Energy 104 (2016) 76–84

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Experimental study on hydrate-based CO_2 removal from CH_4/CO_2 mixture

Fei Wang [a, b], Shanfei Fu [a, b], Gang Guo [a], Zhen-Zhen Jia [c], Sheng-Jun Luo [a, **], Rong-Bo Guo [a, *]

[a] *Shandong Industrial Engineering Laboratory of Biogas Production & Utilization, Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, Shandong, China*
[b] *University of Chinese Academy of Science, Beijing 100049, China*
[c] *Guizhou University, Guiyang 550025, China*

A R T I C L E I N F O

Article history:
Received 24 June 2015
Received in revised form
20 March 2016
Accepted 21 March 2016

Keywords:
CO_2 removal
Hydrates
CH_4/CO_2 mixture
Separation factor
Multistage separation

A B S T R A C T

In this work, hydrate-based CO_2 removal from a CH_4/CO_2 mixture was studied. CH_4/CO_2 led to faster hydrate formation than pure CH_4, because the existence of CO_2 resulted in easier hydrate nucleation. Kinetic separation of CO_2 was observed in the CH_4/CO_2 hydrate formation with different initial CO_2 proportions (1.83–27.76%) due to the higher CO_2 affinity of formation of hydrates. However, the initial CO_2 proportion of CH_4/CO_2 showed no obvious effects on the hydration ratio of CH_4 and CO_2 and the separation efficiency when the gas was superfluous in hydrate formation. In addition, hydrate-based multistage separation of CH_4/CO_2 was established and conducted at different initial pressures (4, 5 and 6 MPa). The CH_4 proportions were increased from 72.24% to 97.30%, 97.22% and 97.14% after separation by four, five and seven stages at initial pressures of 4, 5, and 6 MPa, respectively.

1. Introduction

Biogas, mainly composed of CH_4 and CO_2, is converted from organic waste and considered as one of the most important renewable energy due to the low environmental impact and high energy conversion efficiency during the production [1–4]. However, the existence of CO_2 with high proportion is not conducive to the utilization of biogas, such as, used as fuel for stoves, electricity production, vehicles and fuel cells etc. [5], therefore, removing CO_2 from biogas to improve the CH_4 purity is necessary [6,7].

The conventional techniques, such as water scrubbing, cryogenic separation, physical and chemical adsorptions, pressure swing adsorption and membrane separation have been successfully used for biogas purification, through which the CH_4 proportion could reach 95–98% [5,8,9]. However, some drawbacks also exist in the above techniques, such as the high operation pressure or low operation temperature and the possibility of corrosion to the apparatus [10]. Moreover, the high energy costs of the above techniques could not be ignored, especially for small size plants [2,6]. Therefore, improving the efficiency of the current gas separation techniques or developing novel strategies are of great necessity.

Gas hydrates are clathrate crystalline compounds formed by water and gas molecules, such as CH_4 and CO_2, at suitable temperature and pressure through the occupation of gas molecules in the cavities formed by water molecules under hydrogen-bonding [11]. As different conditions are needed for different gases to form hydrates, gas mixtures can be separated through hydrate formation and dissociation [12,13]. In addition, compared with the conventional techniques for biogas purification, the hydrate-based biogas purification, storage and transportation can be achieved in a one-step manner [14].

Hydrate-based gas separation has been studied for various types of gas mixtures [15–22], among which, the studies on CH_4/CO_2 separation are relatively few. Previous studies showed that CO_2 hydrates exhibited milder equilibrium conditions than CH_4 hydrates [23–27], therefore, the separation of CH_4/CO_2 based on the different phase equilibrium conditions of CH_4 and CO_2 hydrates was proposed. For example, Castellani et al. [27] conducted the hydrate formation of CH_4/CO_2 at different partial pressures of CH_4 and CO_2,

---

[*] Corresponding author. Tel./fax: +86 532 80662708.
[**] Corresponding author. Tel./fax: +86 532 80662750.
E-mail addresses: luosj@qibebt.ac.cn (S.-J. Luo), guorb@qibebt.ac.cn (R.-B. Guo).

http://dx.doi.org/10.1016/j.energy.2016.03.107
0360-5442/

Nomenclature

m	hydration number
Δn	methane consumption
n	number of moles
P	pressure
V	volume of the gas phase in the reactor
R	universal gas constant
T	temperature
z	compressibility factor
ΔV	molar volume difference between hydrates and water
v_g	average hydrate growth rate
η	gas hydration ratio
s	separation factor of CO_2

under which CO_2 could form hydrates while CH_4 could not. However, although high CO_2 proportion in the hydrate phase was achieved, the separation efficiency was low due to the small difference between the phase equilibrium conditions of CH_4 and CO_2 hydrates.

To make the phase equilibrium of CH_4/CO_2 hydrates much milder and enlarge the hydrate stable region, thermodynamic promoters, such as TBA salts (Tetra-n-butyl ammonium Halide) and THF (Tetrahydrofuran) were employed in hydrate-based separation of CH_4/CO_2 [28–34]. Fan et al. [28] measured the hydrate phase equilibrium of CH_4/CO_2 hydrates in the presence of TBAB (Tetra-n-butyl ammonium bromide) or TBAC (Tetra-n-butyl ammonium chloride) or TBAF (Tetra-n-butyl ammonium fluoride) and found that all the three additives could expand the hydrate stable region and TBAB showed the best performance. Hydrate-based separation of CH_4/CO_2 with the existence of THF was conducted by Zhong et al. [34] and CO_2 separation could be achieved at relatively mild conditions. However, based on the different phase equilibrium conditions of CH_4 and CO_2 hydrates, it is theoretically difficult to achieve CH_4 with high purity (>97%) through hydrate-based separation of CH_4/CO_2. For example, the phase equilibrium pressures of CH_4 and CO_2 at 275.15 K were about 3.2 MPa and 1.6 MPa respectively [23], therefore, the CH_4 fraction in gas phase during the hydrate formation would not increase when the CH_4 fraction exceeded 66%, because CH_4 could preferentially form hydrates at low CO_2 proportion.

In recent years, another separation idea called “kinetic separation” has been proposed, which was based not on the different phase equilibrium conditions of CH_4 and CO_2 hydrates but on the different affinities of formation of hydrates [6,35–37]. According to Herri et al. [35], hydrate cavities and gas molecules could act as adsorbent and adsorbate respectively during gas hydrate formation and gas molecules were distributed in the hydrate cavities with respect to the relative affinity. In the hydrate formation with CH_4/CO_2, CO_2 could be removed more quickly due to the higher affinity of formation of hydrates [36–38]. Therefore, based on kinetic separation, it is theoretically possible to increase the CH_4 purity up to 97% through multistage separation to meet the Chinese natural gas standard (GB17820-2012), however, the related studies are relatively few. In addition, two important factors in hydrate-based separation of CH_4/CO_2, the hydrate formation rate and the separation efficiency, especially at a series of initial CO_2 proportions, have also been poorly investigated.

In this work, hydrate-based CH_4/CO_2 separation was carried out at a series of initial CO_2 proportions (1.83%–27.76%) to study the hydrate formation rate and separation efficiency at different initial CO_2 proportions. In addition, multistage separation of CH_4/CO_2 was established through experiments and calculation to evaluate the feasibility of achieving CH_4 with high purity (97%) through hydrate-based separation.

2. Experimental

2.1. Materials

Sodium dodecyl sulphate (SDS, AR (analytical reagent)) was purchased from Xiya Reagent Co., Ltd. CH_4 (99.99%) and CO_2 (99.99%) were provided by Heli Gas Co., Ltd (Qingdao, China). CH_4/CO_2 mixtures with different CO_2 proportions were laboratory-made. The deionized water used in this work was laboratory-made through Millipore SDS 350 water purification system and the conductivity of the obtained deionized water was 1.17 ± 0.1 μs/cm at 298.15 K.

2.2. Apparatus

Fig. 1 shows the schematic diagram of the hydrate formation apparatus used in this work. The main part of the apparatus consisted of a piston container and a reactor with the volume of 1 L and 200 mL, respectively. Both of the piston container and the reactor, with the maximum pressure capability of 20 MPa, were made of 316 L stainless steel with the roughness less than 0.2 μm and were set in the thermostatic water bath with the temperature range of 253.15–373.15 ± 0.1 K. The reactor was equipped with two PT100 temperature transducers with the uncertainty of 0.01 K and one SDD-601 pressure transducer with the uncertainty of 0.05 MPa. All the transducers were connected to YUDIAN AIDCS monitor system for data monitoring and acquisition. The piston container was connected to a metring pump with the maximum pressure ability of 10 MPa and the flow rate of 0.1–100 mL/min. The piston container played an important role in this work. On one hand, in all the hydrate formation experiments, reaction gas was charged into the piston container in advance to reach the reaction temperature and then injected into the reactor from the piston container, which could avoid the pressure change in the reactor caused by the cooling process when the gas was charged into the reactor directly. On the other hand, in the biogas separation experiments, gas mixtures were prepared in the piston container.

In addition, in order to achieve the online measurement of gas composition during the hydrate formation, a sampling device was installed on the reactor, which consisted of two globe valves and a sectional steel pipe with the volume of 0.5 mL. All the globe valves and the steel pipe were made of 316 L stainless steel. During the measurement, opened valve 1 and the gas in the reactor would fill into the steel pipe. Then closed valve 1 and opened valve 2 and the high-pressure gas could expand to the BEIFENG 3420 A gas chromatography for component analysis. All the transducers, gas chromatography and electronic balance were connected to the computer for data record.

2.3. Procedure of gas hydrate formation experiments

Gas hydrate formation was carried out in the unstirred stainless steel reactor described above. Opened the reactor and washed the reactor with deionized water three times. Then 30 mL reaction solution was added into the reactor, which was then sealed and purged with reaction gas three times. In this work, to get rapid hydrate-based separation of gas mixture, SDS solutions were used. Afterwards, the reaction gas was charged into the piston container and cooling was started. After the reaction solution reached 275.15 K, opened the valve between the reactor and piston