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Grand canonical Monte Carlo simulations of pore structure influence on methane adsorption in micro-porous carbons with applications to coal and shale systems

Wenhui Song[a], Jun Yao[a,*], Jingsheng Ma[b,*], Aifen Li[a,*], Yang Li[c], Hai Sun[a], Lei Zhang[a]

[a] Research Centre of Multiphase Flow in Porous Media, China University of Petroleum, No. 66, Changjiang West Road, Huangdao District, Qingdao 266580, China
[b] Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, UK
[c] Department of Oilfield Exploration & Development, Sinopec, Beijing 100029, China

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ABSTRACT

Coal and shale are strong heterogeneous anisotropic media involving nanoscale pore size and variance of microstructure. The complexity of methane adsorption is expressed both in diverse chemical properties and confined pore structures. In this study, Grand canonical Monte Carlo simulations were carried out to assess the influence of pore structure on methane adsorption at temperature 318 K, 333 K and pressure up to 20 MPa. The pore radii of physical carbon-based model range from 0.55 nm to 1.15 nm at the step of 0.1 nm. Simulated results indicate that the excess adsorption isotherms and maximum excess adsorption density are notably different for different pore structures. The triangle pore exhibits largest value of maximum excess adsorption density followed by the slit pore, circle pore and square pore. The maximum excess adsorption density is larger than 6×10^3 mol/m^3 at simulated temperatures for triangle pore with pore radius less than 1 nm. The excess adsorption amount first increases with the increase of pressure and then decreases when the pressure is larger than 7.5 MPa for slit pore and 5 MPa for the circle pore, triangle pore and square pore. The excess adsorption amount for circle pore and square pore drops down to negative value when the pressure is larger than 12.5 MPa while the excess adsorption amount stays above zero across simulated pressure for the slit pore and triangle pore. The adsorption isotherms of micro-porous carbons were obtained by superposition of simulated adsorption isotherms based on the pore size distribution and were compared with coal samples experimental data gathered from the same temperature. The experimental isotherm is more close to slit pore excess isotherm and predicted excess isotherms based on circle pore and square pore under-estimate excess adsorption capacity.

1. Introduction

Finding environmental-friendly and sustainable sources of energy becomes urgent due to depletion of global oil reserves and concerns over increasing carbon dioxide levels in atmosphere [1–3]. Methane is widely distributed in large amounts on earth [4–6] and the specific combustion enthalpy of methane is higher than that of petroleum. Furthermore, the carbon dioxide emission amount from methane combustion is lower compared with petroleum combustion. Therefore, methane is deemed as the substitute energy. Large amounts of methane adsorb in coal and organic matrix of shale [7–12]. The heterogeneities of coal and shale are demonstrated in terms of nanoscale pore size, pore structures, surface chemical properties and mechanical properties [13–16]. Numerous image studies suggest that the pore structures in coal and shale exhibit a wide range of possible shapes [17–23]. Zhao and Elsworth et al. [24] observed slit pore and circle pore for both high- and low-volatile bituminous in the transmission electron microscopy (TEM) images. Nie et al. [25] detected slit pore, bottle-shaped pore, cylindrical pore and wedge-shaped pore on coal surface by Scanning Electron Microscopy (SEM) images. Javadpour et al. [26] categorized the shale pore structures into triangle pore, slit pore, square pore and circular pore and analyzed the liquid slip flow in these different pore structures. Two shale SEM images in Fig. 1 obtained from [27] clearly show the four different pore structures.

Molecular simulation methods are commonly applied to study methane adsorption behavior in nanoscale porous media. Saha et al. [28] reviewed computation models on methane adsorption and purification of natural gas. Keith E. Gubbin et al. [29] performed Grand canonical Monte Carlo (GCMC) simulations to compare methane adsorption capacity in porous carbons and zeolites by slit pores model and cylindrical

* Corresponding authors.
E-mail addresses: rcogfr_upc@126.com (J. Yao), Jingsheng.Ma@hw.ac.uk (J. Ma), aifenli123@163.com (A. Li).

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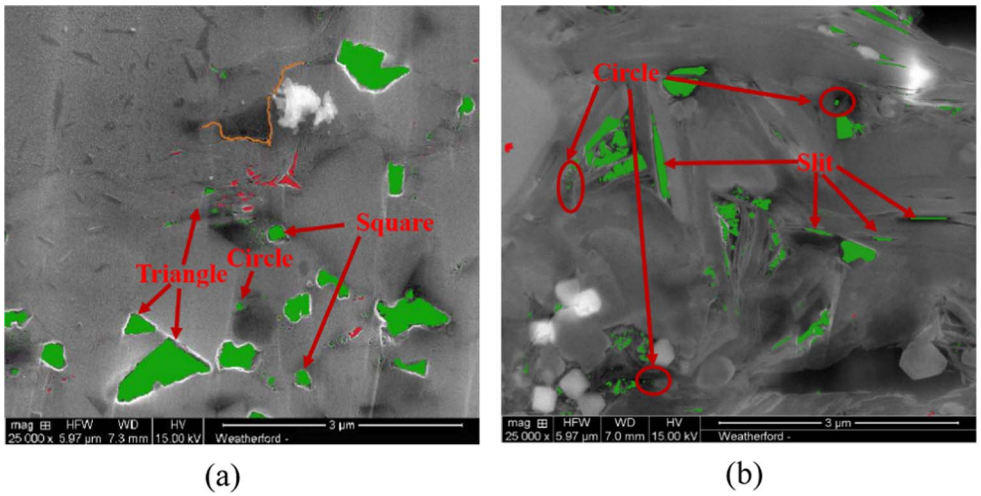

Fig. 1. Shale SEM images, triangle pore, slit pore, circle pore and square pore are illustrated on the image. (a) Eagle Ford shale. (b) Marcellus Shale. Green color represents organic pores, red color represents inorganic pores. The SEM images are obtained from Rine et al. [27] work.

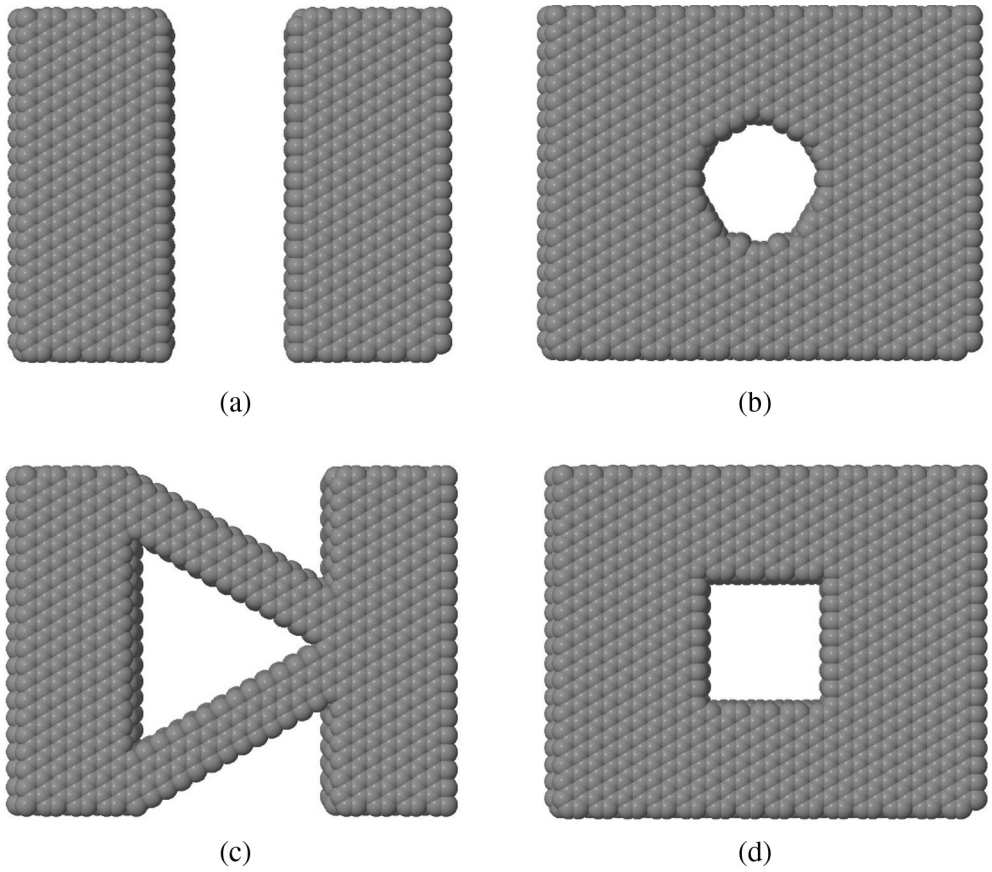

Fig. 2. Visualization of constructed carbon pore structures: (a) slit pore, (b) circle pore, (c) triangle pore, (d) square pore.

Table 1
Force field potential parameters.

	ε_{ff}/k_B (K)	σ_{ff} (nm)
CH4 [51]	148	0.373
C	28	0.34

pores model. Jennifer Wilcox et al. [30] studied the adsorption isotherms of methane change versus pore size in micro- and mesoporous carbons based on slit-shaped pore. Olumide O. Adisa et al. [31] investigated methane adsorption on both graphite and in the region between two aligned single-walled carbon nanotubes. Sergi Vela et al. [32] studied the methane adsorption in single walled carbon nanotubes bundles. Delavar et al. [33] experiment results confirmed that pore structure influences the final methane uptake value. GCMC simulation results by K. Vasanth Kumars et al. [34] indicated that the competitive adsorption of methane molecules from methane and hydrogen mixtures is strongly affected by the pore size distribution and pore geometry. Palmer et al. [35] analyzed the influence of pore structure on the separation of carbon dioxide and methane mixtures by nanoporous carbon structures. Xiong et al. [36] found that methane adsorption capacity in slit pore decreases with the decreasing O/C ratio.

Very few studies have emphasized the pore structure influence on methane storage. Narandalai Byamba-Ochir et al. experimental results indicated that specific surface area of adsorption media is not always a major factor in storing of methane [37]. Qajar et al. [38] extended