Enhanced carbon dioxide hydrate formation kinetics in a fixed bed reactor filled with metallic packing

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HIGHLIGHTS

- CO_2 capture through clathrate hydrate crystallization in fixed bed setup.
- Gas uptake measurement for CO_2 hydrate formation in four different packing materials.
- Use of anionic surfactant, sodium dodecyl sulfate (SDS) for lower induction time and faster hydrate growth.

ABSTRACT

In this fundamental work, two nonporous metallic (SS-316) mesh arrangements having high thermal conductivity compared to silica sand and silica gel were used as a packing material in a fixed bed setup for faster hydrate growth kinetics. Induction time and kinetics of carbon dioxide hydrate formation was investigated at 3.0 MPa and 274.65 K. An anionic surfactant, 1 wt% sodium dodecyl sulfate (SDS) was used as a kinetic promoter in all the experiments. Significantly higher gas uptake rate of 115 mol min^{-1} m^{-3} and water to hydrate conversion of 50% was achieved in an hour of hydrate formation with metallic packing in the presence of SDS. Amount of CO_2 gas captured per mass/volume of packing material was significantly higher for metallic packing compared to silica sand and silica gel, which is an important parameter for evaluating a hydrate crystallization process using fixed bed.

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1. Introduction

Gas hydrates (clathrate hydrates) are ice-like crystalline compounds formed by the combination of hydrogen bonded water molecules and small guest molecules under high pressure and low temperature (Davidson, 1973; Englezos, 1993; Sloan and Koh, 2008). Naturally occurring methane gas hydrates are considered as a vast source of energy (Collett and Kuuskraa, 1998). Moreover, gas hydrates also have a significant role to play in seawater desalination (Lee et al., 2011; Max and Pellenbarg, 2000), hydrogen storage (Lee et al., 2005; Lu et al., 2012; Veluswamy et al., 2014) and carbon dioxide capture through hydrate formation and decomposition cycle (Duc et al., 2007; Li et al., 2011, 2012).

Schematic of a two stage hydrate based gas separation (HBGS) process using fixed bed reactors has been presented in Fig. 1. Flue gas mixture (15 mol% CO_2 + 85 mol% N_2) from a conventional coal based power station can be considered as a feed gas for CO_2 capture. In the HBGS process, packed bed in the first stage captures most of the CO_2 from the feed gas by preferential enclathration of CO_2 (by hydrate formation). The resulting gas phase which is now a lean mixture of CO_2 can be emitted to the atmosphere. CO_2 rich hydrate phase is decomposed and sent for further CO_2 enrichment in the second stage, where fresh bed is available for capturing more CO_2. After hydrate formation in reactor-2 the CO_2 lean gas phase is emitted to the atmosphere whereas the CO_2 rich phase upon decomposition of hydrate phase is sent for sequestration. It is envisioned that a mature HBGS process will be more like a tray dryer; in a continuous manner fresh batches of tray (packing material soaked in water) would come in contact with the gas phase and preferentially take away CO_2, leaving behind a CO_2 lean mixture suitable for atmospheric emission.

The selective partition of CO_2 between the hydrate and gas phase is the basis for its separation from associated gases. Thus it is imperative that (1) faster hydrate formation rate and (2) maximum water to hydrate conversion is achieved. Hydrate formation is essentially a gas–liquid–solid multiphase reaction and thus higher interfacial area is desirable for better gas–water contact
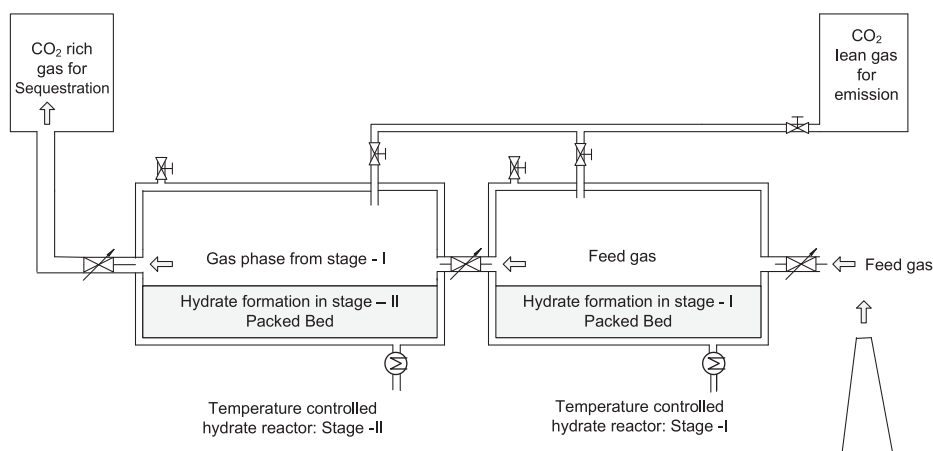
Fig. 1. Schematic of the hydrate based gas separation (HBGS) process in fixed bed arrangement.

to form solid hydrates. Employing a stirred tank reactor results in faster hydrate kinetics; however agglomeration of hydrate crystals on the interface creates a barrier for gas to water contact and thus water to hydrate conversion remains less than 20%. Moreover, it has been shown that stirring cost becomes a significant portion of total process cost, making it a highly energy intensive process (Linga et al., 2010). Thus a fixed bed contact mode having a high surface to volume ratio is ideally suitable; packing material with large intra-pore surface area (silica gel) and large inter-particle surface area (silica sand) has been used in fixed bed arrangement.

Several literature works have been focusing on different porous media like silica gel, silica sand, aluminum foam, polyurethane foam in the recent years to enhance kinetics of hydrate formation employing a fixed bed reactor configuration (Daraboina et al., 2013; Seo and Lee, 2003; Adeyemo et al., 2010; Babu et al., 2013a, 2013b; Kumar et al., 2013; Dicharry et al., 2013; Yang et al., 2011; Fan et al., 2012; Park et al., 2013). Among the porous materials employed in the literature for CO_2 capture studies, silica gel has a gravimetric capacity (weight of water/weight of material) of 0.8–1.0 g/g (Seo and Lee, 2003; Adeyemo et al., 2010; Seo and Kang, 2010; Park et al., 2013), silica sand (Linga et al., 2012; Daraboina et al., 2013; Babu et al., 2013b) has a gravimetric capacity of 0.22 g/g. On a comparative basis, Babu et al. reported that the hydrate formation kinetics is better with silica sand than gel (Babu et al., 2013b). In the silica gel a significant portion of the dispersed water is confined inside intra-particle pore space of the gels, which ultimately does not participate in hydrate formation. Recently Babu et al. has used polyurethane foam having large interconnected channels as a packing material, which showed significantly improved hydrate formation kinetics compared to silica gel and silica sand (Babu et al., 2013a).

It has been shown that hydrate formation rate and water to hydrate conversion can also be increased by using a small percentage of an anionic surfactant SDS as an additive (Kumar et al., 2013; Watanabe et al., 2005; Yoslim et al., 2010; Zhong and Rogers, 2000; Karaaslan and Parlaktuna, 2002). It is assumed that the presence of surfactant molecule reduces the surface tension and helps in better water to gas contact by enhancing the gas diffusion rate to the hydrate nucleating sites. Capillarity driven supply of the water into the porous hydrate layers in the presence of surfactant molecules has been reported by visual observation (Gayet et al., 2005; Okutani et al., 2008). Thus, the use of kinetics promoters (SDS) and porous fixed bed media enhances the rate of hydrate formation.

In this fundamental work, we chose to evaluate two metallic packing in order to evaluate the kinetics of CO_2 hydrate formation kinetics. Pure CO_2 was chosen for this work as most of the gas

hydrate formation applications in the literature have been for CO_2 containing systems pertaining to CO_2 capture, and separation from CO_2/CH_4, coal mine gas, land fill gas, etc. For exothermic hydrate crystallization, better growth kinetics can be achieved by efficient removal of localized heat from the crystallizer, thus a metallic packing with high thermal conductivity should be ideal. Yang et al. have used aluminum foam (AF, average pore size of 1000 μm) as a medium to study the kinetics of methane hydrate formation. It was observed that AF not only reduces the induction time but also enhances the formation and growth significantly (Yang et al., 2011). Out of the two packings used for this work, one resembles a random packing (SS-316 fillings, SSP-1) and the other, structured packing (SS-316 wire mesh, SSP-2), photographs of the packing materials are included in the supplementary information as Figs. S1 and S2. SS-316 has a density of ∼8000 kg/m³ which is approximately 4-times higher than the silica sand density (1560 kg/m³) (Dawson, 2004; Jones and Schoonover, 2002). Thus a very dense metallic packing might unnecessarily increase the column weight resulting in lesser CO_2 capture capacity per unit mass. In this work CO_2 capture capacity under similar experimental condition for CO_2 consumption per unit mass of water, per unit mass of material (combined mass of packing and water) and per unit volume of material (combined volume occupied by the packing and the water) were done and its performance is compared. As explained earlier, to enhance the rate of hydrate formation a kinetic promoter (1 wt% SDS) was also used in all the experiments. 1 wt% SDS–water solution was optimum SDS concentration to achieve maximum water to hydrate conversion rate and ratio. Fig. S3 (supplementary information) shows the comparison of hydrate growth rate at three different SDS concentrations (0.1%, 0.5% and 1.0% by weight) in the presence of silica sand packing.

2. Experimental section

2.1. Materials

Carbon dioxide gas with a certified purity of more than 99.9% was supplied by Vadilal Gases Ltd., India. Silica sand was purchased from Sakalchand & Company Pune, India. The particle size distribution of silica sand is in the range of 30–400 μm. The volume of the water required to completely fill the void space between the sand particles was ∼0.20 cm³/g. Silica gel with the pore diameter of ∼5 nm, particle size distribution 40–65 μm and pore volume of 0.92 cm³/g with 99% purity (LR grade) was purchased from Rankem Ltd. Surfactant, SDS (SQ Grade) with minimum 98% purity were purchased from Fisher Scientific Ltd. India. SSP-1 is a SS-316 filling fabricated on request at the