Hydrate-based carbon dioxide capture from simulated integrated gasification combined cycle gas

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Abstract
The equilibrium hydrate formation conditions for CO_2/H_2 gas mixtures with different CO_2 concentrations in 0.29 mol% TBAB aqueous solution are firstly measured. The results illustrate that the equilibrium hydrate formation pressure increases remarkably with the decrease of CO_2 concentration in the gas mixture. Based on the phase equilibrium data, a three stages hydrate CO_2 separation from integrated gasification combined cycle (IGCC) synthesis gas is investigated. Because the separation efficiency is quite low for the third hydrate separation, a hybrid CO_2 separation process of two hydrate stages in conjunction with one chemical absorption process (absorption with MEA) is proposed and studied. The experimental results show H_2 concentration in the final residual gas released from the three stages hydrate CO_2 separation process was approximately 95.0 mol% while that released from the hybrid CO_2 separation process was approximately 99.4 mol%. Thus, the hybrid process is possible to be a promising technology for the industrial application in the future.

Key words
integrated gasification combined cycle (IGCC); gas hydrate; CO_2 separation; H_2 purification; chemical absorption

1. Introduction

Carbon dioxide (CO_2) is considered as one main contributor to the greenhouse gases resulting in the global warming [1]. Near one third of all CO_2 emissions worldwide is produced by the fuel power plants [2]. Therefore, the prime target is to capture CO_2 from the fuel power plants to slow down the deterioration of the climate. Pre-combustion capture and post-combustion capture are two approaches extensively used for CO_2 capture from the fuel power plants [3]. Pre-combustion capture is capturing or removing CO_2 before the fuel being burnt while post-combustion capture is capturing or removing CO_2 from the flue gas [4]. Presently, the integrated gasification combined cycle (IGCC) is widely utilized in the coal-fired power plants. CO_2 capture from IGCC becomes one promising route of pre-combustion capture. In IGCC plant, coal is firstly gasified and then converted into a stream of hydrogen (H_2) and CO_2 [5]. Once CO_2 is removed

efficiently, the resultant H_2 can be used as a clean fuel. Physical adsorption, chemical absorption, cryogenic fractionation and membrane process are the conventional technologies for capturing CO_2 from the fuel gas. However, the conventional technologies face some challenges, such as low capacity, technology feasibility, high cost and corrosion [6,7]. Therefore, novel and low cost technologies of carbon capture need to be developed.

Gas hydrate-based CO_2 capture technology is one of the novel technologies for capturing CO_2 from IGCC synthesis gas (mixture of CO_2/H_2). The gas hydrates are non-stoichiometric compounds formed by water molecules and small molecule gases such as CO_2, nitrogen (N_2), oxygen (O_2), H_2, methane (CH_4) [8]. The mechanism of hydrate-based CO_2 capture is selective partition of CO_2 component between hydrate phase and gaseous phase [9,10]. Because the equilibrium hydrate formation pressure of CO_2 is much lower than that of H_2 at the same temperature, it is expected that

CO_2 is preferentially encaged into the hydrate phase. The hydrates are then separated and subsequently decomposed to create CO_2-rich stream while the rest constitutes CO_2-lean one. Thereby, CO_2 is captured from IGCC synthesis gas.

IGCC synthesis gas mainly contains approximately 40.0/60.0 mol% CO_2/H_2 gas mixture, and the outlet pressure of the synthesis gas is generally 3−5 MPa [3]. In our previous work [10], the concentration of CO_2 can be reduced from 40.0 mol% in the feed gas to approximately 13.5 mol% in the residual gas after one stage hydrate-based CO_2 separation. Therefore, in order to separate CO_2 from CO_2/H_2 gas mixture completely, two hydrate stages or even three hydrate stages are required. However, the equilibrium hydrate formation pressure is higher with the decrease of CO_2 concentration in the gas mixture. Thus, higher driving forces are required for the gas mixtures containing lower concentration of CO_2 to form gas hydrate, that is, more serious conditions are required for the gas mixtures containing lower concentration of CO_2 to form gas hydrate. Therefore, a hybrid process based on the hydrate and chemical absorption process is developed. Moreover, no complete system configurations with key hybrid process parameters were presented in the papers [11,12].

In our previous work, 0.29 mol% TBAB solution was proved to be an optimal hydrate formation promoter for the hydrate-based CO_2 capture from either flue gases or IGCC synthesis gas [9]. Thus, 0.29 mol% TBAB solution is adopted in this work directly. In addition, the equilibrium hydrate formation conditions for CO_2/H_2/TBAB/H_2O systems with different CO_2 concentrations are measured firstly, and a hybrid process based on two hydrate stages coupled with a chemical absorption process is proposed for CO_2 capture. By the comparison of CO_2 capture efficiencies, the concentrations of H_2 in the residual gas, the energy consumptions between the third-stage hydrate-based CO_2 separation process and the hybrid process, and an optimal separation process are determined.

2. Experimental

2.1. Materials

A CO_2/H_2 gas mixture containing 39.6 mol% CO_2 was used in the work to simulate a pretreated fuel gas mixture. The gas mixture was supplied by Foshan Huate Gas Co., Ltd. Tetra-*n*-butyl ammonium bromide (TBAB) with 99.9% purity was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd., China. Monoethanolamine (MEA) with the purity of more than 99.0% was offered by Tianjin Fuyu Fine Chemicals Co., Ltd. The deionized water used with the resistivity of 18.25 m /cm was produced by an ultra-pure water system supplied by Nanjing Ultrapure Water Technology Co., Ltd., China. The glass-balls with the diameter of 3 mm were supplied by Yunhui Business Co., Ltd., China.

2.2. Apparatus

The experimental apparatus in this work is shown in Figures 1 and 2. The apparatus in Figure 1 was the same as that in our previous work [9]. The crystallizer (CR) with inner volume of 336 mL and the supply vessel (SV) with the inner volume of 1350 mL were made of 316 stainless steels. They were immersed in a glycol-water bath. On the front and back of the CR, there are two circular viewing windows made of Plexiglas. The maximum working pressure of the CR was 25 MPa. A magnetic stirrer (500 r/min) was employed to mix the contents in the CR. The temperatures of the gas phase and the liquid phase in the CR were measured using two Pt1000 thermocouples (JM6081) with uncertainties of ±0.1 K. The pressures in the SV and CR were measured with two Setra smart pressure transducers (model 552, Boxborough, MA, USA) with the uncertainty of ±20 kPa. In addition, the composition of the gas phase in the CR was determined with a HP6890 gas
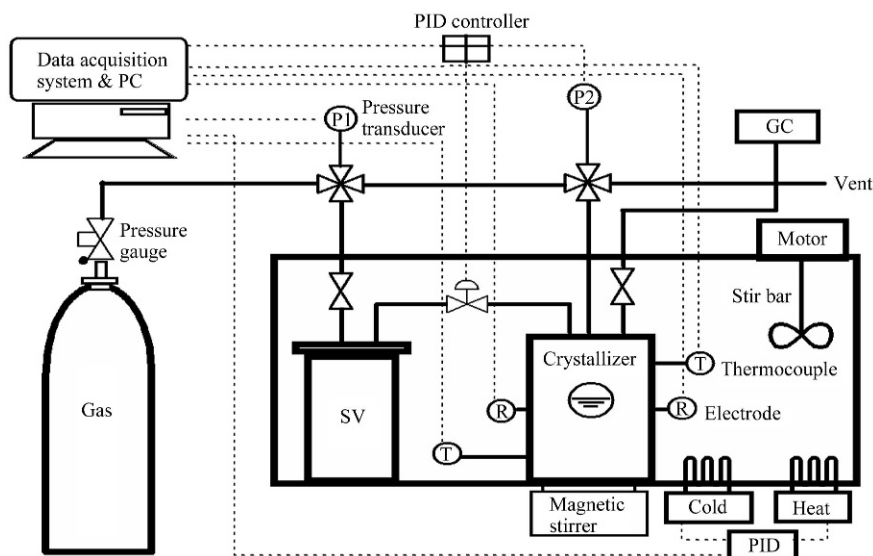

Figure 1. Experimental apparatus for hydrate process

chromatograph (GC) connected on-line with CR and automated with a personal computer (PC). Figure 2 is one simulative MEA CO_2 separation system. The round bottom flask (a) (as an absorption bottle) with effective volume of 500 mL was added into adequate quantities of glass-balls. Then 300 mL MEA solution of 30 wt% was added into the round bottom flask (a) and the solution surface was ensured to be $2-3$ mm higher than the top of the glass-ball stack. The gas mixture was introduced into MEA solution by a right-angle glass tube,

of which one terminal was inserted into the glass-ball stack. The other acute-angle glass tube was used for collecting H_2, of which one terminal went through the rubber stopper. Another round bottom flask (b) was used as a stripper for regenerating MEA solution. The flask (b) was heated with a heater, and the released CO_2 and the solution steam were collected via an acute-angle tube, of which one terminal was connected to a coiled condenser. The final gas was collected with a sealed gaseous envelope, then, it was detected with GC.
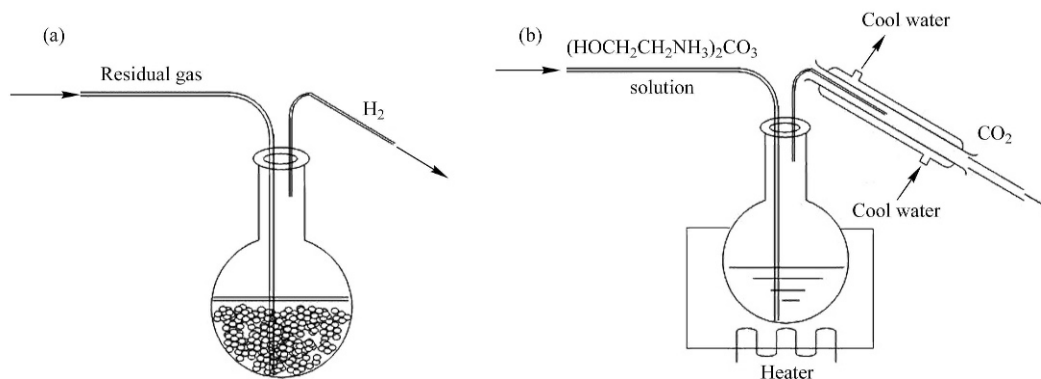

Figure 2. Experimental apparatus for MEA CO_2 separation. (a) Absorption bottle, (b) stripper for MEA regeneration
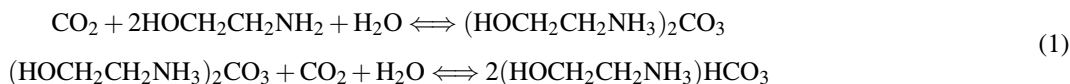
2.3. Procedure

TBAB solution with a desired concentration was introduced into the evacuated high-pressure cell. The content was pressurized up to the desired pressure by supplying CO_2/H_2 gas mixture. In this work, we firstly measured the equilibrium hydrate formation pressure for different CO_2/H_2 gas mixtures (CO_2 concentrations were 39.8 mol%, 18.8 mol% and 10.0 mol%, respectively) in the presence of TBAB. The method of three-phase equilibrium measurement adopted in the work was as same as the "T-cycle method" used by Ohgaki et al. [13]. Each "T-cycle" experiment was repeated for at least three times.

After equilibrium hydrate formation experiments, the procedure for hydrate stage was similar to that in our previous work [9,14]. The crystallizer (CR) was cleaned again using de-ionized water and allowed to dry. Then TBAB solution of 180 mL was introduced into the CR. Subsequently, the

CR is flushed with CO_2/H_2 gas mixture several times to remove gases, and then CO_2/H_2 gas mixture was charged into the CR until the desired pressure. Once the temperature was stabilized (typically within 1 min), the stirrer with a rate of 500 r/min was started, and the experimental time was recorded once every two second. The time when the stirrer was started was defined as t_0. The data of temperature and pressure were recorded during the experiment. As the gas in the crystallizer was consumed because of the hydrate formation, additional gas mixture in the SV was supplied and the pressure in the crystallizer was kept constant with a proportional integral derivative (PID) controller. The measurement of the compositions and the amount of the gas consumed (n_H) as well as the calculation of CO_2 separation efficiency were same as what mentioned in our previous work [10].

The hybrid process proposed in this work included a two-stage hydrate-based process and a chemical absorption process. The mechanism of the chemical absorption process was based on the following reaction [15]:

$$CO_2 + 2HOCH_2CH_2NH_2 + H_2O \Longleftrightarrow (HOCH_2CH_2NH_3)_2CO_3$$

$$(HOCH_2CH_2NH_3)_2CO_3 + CO_2 + H_2O \Longleftrightarrow 2(HOCH_2CH_2NH_3)HCO_3$$

(1)

After two stages hydrate-based capture, the residue gas was introduced into a chemical absorption bottle, in which adequate amount of small glass-balls with the diameter of 3 mm and MEA solution of 30 wt% with desired volume had been added. CO_2 was absorbed completely by MEA solution and formed the compounds of $(HOCH_2CH_2NH_3)_2CO_3$ and $(HOCH_2CH_2NH_3)HCO_3$ while H_2 was not absorbed. Thus, CO_2 is separated from IGCC synthesis gas, and H_2 with high

purity can be obtained. The pressure in the chemical absorption bottle was kept at 1.05 atm in order to ensure that the final gas can be collected easily. Then, the solution was introduced into a regeneration device, in which $(HOCH_2CH_2NH_3)_2CO_3$ and $(HOCH_2CH_2NH_3)HCO_3$ were heated to release CO_2 and regenerate MEA.

Based on the experiments, we further simulated CO_2 separation process in a 500 MW IGCC power plant with two CO_2

separation methods. One was the three stages hydrate-based capture process, and the other was the hydrate/chemical absorption hybrid process. The difference of the two processes was the chemical absorption stage in the hydrate/chemical absorption hybrid process which substituted the third hydrate stage in three stages hydrate-based capture process. The first two hydrate stages were the same for the two processes. Thus, we only need to compare the energy consumptions between the third hydrate stage of the hydrate process and the chemical absorption stage of the hybrid process. The energy consumption was calculated according to the formula listed in the book of Advanced Engineering Thermodynamics [16].

3. Results and discussion

3.1. Equilibrium hydrate formation pressure

We firstly measured the equilibrium hydrate formation pressure for CO_2/H_2 gas mixture with CO_2 concentration of 18.0 mol% in 0.29% TBAB solution. Compared with the results given by Li et al. [17], it is found that the results were in excellent agreement, as shown in Figure 3. This illustrates either the apparatus or the method adopted in this work is reliable.
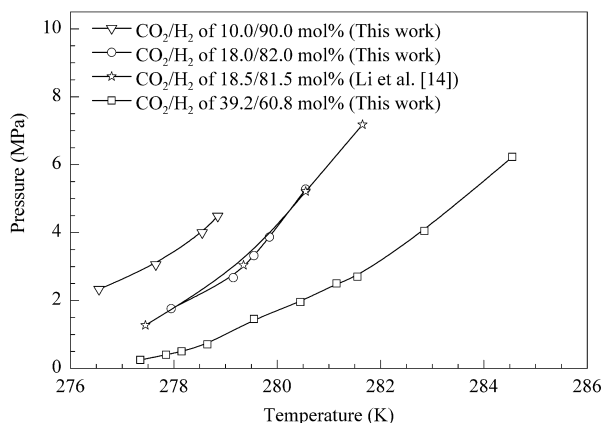
Figure 3. Equilibrium hydrate formation pressure for CO_2/H_2 gas mixtures in the presence of 0.29 mol% TBAB solution

Figure 3 gives the measured equilibrium hydrate formation conditions for CO_2/H_2 gas mixtures with CO_2 concentrations of 10.0, 18.0 and 39.2 mol% in 0.29 mol% TBAB solution. The pressure ranged from 0.25 MPa to 6.23 MPa and the temperature ranged from 276.55 K to 284.55 K. The phase equilibrium data are summarized in Table 1. As shown in Figure 3, the equilibrium hydrate formation pressure decreased considerably with the increase of CO_2 in the gas mixture at the same temperature. For example, the equilibrium hydrate formation pressures were 3.45, 1.80 and 0.50 MPa at 280.15 K for CO_2/H_2 mixtures with CO_2 concentrations of 10.0, 18.0 and 39.2 mol%, respectively. In addition, the equilibrium temperatures at 4.0 MPa were 278.15, 279.75 and 282.65 K for CO_2/H_2 mixtures with CO_2 concentrations of 10.0, 18.0 and 39.2 mol%, respectively. The result illustrates that lower CO_2

concentration in CO_2/H_2 mixture results in higher equilibrium pressure at the fixed temperature or higher equilibrium temperature at the fixed pressure, and further results in forming the gas hydrate more difficultly.

Table 1. Equilibrium hydrate formation pressure for CO_2/H_2 gas mixtures with different concentrations in 0.29 mol% TBAB solution
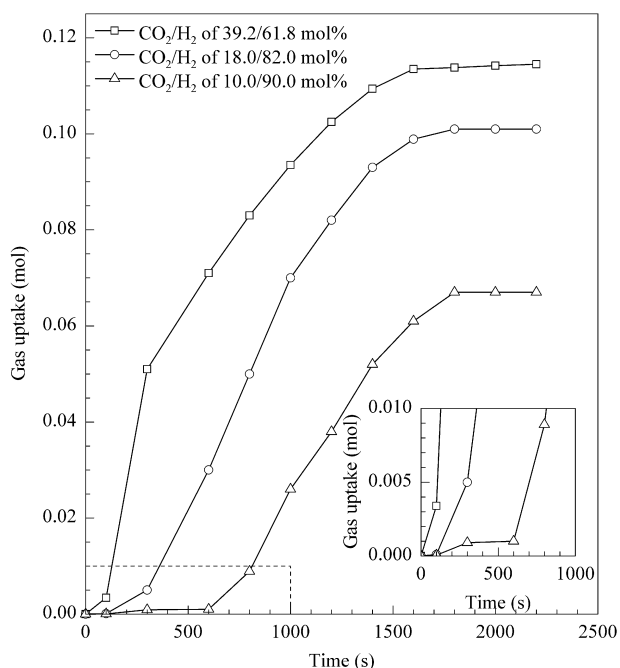
CO_2/H_2 gas mixtures	T/K	P/MPa
10.0/90.0 mol%	276.55	2.33
	277.15	2.72
	277.65	3.06
	278.65	4.00
	278.85	4.49
18.0/82.0 mol%	277.45	1.25
	277.95	1.76
	279.15	2.67
	279.85	3.87
	280.55	5.28
39.2/60.8 mol%	277.35	0.25
	277.85	0.40
	278.15	0.51
	278.65	0.71
	279.55	1.45
	280.45	1.96
	281.15	2.50
	282.85	4.05
	284.55	6.23

3.2. Hydrate-based CO_2 separation

Figure 4 gives the gas uptake changes with time for three CO_2/H_2 gas mixtures with CO_2 concentrations of 10.0, 18.0 and 39.2 mol% at 4.0 MPa and 276.15 K. A typical example is shown in Figure 4. There was an inflexion in the curve for 10.0 mol% CO_2/H_2 gas mixture at the 625th second. The gas uptake increased slowly from 0 to 625 s while dramatically increased after the 625th second. At the 1830th second, the amount of gas uptake was 0.067 mol, and then the amount of gas uptake had little change from the 1830th second to the end of the experiment. Similar phenomenon was also shown for 18.0/88.0 mol% CO_2/H_2 gas mixture. The gas uptake had a slight increase from 0 to 162 s, then, it increased abruptly after the 162th second. At the 1945th second, the amount of gas uptake was 0.101 mol. Subsequently, the amount of gas uptake had little change. For 39.2/60.8 mol% CO_2/H_2 gas mixture, the gas uptake increased slowly from 0 to 66 s, and the amount of the uptake had a considerable increase from the 66th second to the 1578th second. At the 1578th second, the amount of gas uptake was 0.115 mol, and subsequently it had little change. Similar to our previous work [10], the slow increase of the gas uptake are resulted from the dissolving of the gas mixture in TBAB solution while the abrupt increase of the gas uptake is attributed to the gas hydrate formation. Therefore, the time when the gas uptake turns to the increase abruptly is defined as the hydrate formation induction time [18]. Thus, as seen from Figure 4, the hydrate formation induction time for the three CO_2/H_2 gas mixtures at 4.0 MPa and 276.15 K were 625, 162 and 66 s, respectively. The result illustrates that as CO_2 concentration shifts to be lower, the hydrate formation

induction time increases observably. It is attributed to the fact that the gas mixture with lower CO_2 concentration has higher equilibrium hydrate formation pressure, and thus the corresponding driving force for the hydrate formation is lower, resulting in longer hydrate formation induction time [19]. However, for the hydrate-based CO_2 separation, longer induction time is unfavorable for the application in industry. Thus, the hydrate formation induction time for 10.0 mol% CO_2/H_2 gas mixture of 625 s, is too long to meet the requirement of industrial application for the hydrate-based CO_2 separation.

In addition, as seen from Figure 4, as CO_2 concentration shifted to be lower in the gas mixture, the gas uptake decreased remarkably at 4.0 MPa and 276.15 K. For example, for the three CO_2/H_2 gas mixtures, the gas uptake obtained in this work were 0.067 mol, 0.101 mol, 0.115 mol when CO_2 concentrations were 10 mol%, 18.0 mol% and 39.2 mol%, respectively. Although the gas uptakes obtained here were not

Figure 4. Gas uptake changes with time in the presence of 0.29 mol% TBAB solution at 4.0 MPa and 276.15 K

high enough to meet the requirement of treating the large amount of IGCC synthesis gas in the industry, the shift tendency of the gas uptake with CO_2 concentration change in the gas mixture indicates that higher CO_2 concentration in the gas mixture is more helpful for the hydrate-based CO_2 separation from IGCC synthesis gas.

Table 2 shows the hydrate-based CO_2 separation efficiencies along with CO_2 concentrations in the residual gas phase and hydrate slurry phase for the three different CO_2/H_2 gas mixtures at 4.0 MPa and 276.15 K. As seen from Table 2, because CO_2 concentration in the residual gas after the first and the second hydrate separation stages were 16.6 mol% and 10.1 mol%, the values were close to CO_2 concentration in the feed gas mixtures for the two stages (18.0 mol% and 10.0 mol%), respectively. Thus, a three stages hydrate-based CO_2 separation process was proposed. The process flowchart is shown in Figure 5. As seen from Table 2, CO_2 separation fraction and separation factor for CO_2/H_2 gas mixture of 39.2/60.8 mol/mol were obviously larger than those for other two gas mixtures. As CO_2 concentration shifted to lower, CO_2 separation fraction and CO_2 separation factor shifted to lower. For CO_2/H_2 gas mixtures with CO_2 concentrations of 39.2 mol% and 18.0 mol%, CO_2 separation fractions were 0.66 and 0.62, respectively, and CO_2 separation factors were 72.3 and 19.4, respectively. CO_2 separation fraction and separation factor for CO_2/H_2 gas mixture with CO_2 concentration of 10.0 mol% were only 0.45 and 10.3, respectively. The result illustrates that the hydrate-based CO_2 separation from CO_2/H_2 gas mixtures with CO_2 concentrations of 39.2 mol% and 18.0 mol% are feasible. Nevertheless, that from CO_2/H_2 gas mixtures with CO_2 concentrations of 10.0 mol% is unfeasible because of the quite low CO_2 separation efficiency. Due to CO_2 concentration in the feed gas mixture of the third hydrate stage was lower than 10.0 mol%, that separating CO_2 and purifying H_2 from IGCC synthesis gas via a whole three stages hydrate-based process is unfeasible. In other words, the continuous three stages hydrate-based CO_2 separation process (as shown in the flowchart in Figure 5) is unfeasible. Consequently, it is necessary to develop a hybrid process for separating CO_2 and purifying H_2 from IGCC synthesis gas.

Table 2. Hydrate-based CO_2 separation efficiencies along with CO_2 concentrations in residual gas phases and hydrate slurry phases for three different CO_2/H_2 gas mixtures at 4.0 MPa and 276.15 K in this work

Feed gas	Gas uptake (mol)	Decomposed gas (mol)	CO_2 concentration in residual gas phase (mol%)	CO_2 concentration in hydrate slurry phase (mol%)	CO_2 separation fraction	CO_2 separation factor
10.0/90.0 mol% CO_2/H_2 gas mixture	0.067	0.0065	6.7	42.5	0.45	10.3
18.0/82.0 mol% CO_2/H_2 gas mixture	0.10	0.016	10.1	68.5	0.62	19.4
39.2/60.8 mol% CO_2/H_2 gas mixture	0.12	0.033	16.6	93.5	0.66	72.3

3.3. Chemical absorption of CO_2

On one hand, the amounts of MEA used for absorbing CO_2 according to the Equation (1) depend on the amount of CO_2 in the residual gas mixture. On other hand, the target for adopting less MEA in the process is strictly managed ow-

ing to the environmental unfriendliness of MEA and the high energy consumption of the post-treatment for MEA. Therefore, one chemical absorption process is adopted to separate the residual gas released from the second hydrate stage. Figure 6 shows the flowchart of the hybrid CO_2 separation process. Compared with the flowchart shown in Figure 5, the
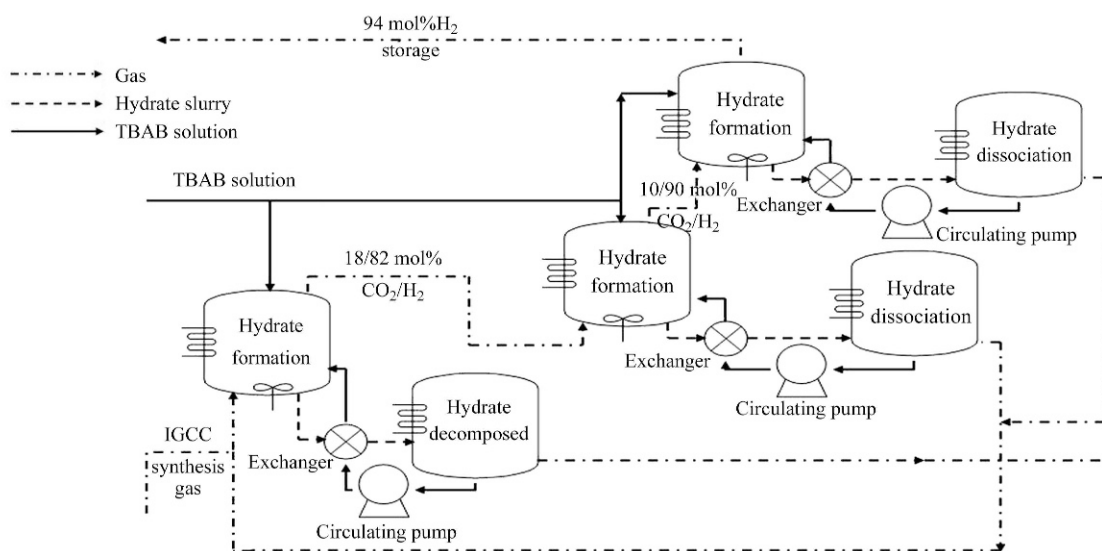
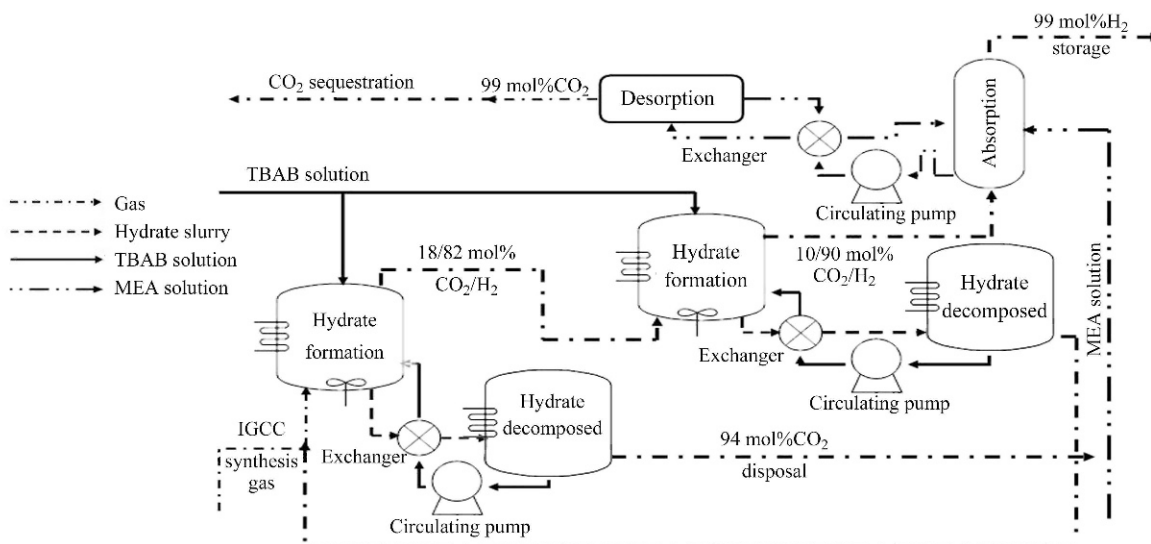**Figure 5.** Flowchart for three hydrate-stage CO_2 separation process

Figure 6. Flowchart for two hydrate-stage/chemical absorption hybrid CO_2 separation process

third stage of the hydrate-based separation process was substituted by a chemical absorption and desorption process in Figure 6. Besides, the residual gas mixture produced in the second hydrate stage was directly introduced into 30.0 wt% MEA solution in the absorption tank. Because excess MEA was added in the absorption tank to absorb CO_2 according to the Equation (1), all CO_2 was considered to be adsorbed. In addition, in order to collect the gas mixture released from MEA solution easily at the outlet, the pressure difference of 0.5 atmosphere pressure was set between the inlet and outlet of the tank. The collected gas was almost pure H_2 with purity of approximately 99.4 mol%. However, H_2 concentration in the residual gas released from the third stage hydrate-based CO_2 separation process was approximately 95.2 mol%, as seen in Figure 7. Therefore, the concentration of H_2 released from the chemical absorption separation process was
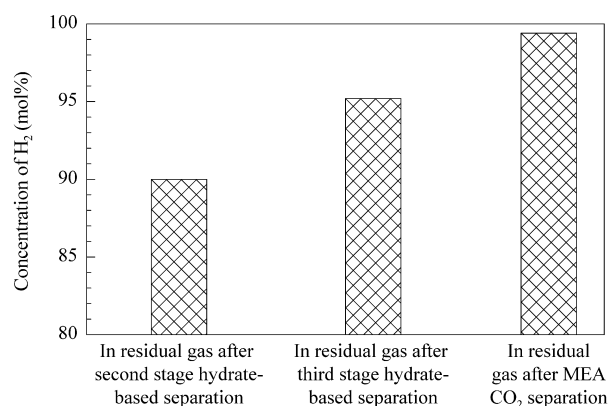
Figure 7. H_2 concentrations in the residual gas after third stage hydrate-based CO_2 separation and chemical absorption for feed gas coming from residual gas after second stage hydrate-based CO_2 separation in this work

4.2 mol% which was higher than that released from the third stage hydrate separation process. Thus, it illustrates that hybrid CO_2 separation process is feasible to obtain highly pure H_2. However, the feasibility of hybrid CO_2 separation process for the industrial application still needs reasonable energy consumption estimation and the estimation will be made in our next work.

4. Conclusions

The equilibrium hydrate formation pressures for CO_2/H_2 gas mixtures with CO_2 concentrations of 10.0, 18.0 and 39.2 mol% in the presence of 0.29 mol% TBAB solution are firstly measured. The results illustrate that the equilibrium hydrate formation pressure increases remarkably with the decrease of the concentration of CO_2 at the fixed temperature. Based on the above investigation, a hydrate-based CO_2 separation from IGCC synthesis gas is studied for its environment-friendly and economic features. In order to realize CO_2 separation from IGCC synthesis gas efficiently, at least three hydrate stages are required. However, with the decrease of CO_2 in CO_2/H_2 gas mixture, CO_2 separation from the gas mixture becomes more difficult because of the increase of the corresponding equilibrium hydrate formation pressure. Especially for the third hydrate separation process, the equilibrium hydrate formation pressure shifts to high and the separation efficiency turns to quite low. Therefore, a hybrid CO_2 separation process with two stages hydrate separation process in conjunction with one chemical absorption process (absorption with MEA) is proposed and analyzed. The experimental results show H_2 concentration in the final residual gas released from the three stages hydrate CO_2 separation process is approximately 95.0 mol% while that released from the hybrid CO_2 separation process is approximately 99.4 mol%. In this work, the energy consumption estimation is not studied, and it will be analyzed in our next work.

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