



Effects of additives on continuous hydrate-based flue gas separation[☆]

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HIGHLIGHTS

- Multiple stage continuous hydrate-based gas separation process was proposed.
- Solution movement characters were observed and analyzed for experimental cycles.
- Hydrate saturation for 5% TBAB + 5% THF was higher than that of 19% THF.
- 80 min is the appropriate time for rapid hydrate formation process.

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ABSTRACT

CO₂ capture from fossil fuel power plants is the main method of CO₂ storage. Hydrate-based gas separation is regarded as a potential method for CO₂ capture from flue gas. In this study, hydrate-based gas separation (HBGS) was used to capture CO₂ from flue gas (19.96 mol% CO₂ and 80.04 mol% N₂), and the continuous experimental process was monitored using magnetic resonance imaging (MRI). The effects of two additives (5 wt% TBAB + 5 wt% THF and 19 wt% THF), two gas injection methods (constant pressure and constant flow rate processes), and of different pressures and flow rates on the hydrate saturation and solution movement were investigated. The results show that both additives effectively promote hydrate formation. The constant pressure process was superior to the constant flow rate process for hydrate formation. Furthermore, the flow rate had little influence on the hydrate saturation. The process was most efficient when a hydrate formation stage time of approximately 80 min was used. The solution movement resulting from the continuous multiple cycles tended to decrease during subsequent cycles. Moreover, the addition of 19 wt% THF had a more obvious effect on the solution movement than 5 wt% TBAB + 5 wt% THF. Solution concentration phenomena were observed in the presence of 19 wt% THF at 285.15 K; these phenomena may have been affected by the formation and dissociation of hydrates. Due to solution movement during the continuous industrial hydrate-based gas separation process, the solution might need to be replenished. Finally, in terms of the resulting hydrate saturation, the use of 5 wt% TBAB + 5 wt% THF was found to be more suitable in this study, while the 19 wt% THF was more suitable for a higher experimental temperature.

1. Introduction

Fossil fuel combustion is the main sources of CO₂ emissions. A high concentration of CO₂ is present in the flue gas produced by fossil fuel power plants. CO₂ capture is an effective way to reduce the emission of CO₂ into the atmosphere [1–4]. Thus, it is necessary to capture CO₂ from flue gas, and the CO₂ separation process is the key step of CO₂ capture. Many methods for CO₂ separation have been reported, including chemical and physical absorption, solid physical adsorption, cryogenic distillation, and membrane gas separation [5]. CO₂ separation is an energy-consumption process [6]. Although some of the above

methods yield satisfactory results for CO₂ separation, their energy cost is still too great for commercial use. Furthermore, the cost of hydrate-based gas separation (HBGS) is believed to be lower than that of chemical absorption [7]. Unlike cryogenic distillation, the operating temperature of HBGS is above the freezing point, and thus less energy is used for refrigeration [8,9]. Furthermore, the water used in HBGS can be recycled, which reducing the raw material costs. The feasibility of HBGS has been proven in the laboratory [10–14]. In HBGS, N₂ and CO₂ are the main components in the flue gas. Because the hydrate phase equilibrium pressure of N₂ is significantly higher than that of CO₂ at the same temperature, CO₂ preferentially enters the hydrate cavities

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making separation the flue gas via HBGS possible [15].

The key limitations of the HBGS process are the hydrate formation rate and the demanding conditions required to reach phase equilibrium. Therefore, researchers have attempted to determine these values through a variety of different methods [16–18]. Enhancing the gas–water contact and the heat and mass transfer are believed to increase the hydrate formation rate. At present, the main methods to enhance gas–water contact and heat and mass transfer are mixing, spraying, bubbling, or porous media; other physical methods and the use of chemical additives have also been considered [19]. The use of porous media in particular is an important method to promote hydrate formation in hydrate applications. The water in porous media could improve the gas–water contact, which could promote hydrate formation by increasing the hydrate formation rate [20]. Babu et al. found that the addition of porous media resulted in 54% conversion of water into hydrate within two hours. In addition, higher gas consumption and a decreased induction time were observed [21]. Park et al. reported increased gas consumption and water conversion when silica gels were employed [22]. Adeyemo et al. observed that the gas consumption, CO₂ recovery, separation factor and the conversion of water to hydrate increased with larger pore and particle size [23]. In our previous work, we found that less solution concentration occurred BZ-01, which contained smaller pores, than in BZ-02 and BZ-04, which contained larger pores [7]. Zhong et al. found that stirring was beneficial for hydrate formation [24]. In addition to physical methods, the use of chemical additives to improve the HBGS process has been widely studied. These chemical additives are divided into two classes: kinetic and thermodynamic additives. Kinetic additives include sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), and alkylpolyglucoside (APG) [25,26]. Thermodynamic additives such as tetrahydrofuran (THF), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium fluoride (TBAF), and cyclopentane (CP) not only accelerate the hydrate formation rate, but can also ease the hydrate phase equilibrium conditions [8,27–33], TBAB and THF are currently in wide use.

The principle behind the use of TBAB as an additive is as follows. During hydrate formation, Br⁻ can displace water molecules in the crystal structure of the hydrate to form hydrate cages. Subsequently, TBA⁺ can occupy the large cages of the hydrate, while CO₂, N₂, H₂S, and other small molecules fill the remaining small cages. TBAB is involved in the formation of hydrate cages, stabilizing the hydrate structure and resulting in a substantial reduction in the pressure of hydrate dissociation [34]. Several studies have verified that TBAB can allow phase equilibrium to be achieved under less demanding conditions. Li et al. measured the phase equilibrium of CO₂ hydrate in the presence of TBAB. Their results showed that TBAB significantly decreased in the phase equilibrium pressure of CO₂ hydrate [35,36]. Furthermore, the TBAB hydrate is believed to have an obvious effect on CO₂ separation from mixed gases. Kim et al. investigated the thermal stability of hydrates of mixed gases (20% CO₂ + 80% N₂) in the presence of TBAB, TBAC, and TBAF, and found that the concentration for CO₂ in the hydrate was as high as about 60%, and that the selectivity of CO₂ did not depend on the type of quaternary ammonium salt used [34]. Hashimoto et al. studied hydrate-based mixed gas (CO₂ + N₂) separation in the presence of TBAB, and found that the CO₂ selectivity was highest at a pressure of 1 MPa and a TBAB concentration of 32 wt %. They also found more CO₂ was captured without gas flow than with gas flow [37]. In addition to these experimental results, models have also been proposed [38,39]. A model for the phase equilibrium conditions for the formation of hydrates of CO₂, CH₄, and N₂ in TBAB or pure water has been proposed, in which the temperature and the TBAB concentration are considered [40,41].

The principle behind the use of THF as a promoter is as follows. When the CO₂/N₂ gas mixture and water form a hydrate in the presence of THF, THF molecules occupy the large cages of the hydrate, while CO₂ fills the small cages to form the S-II THF-CO₂ hydrate. This changes the

phase equilibrium conditions of the original hydrate, reducing the induction time of the process significantly [42]. Several studies have verified that THF can allow phase equilibrium to be achieved under less demanding conditions. Wang et al. investigated the CO₂ hydrate phase equilibrium conditions in the presence of THF using a stepwise heating method; their results demonstrated that the equilibrium pressure of the CO₂ hydrate was significantly reduced in the presence of THF, and that as the THF concentration was increased, the equilibrium pressure was reduced [43,44]. Moreover, THF hydrate is believed to have an obvious effect on gas separation from mixed gases. Cai et al. studied the hydrate-based CO₂ separation process in the presence of THF, using real-time Raman spectroscopy [45]. Park et al. found that CO₂ could be enriched to 90% in the hydrate phase when THF and mixed gas (60% H₂ + 40% CO₂) were used for hydrate formation [22]. Another study verified that more than 99 mol% CO₂ could be recovered from flue gas by HBGS when the hydrate promoter THF was used [46]. Sun et al. used a CO₂ hydrate with THF for refrigeration applications, and proposed a kinetic model of the CO₂-THF hydrate to predict hydrate decomposition [47].

The effect of various mixed additives has also been studied. Our group has investigated the effect of the mixed additive THF + TBAB on the separation of flue gas and found similar phase equilibrium pressure using 5% THF + 5% TBAB and 5% THF + 10% TBAB. Furthermore, as the THF or TBAB concentration was increased, the gas consumption also increased [17]. Lirio et al. measured the storage capacity, induction time, and induction temperature of CO₂ hydrates in pure water, SDS solution, THF solution, and a mixed solution of THF and SDS. Their results showed that while SDS increased the CO₂ hydrate storage capacity, its effect on the CH₄ hydrate was less significant. However, because of the coupling effect, a mixture of SDS and THF reached 121 (± 12)% of the maximum theoretical value, and the induction temperature and the induction time were reduced [48]. Tzirakis et al. studied the phase equilibrium of the hydrate of a CO₂ + N₂ mixture with TBAB, CP, and TBAB + CP as promoters, respectively, and found that the mixture of TBAB and CP had a greater effect on reducing the equilibrium pressure of hydrate than pure TBAB [49]. The results were similar for a TBAF + CP mixture. Moreover, they found that the TBAF + CP mixture had a greater effect on reducing the equilibrium pressure of hydrate than pure TBAF [50]. Xia et al. found that CO₂ and H₂S could be captured simultaneously from biogas or natural gas in the presence of a physical gas solvent (TMS) and TBAB [51]. Moreover, mixtures of many additives, including TBAB, SDS, THF, dimethylsulfoxide (DMSO), and CP have been investigated, and mixed additives have been shown to have a significant effect on gas separation, leading to over 90 mol% CO₂ in the hydrate phase and separation factors as high as 17.82 [52–57].

Therefore, HBGS is a feasible potential method for CO₂ capture, and further investigation the factors affecting industrial CO₂ capture is necessary. In a review of the literature, many works about additives have been reported, while most of them focused on the hydrate phase equilibrium conditions, separate factors and CO₂ concentrations after the gas separation, and their works on separate factor have been studied in great detailed. However, we found that there have been few simulations of continuous industrial hydrate-based gas separation processing in the presence of additives, which is very important for hydrate-based technology. Therefore, the effects of different pressures and reaction times on hydrate formation, as well as the effects of different gas injection methods and additives, and the use of continuous multiple cycles on the continuous industrial hydrate-based gas separation process have been studied in this work.

2. Experimental material and methods

2.1. Apparatus

The experimental apparatus consisted of several parts (see Fig. 1): a

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