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Continuous separation of CO$_2$ from a H$_2$ + CO$_2$ gas mixture using clathrate hydrate

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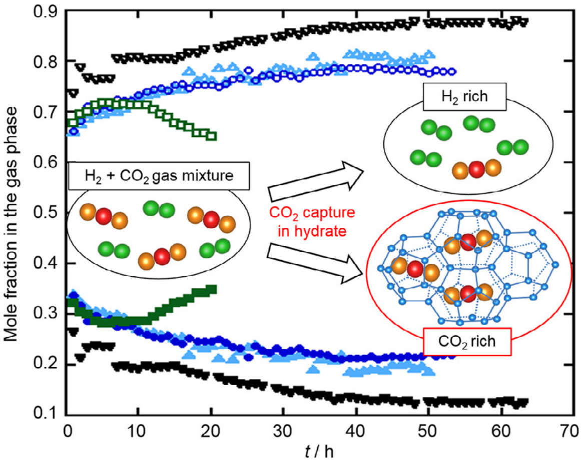
HIGHLIGHTS

- Hydrate-based continuous fuel gas purification experiments.
- Uses tetra-*n*-butylammonium bromide to moderate the process pressure.
- Investigates the H$_2$ and CO$_2$ concentrations in the gas phase and hydrate slurry.
- CO$_2$ mole fraction was increased up to 1.0 only in a single stage.
- Split fraction of CO$_2$ was comparable to or greater than that by batch process.

GRAPHICAL ABSTRACT



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ABSTRACT

CO$_2$ capture using clathrate hydrates is an environmentally friendly separation technology. When considering operational efficiency, it is desirable to operate the separation process continuously. In this experimental study, the continuous separation of CO$_2$ from a model fuel gas was performed for H$_2$ + CO$_2$ + H$_2$O and H$_2$ + CO$_2$ + tetra-*n*-butylammonium bromide (TBAB) + H$_2$O systems with TBAB mass fractions of $w_{\mathrm{TBAB}} = 0$, 0.05, 0.10, and 0.32. Measurements were taken to track the time evolution of compositions of the gas phase and hydrate slurry. After between 37 and 48 h from the start of the experiment, H$_2$ compositions in the gas phase reached steady state values of 0.87, 0.81, and 0.78 for w_{TBAB} values of 0, 0.05, and 0.10, respectively. For the same conditions, CO$_2$ compositions in the hydrate slurry reached steady state values of 1.00, 0.82, and 0.79, respectively. In carrying out this work we have shown that it is possible to successfully separate CO$_2$ using structure I hydrates and ionic semiclathrate hydrates, on a continuous basis. There is the caveat, however, that for $w_{\mathrm{TBAB}} = 0.32$ a continuous separation process is not possible. The split fraction of CO$_2$ we attained were 0.76, 0.64, and 0.62 for w_{TBAB} values of 0, 0.05, and 0.10, respectively. The water system ($w_{\mathrm{TBAB}} = 0$) exhibited the highest H$_2$ compositions in the gas phase, highest CO$_2$ compositions in the hydrate slurry, and highest split fraction of CO$_2$. Although short-term operation, specifically 18 h, is possible with $w_{\mathrm{TBAB}} = 0$, continuous hydrate

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formation cannot be implemented. The concentration of captured CO_2 for $w_{TBAB} = 0$ was comparable to that obtained from hydrate-based gas separation in multistage processes or chemical absorption.

1. Introduction

Worldwide energy consumption has increased since the industrial revolution and it is expected that global energy demand will increase by 30 percent by 2040 [1]. Because fossil fuels are forecasted to continue to be a bedrock of the global energy system for many decades to come [1], the reduction of CO_2 emissions from the burning of fossil fuels has been and will continue to be a significant challenge. One approach to reducing CO_2 emissions is to capture CO_2 prior to combustion in power plants. This approach is called "pre-combustion" capture.

Pre-combustion capture is mainly applied in an integrated gasification combined cycle (IGCC) which is emerging as one of the most promising technologies for power generation [2–5]. A typical fuel gas produced after gasification and shift reaction processes in an IGCC consists of CO_2 and H_2 (H_2: CO_2 = 0.6: 0.4 in mole fraction) at a total pressure of 3.0–7.0 MPa. This gas mixture is typically then treated through a CO_2 capture process. Of the traditional CO_2 separation methods, there are several technologies, such as chemical absorption [6,7] and membrane separation [8,9]. However, chemical absorbents are toxic and corrosive to metals, while membrane separation requires frequent maintenance due to clogging of the membrane.

Hydrate-based gas separation is one of the emerging technologies for CO_2 capture and storage [10,11]. Clathrate hydrates are crystalline compounds consisting of host water molecules which are hydrogen-bonded to form cages that encapsulate different guest molecules [12]. The basis for hydrate-based gas separation is guest compound selectivity which is one of unique properties of hydrates. CO_2 and H_2 molecules are separated into hydrate and gas phases by preferential uptake of CO_2 molecules into the hydrate from the $H_2 + CO_2$ gas mixture.

In previous studies, it has been shown that hydrate-based gas separation is a technology with a great amount of potential [13–20]. Linga et al. [13] performed CO_2 separation experiments for H_2/CO_2 gas mixtures in a semi-batch stirred vessel at 7.5, 8.5 MPa and 273.7 K. CO_2 was preferentially captured into the hydrate phase. However, such a high operating pressure would require large amounts of energy due to compression work. Several studies using additional guests have been performed to reduce the operating pressure from an economic viewpoint. It is known that ionic semiclathrate hydrate forms in the $H_2 + CO_2$ + tetra-*n*-butylammonium bromide (TBAB) + H_2O system. Kumar et al. [14] and Kim et al. [15] measured phase equilibrium conditions for this system and for that of the $H_2 + CO_2$ hydrate system. From their results, it was found that an aqueous solution with a 0.08 mass fraction of TBAB moderates the phase equilibrium pressure from 5.4 MPa down to 0.6 MPa, for a temperature of 280 K and a feed gas phase composition of H_2:CO_2 = 0.6:0.4. Experimental works using TBAB to separate CO_2 from H_2 and CO_2 gas mixtures have been performed at various conditions. These studies have examined the effect of pressure, temperature, and TBAB concentration [15–19]. Table 1 summarizes these results. Li et al. [16] obtained a CO_2 composition of the gas component in the hydrate phase of 0.97 mol fraction and a CO_2 recovery ratio of 0.67, with a 0.05 TBAB mass fraction, at 278.15 K and 3.0 MPa. Babu et al. [17] reported that the 0.05 mass fraction TBAB solution exhibited a maximum gas uptake of 0.0104 mol of gas/mol of water and a maximum CO_2 composition in hydrate phase of 0.95 mol fraction. As mentioned above, these experiments have examined separation efficiency by measuring gas uptake, compositions of CO_2 in the hydrate phase and CO_2 recovery. From these results, it is clear that it is possible to separate CO_2 from fuel gas without the need for chemical absorbents nor membranes.

All the above-mentioned studies were performed using batch type or semi-batch type separation methods. In the batch type operations, two or more sets of reactors are required for the continuous production of purified gas because the gas phase cannot be concurrently taken out of the hydrate-forming reactor. In the continuous operations, the hydrate formation and discharge of the gas phase are performed simultaneously using a single set of reactors for hydrate formation, transportation and decomposition. Thus, the capital investment for plant construction and operational cost can be reduced with continuous operations when compared to those using batch operations. The compositions of the gas component in gas, liquid and hydrate phases would continuously change during hydrate formation. For engineering applications, it is important to investigate the variation with time of these compositions. Kondo et al. [21] were the first to succeed in achieving continuous hydrate formation in their experimental work with a modeled natural gas. They reported gas phase composition changes over 50 h of operation. Akatsu et al. [22] presented a computational scheme for the thermodynamic simulation of continuous multistage separation. They applied this scheme to model the removal of CO_2 and H_2S from low quality natural gas and gave predictions for the simultaneous changes in chemical compositions of gas, liquid and hydrate phases at each stage of a multistage separation process. The validity of these thermodynamic simulations for continuous separation was confirmed experimentally by Tomita et al. [23]. They performed experiments and thermodynamic simulations for continuous gas separation from a model of unconventional natural gases, $CH_4 + CO_2$ gas mixtures. They investigated the time evolutions of compositions in the gas phase and hydrate slurry until they reached steady state values. This experimental work showed that it is possible to continuously separate CO_2. However, continuous CO_2 separation using ionic guest compounds, such as TBAB, has, thus far, not been reported in the literature.

Muromachi et al. revealed the crystal structure of TBAB + CO_2

Table 1
Summary of experimental conditions and results of previous studies.

Authors	Feed gas composition by mole fraction	Experimental method	Experimental condition			Results		Ref.
			Temperature/K	Pressure/MPa	TBAB mass fraction	CO_2 concentration in the hydrate phase	CO_2 recovery ratio[a]	
Kim et al.	H_2/CO_2 = 0.6/0.4	Semi-batch	280.15	3.0	0.15	0.89	0.24	[15]
Li et al.		Semi-batch	278.15	3.0	0.05	0.97	0.67	[16]
Babu et al.		Batch	279.2	6.0	0.05	0.95	–	[17]
Gholinezhad et al.		Semi-batch	273.9	3.8	0.10	0.86	0.47	[18]
Park et al.		Semi-batch	(ΔT_{sub}[b] = 4.0 K)	8.0	0.10	0.95	–	[19]

[a] CO_2 recovery ratio from feed gas or split fraction [13].

[b] Temperature difference between equilibrium and experimental temperatures.