A systematic kinetic study to evaluate the effect of tetrahydrofuran on the clathrate process for pre-combustion capture of carbon dioxide

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ABSTRACT

THF (Tetrahydrofuran) is the most commonly employed promoter for the gas hydrate formation pertaining to applications like carbon dioxide capture and energy storage (for natural gas and hydrogen). In this work, THF was investigated as a promoter for pre-combustion capture of carbon dioxide (CO_2) from fuel gas mixture (CO_2/H_2) in a systematic manner. 0.5, 1.0, 3.0 and 5.56 mol% THF solution were employed with different driving force conditions to study the effect of pressure, temperature and composition of gases in hydrate. The kinetic performance of the CO_2/H_2/THF gas hydrate system was evaluated by reviewing the IT (induction time), normalized gas uptake, normalized rate of hydrate formation and the hydrate phase composition. The optimum operating conditions and optimum THF concentration in this study was found to be 6.0 MPa, 282.2 K, and 5.56 mol% THF respectively. 5.56 mol% THF solution yielded an average gas uptake of 13.9 mmol of gas/mol of water for hydrate growth and an average normalized rate of hydrate formation of 1679.8 mmol s^{-1} m^{-3}.

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1. Introduction

The burning of fossil fuels has led to increasing concentration of carbon dioxide (CO_2) in the atmosphere, amplifying the risks of global warming [1]. Besides the atmosphere, sea oceans are also increasingly exposed to the danger of acidification, having already taken up a third of the CO_2 released into the atmosphere [2]. In order to reduce CO_2 emission from the burning of fuels, application of pre-combustion capture of CO_2 can be adopted, where primary fuels such as natural gas are treated with oxygen to produce mainly hydrogen (H_2) and CO_2 gas mixture. In an IGCC (Integrated Gasification Combined Cycle) power station, the treated gas, consisting of about 40% CO_2 and 60% H_2, will then undergo CO_2 separation process to produce pure H_2 which can be fed to gas turbines for power generation. Various techniques employed for CO_2 separation from fuel gas mixture are absorption, adsorption, membrane separation and cryogenic separation [3–5]. These processes are energy intensive hence there is an ongoing search for new technologies that are less energy intensive and environmentally friendly [3–5]. One such novel and environmental friendly process is the HBGS (hydrate based gas separation) process [6–10].

Understanding the HBGS process requires first the understanding of gas hydrates, also commonly known as clathrate hydrates. Gas hydrates are non-stoichiometric crystalline compounds consisting of nanoscale cage-like structures, which are formed by hydrogen-bonded water molecules [11]. These cages are able to capture and store smaller guest molecules such as CO_2, CH_4, etc. and depending on the size and composition, form mainly three different type of structures namely sI, sII and sH [11]. Gas hydrate formation is a problem to oil and gas industry (flow assurance issues) [11]. Hydrate formation is also considered for several applications of like: CO_2 capture and sequestration [9,10,12]; cold storage [13–16]; gas separation [17–20]; transportation and storage of fuels including hydrogen [21–26]. The concept of HBGS involves formation of hydrate crystals when the treated fuel/flue gas, under suitable conditions in the presence of water. A schematic of the HBGS process for pre-combustion capture is presented in Figure S1 (given in supporting information). Due to a significant difference in hydrate formation pressure between CO_2 and H_2, CO_2 preferentially occupies the hydrate cages compared to H_2. Subsequently, the hydrate can undergo decomposition to obtain a gas that is rich in CO_2 [6]. HBGS process is also applicable for post combustion capture of CO_2 from flue gas mixture. For post combustion capture, CO_2 preferentially occupies the hydrate cages compared to N_2 [6,27–30]. A comprehensive review of the HBGS process for carbon dioxide capture is available in literature [9,10,31].

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Linga et al. [28] evaluated the kinetics of the HBGS process and proposed a two-stage hydrate/membrane process to capture CO_2 from fuel gas in which the first stage operates at 7.5 MPa. The pressure of the typical fuel gas mixture exiting IGCC power plant is in the range of 2.0–7.0 MPa [1]. Therefore it would require compression of the fuel gas mixture before hydrate formation. Compression of the fuel gas mixture would increase the cost of the process. Therefore it is necessary to reduce the operating pressure in the range of 2–7 MPa. In order to reduce the operating pressure, thermodynamic promoters can be employed. Thermodynamic promoters reduce the equilibrium hydrate formation pressure, thereby reducing the operating pressure. The reduction in the equilibrium hydrate formation pressure at any given temperature is due to the fact that the promoter occupy the cages and hence form stable structure at a lower pressure at a given temperature. Several thermodynamic promoters such as propane [32–34], THF (tetrahydrofuran) [35–38], CP (cyclopentane) [39–41], TBANO$_3$ (tetra-n-butyl ammonium nitrate) [42,43] and TBAB (tetra-n-butyl ammonium bromide) [44–49] have been proposed. For example at 277.6 K, minimum pressure required to form hydrate from fuel gas mixture is 9.15 MPa [50] whereas in presence of 5.56 mol% THF, the minimum pressure required for fuel gas mixture to form hydrate is 0.1 MPa at 277.6 K [51]. The use of THF in particular has more advantages than the other promoters due to its ability to completely mix with water and easily achieve hydrate formation conditions (0.1 MPa, 277.6 K) [51].

Hashimoto et al. [36], Lee et al. [37] and Park et al. [38] presented thermodynamic data for the equilibrium conditions of CO_2/H_2 system with 0.5, 1.0, 3.0 and 5.6 mol% THF. The addition of THF significantly reduced the hydrate formation pressure for CO_2 capture. For example, Hashimoto et al. [36] presented that the hydrate formation pressure was reduced from 9.1 to 1.0 MPa with 3.0 mol% THF at 280.1 K. Lee et al. [37] carried out various kinetic experiments (279.6 K, $\Delta P = 0.89$ or 1.87 MPa) at various experimental pressure with 0.5 (Experimental pressures of 4.59 and 5.57 MPa), 1.0 (Experimental pressures of 3.14 and 4.12 MPa) and 3.0 mol% (Experimental pressures of 1.55 and 2.53 MPa) THF and reported 1.0 mol% THF as the optimum concentration for pre-combustion CO_2 capture based on gas uptake (7.66 mmol of gas/mol of water for 1.0 mol% at 279.6 K and 4.12 MPa). Park et al. [38] carried out kinetic studies at 8.0 MPa and ΔT of 4 K (corresponds to $T_{exp} = 283.5$ K for 1.0 mol% THF and $T_{exp} = 287.0$ K for 5.6 mol% THF) with 1.0 and 5.6 mol% THF solution. Park et al. [38] reported very low gas uptake of 3.0 mmol of gas/mol of water for hydrate formation in presence of 1.0 mol% THF solution from fuel gas mixture. They reported that 5.6 mol% THF resulted in higher gas uptake of 20 mmol/mol of water similar to pure water experiments at their experimental condition. It has to be noted that Park et al. [38] presented only one kinetic experimental data for both 1.0 and 5.6 mol% THF solution. The available literature kinetic data for the HBGS process are also at lower experimental pressures or at higher experimental pressure compared to the pre-combustion pressure streams which is typically in the range of 2–7 MPa. Moreover, given the different observations for the kinetics of hydrate formation in literature works done at different experimental conditions and THF concentrations, there is a need for fundamental work to elucidate the effect of experimental conditions and the effect of THF concentration for the HBGS process in a more systematic and comprehensive manner.

Therefore, the objective of this work is to investigate the kinetics of gas hydrate formation from fuel gas mixture to determine the optimal operating conditions and optimal THF concentration. Factors such as induction time (IT), normalized gas uptake, normalized rate of hydrate formation and hydrate composition have been determined and analysed to evaluate the effect of pressure, temperature and THF concentration on hydrate formation kinetics.

2. Experimental

2.1. Materials

THF of 99.99% purity was supplied by Fisher Scientific. Gas cylinder, supplied by SOXAL (Singapore Oxygen Air Liquide Pte Ltd), consisting of 40 mol% CO_2 and 60 mol% H_2 was employed for the experiments.

2.2. Preparation of THF solution

In order to prepare the desired concentration of THF solution, the amount of deionized water required was weighed, with the aid of a weighing machine, and transferred into a 250 ml beaker. After which, the required volume of THF was pipetted into the same beaker. Thorough stirring of the THF solution for about 5 min was conducted to ensure uniform mixing. For various concentrations of THF solution employed in this work, the volume of materials required can be found in Table S1 (given in the supporting information).

2.3. Experimental setup

Detailed illustration of the apparatus and experimental setup for gas uptake measurements is shown in Fig. 1. Mainly, a crystallizer, with internal volume of 150 cm^3 (ID = 5.08 cm) and attached with two circular viewing windows at the front and back side, was immersed in a temperature-controlled bath. A reservoir was connected to the crystallizer to increase the volume of gas available for hydrate formation. The temperature of the bath was controlled by an external refrigerator. In order to measure the temperature of the liquid phase of the THF solution, a T-type omega-constantan thermocouple (0.01 K uncertainty) was connected to the side port of the crystallizer. A pressure transmitter (0.1% uncertainty) and pressure gauge were connected to the crystallizer to measure the pressure. Both the temperature and pressure were recorded using a Data Acquisition (DAQ) system and displayed on a computer. A magnetic stirrer was also used for mixing the contents in the crystallizer.

2.4. Gas uptake measurements

Detailed procedures on gas uptake measurements can be found in the literature [47]. Briefly, for a fresh experiment, 53 ml of the desired concentration of THF solution was injected into the crystallizer and placed in a temperature-controlled bath, where it was cooled to the required experimental temperature. Once the temperature reached steady-state, the crystallizer was flushed 3 times with the fuel gas mixture and then pressurized to the desired experimental pressure. As the temperature and pressure stabilized, the magnetic stirrer was switched on and data was recorded for every 20 s till 2 h after hydrate formation.

After which, the magnetic stirrer was switched off, the pressure of the crystallizer was reduced to atmospheric pressure and the cooling bath was heated to room temperature (297.2 K) for hydrate decomposition to occur. The pressure in the crystallizer increased due to the hydrate dissociation. Samples of this gas mixture were then fed into a GC (gas chromatography) in order to determine the gas composition of the hydrate.

A solution that has previously experienced hydrate formation is generally termed as memory solution [6,43,47]. For a memory experiment, the THF solution was stirred and all gases vented out for 2 h after the end of the fresh experiment. After which, the same