Fuel 188 (2017) 239–245

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

A hybrid methodology to predict gas permeability in nanoscale organic materials; a combination of fractal theory, kinetic theory of gases and Boltzmann transport equation

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HIGHLIGHTS

- A theoretical model is used to predict gas permeability in nanoscale organic materials.
- Boltzmann transport equation is directly solved to predict mass transfer of the adsorbed layer.
- The absolute permeability of porous media is determined by the fractal theory.
- The Knudsen mass transfer is predicted by fundamentals of kinetic theory of gases.
- The gas permeability is well predicted by current approach.

ARTICLE INFO

Article history:
Received 7 July 2016
Received in revised form 29 August 2016
Accepted 3 October 2016
Available online 12 October 2016

Keywords:
Gas permeability
Nanoscale
Gas adsorption
Slippage effect
Organic materials

ABSTRACT

A theoretical methodology is developed to study the permeability of gas in organic tight porous media. In derivation of our equations, three main mechanisms of gas transport in organic porous media are taken into account. The modified fractal theory is used to explain viscous transport. Using the kinetic theory of gases, a similar formula derived in our previous study (Behrang et al., 2016) is applied to study the slippage phenomenon and the Knudsen transport. The surface transport which shows the impact of the gas adsorption on the permeability is addressed by direct solution of the Boltzmann transport equation for a thin layer of adsorbed gas. The final equation is used to explore influences of the adsorbed layer thickness, grain surface specularity and pressure on the gas permeability. The presented approach is validated against available experimental data. An excellent agreement between our proposed theoretical model and experimental results are observed.

1. Introduction

A typical shale gas reservoir consists of organic porous material (known as kerogen) and inorganic matrix. It is found that most pores in a kerogen are in nanoscale [2,3]. Thus, gas flow cannot be described by conventional macroscopic models. Some special transport mechanisms are involved in nanoscale gas flow. In addition to gas slippage phenomenon, adsorption of high density gas on the pore walls of the kerogen influences significantly on gas transport. Note that effects of slippage and adsorbed gas on gas transport is neglected in macro-pores where the conventional transport mechanisms such as viscous transport are dominated. It is worthwhile to note that the adsorption mechanism is not considered in inorganic materials. For a typical nanoscale organic material, three gas transport mechanisms are taken into the account. (i) viscous flow, (ii) Knudsen flow (slippage term) and (iii) surface diffusion (adsorbed gas term). Although both surface diffusion and Knudsen flow exist in kerogen pores, their fundamental transport mechanisms are different. The Knudsen flow depends on the pore size. Under the influence of an external flux, some of the adsorbed molecules can overcome the local interactions with the grain surface and develop a hopping mechanism. This type of transport mechanism, known as surface diffusion, is only important in very small pores [3]. In the presence of these three gas transport mechanisms the total gas flux m_{total} (kg/s/m^2) is given by:

$$m_{total} = \frac{\phi}{\tau}(\xi m_{vis} + (1-\xi)m_{surf} + m_{Kn}) \quad (1)$$

where m_{vis}, m_{Kn}, m_{surf} are viscous, Knudsen and surface diffusion mass flow rates, respectively. Where $\xi = \frac{1}{1+Kn}$ [4,5]. By $Kn = \frac{\Lambda}{a_{eff,h}}$

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http://dx.doi.org/10.1016/j.fuel.2016.10.014
0016-2361/

the Knudsen number is denoted. Λ is the gas mean free path and $a_{eff,h}$ is the effective pore radius. ϕ is the porosity and τ stands for the tortuosity. Before calculating gas flow rate terms, it is pointed out that it is a well-accepted approach to assume porous media as composed of a bundle of tortuous capillary tubes with uniform mean size/radius. Thus, a cylindrical tube can be considered as a good representative of porous media [6–9].

2. Determination of the viscous mass flow rate

To determine the viscous (conventional) term, the Darcy's law is applied:

$$m_{vis} = -\rho_g \frac{k_0}{\mu} \nabla P \tag{2}$$

By ρ_g and k_0, the gas density and the absolute permeability are denoted, respectively. μ stands for the gas viscosity and ∇P is the pressure gradient. Different research methods including experimental measurements [10,11], theoretical studies and numerical simulations [12,13] can be applied to determine the absolute permeability k_0 of a given porous medium. Among different theoretical techniques, the Kozeny-Carman correlation [14–18] and the fractal theory [1,19–21] have been commonly used for predicting the permeability of complex media. Now we proceed to specify the absolute permeability of porous media using the fractal theory. The interspaces in real tight porous media have fractal characteristics in a certain range of scales from micrometer to nanometer [6,22,23]. A porous medium such as a shale gas consists of a combination of numerous irregular and disordered pores of different sizes and complex tortuosity. For a tortuous capillary of diameter λ and tortuous length of $L_t(\lambda)$ along the transport direction, a fractal scaling relation between the diameter and length of tortuous capillaries can be described as

$$L_t(\lambda) = \lambda^{1-D_t} L_0^{D_t} \tag{3}$$

where L_0 is the straight length of the medium [19,24]. Due to the tortuous nature of capillary tubes, $L_t \geqslant L_0$. By $1 < D_t < 2$ the tortuosity fractal dimension is denoted. Obviously for a straight capillary $D_t \to 1$, $L_t = L_0$. The higher is D_t, the more tortuous is the capillary. Eq. (4) can be used to describe the relation between porosity and fractal dimension.

$$\phi = \left(\frac{\lambda_{min}}{\lambda_{max}}\right)^{d_E - D_f} \tag{4}$$

where d_E is the Euclidean dimension (i.e. $d_E = 2$ and 3 in the two- and three-dimensional spaces, respectively). D_f stands for the pore area fractal dimension. λ_{min} and λ_{max} are the pore size and the maximum pore size of the porous media, respectively [20,25].

Size distribution of pores is another important porous medium characteristic that should be determined. It has been shown that the cumulative size distribution of the pores can be mathematically expressed by the fractal power law [26],

$$N(L \geqslant \lambda) = \left(\frac{\lambda_{max}}{\lambda}\right)^{D_f} \tag{5}$$

The number of pores of sizes between λ to $\lambda + d\lambda$ is given by differentiating Eq. (5).

$$-dN = D_f \lambda_{max}^{D_f} \lambda^{-(D_f+1)} d\lambda \tag{6}$$

Minus in Eq. (6) represents that pore population decreases with increasing pore size. The total number of pores (from the smallest size λ_{min} to the largest size λ_{max}) can be given by Eq. (5) as

$$N_t(L \geqslant \lambda_{min}) = \left(\frac{\lambda_{max}}{\lambda_{min}}\right)^{D_f} \tag{7}$$

The probability density function $f(\lambda) = D_f \lambda_{min} \lambda^{-(D_f+1)} \geqslant 0$ is given by dividing Eq. (6) by Eq. (7)

$$-\frac{dN}{N_t} = D_f \lambda_{min} \lambda^{-(D_f+1)} d\lambda \tag{8}$$

According to the probability theory, the probability density function should satisfy the following expression

$$\int_0^\infty f(\lambda) d\lambda = \int_{\lambda_{min}}^{\lambda_{max}} f(\lambda) d\lambda = 1 - \left(\frac{\lambda_{min}}{\lambda_{max}}\right)^{D_f} = 1 \tag{9}$$

Eq. (9) is valid if and only if $\left(\frac{\lambda_{min}}{\lambda_{max}}\right)^{D_f} = 0$. Although this statement is not exactly met for a typical porous medium (i.e., $\frac{\lambda_{min}}{\lambda_{max}} = 10^{-2}$), it is reasonable to use the fractal theory to approximate properties of porous media [19,26,27]. The flow rate through a tortuous capillary tube can be presented by modifying the Hagen-Poiseulle equation

$$q = \frac{\pi}{128} \frac{\lambda^4}{\mu} \frac{\Delta p}{L_t(\lambda)} \tag{10}$$

After integrating Eq. (10) over the entire range of pore sizes and doing some manipulations (for more details see Ref. [19]), the total flow rate is given by

$$Q = -\int_{\lambda_{min}}^{\lambda_{max}} q dN = \frac{\pi}{128} \frac{\Delta p}{\mu} \frac{L_0^{1-D_t}}{A} \frac{A}{L_0} \frac{D_f}{3 + D_t - D_f} \lambda_{max}^{3+D_t} \tag{11}$$

Comparing Eq. (11) with Darcy's law, the permeability of the porous medium is presented by

$$k_0 = \frac{\mu L_0 Q}{\Delta p A} = \frac{\pi}{128} \frac{L_0^{1-D_t}}{A} \frac{D_f}{3 + D_t - D_f} \lambda_{max}^{3+D_t} \tag{12}$$

Note that A stands for the cross-section area. A and L_0 should be determined based on the microstructure of a specific porous medium. The pore space in a cross section can be considered as circles with different diameters λ. The total pore area in the cross section A_p is given by

$$A_p = \int_{\lambda_{min}}^{\lambda_{max}} \frac{\pi}{4} \lambda^2 (-dN) = \frac{\pi D_f \lambda_{max}^2}{4(2 - D_f)} (1 - \phi) \tag{13}$$

and consequently the cross-sectional area A is given by

$$A = \frac{A_p}{\phi} = \frac{1 - \phi}{\phi} \frac{\pi D_f \lambda_{max}^2}{4(2 - D_f)} \tag{14}$$

Considering $L_0 = \sqrt{A}$, the expression for the absolute permeability is written as

$$k_0 = \Xi \lambda_{max}^2 \left(\frac{\phi}{1 - \phi}\right)^{(1+D_t)/2} \tag{15}$$

where

$$\Xi = \frac{(\pi D_f)^{(1-D_t)/2} (4(2 - D_f))^{(1+D_t)/2}}{128(3 + D_t - D_f)} \tag{16}$$

To determine the relationship between the maximum pore diameter λ_{max} and grain radius, a porous medium unit should be defined. A schematic of the porous medium unit is presented in Fig. 1. For the presented unit cell, the total area of the unit cell and the maximum pore area are given by

$$A = \frac{\pi a_p^2}{2} \left(\frac{1}{1 - \phi}\right) \tag{17}$$

and