Numerical Simulation of Adsorption and Heat Transfer in Porous Media Using Lattice Boltzmann Method

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Abstract. An adsorption model for fluid flow, heat, and mass transfer of the adsorbent bed was established. Based on the single relaxation time lattice Boltzmann method, a dual-distributed lattice Boltzmann model of density and concentration was established to solve the fluid flow and mass transfer process in the surface area of the adsorbent bed. The adsorption and heat transfer process on the surface of the adsorbent bed was incorporated into the dual-distributed lattice Boltzmann model by the fourth-order Runge-Kutta finite difference method. The multiphysics fields under Poiseuille flow were simulated by the presented model, and the adsorption capacity and temperature distribution during the adsorption process were investigated.

Keyword. Adsorption, heat transfer, lattice Boltzmann method, porous media.

1. Introduction
As a storage medium for gases such as H₂ and CH₄, porous media adsorbents have been widely used in the engineering industry [1]. The adsorption of gases such as methane occurs on the surface of porous media while giving off heat, and it is necessary to study the heat transfer process in the area near the adsorption bed during the adsorption process and the effect on the adsorption amount.

As an emerging and effective numerical simulation method at the mesoscopic level, LBM has been widely used in fluid flow, heat, and mass transfer problems, such as porous media flow, due to its advantages of simple programming, inherent parallelism, and easy handling of complex boundaries [2]. The heat of adsorption effect, however, was few incorporated in LB simulations for adsorption.

In this paper, a two-dimensional adsorption and heat transfer model is established based on LBM, and a Maxsorb adsorption bed of a specific size is selected for numerical simulation. The kinetic adsorption characteristics are investigated combining the heat of adsorption effect.

2. Numerical model
2.1. Dual-Distributed Lattice Boltzmann Model
The single relaxation time lattice Boltzmann method is used to solve the density field and concentration field in the fluid flow and mass transfer governing equations, in which the D2Q9 and D2Q5 models are selected respectively [3].

\[
f_i \left( \mathbf{r} + \Delta t \mathbf{e}_i, t + \Delta t \right) - f_i(\mathbf{r}, t) = -\frac{1}{\tau_f} \left[ f_i(\mathbf{r}, t) - f_i^{eq}(\mathbf{r}, t) \right]
\]  

(1)
\[ g_i \left( \mathbf{r} + \Delta \mathbf{r}_i, t + \Delta t \right) - g_i (\mathbf{r}, t) = -\frac{1}{\tau_d} \left[ g_i (\mathbf{r}, t) - g_{eq,i} (\mathbf{r}, t) \right] \]  
\[ \text{where } f_i \text{ is the density distribution function; } f_{eq,i} \text{ is the density equilibrium distribution function; } g_i \text{ is the concentration distribution function; } g_{eq,i} \text{ is the concentration equilibrium distribution function; } \tau_f \text{ and } \tau_s \text{ are the dimensionless relaxation times of the density distribution function and concentration distribution function, respectively.} \]  

2.2. Adsorption Kinetic Model and Heat Transfer Model

Adsorption occurs on the surface of porous media. Langmuir adsorption kinetics is generally used to describe the adsorption process on the surface of porous media.

\[ D_f \frac{\partial C}{\partial n} = \frac{\partial N}{\partial t} = k_1 C (N_m - N) - k_{-1} N \]  
\[ \text{where } k_1 \text{ and } k_{-1} \text{ are the constant adsorption and desorption rates; } N \text{ is the adsorption capacity at that moment; } N_m \text{ is saturated adsorption capacity.} \]

The crystallite pore diffusion of methane in porous media [4] is also considered, and its governing equation is described as

\[ \frac{\partial N}{\partial t} = D_s \left( \frac{\partial^2 N}{\partial x^2} + \frac{\partial^2 N}{\partial y^2} \right) \]  
\[ \text{where } D_s \text{ is the solid diffusion coefficient in porous media.} \]

The heat transfer governing equation includes three regions: fluid domain, porous medium interface, and porous medium interior [5], which are respectively described as

\[ \text{fluid domain: } \left( \rho c_p \right)_f \frac{\partial T}{\partial t} + \nabla \cdot (\lambda_f \nabla T_f) = \nabla \cdot (\lambda_f \nabla T_f) \]  
\[ \text{interface: } \left( \rho c_p \right)_s \frac{\partial T_s}{\partial t} = \nabla \cdot (\lambda_s \nabla T_s) + \frac{\partial N}{\partial t} H_{ads} \]  
\[ \text{interior: } \left( \rho c_p \right)_s \frac{\partial T_s}{\partial t} = \nabla \cdot (\lambda_s \nabla T_s) \]  
\[ \text{where } c_p \text{ is specific heat capacity; } \lambda \text{ is coefficient of thermal conductivity; } H_{ads} \text{ is the heat of adsorption.} \]

The adsorption capacity and temperature field are calculated iteratively using the fourth-order Runge-Kutta finite difference method [6], and the calculation variance is as follows

\[ \frac{\partial T}{\partial t} \equiv K_1 (T), \quad \frac{\partial N}{\partial t} \equiv K_2 (N) \]  
\[ h_1 = K(\chi''), h_2 = K(\chi'' + h_1 \frac{\Delta t}{2}), h_3 = K(\chi'' + h_2 \frac{\Delta t}{2}), h_4 = K(\chi'' + h_3 \cdot \Delta t) \]
\[ \chi''^{n+1} = \chi'' + \frac{\Delta t}{6} (h_1 + h_2 + h_3 + h_4) \]
3. Adsorption Process Simulation

3.1. Adsorption Isotherm
In this paper, the Tóth adsorption isotherm model is selected to calculate the saturated adsorption capacity, which can be represented by

$$\frac{N_m}{N_0} = \frac{k_0 \exp \left( \frac{H_{ads}}{RT} p \right)}{1 + \left[ k_0 \exp \left( \frac{H_{ads}}{RT} p \right) \right]^s}$$  \hspace{1cm} (11)

where $s$ is adsorbent structural heterogeneity parameter, $k_0$ and $N_0$ are fitting parameters. The result of fitting experimentally measured adsorption uptake of methane onto Maxsorb III [7] based on the Tóth adsorption isotherm model is shown in figure 1, meanwhile fitting parameters and fitting errors are shown in table 1.

$$\begin{align*}
N_0 & \text{(mol/m}^3) \hspace{1cm} 174915.1 \\
H_{ads} & \text{(J/mol)} \hspace{1cm} 15078.3 \\
k_0 & \text{0.0036} \\
s & \text{0.2705} \\
R^2 & \text{0.9969}
\end{align*}$$

3.2. The Simulation Process of LBM
The surface of porous media is rough and there are a lot of pores. Therefore, the structure diagram of maxsorb III adsorption bed with a lattice size of 500*500 is drawn in this paper, as shown in figure 2. The black part in the figure is Marsorb III particles, and the red part is the fluid domain.
In each lattice time step, the simulation process is calculated according to the time sequence of fluid flow, mass transfer, adsorption, and heat transfer. The fluid flow and mass transfer process are subjected to obtain information such as density, concentration, the velocity of each lattice point after collision and migration according to equation (1)-(2). According to equation (3)-(10), the fourth-order Runge-Kutta finite difference method is used to calculate the adsorption capacity and heat transfer process of the Maxsorb III adsorption bed at the same time.

The variables in the LBM simulation process are all dimensionless lattice units, so the relevant physical parameters need to be converted to dimensionless lattice units by dimensionless correlation numbers, as shown in Table 2.

Table 2. Conversion of dimensionless lattice units and physical parameters.

| Physical parameters               | Units         | Physical symbol | Physical value | Lattice value |
|-----------------------------------|---------------|-----------------|----------------|---------------|
| Sound velocity                    | m/s           | c_s             | 340.40         | 0.5774        |
| Domain length                     | m             | L               | 1×10^{-4}      | 500           |
| Time Step                         | s             | Δt              | 3.40×10^{-10}  | 1             |
| Gas density                       | kg/m^3        | ρ_f             | 1.6550         | 1             |
| Kinematic viscosity               | m^2/s         | ν_l             | 2.8203×10^{-6} | 0.024         |
| Gas velocity                      | m/s           | u_{max}         | 5.89           | 0.01          |
| Gas concentration                 | mol/m^3       | C_0             | 103.44         | 10            |
| Gas diffusion coefficient         | m^2/s         | D_f             | 1.96×10^{-5}   | 1/6           |
| Saturated adsorption capacity     | mol/m^3       | N_m             | -              | /10.344       |
| Solid diffusion coefficient       | m^2/s         | D_s             | 3.92×10^{-8}   | 1/3000        |
| Constant adsorption rate          | m^3/mol·s     | k_i             | 1.47×10^{2}    | 0.0161        |
| Constant desorption rate          | s^{-1}        | k_{ij}          | 2.94×10^{6}    | 0.0010        |

4. Results and Discussion

4.1. Effect of Fluid Flow and Mass Transfer
The simulation conditions are 120 K temperature and 0.1 MPa pressure, while the left inlet velocity satisfies the Poiseuille flow with a maximum velocity of 0.01 (lattice units), and the inlet methane concentration is maintained at 10 (lattice units).

Figure 3 shows the change of methane concentration in the calculation domain at 4000-500000 lattice time steps. It can be found that when adsorption starts to occur, the methane in the pores of the Maxsorb III adsorption bed is rapidly adsorbed and the methane concentration in the pores drops to 0. The pore size of Maxsorb III is very small, and the fluid-solid boundary used in LBM simulation is a rebound boundary without slip, so the fluid flow rate in the pore is very small, close to 0, and the diffusion rate of methane is very small compared to the adsorption rate. Therefore, in the whole simulation process, the methane concentration is always 0 after the initial methane is adsorbed in the
pore. Only when Maxsorb III particles outside the pore reach saturation adsorption, methane begins to diffuse into the pore.

Figure 3. Figure with the change of methane concentration in the calculation domain at 4000-500000 lattice time steps.

4.2. Effect of Adsorption and Heat Transfer
The change of adsorption capacity of Maxsorb III adsorption bed and temperature change in computational domain with 4000-500000 lattice time steps are shown in figure 4. At the beginning, the methane adsorption rate is very fast, and the adsorption capacity on the surface of adsorption bed reaches 3312 (lattice unit) in 2000 lattice time steps. According to the content in the previous section, after methane concentration within the pores of the adsorbent bed drops to 0, the adsorption only occurs on the surface of the adsorption bed. After 500,000 lattice time steps, the diffusion of methane in Maxsorb III particles is only close to the adsorption amount on the surface of the adsorption bed in the area with a thickness of about 12 (lattice unit).

Figure 4. Figure with the change of adsorption capacity of Maxsorb III adsorption bed and temperature change in computational domain with 4000-500000 lattice time steps.

Adsorption is an exothermic process and the temperature change in the computational domain is directly influenced by the adsorption rate. The upper left region of the adsorption bed is near the inlet, where the methane concentration is high and the adsorption rate is high, so the temperature increase in this region is the largest. The variation of the adsorption capacity and temperature in the calculation domain is shown in figure 5. The temperature increases rapidly at the initial stage and reaches a peak value of 167K at 18000 lattice time step. Then the adsorption gradually reaches saturation, and the adsorption rate decreases and heat conducts to the fluid domain and the interior of the adsorption bed, so the temperature decreases gradually. As the temperature drops, the saturated adsorption capacity
increases, the adsorption capacity increases slowly. Finally, the adsorption capacity and the temperature stabilize at 7650 (lattice unit) and 148K, respectively, in the later simulation period.

**Figure 5.** Figure with the variation of the maximum adsorption capacity and maximum temperature.

5. Conclusions

The adsorption heat transfer process at the pore-scale level of porous media was studied based on LBM. The experimental data of Maxsorb III particle saturated adsorption capacity were fitted by Tóth adsorption isotherm model. The methane concentration and adsorption rate on the surface of the adsorption bed were calculated according to Langmuir adsorption kinetics model. The methane adsorption capacity and temperature field in the calculation domain were calculated by the fourth-order Runge-Kutta finite difference method. It is concluded that the maximum temperature increase in the adsorption process reaches 47K, and the temperature change caused by the adsorption exotherm will have a significant impact on the saturated adsorption capacity.

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