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Hydrate-based pre-combustion carbon dioxide capture process in the system with tetra-n-butyl ammonium bromide solution in the presence of cyclopentane

Xiao-Sen Li [a,b,*], Chun-Gang Xu [a,b,c], Zhao-Yang Chen [a,b], Hui-Jie Wu [a,b]

[a] Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China
[b] Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, PR China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100083, PR China

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ABSTRACT

Effects of 0.29 mol% tetra-n-butyl ammonium bromide (TBAB) solution in conjunction with cyclopentane (CP) on the hydrate-based pre-combustion CO_2 capture are investigated by the measurements of the gas uptakes, CO_2 separation efficiencies and induction time of the hydrate formation at the different temperature–pressure conditions. The results show that the volume of the TBAB has an effect on the CO_2 separation and the induction time, and the addition of the CP into the TBAB solution remarkably enhances the CO_2 separation and shortens the induction time. The system with the CP/TBAB solution volume ratio of 5 vol% and TBAB solution/reactor effective volume ratio of 0.54 is optimum to obtain the largest gas uptake and the highest CO_2 separation efficiency at 274.65 K and 4.0 MPa. Compared to the results with tetrahydrofuran (THF) as an additive [1], the gas uptake is enhanced by at least 2 times and the induction time is shortened at least 10 times at the similar temperature–pressure condition. In addition, the CO_2 concentration in the decomposed gas from the hydrate slurry phase reaches approximately 93 mol% after the first-stage separation at 274.65 K and 2.5 MPa. The gas uptakes of more than 80 mol% are obtained after 400 s at the temperature range of 274.65–277.65 K and the pressure range of 2.5–4.5 MPa.

1. Introduction

Carbon dioxide discharged from the burning of fossil fuels has been identified as the main contributor to the greenhouse gases and the global warming [2]. Among all the CO_2 emissions worldwide, about one third of CO_2 emissions come from fossil fuel electric power plants [3]. In order to deal with the challenge of the global warming, the technique of CO_2 sequestration (capture and storage) has been developing. The current main techniques for the CO_2 capture include physical adsorption, chemical adsorption, cryogenic fractionation and membrane process. However, these techniques have their individual issues of either high cost, large energy consumption, low capacity or high corrosion [4]. Therefore, for the purpose of utilizing fossil fuels in the power plants continuously, it is necessary to develop the new technologies to capture CO_2 efficiently and cost-effectively.

A novel method for separating CO_2 is via the gas hydrate crystallization [4–7]. The basis for the separation is the selective partition of the CO_2 component between the hydrate phase and the gaseous phase. Spencer et al. [8] gave an economic assessment that the cost of the hydrate technique for CO_2 separation from IGCC (Integrated gasification combined cycle) power plant was approximately 10 U.S. dollars per ton of CO_2, which is much lower than that of other methods. Hence, the hydrate separation technique is promising for separating CO_2 from IGCC syngas.

Linga et al. [1] studied on the hydrate kinetics of CO_2/H_2 mixture in pure water system. They found that the induction time is 9.7 min and the hydrate formation rate is 0.0048 mol/min for the first 5 min for $CO_2/H_2/H_2O$ system at 273.7 K and 7.5 MPa. Especially, the operating pressure of 7.5 MPa was higher than the outlet pressure of the fuel gas. Hence, there is a continuous interest in using the additives to shorten the induction time, accelerate the formation rate, and reduce the operating pressure. Tetrahydrofuran (THF) is identified to have a significant effect on reducing the equilibrium hydrate formation condition for the $CO_2/H_2/H_2O$ mixture [1], and the 1.0 mol% THF was found to be the optimum concentration for the CO_2 capture based on the thermodynamic experiments. Zhang and Lee found that the H_2/cyclopentane (CP) hydrate system has

* Corresponding author. Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, No. 2, Nengyuan Road, Wushan, Guangzhou 510640, PR China. Tel.: +86 20 87057037; fax: +86 20 87034664.
E-mail address: lixs@ms.giec.ac.cn (X.-S. Li).

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a lower equilibrium pressure at the same temperature, compared with the H_2/THF hydrate system [6]. Furthermore, they studied on the phase equilibria of the CO_2/H_2/CP ternary hydrate systems and proposed a hydrate-based pre-combustion CO_2 capture process [7]. The results showed that the equilibrium hydrate dissociation pressure of the CO_2/H_2/CP/H_2O system is lower than that of the CO_2/H_2/THF/H_2O system with the same initial gas compositions at the same temperature. Thus, the operating pressure of the hydrate-based pre-combustion CO_2 capture can be reduced. However, in the CO_2/H_2/CP/H_2O system, the selectivity of CO_2 over H_2 in the hydrate phase reduces significantly due to H_2 competed with CO_2 for the small cages of the hydrates with structure II [7]. Kumar et al. studied on the incipient hydrate phase equilibria for the gas mixtures containing hydrogen, carbon dioxide and propane, and found that the propane (C_3H_8) as a promoter can reduce the equilibrium hydrate formation pressure [9]. Afterwards, C_3H_8 was employed in a two-stage clathrate hydrate process for pre-combustion capture of carbon dioxide and hydrogen, and the results showed that the 3.2 mol% C_3H_8 can reduce the operating pressure from 7.5 MPa (in a system without propane) to 3.8 MPa in the first stage [10].

Recently, tetra-n-butyl ammonium bromide (TBAB) as an environmental friendly compound is investigated in the process of hydrate-based gas capture, which can significantly reduce the equilibrium hydrate formation pressures of the CO_2/H_2 mixtures [11,12]. Li et al. found that approximately 0.29 mol% TBAB is the optimum concentration to obtain a high gas storage capacity based on the experiments of the gas hydrate formation process for the CO_2 separation from the fuel gas mixture [13]. Although some work [1,7,10,11] has carried out the investigations into the gas uptakes, the CO_2 separation efficiencies, the induction time of hydrate formation etc. in the processes of the hydrate-based pre-combustion gas separations, the CO_2 capture still needs to be further improved to meet the requirement of the industrial application. As mentioned above, the TBAB and CP are excellent promoters for the hydrate-based gas separation. However, few studies on the kinetic behaviors of the hydrate formation for the CO_2/H_2 gas mixtures in the TBAB solution in the presence of CP are reported.

In this work, the gas uptakes, the CO_2 separation efficiencies and the induction time of the hydrate formation for the hydrate-based pre-combustion CO_2 capture process in the systems with the different amount of the 0.29 mol% TBAB solution in the presence of CP with various corresponding volume ratios with the TBAB solution are investigated at the pressure range from 2.5 MPa to 4.5 MPa and the temperature range from 273.65 K to 277.65 K. In the following, the ratio of the volume of CP to the volume of the TBAB solution is abbreviated as the CP/TBAB ratio.

2. Experimental

2.1. Materials

A treated synthesis gas coming out of an IGCC power station consists of approximately 40 mol% CO_2/H_2 gas mixture at the pressure of 2.5–5.0 MPa [5]. Thus, a CO_2/H_2 gas mixture containing the 38.6 mol% CO_2 is used in the work to simulate a pretreated fuel gas mixture. The gas mixture is supplied by Foshan Huate Gas Co., Ltd. TBAB with 99.9% purity is supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd., China. CP with the purity of more than 99.0% is supplied by Xiamen Pioneer Chemical Reagent Co., Ltd. The de-ionized water used with the resistivity of 18.25 $m\Omega\,cm^{-1}$ is produced by an ultra-pure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China.

2.2. Apparatus

The experimental apparatus in this work is shown in Fig. 1. The crystallizer (CR) with inner volume of 336 ml and the supply vessel (SV) with the inner volume of 1350 ml are made of 316 stainless steels, respectively. They are immersed in a temperature-controlled water bath. On the front and back of the CR, there are two circular

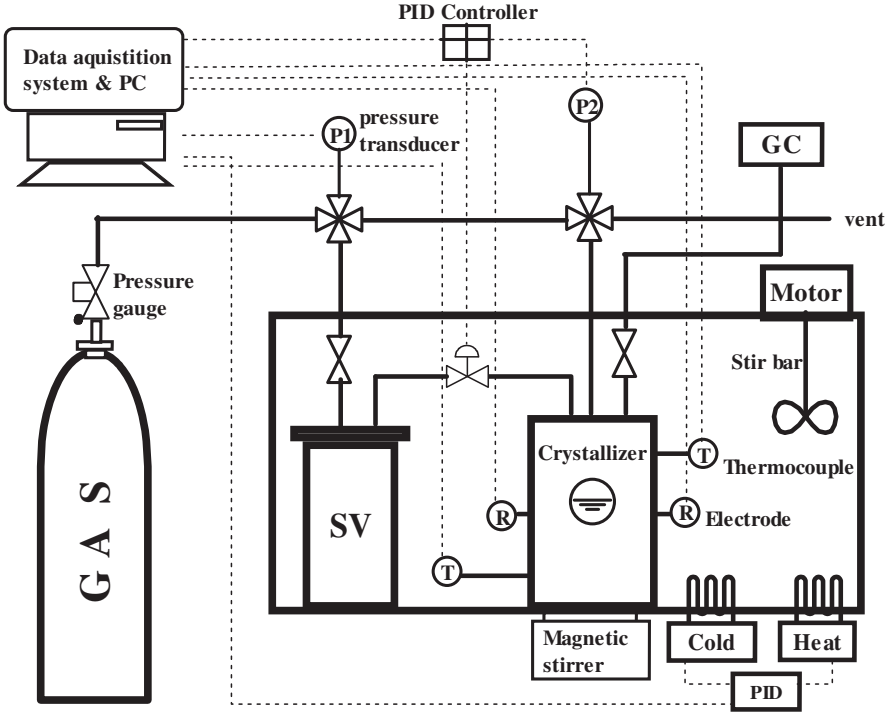

Fig. 1. Experimental apparatus.