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Hydrate-based acidic gases capture for clean methane with new synergic additives ☆

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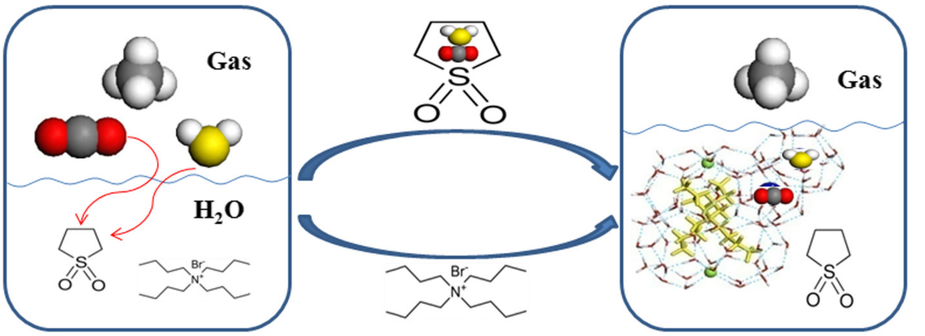
HIGHLIGHTS

- Hydrate-based acidic gases capture with synergic additives was investigated.
- Synergic additives was comprised by TMS and TBAB.
- CO_2 and H_2S could be synchronously captured.
- Synergic additives enhance the dissolution and diffusion of acidic gases.
- Synergic additives promoted hydrate-based capture process.

GRAPHICAL ABSTRACT



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ABSTRACT

The widespread need for carbon dioxide (CO_2) and hydrogen sulfide (H_2S) removal from potential gaseous fuel processes associated with upgrading of natural gas, biogas and landfill gas has led to a continuing interest in developing acid gas capture technologies. This work experimentally investigated the hydrate-based acidic gases (CO_2 and H_2S) capture for clean methane (CH_4) fuel from biogas or natural gas with new synergic additives, which comprised physical gas solvent (TMS) and traditional hydrate promoter (TBAB). The results show that, with the synergic additives, the equilibrium hydrate formation pressures were moderated by about 90% relative to pure water, the selectivity of CO_2 over CH_4 and the selectivity of H_2S over CH_4 could achieve 18.56 and 11.38, respectively. Compared with TBAB, the synergic additives could improve the hydrate formation rate and the gas storage capacity by 149% and 84%, respectively. Furthermore, the promotion effect could be enhanced when with the help of H_2S. It has been shown that CO_2 and H_2S could be synchronously captured through the hydrate formation process. It will be of importance to the fundamental study of enhancing gas hydrate formation process, and of practical significance for the hydrate-based application industry.

1. Introduction

Natural gas has attracted high attention in the last few decades because of the increasing demand for alternative energy sources owing to depleting conventional energy sources. Refer to the Paris Agreement, the World Energy Outlook 2016 studied the 450

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Scenario (consistent with a 50% chance of limiting global warming to 2 °C) and reported that, there will be a 30% rise in global energy demand to 2040, and natural gas fares best among the fossil fuels, with consumption rising by 50% [1]. Raw natural gas consists of several contaminants (i.e. water, CO_2, H_2S, and many others) that need to be processed and purified before used. Approximately 5% of worldwide natural-gas reserves are contaminated with H_2S in excess of 15% concentration [2]. Over 30% of the current natural gas production in the US is in the form of low-quality natural gas that contains significant amounts of CO_2 and H_2S [1,2]. Acid gases must be removed from natural gas in order to: (1) increase the heating value of natural gas; (2) decrease the volume of gas transported in pipe-lines; (3) reduce corrosion during the transport and distribution of natural gas; and (4) prevent atmospheric pollution by SO_2, which is generated during the combustion of natural gas containing H_2S [3]. H_2S removal from natural gas is even more challenging than CO_2 removal. The typical specifications of natural gas pipeline require that, CO_2 component should be reduced to 1–3%, whereas H_2S component needs to be reduced to as low as 3 ppm (v/v) of total sulphur. H_2S also represents a greater health and safety hazard as compared to CO_2. Additionally, water vapor, as the main reason for blockage or corrosion of pipelines and facilities because its existence can lead to the creation of natural gas hydrates, needs to be removed before further processing.

Meanwhile, the limited global petroleum resources, as well as the social and environmental effects of fossil fuel consumption, have encouraged people to invest in the renewable energy. Biogas clearly is a very versatile source of renewable energy that can serve as a natural gas replacement or supplement, or as vehicle fuel due to the high calorific value [4]. For instance, the biogas calorific values varies from 15 to 20 MJ/m^3 when the CH_4 component ranges from 45% to 60% mole fraction [5]. However, other contaminants (H_2S and CO_2) almost always coexist in biogas, as well as saturated with water when it is produced. Therefore, removal of acid gases (H_2S and CO_2) and water vapor from biogas is very important in this case since it is the prerequisite process to enhance its calorific values and to reduce corrosion and the greenhouse effect. Thus, it can be expected that, with effective disposal technology for the contaminants, biogas will serve as an important methane resource in future, especially for those countries that have to import natural gas or other fossil fuel.

Acid gases (H_2S and CO_2) and water vapor have to be removed from raw natural gas or biogas for operational, economical or environmental reasons [6]. The most common approach for the removal of H_2S and CO_2 is amine treatment or adsorption by zeolites [7–9]. However, these approaches involve the corrosion or the energy cost, especially almost could not dispose H_2S, CO_2 and water vapor synchronously. Thus, novel approaches should be considered. It is well known that natural gas emerges from the ground at a pressure of 5–25 MPa, and both CO_2 and H_2S are known to form clathrate hydrates at lower pressures than CH_4. So it is expect that the capture technology utilizing hydrate crystallization can be effective for acidic gases removal from natural gas or biogas. Gas hydrate crystallization processes has evolved as potential novel capture technology for CO_2 capture and storage (CCS) or for acidic gases removal from fuel gas, flue gas, landfill gas, natural gas streams and so on resource [10–39]. Compared with conventional gas capture technologies, the hydrate-based gas capture is energy saving and environment friendly due to the following factors: (1) the only material needed is water, no other hazardous or expensive materials are involved, it also can be re-circulated used, almost without any material loss [40]; (2) the contained water vapor, hindering the uptake capabilities for other technologies, inversely is beneficial to the hydrate-based capture technology due to that hydrates rely on water molecules to enclathrate the gas; (3) additionally, relative to the conventional capture methods, it is remarkably energy potential due to the less temperature difference and the low pressure loss [41].

Previous researches mainly focus on the thermodynamic studies to moderate the operation condition. Some outstanding thermodynamic additives such as tetrahydrofuran (THF) [42], Tetra-b-utyl ammonium/phosphonium salts [43–45], and cyclopentane (CP) [46] have been testified that they could remarkably moderate the hydrate formation conditions. Our previous research found that, for instance, the equilibrium hydrate formation pressure of landfill gas with 0.0234 mol fraction tetra-n-butyl ammonium bromide (TBAB) is only 0.67 MPa at 285.95 K, which means approximately 90% pressure drop relative to that with pure water [45]. However, Babu et al. found that the CO_2-TBAB hydrate formation process had the lower gas consumption and water conversion ratio [35]. Both hydrate formation rate and gas storage capability would have been prerequisite if the hydrate-based process is commercially viable for natural gas or biogas purification [47–50]. Hence, how to improve the rate and the intensity is essential for the hydrate-based gas capture technology. It has been proposed in previous researches that, the higher solubility the hydrate former has and the larger contact area between the hydrate former and water molecules, the faster hydrate formation formed [48,51,52].

Therefore, as an innovative work to research the essential approach for accelerating the hydrate formation rate and improving the hydrate storage capability, new synergic additives were proposed for the hydrate-based natural gas or biogas purification process. It comprised physical gas solvent (tetramethylene sulfone, TMS) and traditional hydrate promoter (tetra-n-butyl ammonium bromide, TBAB). TMS, an acidic gas solvent with high values of boiling point and dielectric constant, can remarkably dissolve the slight polar gas acidic CO_2 [53]. This work conceived that the physical gas solvent (TMS) itself could freely dissolve and diffuse in water but could not chemically react with other components (such as CO_2 and TBAB), and could dissolve and diffuse the acidic gas (H_2S and CO_2) as a carrier. In this case, on the one hand, TMS can not only promote the solubility and diffusivity of acidic gas in the solution, but also carry acidic gases molecules to the locality where far from the gas/liquid interface, and make acidic gases fully contact with water molecules. On the other hand, the traditional hydrate promoter (TBAB) can moderate the hydrate formation conditions and promote the hydrate formation process. Therefore, it would be interesting to insight the effect of the new synergic additives on the hydrate-based natural gas or biogas purification processes. The two gas samples (G1: 0.45 CO_2/0.55 CH_4; G2: 0.44 CO_2/0.55 CH_4/0.01 H_2S) were simulated as natural gas or biogas in this work due to its realistic composition [54,55]. This work will be of importance to the fundamental study of enhancing gas hydrate formation, and of practical significance for the hydrate-based capture technology.

2. Experimental section

2.1. Materials

Both Tetra-n-butyl ammonium bromide (TBAB) and Tetramethylene sulfone (TMS) purity with 99.99% were purchased from Aladdin Industrial Corporation (Shanghai, China). The chemicals were used without any further purification. The simulated biogas and natural gas with the corresponding compositions as followed were purchased from Huate Gas Co., Ltd., China:

Gas sample G1: mole fraction (CO_2) = 0.45; mole fraction (CH_4) = 0.55;

Gas sample G2: mole fraction (CO_2) = 0.44; mole fraction (CH_4) = 0.55; mole fraction (H_2S) = 0.01;

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