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Enhanced kinetics for the clathrate process in a fixed bed reactor in the presence of liquid promoters for pre-combustion carbon dioxide capture

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ABSTRACT

In this work, we present enhanced kinetics of hydrate formation for the clathrate process in the presence of two liquid promoters namely THF (tetrahydrofuran) and TBAB (tetra-n-butyl ammonium bromide) in a FBR (fixed bed reactor) for pre-combustion capture of CO_2. Silica sand was used as a medium to capture CO_2 from CO_2/H_2 gas mixture by hydrate crystallisation. Experiments were performed at different temperatures (274.2 K and 279.2 K) and 6.0 MPa to determine the total gas uptake, induction time and rate of hydrate formation. The observed trends indicated that higher driving force resulted in higher gas consumption and significantly reduced induction time. For the same driving force, higher gas consumption and shorter induction time was achieved by THF as compared to TBAB. 5.53 mol% THF attained higher gas consumption than 1.0 mol% THF whereas 3.0 mol% TBAB attained lower gas consumption than 0.3 mol% TBAB. A highest gas uptake of 51.95 (±5.183) mmol of gas/mol of water and a highest rate of 51.21(±8.91) mol.min^{-1}.m^{-3} were obtained for 5.53 mol% THF at 6.0 MPa and 279.2 K. Overall, this study indicated better hydrate formation kinetics with the use of THF in an FBR configuration for CO_2 capture from a fuel gas mixture.

1. Introduction

Gas hydrates or clathrate hydrates are ice-like crystalline compounds with water forming cages (water molecules hydrogen-bonded together) to encapsulate the guest molecules such as hydrogen, methane, carbon dioxide, etc. [1–3]. Typically, gas hydrates are non-stoichiometric in nature. In other words, the ratio of guest-to-water molecules (hydration number) can vary based on formation conditions. Gas hydrates can form three well-known structures, each of which have different cage sizes and number of cages that can accommodate different molecules accordingly. Thus, the cages in gas hydrate present potential storage capacity for different types of guest molecules which led to the ongoing research on gas hydrates for natural gas/hydrogen storage and the exploitation of these guest molecules as energy source trapped in the form of natural gas hydrates.

Over the past century, the quantity of CO_2 (carbon dioxide) in the atmosphere has increased tremendously as a result of heavy reliance and usage on fossil fuels. Being a greenhouse gas, CO_2 will enhance the greenhouse effect, worsening the global climate warming situation [4]. Fossil fuel based electric power plants are responsible in contributing one-third of CO_2 emission worldwide. Hence, its disposal is a significant concern worldwide. Without CO_2 capture and storage, the IEA (International Energy Agency) forecasts that the cost of controlling climate change will be 70% more expensive in 2050 [5].

To drive the reduction in carbon dioxide emission, several useful technologies have been proposed with the purpose of capturing carbon dioxide either before or after combustion. One such approach is the development of IGCC (integrated gasification combined cycle) power plant or IG-SOFC (integrated gasification solid oxide fuel cell) for the generation of electricity [6]. Taking the syngas from coal gasification, a process involving WGS (water–gas shift) reaction is applied to concentrate the H_2 content in syngas along with CO_2 production. Prior to combustion, the CO_2 can be then removed by Selexol process, a physical absorption-based separation process or through the use of chemical absorption

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with amines like MDEA (methyl diethanolamine) [6]. Another novel/environmental friendly method for pre-combustion capture of CO_2 is the development of HBGS (hydrate based gas separation) technology [7–9] by employing water as a solvent. HBGS technology is an efficient and cost-effective separation method for CO_2 capture [10–12]. The pre-combustion stream known as fuel gas is a mixture of CO_2/H_2 and is available at elevated pressures (2–7 MPa) making it suitable to apply the HBGS technology. In HBGS process, gas molecules are captured inside the ice-like crystalline cavities formed by water molecules. Since the equilibrium hydrate formation pressure of CO_2 is significantly lower than that of H_2 at a given temperature, CO_2 is preferentially encaged into the hydrate crystal phase, thus separating CO_2 from the CO_2/H_2 gas mixture [7]. In order to form CO_2 hydrates quickly and efficiently, it is necessary to understand the thermodynamics and kinetics of CO_2 hydrate formation and dissociation from fuel gas mixture. A fuel gas mixture (40% CO_2/60% H_2) at 273.7 K would require a pressure of 5.1 MPa to form hydrates [13]. This is a thermodynamic limit and actually a considerably higher pressure from equilibrium is required to create a driving force (over pressure) to form hydrates at a reasonable experimental time and rate. Linga et al. [14] evaluated the kinetics of the hydrate formation from fuel gas mixture and suggested that a minimum operating pressure of 7.5 MPa would be needed to form substantial amount of hydrates (~12.9 mmol of gas/mol of water).

Several studies have been reported to mitigate the hydrate formation conditions so as to increase hydrate formation rate and gas uptake capacity. The use of promoters has been employed to investigate their effect on the thermodynamic equilibrium, process and separation efficiency. Among the water soluble promoters, THF (tetrahydrofuran) [14–22] and TBAB (tetra-n-butyl ammonium bromide) [23–29] are the most extensively tested promoters for the clathrate process for carbon dioxide capture. Lee and his co-workers [16,30,31] reported that the use of THF can significantly shift the hydrate phase equilibrium for a flue gas mixture making it attractive to employ the clathrate process for carbon dioxide capture. Linga et al. [18] reported that the addition of THF greatly reduced the operating pressure and also resulted in a shorter induction time for hydrate formation. However, it was noticed that the hydrate formation rate and gas consumption in a semi-batch stirred vessel for CO_2/N_2 gas mixture reduced significantly with the addition of THF as compared to without the addition of THF. Similar observations of 1.0 mol % THF resulting in lower gas uptake and lower hydrate growth rates for the CO_2/H_2 gas mixture were also observed by Lee et al. [17] and Park et al. [19]. Lee et al. [17] reported a gas uptake of 8.36 mmol of gas/mol of water and Park et al. [19] reported 0.71 mmol of gas/mol of water for 1.0 mol% THF concentration at different experimental conditions. Li and his co-workers investigated the effect of TBAB on the kinetics of CO_2 separation from the CO_2/H_2 gas mixture [27–29]. The group reported that TBAB was capable of shifting the phase equilibrium to lower boundary which presented milder conditions for hydrate formation and the presence of TBAB resulted in shorter induction time for hydrate formation. However, it was also noticed that gas consumption and hydrate growth rate decreased with increase in TBAB concentration. In the presence of 0.29 mol% TBAB, Xu et al. [28] reported a maximum gas uptake of 13.9 mmol of gas/mol of water for the experiment conducted at 3.08 MPa and 274.15 K. However, lower gas uptake capacities were also reported in the literature for the CO_2/H_2 system in the presence of TBAB in a stirred vessel [24,32–34]. The lower gas capacities obtained in the presence of promoters in a stirred vessel was attributed from the substantial formation and agglomeration of gas hydrates at the gas/liquid interface that inhibits further gas dissolution into aqueous liquid phase to form hydrates [34]. In general, promoters are desired for their capability in reducing the operating conditions of gas hydrate formation. Hence, there is also an ongoing effort in search of the best multi-phase reactor for gas hydrate technology.

To accelerate the rate of hydrate formation and to increase the gas uptake capacity, hydrate technology has to be looked into with innovative reactor designs [35,36]. For gas hydrate technology to be successful, there needs to be an improvement of gas/liquid contact to boost hydrate growth significantly thereby increasing the gas uptake capacity as well [35,36]. HBGS technology that uses mechanical agitation is not commercially viable for CO_2 capture since large amounts of power will be required for hydrate crystallisation. It is noted that operating the HBGS technology for CO_2 capture process in a continuous mode would not be a practically and economically viable option due the well-known affinity of hydrate formation in oil and gas pipelines. A continuous operation could result in drastic plug formation in the process flow lines due to hydrate formation at favourable conditions leading to frequent shutdown and stoppage in operations. It is extremely difficult to precisely control the hydrate formation in flow lines at favourable conditions, hence the oil and gas industry has been employing very high concentrations of thermodynamic inhibitors to prevent hydrate formation for flow assurance for the past several decades [1]. In a continuous operation mode, the hydrate content in the liquid flow stream should be kept at low levels to avoid plug formation which then implies that the eventual operating volumes to capture carbon dioxide would be very large.

Recently, the use of porous media in a FBR (fixed bed reactor) has been studied extensively to enhance the kinetics of hydrate formation. Several studies have investigated different types of silica gels as a medium to enhance the kinetics of hydrate formation [8,37–39]. In silica gels, the intra particle (inner particle) pore space is important as the water is dispersed inside the pores. Adeyemo et al. [28] studied the effectiveness of silica gel bed on the separation efficiency of CO_2 from CO_2/H_2 gas mixture through hydrate crystallisation. The amounts of gas uptake and hydrate yield were significantly enhanced in separating CO_2 from gas mixture in the absence of stirring. Besides, the gel pore size was found to relate positively with gas consumption. Similar result with high yield of conversion of water to hydrates was reported earlier by Seo et al. [39] in clathrate hydrate formation in porous silica gels for flue gas separation. Linga et al. [40] investigated the effect of silica sand as a porous media and compared the performance with a stirred tank reactor. Silica sands are finely grained particles of different shapes which can increase the bed porosity via the presence of inter particle space. In silica sand, the water is present in the interstitial particle space. It was reported that the gas uptake was significantly higher in a fixed bed column than stirred tank for several gas/gas mixtures which also consequently resulted a higher percent conversion of water to hydrates [40]. Recently, Linga and his co-workers [9,41] evaluated the use of silica gel and silica sand as medium in a fixed bed column for CO_2 capture through hydrate crystallisation qualitatively and quantitatively with and without propane as an promoter. Silica sand as a medium was reported to result in a higher hydrate growth rate, higher gas uptake capacity and subsequent higher percent water conversion than silica gel, concluding that it was a better medium for separation of CO_2 from a fuel gas mixture in an FBR configuration.

The objective of the present study is to investigate the effectiveness of the two most important water soluble promoters: THF and TBAB in an FBR with silica sand as a porous media for the separation of CO_2 from a typical fuel gas (CO_2/H_2) mixture from an integrated coal gasification cycle through hydrate crystallisation. The effect of driving force on hydrate formation, gas uptake, induction time and conversion of water to hydrates were evaluated.

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