Energy 63 (2013) 252–259

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

HBGS (hydrate based gas separation) process for carbon dioxide capture employing an unstirred reactor with cyclopentane

Leong Chuan Ho [a,1], Ponnivalavan Babu [a,1], Rajnish Kumar [b], Praveen Linga [a,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117 576, Singapore
[b] Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune, India

ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form
24 August 2013
Accepted 11 October 2013
Available online 9 November 2013

Keywords:
Gas hydrates
Gas separation
Pre-combustion
Cyclopentane
Carbon dioxide capture
Unstirred reactor

ABSTRACT

The effect of CP (cyclopentane) as a promoter/additive, in the HBGS (hydrate based gas separation) process for pre-combustion gas mixture was investigated by employing an unstirred reactor configuration. Gas uptake measurements were performed at two different temperatures (275.7 K and 285.7 K) and at an experimental pressure of 6.0 MPa to determine the kinetics of hydrate formation. Experiments were conducted with three different volumes (7.5, 15 and 22 ml) of CP and based on induction time and the rate of hydrate growth, 15 ml of CP was determined to be the optimal volume for carbon dioxide capture at 6.0 MPa and 275.7 K. In addition, the effect of a kinetic promoter, SDS (sodium dodecyl sulfate), was investigated. Surprisingly, no improvement in kinetic performance was observed at 6.0 MPa and 275.7 K in the presence of SDS and CP. From the study, it was found that at the optimal 15 ml CP (CP layer thickness of 1.8 mm), the average composition of carbon dioxide in the hydrate phase was 90.36 mol% with a separation factor of 17.82. Furthermore, the unstirred reactor also yielded better kinetic performance over the stirred tank reactor with the unstirred reactor having a 2.28 times higher average gas uptake.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Increasing emissions of greenhouse gases, like carbon dioxide, have been established as a cause for global warming, and there is therefore a need to research into the technologies behind carbon dioxide capture. With reference to a report by the IPCC (Intergovernmental Panel on Climate Changes) [1], there exist three main types of carbon dioxide capture from point sources, post-combustion capture, pre-combustion capture, and oxy-fuel combustion. Both post-combustion capture and oxy-fuel combustion involve the capture of carbon dioxide from flue gases but with key differences in the combustion process. In post-combustion capture, the flue gas produced is a result of combustion between fuel and air while in oxy-fuel combustion; oxygen with high purity is used in place of air. This result in the carbon dioxide concentration in oxy-fuel combustion to be significantly higher than in post-combustion capture (>80 vol% in oxy-fuel combustion compared to 3 vol%–15 vol% carbon dioxide in post-combustion capture). As the focus of this paper will be on the pre-combustion capture of carbon dioxide, the process behind post-combustion capture and oxy-fuel combustion will not be further detailed.

In pre-combustion, fossil fuels are partially oxidized, resulting in the formation of "synthesis gas" (syngas), which consists of a mixture of carbon monoxide and hydrogen. The syngas then undergoes a water–gas shift reaction with steam to yield a carbon dioxide–hydrogen gas mixture, which is called as "Fuel gas" mixture. Carbon dioxide can then be captured while hydrogen can be used as the fuel for combustion. The presence of a relatively pure emission stream with hydrogen as the output is one of the key advantage of pre-combustion capture as the combustion process of hydrogen is carbon-free and will not contribute to the emission of greenhouse gases. Furthermore, the above processes produce gases at high pressure that will be favorable for separation processes.

There exists a myriad of options available for carbon dioxide capture [1–5] and the focus of this paper will be on HBGS (hydrate based gas separation) process. Gas hydrates, also known as clathrate hydrates, are non-stoichiometric crystalline structures made up of water and gas molecules. Water molecules act as a "cage" with hydrogen bonds between the molecules while gas molecules are held within it. Gas hydrate formation is an exothermic process and it occurs above a specific temperature and pressure that are a function of the type of gas involved, and the amount of gas and water used. With the better understanding of gas hydrate

---

[*] Corresponding author. Tel.: +65 6601 1487; fax: +65 6779 1936.
E-mail addresses: chepl@nus.edu.sg, praveen.linga@nus.edu.sg (P. Linga).

[1] Both authors equally contributed to the work.

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.10.031

formation over the years, there has been a growing interest in the research of gas hydrate due to the large potential across many applications. Some of the possible applications include the use of gas hydrate for transportation of natural gas/hydrogen [6–11], a source of energy [12–18], and as a technology for carbon dioxide capture, storage/sequestration [19–24].

The equilibrium condition for hydrate formation is a function of the type of gas involved. At 280 K, the dissociation pressure of hydrogen gas is 300 MPa while the dissociation pressure of carbon dioxide is 2.91 MPa [25,26]. As such, the use of gas hydrate separation as a means to capture carbon dioxide from pre-combustion gas mixture is promising as carbon dioxide gas will be preferably held in the water molecules "cage" at lower pressures [19,27,28]. Linga et al. [19] proposed a two stage HBGS process for capturing carbon dioxide from a pre-combustion fuel gas mixture consisting of 40% CO_2 and rest H_2 with the first stage requiring an operating pressure of 7.5 MPa at 273.65 K. As the equilibrium pressure for this gas mixture at 273.65 is 5.1 MPa [29], a higher operating pressure provides the necessary driving force for gas hydrate formation to occur at an appreciable rate, which also results in an increase in compression costs for the HBGS process. There is therefore an ongoing effort to search for additives that can lower the equilibrium conditions required for gas hydrates.

In an attempt to lower the operating pressure required for the HBGS process, the use of additives has been investigated by several researchers by employing a STR (stirred tank reactor) [30–34]. In a two-stage medium pressure hydrate process, Kumar et al. [30] investigated the use of 2.5 mol% propane as an additive and reported a significantly lower rate of hydrate formation and total moles of gas consumed. As for the study on THF (tetrahydrofuran) by Lee et al. [31], it also yielded similar observations with 1.0 mol% THF reported as the optimal concentration. Kim et al. [35] and Li et al. [32] investigated the use of TBAB (tetra-n-butyl ammonium bromide) and the total number of moles of gas consumed on a water free basis was lower compared to the THF experiments. From the above investigations, it can be noted that in general, the use of additives in the stirred tank reactor (STR) resulted in a lower rate of hydrate formation and lower gas consumption when using the clathrate process. Furthermore, it has also been established that the use of stirred tank reactor leads to an agglomeration of hydrate crystals, creating a barrier at the gas/liquid interface [22,36,37].

There is therefore a need to identify innovative reactor designs in place of STR. One possible configuration was proposed by Linga et al. [22] where a modular, mechanically agitated gas-inducing crystallizer was used for both post- and pre-combustion carbon dioxide capture. However, even though the gas uptake and separation efficiency were higher than a STR, they reported that the cost involved due to the mechanical agitation was significant and hence prohibited industrial adoption. Other ways proposed to enhance the performance of hydrate formation include the use of a fixed bed reactor with silica gel or silica sand as a medium [38–40], a fluidized bed reactor by employing a slurry bed or a gas bubble column [41–43] or using an unstirred reactor configuration [44,45].

One of the possible approaches to overcome the above limitations (higher operating pressure and effective gas–liquid contact) is the use of CP (cyclopentane), as a promoter. CP has been identified as a possible candidate in the literature [26,33,45–48] and has been shown to lower the equilibrium pressure and temperature required for hydrate formation. Furthermore, CP can be used in an unstirred reactor configuration [45], which is also associated with an additional cost advantage in the practical implementation of the HBGS process as highlighted by Linga et al. [22]. Zhang et al. [45] reported faster kinetics for pure CO_2 hydrates in an unstirred reactor configuration. Li et al. [33] investigated the CO_2 separation efficiencies of a fuel gas stream with CP in a stirred tank reactor and reported a highest gas uptake of 0.003 mol of gas/mole of water for the 36.0 ml CP at 4.5 MPa and 273.15 K. Recently, Lim et al. [48] investigated the morphology of CO_2/H_2/CP mixed hydrates and presented the mechanism of hydrate formation in quiescent conditions. They proposed that for experiments with a CP layer thickness of 1.8 mm, the gas diffuses into the CP layer and reaches the water layer and nucleation begins at the CP–water interface, hydrates then begin to grow upward and radially inward towards the center of the reactor. The formation of hydrate layer then further resulted in a faster rate of gas consumption for hydrate formation.

The objective of this paper is to evaluate the macroscopic kinetics of cyclopentane (CP) as a promoter for effective separation of CO_2 from CO_2/H_2 mixture at moderate pressures in an unstirred reactor configuration. Effect of the use of CP with SDS (sodium dodecyl sulfate), a kinetic promoter, is also investigated with varying temperature as a driving force for both sets of experiments. Finally, the kinetic comparison between STR and unstirred reactor is also presented.

2. Experimental

2.1. Materials

A 40 mol% CO_2/60 mol% H_2 gas mixture, provided by Soxal Pte., Ltd., was used in the experiment. Cyclopentane with purity 99.98% and SDS with purity 99% were supplied by Alfa Aesar and Amresco respectively. Distilled and deionized water was used in all experiments.

2.2. Apparatus

2.2.1. Unstirred reactor

The apparatus for the hydrate kinetic experiments has been described elsewhere in the literature [40]. The adapted schematic of the experimental setup is shown in Fig. 1. Briefly, the setup consists of a crystallizer immersed in a temperature controlled water bath coupled with an external refrigerator. Thermocouples with uncertainty of 0.1 K are used to measure the temperature of the gas phase and liquid phase in the crystallizer. Pressure transmitter and pressure gauge are employed to measure the pressure of the crystallizer. The temperature and pressure data are recorded using a data acquisition system coupled with a computer. Hydrate formation experiments are carried out in a batch manner (constant volume) at a constant temperature.

2.2.2. Stirred tank reactor (STR)

Detailed description of stirred tank reactor (STR) is available in our previous work [49]. Briefly, the setup consists of a crystallizer with a pair of circular sapphire glass viewing windows at the side of the reactor to observe the hydrate formation process. The in-built cooling arrangement in the crystallizer is connected to an external refrigerator to create a temperature-controlled environment. A thermocouple with uncertainty of 0.1 K is located at the fixed head of the crystallizer to measure the temperature of the liquid phase in the crystallizer. Pressure transmitter and pressure gauge are employed to measure the pressure of the crystallizer. A mechanical stirrer connected to a controller is also employed to control the stirring speed (rpm). The temperature and pressure data are recorded using a data acquisition system coupled with a computer. Hydrate formation experiments are carried out in a batch manner (constant volume) at a constant temperature.

2.3. Procedures

2.3.1. Preparation of SDS solution

SDS is a white powdered solid at room temperature and pressure. To prepare the SDS solution, the required amount of SDS (0.1,

Download English Version:

https://daneshyari.com/en/article/8078980

Download Persian Version:

https://daneshyari.com/article/8078980

Daneshyari.com