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Separation and capture of carbon dioxide from CO_2/H_2 syngas mixture using semi-clathrate hydrates

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ABSTRACT

The relation between anthropogenic emissions of CO_2 and its increased levels in the atmosphere with global warming and climate change has been well established and accepted. Major portion of carbon dioxide released to the atmosphere, originates from combustion of fossil fuels. Integrated gasification combined cycle (IGCC) offers a promising fossil fuel technology considered as a clean coal-based process for power generation particularly if accompanied by precombustion capture. The latter includes separation of carbon dioxide from a synthesis gas mixture containing 40 mol% CO_2 and 60 mol% H_2.

A novel approach for capturing CO_2 from the above gas mixture is to use gas hydrate formation. This process is based on selective partition of CO_2 between hydrate phase and gas phase and has already been studied with promising results. However high-pressure requirement for hydrate formation is a major problem.

We have used semiclathrate formation from tetrabutylammonium bromide (TBAB) to experimentally investigate CO_2 capture from a mixture containing 40.2 mol% of CO_2 and 59.8 mol% of H_2. The results shows that in one stage of gas hydrate formation and dissociation, CO_2 can be enriched from 40 mol% to 86 mol% while the concentration of CO_2 in equilibrium gas phase is reduced to 18%. While separation efficiency of processes based on hydrates and semi-clathrates are comparable, the presence of TBAB improves the operating conditions significantly. Furthermore, CO_2 concentration could be increased to 96 mol% by separating CO_2 in two stages.

Keywords: Gas hydrates; TBAB; Gas separation; CO_2 capture; Hydrogen

1. Introduction

It is now widely accepted that anthropogenic CO_2 emissions from burning of fossil fuels are largely responsible for the rapid rise in global temperatures recorded over the past century. Worldwide concerns over the threat of global warming have led industrialised countries to agree to reduce carbon emissions. In order to meet this goal, the research communities are trying to develop new solutions for reducing CO_2 (and other greenhouse gas) emissions from existing and new fossil fuel usage.

Integrated gasification combined cycle (IGCC) is rapidly emerging as one of the most promising technologies in power generation, hydrocarbons (gas, coal and oil) are broken down to yield a high value natural gas type fuel also called synthesis gas (Barchas and Davis, 1992). This synthesis gas can be converted (by a shift reaction) into a mixture of CO_2 and H_2. A typical synthesis gas from an IGCC power station consists approximately of a 40 mol% CO_2 and 60 mol% H_2 mixture at a total pressure of 2.5–5 MPa (Klara and Srivastava, 2002). The separation of carbon dioxide from this mixture, also called "pre-combustion capture", is an essential element of these processes. The resultant stream of H_2 could be used in fuel cells or in a gas turbine and the carbon dioxide could be geologically sequestered. There is an ongoing effort to reduce operating cost of an IGCC plant, particularly for CO_2 capture.

A novel method for CO_2 capture and storage is to use gas hydrates (Spencer, 1997; Aaron and Tsouris, 2005; Linga et al., 2007a; Kumar et al., 2009; Zhang et al., 2009). The basis for the separation is the selective partition of CO_2 between the hydrate phase and the gaseous phase. The kinetics of hydrate formation in the system CO_2/H_2–water was studied by Linga et al. at 273.7 K and 7.5 MPa (Linga et al., 2007a). However, the 7.5 MPa operating pressure was higher than the typical pres-

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sure of the fuel gas. There is an ongoing interest in using additives to reduce the operating pressure. Several additives have been used for this purpose including tetrahydrofuran, hereafter THF (Lee et al., 2009), propane (Kumar et al., 2009), cyclopentane (Zhang et al., 2009).

Recently, tetra-n-butyl ammonium bromide (TBAB) has attracted significant attention as a suitable additive for different hydrate applications such as hydrogen storage (Chapoy et al., 2007; Struzhkin et al., 2007; Tohidi et al., Int. patent, 2006), air conditioning (Darbouret et al., 2005; Delahaye et al., 2008; Daitoku and Utaka, 2009) and CO_2 capture (Kang and Lee, 2000; Klara and Srivastava, 2002; Aaron and Tsouris, 2005). This is due to the fact that small gas molecules (CH_4, CO_2) could be encaged into the dodecahedral cavities (S-cage, 5^{12}) of TBAB hydrate at favourable pressure and temperature conditions (Shimada et al., 2005; Arjmandi et al., 2007). TBAB forms semi-clathrates that could offer greater benefits for CO_2(H_2 separation: operating pressures could be lowered significantly and therefore less cooling being required for hydrate formation.

TBAB forms semi-clathrate hydrates with water at ambient conditions, i.e. at 1 atm and 12 °C (Jeffrey and McMullan, 1967; Dyadin and Udachin, 1984; Oyama et al., 2005). If a gas or mixture of gases is associated with these hydrates, the thermodynamic stability of the mixture becomes even more favourable (Hashimoto et al., 2006; Arjmandi et al., 2007; Li et al., 2007). Li et al. measured the dissociation conditions for the system CO_2/H_2–TBAB–water for a 39.2% CO_2 and 60.8% H_2 gas mixture with different concentrations of TBAB (Li et al., 2009). They found that with the addition of 5 wt% TBAB, the equilibrium hydrate formation pressure for the typical gas mixture reduces from 11.01 MPa at 278.75 in the case of pure water to 0.85 MPa at the same temperature which shows an approximate reduction of 92.3% in the equilibrium pressure. However, no data were given by Li et al. on the separation efficiency and gas compositions after hydrate formation.

In this study, we have used TBAB to investigate the capture efficiency of CO_2 from CO_2/H_2 mixture and the kinetics of gas uptake by semi-clathrates formed in the systems CO_2/H_2–TBAB–water for TBAB concentrations of 5% and 10% in aqueous solutions. The results have been compared with systems in which other additives have been used.

2. Experimental

2.1. Materials

Tetra-n-butylammonium bromide, 50 weight percent in water, was purchased from Aldrich. Deionised water was used to dilute the tetrabutylammonium bromide solution to different desired mass fractions in the experiments. Hydrogen was purchased from BOC gases with a certified purity greater than 99.995 vol.%. Carbon dioxide (>99.9% purity) was purchased from Air Product Ltd.

2.2. Apparatus

The setup used in this work, is shown in Fig. 1 The equilibrium cell has an inner volume of 527 ml and a maximum working pressure of 40 MPa and is hosted in a cooling jacket. The cell temperature is measured by means of platinum resistance thermometer, PRT within a precision of ±0.01 K. The pressure is measured by a DRUCK pressure transducer within a precision of ±0.008 MPa for the complete operating range of 0–138 MPa. The cell temperature is controlled by a programmable cryostat, which can be kept stable to within ±0.02 K. The stirrer is used to agitate the test fluids. A Varian CP-3800 gas chromatograph (GC) equipped with a thermal conductivity detector, TCD was used to determine the composition of the gas samples. The temperature and pressure are continuously monitored and recorded by a computer. The piston vessel containing the gas mixture is connected to the cell while a pump is used to keep the pressure constant.

2.3. Procedures

In a typical separation experiment, the cell was first vacuumed and a known amount of TBAB aqueous solution (5 wt% or 10 wt%) was then loaded into the cell to occupy 50% of its volume. A certain amount of the CO_2/H_2 gas mixture was injected to reach the desired pressure. A piston vessel was kept connected to the cell to maintain the pressure by injecting water to the bottom of piston vessel with a high-precision Quizix pump. The number of moles of gas in the cell and the vessel can be determined and controlled by the amount of fluid injected behind the piston. During the experiment, temperature and pressure in the system were recorded. The stirrer was started to operate with the speed of 600–700 rpm. The cap gas was sampled and compositionally analyzed by GC in order to determine the amount of gas dissolved in the liquid at equilibrium before hydrate formation.

When loaded and equilibrated, the cell temperature was lowered until clathrate formation began. This was confirmed by a rapid rise in the cell temperature as well as an increase of the rate of fluid injection. When there was no further clathrate formation and the injection of pump fluid was stopped, the gas in equilibrium with hydrates was sampled and analyzed by GC in order to determine its composition. The residual gas was rapidly vented to the atmosphere and hydrates were dissociated by increasing the temperature of the cell. The gas released from hydrates (including the dissolved gas) was collected, sampled and analyzed by GC, thus giving the composition of the gas in hydrate.

3. Results and discussion

The separation tests were carried out with 5 wt% and 10 wt% TBAB aqueous solutions and volumetric calculations were performed for each concentration. The number of moles of gas consumed at any time during hydrate formation (Δn_H) can be calculated by the following equation:

$$\Delta n_H = n_{G,0} - n_{G,t} = \left(\frac{PV}{zRT}\right)_{G,0} - \left(\frac{PV}{zRT}\right)_{G,t} \quad (1)$$

where $n_{G,0}$ and $n_{G,t}$ are the number of moles of free gas in the cell before and after hydrate formation, respectively. P, T, V, z, and R are the system pressure (constant in these experiments), the system temperature, the volume of the cell occupied by free gas, the gas compressibility factor and the universal gas constant, respectively. Figs. 2 and 3 show the changes in temperature and moles of gas consumed during hydrate formation in 5 and 10 wt% TBAB aqueous solutions, respectively. The pressure is maintained constant at 3.8 MPa during the process. The trend of gas consumption was similar in both cases. Initially there is a short period of slow gas uptake which could be mainly due to the reduction in the system tem-