem software from Center of Hydrate Research of Colorado School of Mines (CHR, 2015).

To run each experiment, the reactor was put on the vacuum for half an hour and the settler tank was filled with deionized water. Then, the proper CO₂ to CH₄ ratio was set on the HMI program and the reactor was pressurized by gas to the designed pressure. CO₂ and CH₄ gases are supplied by AirProduct Sdn. Bhd. with the purity of 99.95 %. Gas phase composition was checked by sending samples to the gas analyser. The thermo-stated bath temperature and settler tank temperature were set to the desired temperature. After stabilization of temperature, water was sprayed to the reactor for 10 min. During this period, pressure and temperature of reactor was measured. After that, another gas sample was sent to the gas analyser.

3. Theory

Gas hydrate is a nonstoichiometric compound and thus, it is not practical to measure the number of gas molecules in hydrate phase without molecular analysis such as RAMAN spectroscopy. Hence, in common gas hydrate studies gas consumption rate is normally measure as an indication of hydrate formation rate. By using an equation of state such as Peng-Robinson for gas mixtures (Peng and Robinson, 1976) and mass balance, the amount of captured gas during the process is measured by Eq(1):

$$\Delta n = \left(\frac{VP}{ZRT} \right)_i - \left(\frac{VP}{ZRT} \right)_f \quad (1)$$

where, subscript i and f are referring to initial and final time of experiment. V is the gas phase volume, P is reactor pressure and T is the average temperature of gas phase in the length of reactor and Z is the compressibility factor. The average gas consumption rate is then calculated by Eq(2).

$$\bar{R} = \frac{\Delta n}{\Delta t} \quad (2)$$

where, Δt is the experiment time, i.e. 10 min in this work. In addition, the separation factor (S.F.) is determined as follow Eq(3)

$$S.F = \frac{n_{CO_2}^c \times n_{CH_4}^g}{n_{CO_2}^g \times n_{CH_4}^c} \quad (3)$$

where, superscripts c and g are referring to number of moles of captured gases and number of remaining gas moles in the gas phase.

4. Results and Discussion

Gas hydrate formation is a thermodynamic driven process and like any other crystallization process requires super-saturation condition to form crystals. Therefore, any proposed process should always maintain the super-saturation condition. For gas hydrate process, this condition is satisfied when operating condition be inside the gas hydrate region. Figure 2 shows a sample of P-T diagram during one of experimental work of this study. As shown in this Figure 2, starting condition is well inside the gas hydrate region. After starting the experiment, the reactor temperature is increased as a result of startup condition and generation of heat by gas hydrate production. However, after almost one minute, the temperature profile becomes stable and still inside hydrate formation region. Therefore, there is no thermodynamically barrier for gas hydrate formation within the whole experiment time and the new reactor design is good enough to remove the heat of gas hydrate formation from the hydrate forming area. In addition during these experiments, no induction time is observed as a result of large contact area produced by spraying liquid water into gas phase.

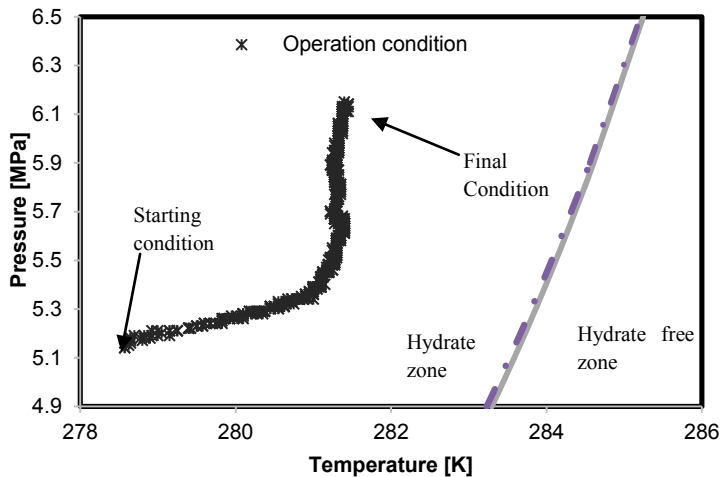


Figure 2: Pressure-temperature profile during injection of 150 mL/min deionized water for 10 min into the reactor at starting condition of 51 bar and 278.5 K with initial 65.6 mol% CO₂

The analysis of data from all experimental conditions via RSM linear method indicates that pressure and gas phase composition has the most significant effect on the gas consumption rate. Liquid flow rate and degree of subcooling effects are not significant; however their effect cannot be neglected on the gas consumption rate. Figure 3 shows the gas consumption rate per liquid flow rate as a function of gas phase

composition for three different pressures. One may notice that by increasing flow rate, the amount of liquid water entering the reactor is increased and consequently, increasing the amount of hydrates crystals forming during the constant experiment time. Therefore, as shown in Figure 3, gas consumption rate is divided by liquid flow rate to normalize the effect of liquid flow on the results.

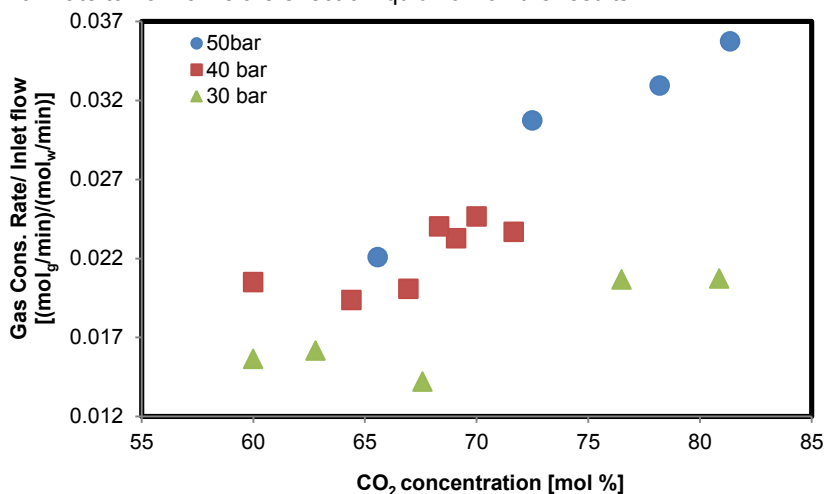


Figure 3: Effect of gas phase composition and pressure on gas consumption rate per liquid flow rate

It is clearly shown that the increasing in CO₂ concentration increases the gas consumption rate. In addition, pressure has significant effect on the formation rate. At higher pressure, the CO₂ solubility in water increases and consequently increases the chance of hydrate formation as the liquid water is more saturated with CO₂. Therefore, the overall gas consumption is also increasing with pressure. The same explanation is valid for effect of gas phase composition on solubility and hydrate formation rate. CO₂ solubility is higher than CH₄, thus, increasing the amount of CO₂ in gas phase is increasing the gas solubility and hydrate formation rate.

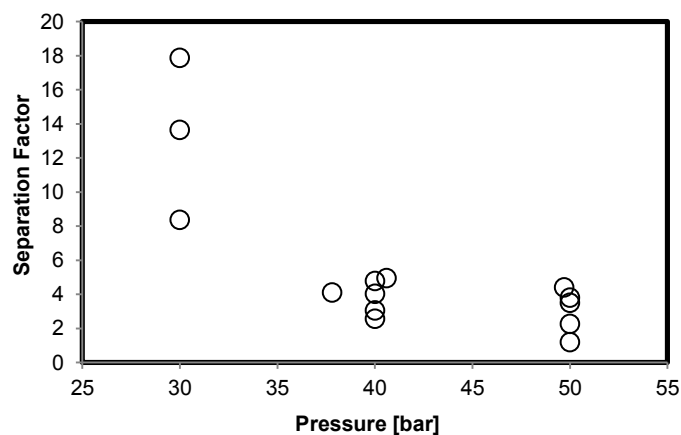


Figure 4: Effect of pressure on separation factor of CO₂ over CH₄

Analysis of separation factor with RSM linear method is indicated that pressure has the greatest effect on the separation of CO₂ from CH₄, while the effect of subcooling is not significant and can be eliminated from affecting parameters. As shown in Figure 4, an increase in pressure resulting in a reduction of the separation factor. This effect is probably due to the increase in solubility of gases in water at higher pressure. Therefore, CH₄ solubility is also increasing with pressure and accordingly, more CH₄ is entering the gas hydrate crystalline structure. CO₂ and CH₄ mixture is forming structure sI where, the ratio of small to large cavities is 3:1. As CO₂ molecules are larger than CH₄, they tend to occupy large cavities, while CH₄ molecules are inclined to occupy small cavities. Therefore, when pressure drives CH₄ molecules into the hydrate crystals, separation of CO₂ from CH₄ becomes more difficult which is shown by smaller separation factor at higher pressure. It should be noticed that variation of separation factor at constant pressure is due to effects of liquid flow rate and gas phase composition. However, the decreasing trend is obvious in Figure 4.

5. Conclusion

Gas hydrate formation is studied by a newly designed gas hydrate crystallizer. The new reactor along with the proposed process is used to form gas hydrate in a semi-batch process. The results indicate that new reactor has the ability to maintain the required gas hydrate conditions during the experiments. In addition, analysis of experimental data shows that rate of gas hydrate formation for the CO₂/CH₄ system is mostly affected by the pressure and gas phase composition. Increasing pressure and CO₂ content of mixture is increasing the gas hydrate formation rate. Furthermore, for this system, pressure has the most influence on the separation factor: increasing pressure is decreasing the separation of CO₂ from CH₄. Therefore, the optimum operating pressure cannot easily detect for such system, and it will depend on other properties.

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