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Effect of swing on removing CO₂ from offshore natural gas by adsorption

Shujun Chen^{a,b,c,*}, Miaomiao Tian^a, Zhicheng Tao^{d,*}, Yu Fu^e, Yanfang Wang^a, Yongqiang Liu^a, Bo Xiao^f

^a College of Pipeline and Civil Engineering, China University of Petroleum (East China), Qingdao 266580, China

^b Shandong Key Laboratory of Oil & Gas Storage and Transport Safety, Qingdao 266580, China

^c Qingdao engineering research center of efficient and clean utilization of fossil energy, Qingdao 266580, China

^d Qiannan Polytechnic for Nationalities, Duyun 558000, China

^e College of New Energy, China University of Petroleum (East China), Qingdao 266580, China

^f School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK

ABSTRACT: Removing CO₂ from CH₄/CO₂ mixture gas is significantly important in natural gas upgrading and greenhouse gas emission control. In order to improve the separation effect, the influence of swing on removing CO₂ from offshore natural gas by the adsorption was studied systematically by experiment and simulation. Firstly, the adsorption experiment was carried out under the quiescent condition, single direction swing with a frequency of 0.12Hz, bidirectional coupling swing with a frequency of 0.12 Hz and quiescent condition with a tilting angle of 20° by the swing experiment platform. The results indicated that the swing of the adsorber can reduce the adsorption purification effect, and which is not caused by the decrease of the adsorbent performance. Then, the adsorption purification model was established and the validity of the model was verified by experiments. Finally, the effects of tilting angle and L/D ratio of the porous zone, inlet flow rate of the mixture gas, particle diameter of adsorbent, and gas inlet distribution of the adsorber on adsorption purification under the quiescent and swing conditions were studied in detail. The results showed that decreasing the tilting angle of the porous zone and inlet flow rate of the mixture gas, or increasing the L/D ratio of the porous zone, the particle diameter of the adsorbent and the inlet amounts of the adsorber can reduce the adverse effect of swing on purification of natural gas. It is of great significance to improve the effect of adsorption purification of natural gas under swing condition by changing the adsorption conditions and structure of the adsorber. The research will provide a certain guidance for removing CO₂ from offshore natural gas by adsorption.

ARTICLE INFO

Keywords: Adsorption purification effect, Swing, Adsorption purification model, removing CO₂, adsorber structure.

1. Introduction

Climate change is considered to be one of the greatest environmental threats of our times. Thus, more and more attention has been paid toward reduction air pollutant emissions as a global environmental challenge. Taking into account actual uncleanly nature of petroleum and coal, the natural gas is regarded as a prospective alternative because of its higher specific combustion enthalpy and the lower emission of carbon dioxide upon combustion. It is predicted that the world natural gas consumption will grow up from 110 quadrillion btu in 2010 to 180 quadrillion btu in 2040 which will exceed the consumption of coal¹, increasing by 64%. To meet the world's growing demand for natural gas requirement, continuous growth in natural gas will remain active in the next decades. Therefore, besides the exploitation of onshore natural gas, an increase in exploitation of offshore natural gas offers an alternative way to satisfy this growing worldwide

* Corresponding authors.

E-mail addresses: shujunchenfu@126.com (S. Chen), kevintaocheng@hotmail.com (Z. Tao).

demand of natural gas.

For offshore natural gas production, the floating liquefied natural gas production storage and off-loading platform (LNG-FPSO) are used for offshore natural gas exploitation, pretreatment, liquefaction, storage, transportation and offloading²⁻⁷. The pretreatment is one of the key points of the offshore natural gas development. Raw natural gas contains a variety of impurities, including acid gas, water vapor, nitrogen, etc..⁸⁻¹⁰ The existence of CO₂ in acidic gas contributes to climate change, causes corrosion to LNG-FPSO equipment, and reduces the combustion heat value of natural gas.¹¹ Therefore, it is necessary to remove CO₂ from offshore natural gas.

To date, the major technologies for gas separation/purification are absorption,¹²⁻¹⁶ membrane separation,^{11,17-19} and adsorption separation.²⁰⁻²⁵ Considering the limited space of the LNG-FPSO as well as swing caused by waves and typhoons, the CO₂ removal device on the LNG-FPSO should be compact, safe and reliable. Moreover, the technology should be mature. According to the characteristics of above methods of gas separation, adsorption based techniques show promise due to their inherently simplicity, low operational requirements, low cost, ease of control and high efficiency. 13X zeolites which have good availability, large surface area, porous texture, high CO₂ adsorption capacity and selectivity, and good stabilities, have traditionally been the most widely used adsorbent.²⁶⁻²⁹ Additionally, it has been mentioned in the literature as one of the best performing candidates for CO₂ removal from natural gas.^{27,30-34} Therefore, 13X zeolite was selected as the adsorbent for removing CO₂ from offshore natural gas.

At present, many investigations have been conducted on large-scale hull sloshing.³⁵⁻³⁸ With the extensive use of floating platforms, its tilt and sloshing influenced the adsorption performance.³⁶ Based on the practical data for South sea of China, Gu et al.³⁷ studied the cryogenic liquid transport in pitching motion with a swing angle of 6-15 ° and a frequency of 0.06-0.24 Hz. Zhao et al.³⁸ studied the coupling effects and interactions between ship motion and inner-tank sloshing. These researches on liquid sloshing provided a guiding for the study of the solid swing. Currently, our group has conducted some studies on the application of adsorption for offshore natural gas purification. Chen et al.³⁹ compared the CO₂ adsorption performance of 13X zeolite under swing and quiescent conditions. The moderate swing was beneficial to adsorption. However, the effect the swing on the adsorption purification of the mixture was not considered. Because the swing can affect the voidage of the adsorber, the best voidage was obtained through the experiments by Chen et al.⁴⁰ But the movement of the adsorbent was not clarified during the swing process.

The adsorption effect can be improved by changing the adsorption conditions and the structure parameters of the adsorber. Sui et al.⁴¹ found that the adsorption of o-xylene on silica gels could be significantly enhanced by increasing the height to diameter ratio. Abdullah et al.⁴² suggested that inlet flow rate and CO₂ concentration could influence the adsorption performance of the

CH₄/CO₂ mixture. Other studies have revealed that the adsorption properties could be affected by the particle size of the adsorbent.^{41,43-46} Most of above experimental and theoretical studies were focused on the adsorption under static conditions. However, there were few literatures on the adsorption properties of the solid adsorbents swing. Therefore, it is urgent to carry out corresponding researches for offshore natural gas purification.

The objective of this study is to systematically investigate the effect of swing on removing CO₂ from offshore natural gas by adsorption. Firstly, the adsorption breakthrough experiments were carried out under quiescent and different swing conditions. The experimental results were analyzed and the separation factors under various conditions were calculated. Secondly, the adsorption purification model was established, and the validity of the model is verified. Thirdly, the effects of tilting angle and length/diameter (L/D) ratio of porous zone, inlet flow rate of the mixture gas, particle diameter of adsorbent, and gas inlet distribution of the adsorber on adsorption purification under the quiescent and swing conditions were respectively discussed.

2. Materials and experiments

2.1 Materials

13X zeolite consisting of spherical particles with diameters of 1-3 mm was provided by Pingxiang Xintao Chemical Packing Co., Ltd. (China). The average pore diameter, BET surface area and pore volume of 13X zeolite were about 2.01 nm, 536.62 m²/g and 0.27 ml/g, respectively. High-purity CO₂ and CH₄ (99.999%) were used in the adsorption experiments.

2.2 Experimental setup and procedures

The experimental setup is shown in Fig.1. The details of the experimental setup for the gas adsorption has been described in previous works.³⁹ The mole fractions of CH₄ and CO₂ in the mixture gas were 97% and 3%, respectively, and were adjusted by a computer automatic gas distribution system. The inlet flow rate of the gas mixture was 0.00008 kg/s. The height of 13X zeolite in the adsorber was 100 mm, and the voidage was 0.40. In the adsorption process, the adsorption temperature and pressure were 298 K and 101325 Pa, respectively. For the swing platform, the single direction swing is approximate to a sine function, while the bidirectional coupling swing is the superposition of two sine functions, as shown in Fig.2. The movement locus for the bidirectional coupling swing can be explained as follows.

The function of single direction swing 1:

$$x = A \sin(\omega t + \theta) \quad (1)$$

The function of single direction swing 2:

$$y = B \sin(\omega t + \beta) \quad (2)$$

The movement locus for the bidirectional coupling swing consists of equations (1) and (2).

When $\theta = \beta$ and $A = B$, equation (3) turns into equation (4), which is plotted in Fig.2(b).

$$\frac{x^2}{A^2} + \frac{y^2}{B^2} - \frac{2xy}{AB} \cos(\beta - \theta) = \sin^2(\theta - \beta) \quad (3)$$

$$y = x \quad (4)$$

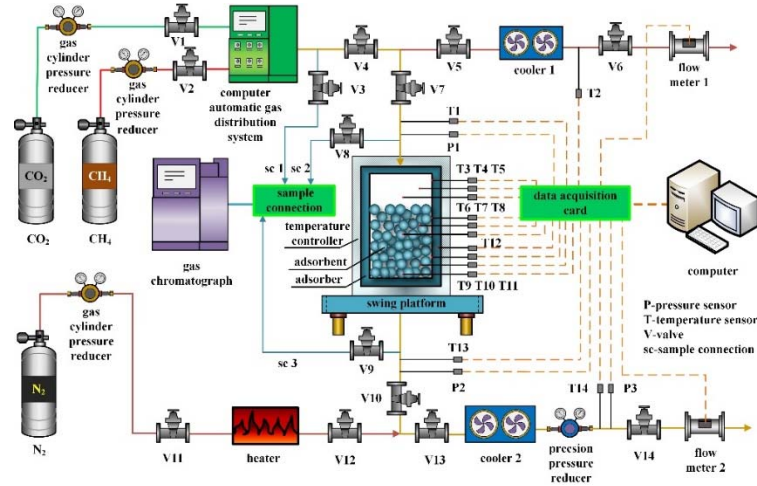


Fig.1. Experimental apparatus for gas adsorption on 13X zeolite.

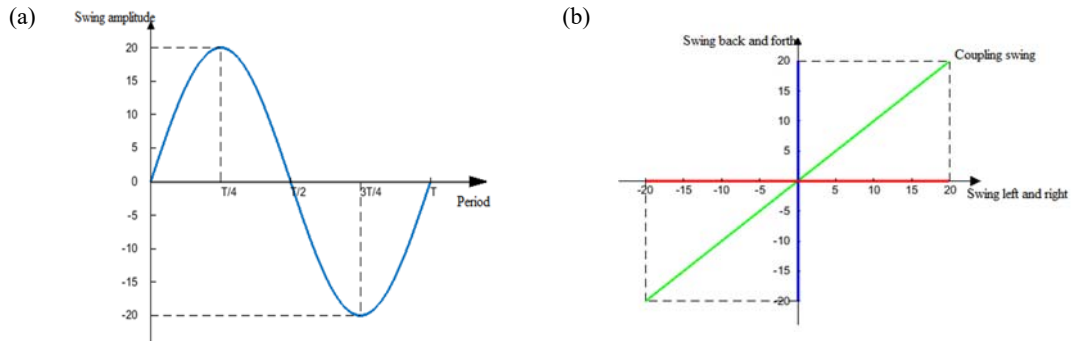


Fig.2. Schematics of swing amplitude. (a) Single direction swing. (b) Bidirectional coupling swing.

Immediately before the adsorption experiment was conducted, 13X zeolite was degassed for 6 h at 553 K to remove any adsorbed species. As shown in Fig.1, the swing of the adsorber was performed by the swinging platform which could control the frequency and direction of the swing. Adsorption experiments were carried out under the quiescent conditions, single direction swing with a frequency of 0.12 Hz, bidirectional coupling swing with a frequency of 0.12 Hz and quiescent condition with a tilting angle of 20° , respectively. After each pipeline was connected, the gas from the gas distribution system flowed into the pipelines via V4, and then entered the adsorber after passing through V7. In this process, CO_2 was adsorbed by 13X zeolite in the adsorber. The purified gas passed through V10, V13 and cooler 2. Finally, the purified gas was

discharged after the gas flow and volume fraction of CO₂ were measured by the flowmeter and gas chromatographic analyzer respectively. In order to recycle the adsorbent, the saturated adsorbent was regenerated by hyperthermal N₂ from V10 at the bottom of the adsorber. After N₂ flowed out of V7 and passed V5, it entered the cooler1 to be cooled to the room temperature. At last, the flow was measured by flow meter 1.

2.3 Experimental results and analysis

CO₂ breakthrough curves under four conditions are depicted in Fig.3. As illustrated in Fig.3, the start breakthrough time of the quiescent condition, the single direction swing with a frequency of 0.12 Hz and the bidirectional coupling swing with a frequency of 0.12 Hz were 8 min, 7 min and 6 min respectively, and the complete breakthrough time of those were 79 min, 67 min and 40 min respectively. The order of the start and complete breakthrough time for above three conditions were all as follows: quiescent condition>single direction swing>bidirectional coupling swing, which indicates that swing have adverse effect on adsorption purification. The reduction of the breakthrough time is attributed to two things. On the one hand, changing in the effective specific surface area, voidage and bulk density of the adsorbent caused by swing lead to changes in mass transfer resistance; On the other hand, the gas-solid contact, such as flow pattern (laminar and turbulent flow) and actual flow rate, had changed due to the above mentioned reasons. At the same swing frequency, the breakthrough time of the bidirectional coupling swing was less than that of the single direction swing. This can be explained by the motion rule of the swing platform. In the bidirectional coupling swing experiment, the motion rule of each direction is same, namely the bidirectional coupling swing is equivalent to the superposition of two sine functions with the same cycle. When the tilting angle of a single sine function gradually increased from 0 ° to 20 °, the tilting angle of the superimposed sine function would gradually increase from 0 ° to the maximum angle which could be greater than 20 °. Consequently, as shown in Fig.2, the tilting angle of the bidirectional coupling swing is larger than that of the single direction swing.

In addition, the swing will tilt the adsorber. Therefore, the adsorption experiment under quiescent condition with a 20 ° tilt angle was performed. It was found that the complete breakthrough time of quiescent condition with a 20 ° tilt angle was 52 min which was longer than that of bidirectional coupling swing, but the start breakthrough time was the shortest which was only 3 min. As depicted in Fig.3, in the early stage of the adsorption, CO₂ concentration under the tilting condition increased faster than that under the coupling swing condition, while CO₂ concentration increased slowly with time passed away, which may be attributed to the stacking and unevenness of adsorbent due to tilt of adsorber.

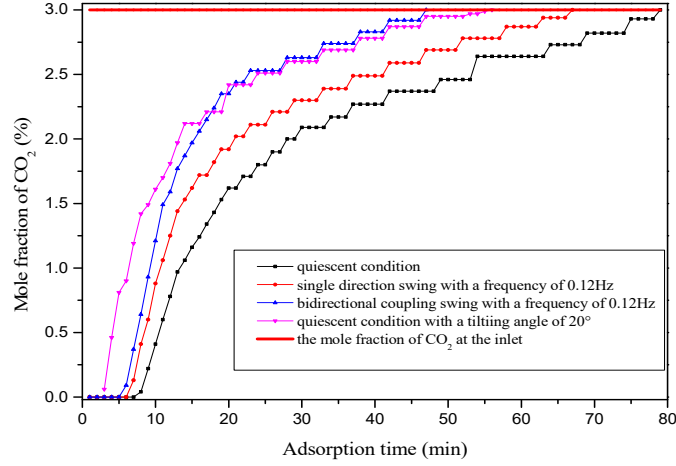


Fig.3. Breakthrough curves of CO₂.

To quantify the separation effect, the separation factor was calculated using the equation (5).

$$a_{ij} = \frac{(x/y)_i}{(x/y)_j} \quad (5)$$

where a_{ij} is separation factor, x is the adsorption phase molar fraction of one component, y is the gas phase molar fraction of one component, the subscripted variables i and j represent the component.

According to equation (5), the separation factors of quiescent condition, single direction swing with a frequency of 0.12 Hz, bidirectional coupling swing with a frequency of 0.12 Hz and quiescent condition with a tilting angle of 20 ° were 3.52, 3.47, 3.44, and 3.48, respectively. There was no significant difference in the numerical value among them, indicating that the decrease of adsorption purification performance caused by swing did not relate to the adsorbent properties. Therefore it is necessary to further analyze the reasons for the decrease of adsorption purification effect under swing conditions.

3. Adsorption purification model

3.1 Governing equations of the numerical model

The gas adsorption in 13X zeolite can be not only investigated by experiment but also by simulation. Compared to experiment, the most advantage of simulation is to save time and cost. In order to obtain the reliable simulation result, it is necessary to set up the reasonable governing equations. The mass conservation equation, momentum conservation equation, energy conservation equation, and adsorption model are all considered.

Considering the mass source term, the mass conservation equation in porous media can be written as follows.

$$\frac{\partial(\varepsilon\rho_f Y_i)}{\partial t} + \nabla \cdot (\varepsilon\rho_f \mathbf{v} Y_i) - \nabla \cdot (\varepsilon\rho_f B_{i,m} Y_i) + M_i \rho_p (1 - \varepsilon) \frac{\partial q_i}{\partial t} = 0 \quad (6)$$

where ε is voidage, ρ_p is the density of adsorbent particles, q_i is the adsorption capacity of component i , M_i is molar mass of component i .

The porous media model was modified by adding a momentum source term formed by the conventional momentum source term and a momentum transfer caused by gas adsorption to the standard fluid Navier-Stokes (N-S) equation.⁴⁷ The modified N-S equation is written as follows.

$$\frac{\partial(\rho_f \vec{v})}{\partial t} + \nabla(\rho_f \vec{v} \vec{v}) = -\nabla p + \nabla(\vec{\tau}) + \rho_f \vec{g} - \mu \frac{\vec{r}}{\alpha} - \left(C_2 \rho_f |\vec{v}| - \left(M_i \rho_p (1 - \varepsilon) \frac{\partial q_i}{\partial t} \right) \right) \vec{v} \quad (7)$$

where $\frac{1}{\alpha}$ is the viscous resistance coefficient, C_2 is the inertia resistance coefficient, which can be calculated using the Ergun equation.

$$\frac{1}{\alpha} = \frac{150(1 - \varepsilon)^2}{d_p^2 \varepsilon^3} \quad (8)$$

$$C_2 = \frac{1.75(1 - \varepsilon)}{d_p \varepsilon^3} \quad (9)$$

where d_p is the adsorbent particle diameter.

Taking into account the conservation laws of the accumulated energy in the adsorber and the change of energy caused by pressure, heat conduction, heat transfer, and adsorption, the energy conservation equation can be expressed as follows.

$$\begin{aligned} \frac{\partial}{\partial t} (\varepsilon \rho_f E_f + (1 - \varepsilon) \rho_p E_p) + \nabla(\vec{v}(\rho_f E_f + p)) = \\ \nabla[k_{eff} \nabla T + (\vec{\tau} \vec{v})] + \sum_{i=1}^n (-\Delta H_i \left(-M_i \rho_p (1 - \varepsilon) \frac{\partial q_i}{\partial t} \right) / M_i) \end{aligned} \quad (10)$$

The adsorption model includes the linear driving force model and two-phase equilibrium model, which can be expressed as follows.

$$\frac{\partial q_i}{\partial t} = k_i \left(\frac{a_i p_i}{1 + \sum_{i=1}^n b_i p_i} - q_i \right) \quad (11)$$

where a and b are fitting parameters.

The geometrical models of the adsorber under the quiescent and tilting condition caused by the swing were constructed, as presented in Fig.4. The tilting angle (ϕ) of the adsorber was shown in Fig.4(b). In the simulation process, the geometry models of the quiescent and tilting conditions were represented by changing the shape of the porous zone, and the boundary conditions were shown in Table 1.

Table 1
Boundary conditions.

Boundary	Flowing adsorption
Entrance	Mass flow rate inlet
Vent	Pressure outlet
Adsorber wall	Wall
Adsorber	axial symmetry

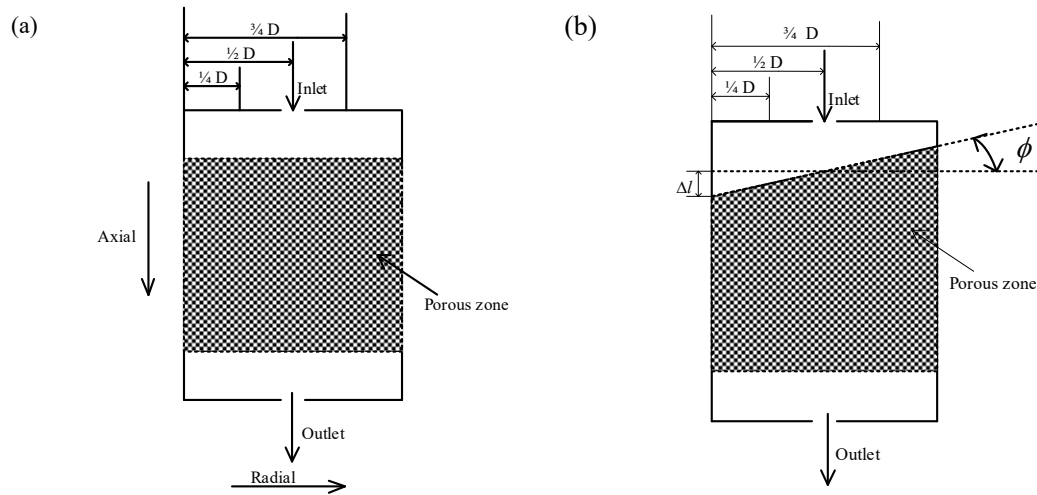


Fig.4. Geometry models of adsorber under (a) quiescent and (b) tilting conditions.

3.2 Model validation

In order to prove the validity of the model, the adsorption breakthrough experiment of mixed gas with 3% molar fraction of CO_2 under quiescent condition was performed at 298 K and 101325 Pa. At the same time, the numerical simulation was carried out using the adsorption purification model under the same conditions. As shown in Fig.5, the results calculated by the model fitted the experimental data well, and the average relative error between the simulation and experiment was only 2.51%, suggesting that the simulation results are reliable.

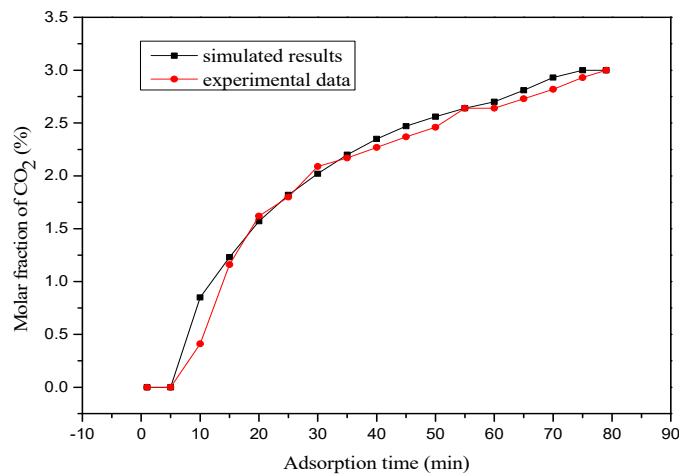


Fig.5. Comparison of simulated results and experimental data.

4. Results and discussion

4.1 Influence of quiescent and tilting conditions on adsorption purification effect

The adsorption of CO₂/CH₄ mixture was simulated under the quiescent and tilting conditions, respectively. The L/D ratio of porous zone is 1. The distribution map for mass fraction of CH₄ at 10 s was displayed in Fig.6. It can be seen that the CH₄ concentrations exhibited a symmetrical distribution under the quiescent condition which is similar to the parabolic curve. However, the distribution for the mass fraction of CH₄ under the tilting condition is asymmetric. The adsorbent would accumulate to one side of the adsorber under tilting condition. The accumulated adsorbent can adsorb more CO₂, which makes the CH₄ concentration of the inlet at the stacking side of adsorbent higher. But the CH₄ concentration at the outlet under the tilting condition is generally lower than that of the quiescent condition, which indicates that adsorption purification effect under the quiescent condition is better. The result can be attributed to the difference in the flow of gas. The inertial and viscous resistance of the CO₂/CH₄ mixture in gas phase is smaller than that in porous region. When the adsorbent was piled onto one side, more gas will autonomously flow toward another side with less resistance. This makes that the adsorbent at the inlet of stacking side is not fully utilized for the flow adsorption. The start breakthrough time under the tilting condition depends on the time of adsorption saturation of the adsorbent at the opposite side of the stacking side. This also provides the reason that the adsorption purification effect under tilting condition is worse than that under quiescent condition.

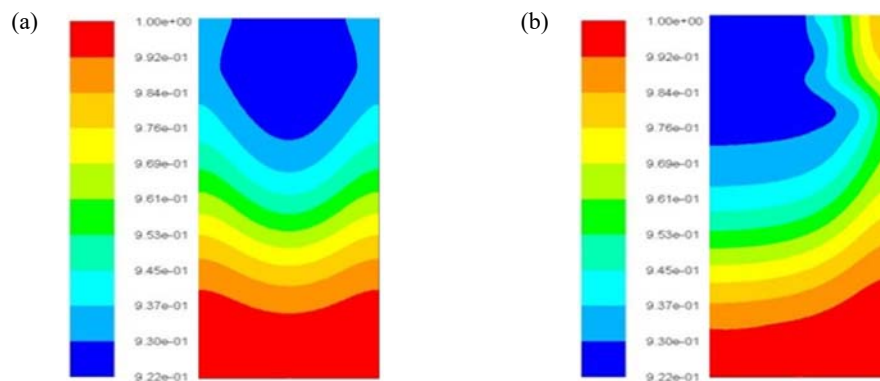


Fig.6. Concentration distribution of CH₄ under (a) quiescent and (b) tilting conditions.

The adsorption simulation of CO₂/CH₄ mixture with a certain adsorber size was performed under the tilting angles of 5 °, 10 °, 15 ° and 20 ° respectively. Fig.7 is the mass fraction of CH₄ along the radial direction at 1/4D, 1/2D and 3/4D of the adsorber when the adsorption time is 10 s.

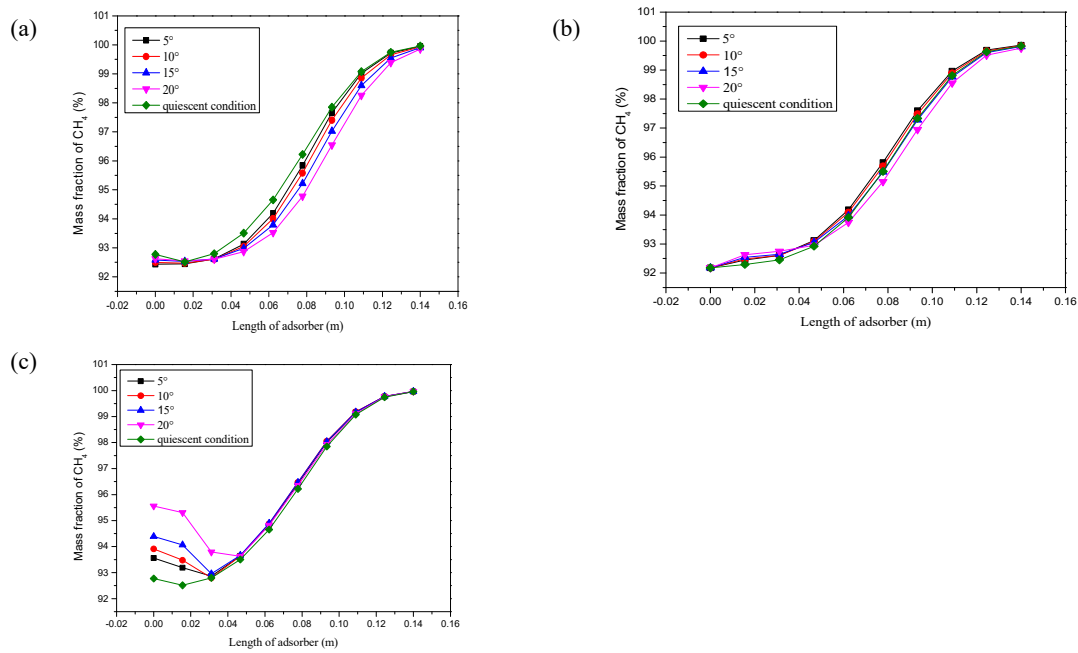


Fig.7. Mass fraction of CH₄ at different angles and (a) 1/4D, (b) 1/2D, and (c) 3/4D of the adsorber.

Fig.7(a) shows the variation in mass fraction of CH₄ along the length of the adsorber at 1/4D. With the increases of the tilting angle, the mass fraction of CH₄ gradually decreases, indicating that the larger the tilting angle, the worse the effect of adsorption purification. This can be ascribed the fact that the air area will enlarge with the increase of the tilting angle at the 1/4D of the adsorber. Fig.7(b) is the mass fraction of the CH₄ along the length of the adsorber at 1/2D. As shown in Fig.7(b), there is little difference in the CH₄ mass fraction at different tilting angle. This is due to the fact that the influence caused by the tilt is small for the adsorbent at the center line of the adsorber. The mass fractions of CH₄ at the tilting angle of 5 ° and 10 ° are slightly higher than that at the quiescent condition while that at the tilting angle of 20° is a few lower. Fig.7(c) shows the mass fraction of CH₄ along the length of the adsorber at 3/4D. At the inlet of the adsorber, as depicted in the Fig.7(c), the larger the tilting angle is, the thicker the adsorbent accumulates, and the better the effect of adsorption purification is. Therefore, the mass fraction of CH₄ at the inlet of the adsorber is the highest at the tilting angle of 20 °. With more CO₂ spreading to adsorber, the mass fraction of CH₄ along the length of the adsorber is decreased. At the last part of the adsorber, it shows a trend of increasing gradual, and the difference between the quiescent and tilting conditions is very small.

By comparing the mass fraction of CH₄ at different angles, it can be seen that the larger the tilting angle of the adsorber is, the lower the mass fraction of CH₄ will be. The tilting of adsorber has an adverse effect on adsorption purification. To reduce the adverse effect, it is critical to reduce the tilting degree of the adsorbent when the adsorber tilts, which can be decreased by changing the tilting angle and the adsorber diameter.

4.2 Influence of L/D ratio of the porous zone on adsorption purification effect

In order to be comparable, the area of the porous mediums with different L/D ratios was the same in the simulation. The detailed parameters of porous area with different L/D ratios were shown in Table 2. Fig.8 shows the mass fraction of CH₄ with different L/D ratios at the 1/4D and 3/4D of the adsorber. The L/D ratios are 1.000, 4.000 and 10.24 respectively. For more effective comparison, the curves depicted in Fig.8 are the date when the breakthrough of CO₂ started. The breakthrough time with L/D ratios of 1.000, 4.000 and 10.24 are 10 s, 12 s and 12 s respectively. It can be seen from Fig.8(a) that the mass fraction of CH₄ under the quiescent condition is higher than that under the tilting condition at 1/4D of the adsorber. When the area of porous media is constant, the difference in the mass fraction of CH₄ between the quiescent and tilting conditions decreases with the increase of the L/D ratio. It is negligible when the L/D ratio reaches 10.24. As shown in Fig.8(b), at 3/4D of the adsorber, the mass fraction of CH₄ at the inlet of the adsorber with the L/D ratio of 1.000 under tilting condition is much higher than that under the quiescent condition. With the increase of the L/D ratio, the difference between these two conditions is gradually reduced. When the L/D ratio reaches 10.24, the difference can be ignored. It can be concluded that increasing the L/D ratio can improve the adsorption purification effect under the tilting condition. There are two reasons, on the one hand, the length of the porous area increases with the increasing of the L/D ratio when the porous media area is constant. Therefore, the time that the CO₂/CH₄ mixture flows through the porous area will increase. On the other hand, the increase of the L/D ratio can reduce the adsorbent stacking height caused by tilt, which reduces the influence of the tilt on the adsorption.

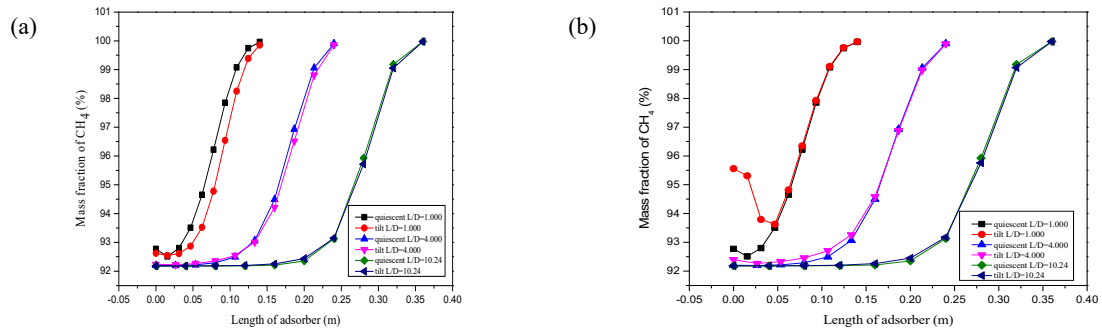


Fig.8. Mass fraction of CH₄ at different L/D ratios and (a) 1/4D and (b) 3/4D of the adsorber.

Table 2

Parameters of porous area with different L/D ratios.

L/D	L(m)	D(m)	Δl (m)
1.000	0.10	0.100	0.018
4.000	0.20	0.0500	0.0090
10.24	0.32	0.0313	0.0057

The radial distributions for mass fraction of CH₄ with different L/D ratios were depicted in

Fig.9. As can be seen from Fig.9(a), when L/D ratio is 1.000, the distribution for mass fraction of CH₄ under quiescent condition is axisymmetric along the radial direction and the lowest value is at 1/2D of the adsorber, while it monotonically increases under the tilting condition. The mass fraction of CH₄ at the stacking side of adsorbent under the tilting condition is higher than that under the quiescent condition. With the increase of L/D ratios, the distribution for mass fraction of CH₄ gradually becomes horizontal and linear. As shown in Fig.9(c), when L/D ratio is 10.24, the mass fraction of CH₄ under two conditions both presents a similar horizontal linear distribution indicating that the tilt of adsorber has no effect on adsorption purification. When L/D ratios are 1.000, 4.000 and 10.24, the relative differences for the mass fraction of CH₄ between adsorber wall and center under the quiescent condition are 20.57%, 0.15% and 0.04%, respectively, and the relative differences are 39.02%, 6.52% and 0.68% under the tilting condition. It illustrates that increasing L/D ratio can make CO₂ adsorbed evenly and the utilization of adsorbent will be improved.

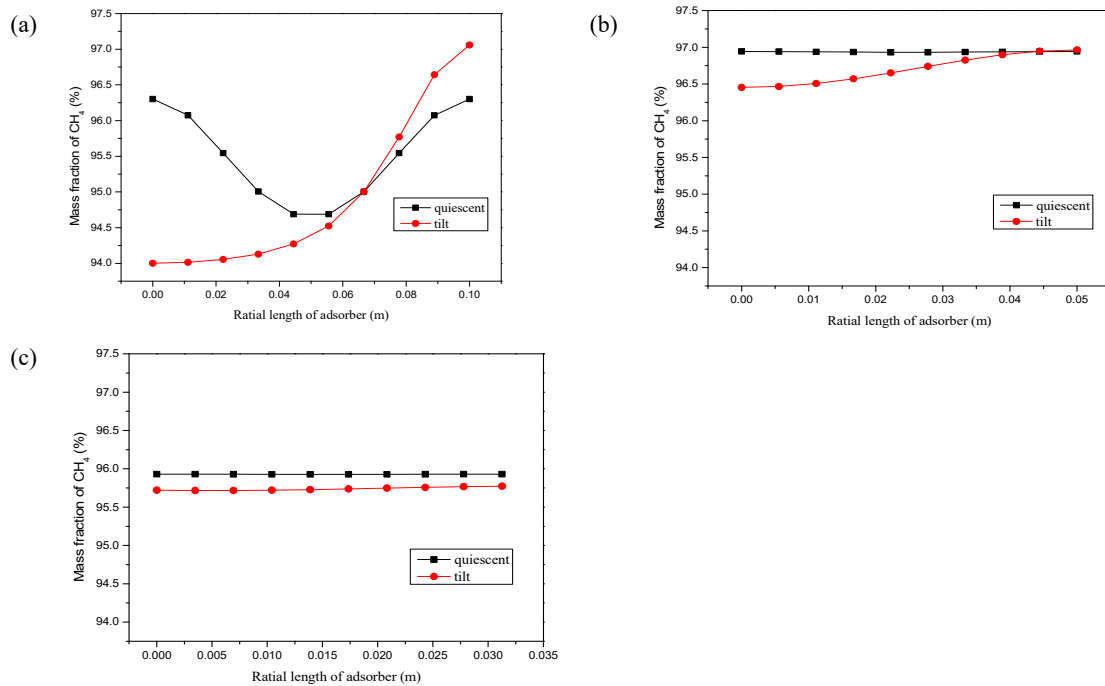


Fig.9. Radial distribution of mass fraction of CH₄ with L/D ratios of (a) 1.000, (b) 4.000, and (c) 10.24.

Fig.10 shows the concentration distribution of CH₄ under the quiescent and tilting conditions at adsorption time of 10 s and L/D ratios of 4.000 and 10.24, respectively. The waveforms tend to be linear with the increase of the L/D ratio which also agrees well with the results of the Fig.9.

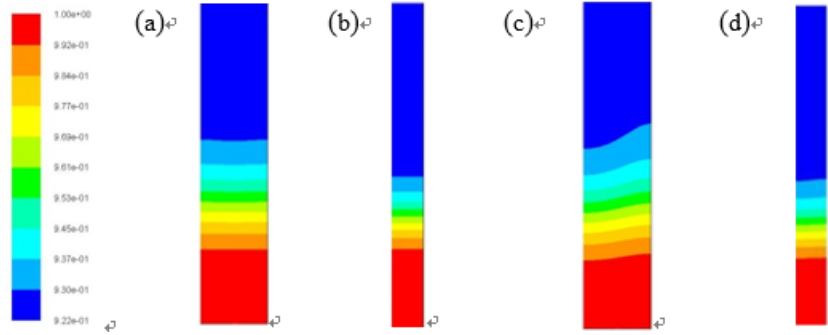


Fig.10. Concentration distributions of CH₄ at adsorption time of 10 s under quiescent condition with L/D ratios of (a) 4.000 and (b) 10.24, and under tilting condition with L/D ratios of (c) 4.000 and (d) 10.24.

4.3 Influence of the inlet flow rate of the mixture gas on adsorption purification effect

The distribution curves for mass fraction of CH₄ with different flow rates at 1/4D, 1/2D and 3/4D of the adsorber under the quiescent and tilting conditions were shown in Fig.11. The mixture gas flow rates are 0.01 kg/s, 0.0005 kg/s and 0.0001 kg/s respectively. Table 3 listed the start breakthrough time at various flow rates. As shown in Fig.11, with the reduction of the flow rate, the mass fraction of CH₄ increases. Due to the tilt of the adsorber, the differences for the mass fraction of CH₄ near the inlet between the quiescent and tilting conditions is big at 1/4D and 3/4D of the adsorber. At 1/4D of the adsorber, as shown in Fig.11(a), when the flow rate is 0.01 kg/s, except the mass fraction of CH₄ near the inlet, the difference for mass fraction of CH₄ along the length of the adsorber between the quiescent and tilting conditions is small. This can be attributed that the flow rate is too fast to be adsorbed. When the flow rates are 0.0005 kg/s and 0.0001 kg/s, the mass fraction of CH₄ at 1/4D of the adsorber under quiescent condition is higher than that under the tilting condition, and the difference gradually decreases. At 1/2D of the adsorber, as shown in Fig.11(b), when the flow rate is 0.0005 kg/s, although the mass fraction of CH₄ under the quiescent condition is still higher than that under the tilting condition, the difference is greatly reduced. When the flow rate reduces 0.0001 kg/s, the mass fraction of CH₄ under the tilting condition starts to be higher than that under the quiescent condition. At 3/4D of the adsorber, as shown in Fig.11(c), when the flow rate is 0.0005 kg/s, the mass fraction of CH₄ under the tilting condition is completely higher than that under the quiescent condition. Furthermore, as depicted in Figs.11(a) and (c), when the flow rate reduces 0.0001 kg/s, the mass fraction of CH₄ near the inlet under tilting conditions is more even at 1/4D and 3/4D of the adsorber, which indicates that the influence of the tilt is reduced. The above analysis illustrates that low flow rate of mixed gas is conducive to the purification of natural gas under the tilting condition.

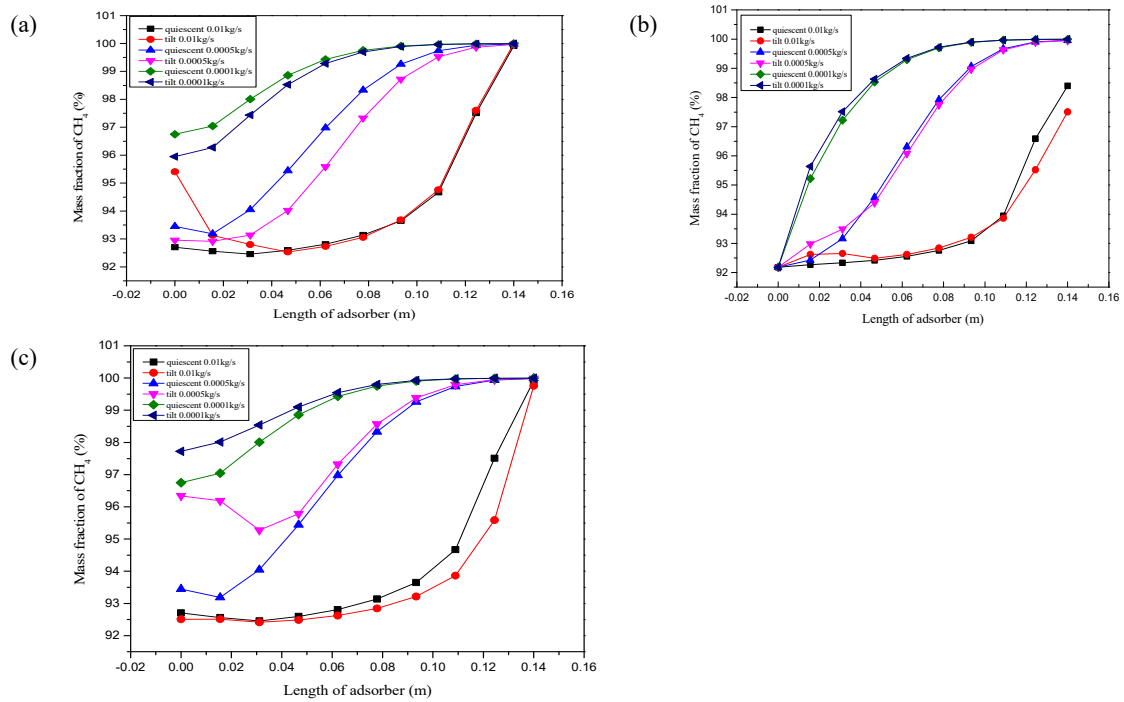


Fig.11. Effect of flow rates under quiescent and tilting condition at (a) 1/4D, (b) 1/2D and (c) 3/4D of the adsorber.

Table 3

Start breakthrough time at different flow rates.

Flow rate	0.01 kg/s		0.0005 kg/s		0.0001 kg/s	
	quiescent	tilt	quiescent	tilt	quiescent	tilt
Time (s)	1.5	1.1	14	14	24	28

It can be seen from table 3 that the start breakthrough time of the quiescent condition at the flow rate of 0.01 kg/s is greater than that of the tilting condition, which is consistent with the analysis of Fig.6. With the decrease of flow rate, the start breakthrough time increases. When the flow rate reduces 0.0001 kg/s, the start breakthrough time of the tilting condition is higher than that of the quiescent condition, indicating that the tilt of the adsorber is more beneficial to the purification of natural gas. This is consistent with the conclusion in Fig.11. The decrease of the flow rate of the mixture gas can reduce the diffusion resistance and enhance the contact time between the gas and adsorbent particles.

In Fig.11, the curves for the mass fraction of CH_4 transfers from concave to convex as the flow rate decreases. The diffusion of gas occurs preferentially at high flow rate. Owing to the effect of the resistance, the flow rate of gas along the length of the adsorber will gradually decrease, which makes CO_2 fully adsorbed at the second half of the adsorber. However, the mixture gas can be fully adsorbed near the inlet of the adsorber at low flow rate. Therefore, the mass fraction of CH_4 increases rapidly in the first half of the adsorber, which makes the curve convex. In addition, the resistance in the air and porous zone decreases at the low flow rate. More gas will flow into the adsorbent at the stacking side of the adsorber. This will lead the increase of CH_4 concentration in

the gas mixture. Therefore, the smaller flow rate of gas mixture can improve the effect of adsorber tilt on adsorption purification. This result also provides the direction for the improvement of the adsorber structure, and the subsequent attempts to change the adsorber from single inlet to double inlets. Meanwhile allows more gas to flow into the adsorbent at the stacking side of the adsorber.

4.4 Influence of particle diameter of the adsorbent on adsorption purification effect

Figs.12 and 13 are respectively concentration distribution of CH₄ at different particle diameters with adsorption time of 6 s under quiescent condition and 4 s under tilting conditions. As shown in Fig.12, the area of the dark blue region at fixed flow rate gradually decreases as the particle diameter increases under the quiescent condition, which indicates that the increase of particle diameter leads to an improvement in the adsorption purification effect. Under the tilting condition, as shown in Fig.13, with the increase of particle diameter, concentration distribution of CH₄ becomes gradually axisymmetric. In addition, the waveforms of CH₄ at the stacking side of the adsorbent transfer from the concave to convex, indicating that the influence of adsorber tilt on adsorption purification decreases gradually. When the voidage of the adsorber is constant, according to the Ergun equation (equations (8) and (9)), the larger the particle diameter is, the smaller the parameters of C_2 and $\frac{1}{\alpha}$ become, which means the viscous resistance and inertia resistance between the adsorbent and gas reduce. The gas is more likely to spread to the stacking side of the adsorbent, thereby reducing the influence of adsorber tilt on the adsorption purification. It can be conclude that increasing the diameter of adsorbent is an effective method to improve the adsorption purification effect.

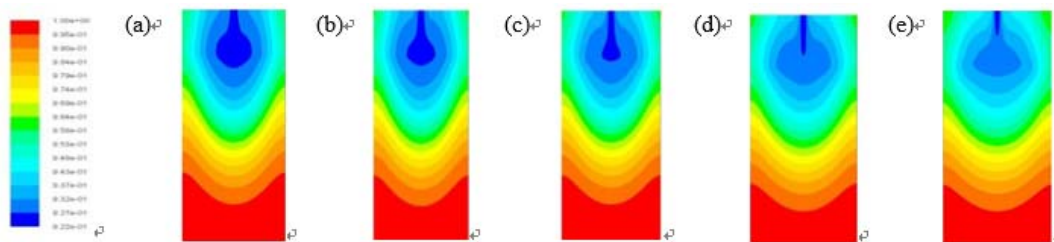


Fig.12. Concentration distributions of CH₄ under quiescent condition when the particle diameters of the adsorbent are (a) 0.800 mm, (b) 1.60 mm, (c) 3.20 mm, (d) 6.40 mm and (e)12.8 mm, respectively.

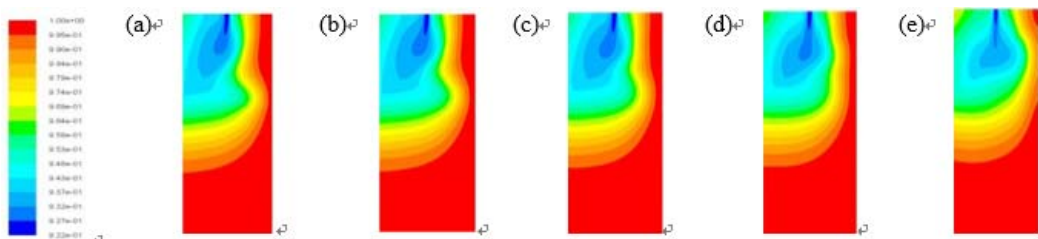


Fig.13. Concentration distributions of CH₄ under tilting condition when the particle diameters of the adsorbent are (a) 0.800 mm, (b) 1.60 mm, (c) 3.20 mm, (d) 6.40 mm and (e)12.8 mm, respectively.

4.5 Influence of gas inlet distribution on adsorption purification effect

In order to reduce the effect of adsorber tilt on the adsorption purification, the influence of inlet distribution on the adsorption was studied. Fig.14 is the mass fraction of CH₄ along the radial direction at the 1/2 axial length of the adsorber with different inlet distribution under the quiescent and tilting conditions. The adsorption time is 8 s. As shown in Fig.14, with the increase of the radial length of the adsorber, the mass fraction of CH₄ is axisymmetric for the single inlet under quiescent condition. However, it increases gradually for the single inlet under tilting condition. When another inlet is added under the tilting condition, the mass fraction of CH₄ is higher than that under quiescent condition with single inlet, indicating that the adsorption purification effect under tilting condition can be improved by increasing the inlet amounts of adsorber.

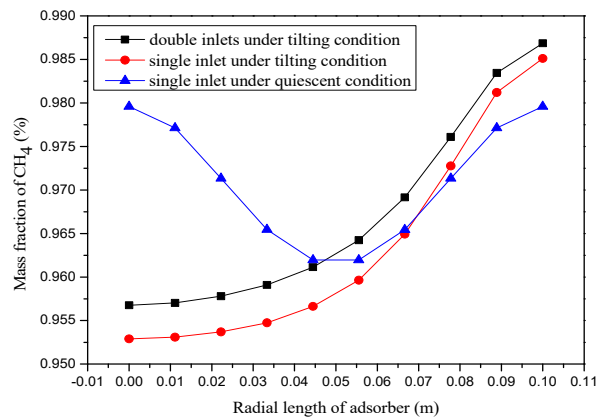


Fig.14. Mass fraction of CH₄ along radial direction of adsorber under different inlet distribution.

In order to improve the utilization of adsorbent at the stacking side of the adsorber under tilting condition, double inlets were set at the radial tripartite point of the adsorber. The mass flow rate of mixture gas at the stacking side of the adsorbent accounted for 90%, and that at the other inlet accounted for 10%. The mass fraction of CH₄ along axial direction for 1/3D and 2/3D of adsorber under different inlet amounts were shown in Fig.15, where the adsorption time is 8 s. As shown in Fig.15(a), except for the air zone, the mass fraction of CH₄ with the double inlets is higher than that with the single inlet. It can be seen from Fig.15(b) that the mass fraction of CH₄ at 2/3D of the adsorber with the single inlet decreases gradually in the axial length range from 0 to 0.05 m in the adsorber, while that with the double inlets increases in the same range, indicating that the double inlets can eliminate the negative influence of tilt on adsorption, and the adsorbent at the stacking side of the adsorber can be fully utilized. The mass fraction of CH₄ with the double inlets from 0.05 m to 0.14 m at the axial direction of the adsorber is higher than that with the single inlet, which demonstrates that the adsorption purification effect of the adsorber with double inlets is better. Therefore, adding an inlet at the stacking side of the adsorbent is one of the effective ways to improve the adsorption purification effect of the natural gas under the tilting condition.

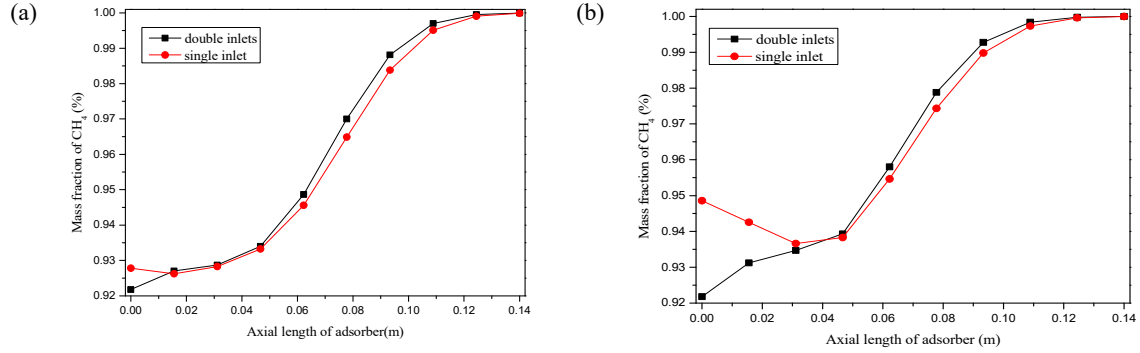


Fig.15. Mass fraction of CH₄ along axial direction for (a) 1/3D and (b) 2/3D of adsorber under different inlet amounts.

5. Conclusions

The effect of swing on removing CO₂ from offshore natural gas by the adsorption was studied using the experiment and simulation methods. Experimental results showed that the swing of the adsorber can reduce the adsorption purification effect, of which the bidirectional coupling swing is worse than that of the single swing. The starting breakthrough time under the quiescent condition with a tilting angle of 20 ° is shorter than that of the bidirectional coupling swing, but the total breakthrough time is longer than it. The separation factors of the quiescent condition, single direction swing, bidirectional coupling swing, and quiescent condition with a tilting angle of 20 ° are 3.52, 3.47, 3.44, and 3.48, respectively. The difference of the separation factors under four conditions is very little, indicating that the reduction of the adsorption purification effect is not caused by the decrease of the adsorbent performance. The adsorbent was stacked at one side of the adsorber owing to the influence of the tilt, which decreases the utilization of the adsorbent. This is the main reason for the reduction of adsorption purification effect. In order to obtain the influence of swing on adsorption purification, the adsorption purification model was firstly established and the validity of the model was verified by experiments. Then the influences of the tilting angle, L/D ratio of adsorber, inlet flow rate of the mixture gas, particle diameter of adsorbent, and gas inlet distribution of the adsorber on adsorption purification were studied systematically. The larger the tilting angle of the adsorber is, the worse the adsorption purification effect becomes. When the area of porous zone is constant, the adsorption purification effect is improved by increasing L/D ratio of the porous zone or decreasing the flow rate of mixture gas. When the inlet flow rate of the mixture gas is constant, the viscous resistance and inertia resistance decrease with the increase of the particle diameter of the adsorbent. Therefore, the gas will be easily to diffuse at all directions in the adsorber and the mixture gas at the stacking side of the adsorbent will increase gradually, which can reduce the adverse effect of swing on the adsorption purification of natural gas. When double inlets were set at the radial tripartite point of the adsorber and the mass flow rates of the mixture gas at the two inlets accounted for 90% and 10% respectively, more gas would flow into the stacking side of the adsorbent. This makes the utilization of the adsorbent higher. In a world,

decreasing the tilting angle and inlet flow rate, or increasing the L/D ratio of the porous zone, the particle diameter of the adsorbent and the inlet amounts of the adsorber are effective ways to improve the adsorption purification effect of the natural gas under the tilting condition.

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References

- [1] EIA. International Energy Outlook .2018.
- [2] K. Song, S. Lee, S. Shin, H.J. Lee, C. Han, *Ind. Eng. Chem. Res.* 53 (2014) 5539-5544.
- [3] Y. Gu, *Appl. Energy.* 87 (2010) 3393-3400.
- [4] T.V. Nguyen, S.O. Júnior, *Energy.* 144 (2018) 594-606.
- [5] S. Gowid, R. Dixon, S. Ghani, *J. Nat. Gas Sci. Eng.* 27 (2015) 1495-1511.
- [6] S. Dan, C.J. Lee, J. Park, D. Shin, E.S. Yoon, *Process Saf Environ.* 92 (2014) 430-441.
- [7] S. Park, B. Jeong, B.S. Lee, S. Oterkus, P. Zhou, *Ocean Eng.* 149 (2018) 423-437.
- [8] Z. M. Xia, X.S. Li, Z.Y. Chen, G. Li, J. Cai, Y. Wang, *Appl. Energy.* 207 (2017) 584-93.
- [9] B. ZareNezhad, M. Ziaee, *Fluid Phase Equilibr.* 356 (2013) 321-328.
- [10] R.W. Baker, K. Lokhandwala, *Ind. Eng. Chem. Res.* 47 (2018) 2109-2121.
- [11] K. Kida, Y. Maeta, K. Yogo, *Sep. Purif. Technol.* 197 (2018) 116-121.
- [12] C.F. Song, Q.L. Liu, N. Ji, S. Deng, J. Zhao, Y. Kitamura, *Appl. Energy.* 204 (2017) 353-361.
- [13] L.D. Wang, Y.F. Zhang, R.J. Wang, Q.W. Li, S.H. Zhang, M. Li, J. Liu, B. Chen, *Environ. Sci. Technol.* 52 (2018) 14556-14563.
- [14] B.H. Li, N. Zhang, R. Smith, *Appl. Energy.* 161 (2016) 707-717.
- [15] T. Nagy, P. Mizsey, *Environ. Sci. Technol.* 47 (2013) 8948-8954.
- [16] Y. Li, H.P. Wang, C.Y. Liao, X.L. Zhao, T.L. Hsiung, S.H. Liu, S.G. Chang, *Environ. Sci. Technol.* 51 (2017) 8824-8831.
- [17] H. Zhai, E.S. Rubin, *Environ. Sci. Technol.* 47 (2013) 3006-3014.
- [18] T. Wang, C. Cheng, L.G. Wu, J.N. Shen, B.V. Bruggen, Q. Chen, D. Chen, C.Y. Dong, *Environ. Sci. Technol.* 51 (2017) 6202-6210.
- [19] Z. Jahan, M.B.K. Niazi, M.B. Hägg, Ø.W. Gregersen, *J. Membrane. Sci.* 554 (2018) 275-281.
- [20] N. Hedin, L. Andersson, L. Bergstrom, J.Y. Yan, *Appl. Energy.* 104 (2013) 418-433.
- [21] N.A.A. Qasem, B.M. Rached, *Appl. Energy.* 209 (2018) 190-202.
- [22] A.E. Creamer, B. Gao, *Environ. Sci. Technol.* 50 (2016) 7276-7289.
- [23] J. Zhang, P.A. Webley, *Environ. Sci. Technol.* 42 (2008) 563-569.
- [24] B. Yuan, X.F. Wu, Y.G. Chen, G.H. Huang, H.M. Luo, S.G. Deng, *Environ. Sci. Technol.* 47 (2013) 5474-5480.
- [25] V. Jiménez, A.R. Lucas, J.A. Díaz, P. Sánchez, A. Romero, *Environ. Sci. Technol.* 46 (2012) 7407-7414.
- [26] S.J. Chen, Y. Fu, Y.X. Huang, Z.C. Tao, *J. Porous Mater.* 23 (2016) 713-123.
- [27] S. Cavenati, C.A. Grande, A.E. Rodrigues, *Chem. Eng. J.* 49 (2004) 1095-101.
- [28] F. Gholipour, M. Mofarahi, *J. Supercrit. Fluid.* 111 (2016) 47-54.

- [29] F.S. Su, C.S. Lu, *Energy Environ. Sci.* 5 (2012) 9021-9027.
- [30] J. McEwen, J. Hayman, A.O. Yazaydin, *Chem. Phys.* 412 (2013) 72-76.
- [31] A.A. Pour, S. Sharifnia, *J. Nat. Gas Sci. Eng.* 26 (2015) 1246-1253.
- [32] M.C. Campo, A.M. Ribeiro, A.F.P. Ferreira, *Fuel Process. Technol.* 143 (2016) 185-194.
- [33] T. Montanari, E. Finocchio, E. Salvatore, G. Garuti, A. Giordano, C. Pistarino, *Energy.* 36 (2011) 314-319.
- [34] J.A.C. Silva, A.F. Cunha, K. Schumann, A.E. Rodrigues, *Micropor. Mesopor. Mat.* 187 (2014) 100-7.
- [35] Y.H. Kim, *Energy.* 70 (2014) 435-443.
- [36] Z.D. Duan, T. Ren, G.L. Ding, J. Chen, X.G. Mi, *Appl. Energy.* 206 (2017) 972-982.
- [37] Y. Gu, Y.L. Ju, J. Chen, Z.J. Shi, *Cryogenics.* 52 (2012) 530-537.
- [38] W.H. Zhao, Z.Q. Hu, J.M. Yang, Y.F. Wei, *Journal of Ship Mechanics.* 15 (2011) 227-237.
- [39] S.J. Chen, Y. Fu, Y.X. Huang, Z.C. Tao, M. Zhu, *Appl Energy.* 179 (2016) 329-337.
- [40] S.J. Chen, Z.C. Tao, Y. Fu, M. Zhu, W.L. Li, X.D. Li, *Appl Energy.* 205 (2017) 1435-1446.
- [41] H. Sui, P. An, X.G. Li, S. Cong, H. Lin, *Chem. Eng. J.* 316 (2017) 232-242.
- [42] M.Z. Abdullah, A. Qasim, *Procedia Engineering.* 148 (2016) 1416-1422.
- [43] W.C. Huang, C.T. Chou, *Ind. Eng. Chem.* 42 (2003) 1996-2006.
- [44] S. Mitra, M. Muttakin, K. Thu, B.B. Saha, *Appl. Therm. Eng.* 133 (2018) 764-773.
- [45] R.R. Kalluri, D.R. Cahela, B.J. Tatarchuk, *Sep. Purif. Technol.* 62 (2008) 304-16.
- [46] S. Jafari, F. Ghorbani-Shahna, A. Bahrami, H. Kazemian, *Micropor. Mesopor. Mat.* 268 (2018) 58-68.
- [47] X.G. Zheng, Y.S. Liu, W.H. Liu, *Ind. Eng. Chem. Res.* 49 (2010) 11814-11824.