

## Evaluating adsorption shale gas during CO<sub>2</sub> huff-n-puff

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**Abstract:** On one hand, the microscopic underlying mechanism of CO<sub>2</sub> huff-n-puff process remains ambiguous. On the other hand, realistic shale organic matter should be simplified as a slit one. In this work, basic on grand canonical Monte Carlo (GCMC) simulations, we study competitive adsorption between CO<sub>2</sub> and CH<sub>4</sub> with pressures up to 30 MPa and then insight into recovery mechanisms during CO<sub>2</sub> huff-n-puff processes in kerogen-based slit nanopores at 353K. With increasing pressure, the selectivity of carbon dioxide relative to methane decreases and tends to approach a constant. Enlarging the pore suppresses the selectivity of carbon dioxide over methane. We also discuss the process of CO<sub>2</sub> huff-n-puff. This study provides the fundamental understanding of the recovery mechanisms in kerogen slit and sheds light on CO<sub>2</sub> enhanced hydrocarbon recovery in shale gas reservoirs.

### 1. Introduction

Natural shale gas has recently emerged as an important alternative clean source to conventional fossil energy because of the low emissions and high energy efficiency in the world [1]. Therefore, exploration and development of shale gas have attracted global focus.

Gas shales can be described as a self-contained reservoir system with low permeabilities, pores in the range of nanometres and geology of fine grained sedimentary rocks that might result in a speedy decrease by degrees of production. Consequently, the recovery of the gas is rather complex and how to improve the recovery of shale gas by adopting appropriate technological measures is the key problem to be solved urgently. Therefore, enhanced gas recovery (EGR) by injecting CO<sub>2</sub> into shale formations is considered as a promising option that can enhance shale gas productivity and, in the meantime, mitigate the global warming via geological CO<sub>2</sub> sequestration.

There have been a number of experimental studies on CH<sub>4</sub> adsorption and the competitive adsorption between CH<sub>4</sub> and CO<sub>2</sub> on shales. Zhang et al. [2] studied CH<sub>4</sub> adsorption on different bulk organic rich shales and isolated kerogen samples up to 15 MPa. Khosrokhavar et al. [3] measured the competitive adsorption of CO<sub>2</sub> and CH<sub>4</sub> on a carboniferous shale from Belgium by a manometric setup, indicating that CO<sub>2</sub> is preferentially adsorbed over CH<sub>4</sub>. Some other works have confirmed the similar conclusions revealing that enhance gas recovery by CO<sub>2</sub> injection can be an effective method [4]

Molecular simulation provides an effective means to make the study of the occurrence state of shale gas go to the molecular scale and be closer to the reservoir temperature and pressure conditions. On the basis of grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations, Huang et al. [5] simulated the competitive adsorption between CH<sub>4</sub> and CO<sub>2</sub> on kerogen matrix and suggested the more remarkable impact of moisture. Rezlerováat al. [6] probed the adsorption performance and the selectivity of CO<sub>2</sub>/CH<sub>4</sub> binary mixture in kerogen slit pores.

Although some advances have been achieved in understanding the competitive adsorption of CO<sub>2</sub> and CH<sub>4</sub>, there are still two problems to be solved. The researchers only study the competitive adsorption of CO<sub>2</sub> and CH<sub>4</sub>, but do not explore the process of CO<sub>2</sub> huff and puff; the adsorption model of kerogen is too simple, which is often simulated by the matrix block of cube. The pore diameter of the matrix block is too small, generally less than 1 nm. It is different from the actual pore size of the layer (2-100 nm).

In this paper, we use MD simulation to build a kerogen-based slit nanopores and then GCMC simulations are employed to systematically simulate shale gas production by CO<sub>2</sub> huff-n-puff. We also discuss the effect of pressure and aperture size during CO<sub>2</sub> huff-n-puff process.

## 2. Models and methods

### 2.1 Construction of Kerogen Slit Nanopores

In this work, we selected the kerogen (type II-D) to construct a three-dimensional rough kerogen-based nanopores. Overmature type II kerogen (exemplified by sample II-D) is a typical unconventional reserves such as the Barnett shale. On the basis of the several analytical experimental results from Kelemen et al. [7], Ungerer et al. [8] developed the molecular structure of our kerogen unit used in the simulation. And the detail of compositions and structural parameters can match fairly well with technical experimental data of solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) methods and X-ray photoelectron spectroscopy. Besides, type II-D kerogen has been employed by Zhou et al. [9] study the adsorption of CH<sub>4</sub> in shale.

As suggested by Ungerer P and Collell J et al. [8] we perform series of MD (Molecular dynamics) simulations in the NVT (canonical ensemble) and NPT (isobaric-isothermal ensemble) to get kerogen-based nanopores by the Materials Studio software. The particular molecular structures of molecules are present in Figure 1, and chemical formula for our kerogen is C<sub>175</sub>H<sub>102</sub>O<sub>9</sub>N<sub>4</sub>S<sub>2</sub>, whose mass is 2466 g/mol. First, we integrate 12 optimized kerogen units into a large simulation box at a density of 0.1g/cm<sup>3</sup>, and the high temperature structural relaxation with NVT ensemble is carried out for the initial configuration at 900 K and 400ps. Then, the system undergoes a series of NPT simulations at a fixed pressure of 20MPa, with temperature stepwise decreased from 900 K to 700 K, 500 K, and finally to 300 K. In addition, the duration of each step simulation is long enough (400 ps) to reach equilibrium. As shown in Figure 1, we built a kerogen matrix, and then we constructed the slit pores by placing an empty space between the two kerogen matrices. The slit aperture is defined as the length of the blank space in the z direction. Two models with the slit aperture of 2 nm and 4 nm were constructed to study the effect of pore size. The kerogen structure remains fixed and the periodic boundary conditions are applied in each direction.

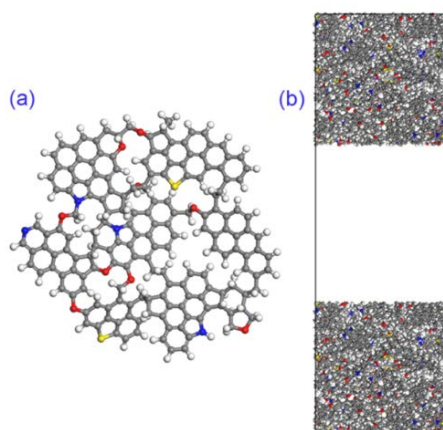


Figure 1. Molecular model of (a) type II-D kerogen unit and (b) slit-shaped kerogen having an aperture of 2 nm.

#### 2.1.1 Force Filed.

The COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field is employed to represent interatomic interactions, which is a common all-atom force field for its good accuracy in predicting structural, conformational, and thermophysical properties for a broad range of molecules in condensed phases. This force field describes dispersion-repulsion by means of Lennard-Jones 6–9, and Nose/Hoover thermostat is used to keep the

temperature constant. Atom-based nonbonded interaction with a cutoff distance of 12.5 Å is selected for the Coulomb and the Van der Waals energy summation.

## 2.2 Simulation Detail

The adsorption capacity of shale gas and CH<sub>4</sub> are calculated by the grand-canonical Monte Carlo (GCMC) method keeping the chemical potentials ( $\mu$ ), the volume ( $V$ ), and temperature ( $T$ ) fixed. During this simulation, the kerogen is kept rigid and the periodic boundary condition is imposed in the X- Y- and Z-directions. In the GCMC simulations, gases are allowed to be in equilibrium with a bulk gas reservoir under the same chemical potential (or fugacity) and temperature. The fugacity is estimated by the Peng–Robinson equation of state (PR-EOS) in this paper. Random insertion, translation, and deletion moves is applied in each GCMC cycle. The simulation consists of  $1 \times 10^7$  steps for each point in total, wherein the first  $5 \times 10^6$  cycles for equilibrium, while the other steps are utilized to calculate the adsorption amount. The absolute adsorption amount of hydrocarbons in the nanopores can be given as

$$N_{ab} = \frac{\langle N_i \rangle}{V \cdot N_A} \quad (1)$$

Here,  $\langle N_i \rangle$  is the number of adsorbate molecules in our kerogen;  $N_A$  presents Avogadro constant ( $6.022 \times 10^{23}$  1/mol);  $V$  denotes free pore volumes of this kerogen. We detected  $V$  by the helium of probe insertion in Materials Studio Atom Volumes & Surface tool at 353°C because helium is small enough to probe the pore and it hardly adsorbs on kerogen. Moreover, Connolly radius is adopted to detect the free pore volume.

## 3. Results and Discussion

### 3.1 Adsorption Behaviors

We first performed GCMC simulations to analyze adsorption and absorption behavior of methane in kerogen slits. The computed adsorption isotherms at 2.0 nm slit are depicted in Figure 2 ( $T = 353$  K). It can be clearly seen that all isotherms of methane increase monotonically with pressure and level off at high pressures. A similar trend has also been reported in other nanoporous materials, such as clays [10] and CNTs [11]. Based on the classification recommended by the International Union of Pure and Applied Chemistry (IUPAC), these isotherms belong to the type I (Langmuir) adsorption behavior, which is typical of nanoporous adsorbents.

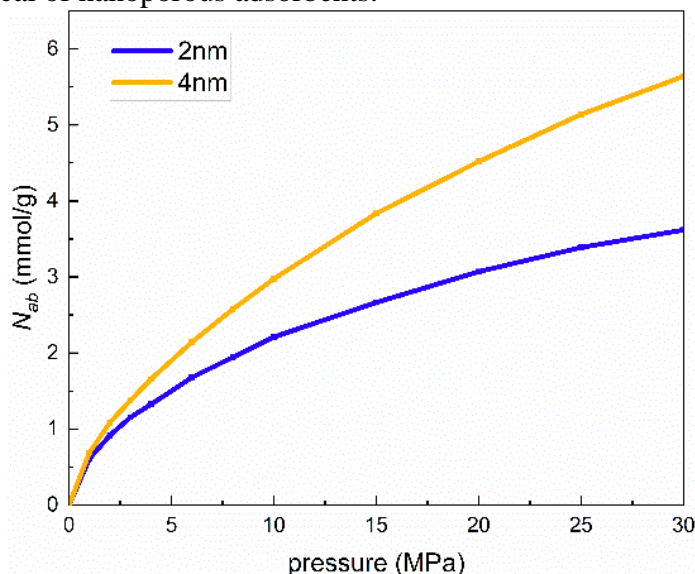


Figure 2. Adsorption isotherms of pure CH<sub>4</sub> in 2nm and 4 nm slits at T=353 K.

The effect of pore size is also shown in Figure 2, where the adsorption increases with increasing pore size, and the result is consistent with previous studies [12]. The aperture size of our slits are distinct, but the masses are almost the same. Therefore, direct quantification of total uptake of adsorption molecules in mmol/g gives a positive correlation with pore size. Larger pores facilitate the formation of layered structures, so more gas molecules are adsorbed.

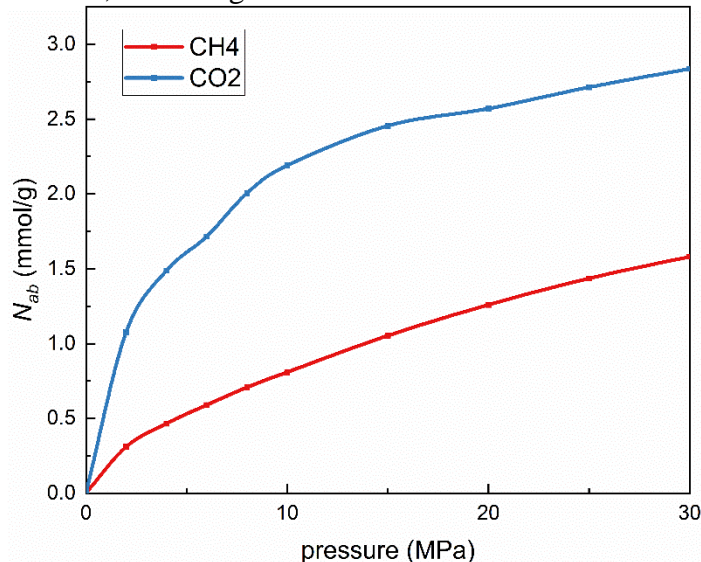


Figure 3. Absolute adsorption isotherms of CH<sub>4</sub> and CO<sub>2</sub> in 2nm kerogen slit.

The competitive adsorption of methane and CO<sub>2</sub> is shown in Figure 3. When the CO<sub>2</sub> mole fraction is 0.5 ( $y_{CO_2} = 0.5$ ), the adsorption amount of CO<sub>2</sub> is much more than that of CH<sub>4</sub>. It can be noted that CO<sub>2</sub> has a larger adsorption capacity than CH<sub>4</sub> to be adsorbed preferentially on this kerogen model in CH<sub>4</sub> and CO<sub>2</sub> binary mixtures.

To further gain insight into the mechanisms of the thermodynamic property for competitive adsorption. We also calculate the isosteric heat,  $Q_{st}$ , using the Clausius-Clapeyron equation [13]. The changes of  $Q_{st}$  as a function of the adsorption quantity of CO<sub>2</sub> and hydrocarbons are shown in Figure 4. The isosteric heat of CO<sub>2</sub>, 5.89 kJ/mol, is  $\sim 1.54$  times larger than that of CH<sub>4</sub>, 3.84 kJ/mol, indicating a superior fluid–solid interaction for CO<sub>2</sub> compared with CH<sub>4</sub>, which is consistent with the conclusion from Figure 3.

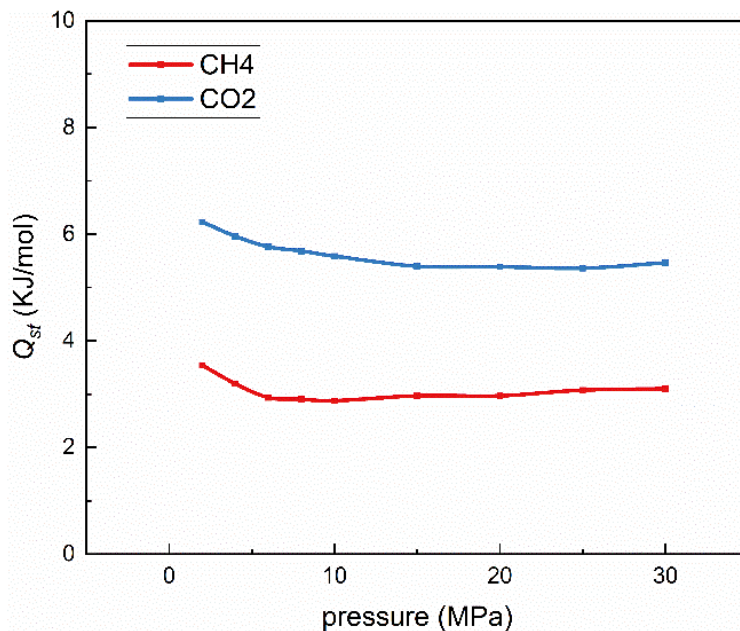


Figure 4. Isosteric heats of adsorption,  $Q_{st}$ .

For the effect of pore size, it can be seen that at different phase compositions, there are more molecules within the larger kerogen slits, which is similar to the result of pure methane mentioned above. In addition, to further compare the competition of CH<sub>4</sub> and CO<sub>2</sub>, the selectivity of CO<sub>2</sub> against CH<sub>4</sub> is defined to quantify the competitive adsorption in a binary mixture.

$$S_{CO_2/CH_4} = \frac{x_{CO_2} / x_{CH_4}}{y_{CO_2} / y_{CH_4}} \quad (2)$$

Where  $x_i$  and  $y_i$  represent the mole fraction of component  $i$  in the adsorbed and bulk phases, respectively, which can be readily obtained from GCMC simulations of CH<sub>4</sub>/CO<sub>2</sub> binary. When the selectivity is greater than 1, CO<sub>2</sub> is preferentially adsorbed or absorbed; otherwise CH<sub>4</sub> is more easily. The higher the selectivity is, the stronger the adsorption capacity of CO<sub>2</sub> on CH<sub>4</sub>.

We illustrate in Figure 5, the competitive absorption and competitive adsorption of CH<sub>4</sub> and CO<sub>2</sub> in different kerogen slit pores. The S values decrease with the increase of pressure, but all of them are greater than 1, indicating that CO<sub>2</sub> is more easily adsorbed on the pore surface and has a greater absorption tendency. For the effect of size, due to the relatively low adsorption amount of CH<sub>4</sub>, the adsorption selectivity of CO<sub>2</sub> to CH<sub>4</sub> in the narrow pores was relatively high, which was supported by previous studies [14].

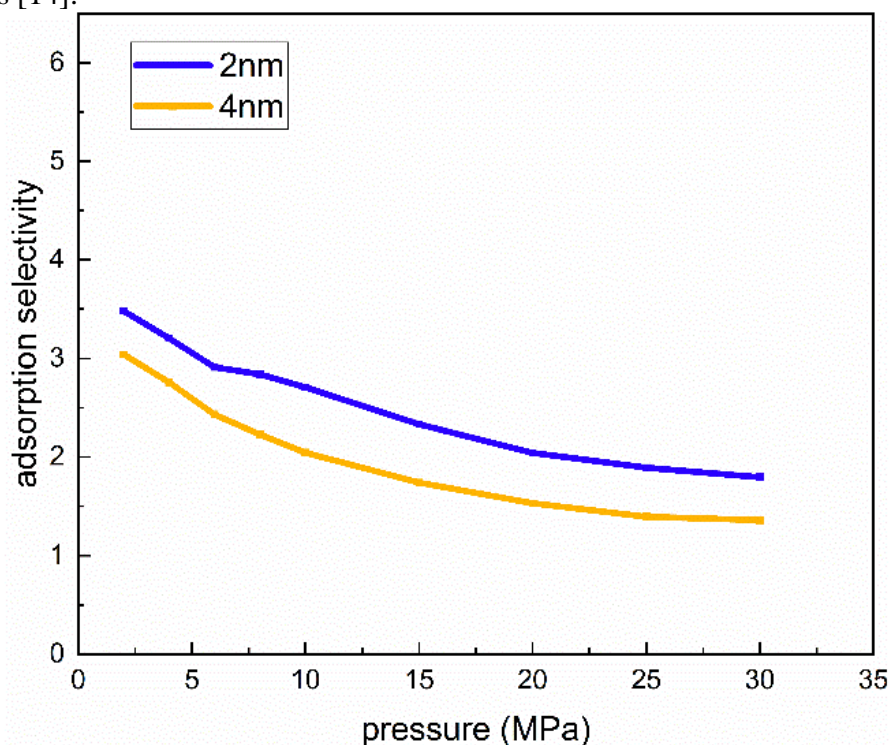


Figure 5. Selectivity of CO<sub>2</sub> relative to CH<sub>4</sub> versus pore pressure ( $y_{CO_2} = 0.5$ ).

### 3.2 CO<sub>2</sub> huff-n-puff

To explore the recovery mechanism through CO<sub>2</sub> huff-n-puff, evaluate the shale gas recovery efficiency, and study the range of gas produced (adsorption or absorption) during CO<sub>2</sub> injection, the evolution of average density in kerogen slit pores at 2 nm during CO<sub>2</sub> huff-n-puff is shown in Figure 6. This process generally includes three different stages: CO<sub>2</sub> injection (huff), soaking, and pressure drop (puff). A simplified process is proposed in this work. For shale reservoir with 15 MPa, firstly inject CO<sub>2</sub> to achieve the mole fraction of CO<sub>2</sub> reach 0.5 (P=18.9 MPa), and then reduce the pressure to 15MPa for extraction. Finally, the pressure of shale reservoir is reduced to 15MPa with the constant bulk mole fraction.

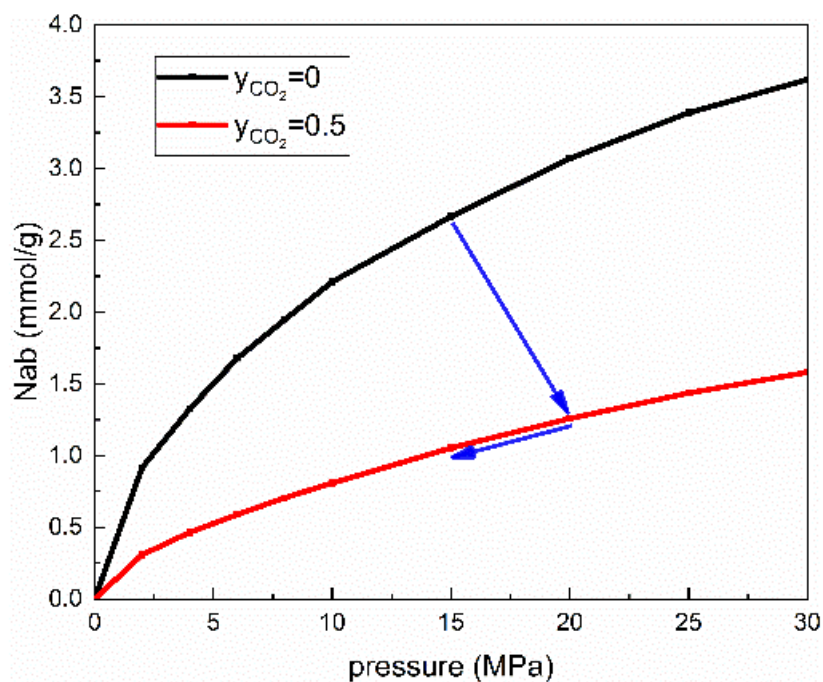


Figure 6. Density distribution of shale gas when injecting CO<sub>2</sub> molecules in the 2nm kerogen slit pores. The arrows in the figure indicate the direction of the recovery process.

It can be seen from the figure that with the injection of CO<sub>2</sub>, the methane content is significantly reduced. In the original reservoir, only shale gas is contained in the pores, and the pressure rises once with CO<sub>2</sub> injection. Then as the pressure drops, a small amount of CO<sub>2</sub> is released, and the methane content is also significantly reduced. On the whole, CO<sub>2</sub> injection is conducive to the recovery of shale gas. Owing to the stronger interaction between the adsorbent and CO<sub>2</sub>, CO<sub>2</sub> molecules occupy the original position of methane, thereby displacing shale gas.

#### 4. Conclusions

In this work, the adsorption behavior of shale gas and the recovery process of CO<sub>2</sub> huff-n-puff are investigated through GCMC simulations.

We find that absolute adsorption amounts of pure CH<sub>4</sub> follow the Langmuir type. Then, we study the competitive adsorption of CO<sub>2</sub> and CH<sub>4</sub>. Owing to the stronger attractions from the solid surface, the adsorption isotherm of CO<sub>2</sub> is larger than that of CH<sub>4</sub>. Under the studied conditions, CO<sub>2</sub>/CH<sub>4</sub> adsorption selectivity in kerogen nanopores decreases monotonically with increasing pressure and approaches to a constant. Thus, the injected CO<sub>2</sub> drives the adsorbed hydrocarbon molecules from the surface and leads to an enhanced gas recovery.

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