MODELING OF RADIAL AND AXIAL NON-ISOTHERMAL ADSORPTION OF METHANE ON ACTIVATED CARBON IN CYLINDRICAL VESSELS

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Two non-isothermal adsorption models have been presented to calculate the amount of adsorbed gas on adsorbents and temperature distribution in a cylindrical tank. In the first model, gas enters the bed radially and it enters in axial direction at the second model. In each model the continuity, energy balance and diffusion equations of adsorbent particles have been solved simultaneously. The models have been used to simulate methane adsorption on activated carbon using in adsorbed natural gas technology (ANG). Simulations indicate that radial entrance results in faster adsorption and slower rise in bed temperature. Effect of the gas velocity on the uptake curve and gas concentration profile in two models has been studied and results indicated that velocity in radial model were more important than axial model.

Keywords: Modeling, Adsorption, methane, Activated carbon, ANG

1. Introduction

ANG (Adsorbed Natural Gas) technology, based on adsorption of natural gas in porous materials at relatively low pressures 3.5-4 MPa and ambient temperature, is a challenge to the LNG (Liquid Natural Gas) and CNG (Compressed Natural Gas) applications [1].

This storage technology rests on the assumption that the high density of the adsorbed gas confined within the pores of the adsorbent compensates for the volume taken up by the solid and for the lower density of the compressed gas in the inter particle void space. Activated carbons, because of the high micro pore volume they may contain, have shown to be an appropriate material, for adsorption of hydrocarbons [2-13].

One of the first experiments with ANG storage system was performed in Russia, Institute of Rural Mineral Resources, under Professor Dubinin's leadership [14]. Two types of active carbons were used for methane storage at the pressure interval 0.1– 100 MPa and room temperature. Rise in the methane

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adsorption capacity was found with the pressure increasing up to 5–6 MPa. Application of the pulverized active carbon for ANG tanks in which methane storage capacity was increased 5–10 times was discussed [15]. Methane adsorption on activated carbon is an exothermic process and as a result, the bed temperature tends to increase during charging. Thus, the ability of the bed to store natural gas strongly depends on the removal of heat of adsorption. Thus, ANG technology does not solely depends on the development of better carbon adsorbents and improving the heat transfer mechanism. Although, a good adsorbent is paramount for the success of ANG, its potential will be limited if it is not integrated with a well designed system which compensates for inherent weaknesses of the adsorption process. Description of the charge and discharge cycle dynamics of an ANG reservoir has been the subject of several studies in recent years [16-24]. Modeling strategies are usually based on the formulation of mass and energy balances.

The aim of this work is to compare the thermal effects resulting from the heat of adsorption on the performance of an ANG storage vessel during radial and axial introduction of the gas to a cylindrical bed of active carbon.

2. Theoretical models

The geometrical model of the storage system under study is depicted in Fig. 1. It consists of a portable cylindrical reservoir of length L, and outer radius Ro, filled with spherical activated carbon particles of uniform size.
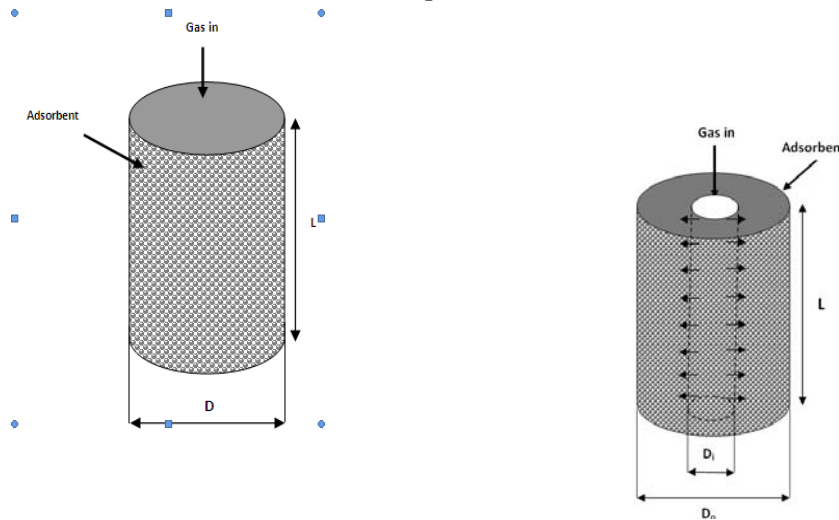

Fig. 1. Schematic presentation of the radial and axial gas distribution

Two models are proposed for analysis of the ANG system denoted by model A and model B. In the model A, methane enters the bed radially through the perforated tube of radius Ri, and in the model B the gas enters axially.

Methane adsorption on activated carbon is an exothermic process and, as a result, the bed temperature tends to increase during charging. Thus, the ability of the bed to store natural gas strongly depends on the removal of heat of adsorption. The methane flows into the cylinder at 298 K and 3.5 MPa at constant mass flow rate.

The output variables of the two models are, mean temperature versus time and uptake data (M_t/M_∞), which are obtained from the simultaneous solution of the differential mass and energy balance and also diffusion equations, subject to the appropriate boundary and initial conditions imposed to the bed.

3. Governing equations

Continuity equation

As mentioned before, model A and model B are presented in this work to compare the radial and axial gas flow in the cylindrical vessel filled with activated carbon. Consequently, continuity and energy equations have been written for both cases.

The continuity equation of the bed in radial direction (R) is:

$$\varepsilon \frac{\partial C}{\partial t} + (1-\varepsilon)\frac{\partial \bar{q}}{\partial t} = -u\frac{\partial C}{\partial R} \tag{1}$$

With the initial and boundary conditions:

$$\begin{cases} t = 0 & C = 0 \\ R = R_o & \dfrac{\partial C}{\partial R} = 0 \end{cases}$$

The continuity equation of the bed in axial direction (Z):

$$\varepsilon \frac{\partial C}{\partial t} + (1-\varepsilon)\frac{\partial \bar{q}}{\partial t} = -u\frac{\partial C}{\partial Z} \tag{2}$$

With the initial and boundary conditions:

$$\begin{cases} t = 0 & C = 0 \\ Z = 0 & C = C_0 \end{cases}$$

Each element of the bed is containing methane in two sections, methane in the bulk (C) and also methane adsorbed in the pore of activated carbon ($\bar{q}$ = mass

of methane adsorbed /mass of activated carbon). Left side of equation provides an expression for the total variation of the gas mass inside the reservoir as a function of time. The parameters ε , u and ρ_s which shown in equations (1) and (2) are bed porosity, gas velocity and bed density.

It is assumed that initially the bed has no methane and, at the entrance of the bed, gas concentration reaches its maximum value of C0.

To calculate the mean adsorbed methane, diffusion equation of the adsorbent particle was written for spherical pellet.

Spherical particle diffusion equation

Activated carbon has high volume of micropore and adsorption of gas occurs mainly in these pores. So, in this study inter particle diffusion of spherical and also cylindrical particles is applied to calculate amount of adsorbed gas. On the external surface of particles the Langmuir equilibrium relation is applied between the gas pressure and gas adsorbed on the surface of adsorbent.

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} D_{eff} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right)$$

(3)

In this equation r is the radius of the activated carbon particle; D_{eff} is effective diffusivity of methane on activated carbon which is calculated from experiments. Adsorbed methane (q) which is function of time and radius of a particle is obtained by solving above equation with appropriate initial and boundary conditions.

$$\begin{cases} \forall t = 0 \quad for\,all\,r \quad q = 0 \\ \forall r = 0 \quad for\,all\,t \quad \dfrac{\partial q}{\partial r} = 0 \\ \forall r = r_p \quad for\,all\,t \quad q_s(r_p,t) = \dfrac{q_m bP}{1+bP} \end{cases}$$

At t=0 the amount of methane adsorbed in the particle is zero and particle is free of methane at the beginning of process. The adsorbed gas concentration in the spherical pellet is symmetrical, while the outer surface of particle corresponds to r=rp. In the last boundary condition q_m and b are two parameters which have been obtained from the experimental results. The mean adsorbed gas is obtained from integration of adsorbed gas profile along the radius of particle.

$$\overline{q} = \frac{3}{r_p^3} \int_0^{r_p} q.r^2.dr$$

(4)

Uptake curve data

To obtain the uptake data of adsorption of methane on activated carbon in the model A and model B, analytical solution of equations 3 and 4 are used, that is:

$$\frac{\overline{q}}{q_s} = \frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{eff} n^2 \pi^2 t}{r_p^2} \right)$$

(5)

where Mt is the total mass of the diffusing species that has adsorbed in the particle at time t, and M∞ is the total adsorbed mass.

Energy equation

To obtain the energy balance equation for the bed, the contribution of the energy transfer by heat diffusion in the solid phase is considered. The heat of adsorption is considered as a rate of internal heat generation. The pressure gradient inside the cylinder is also considered. According to these assumptions, the energy equations for two models are written as follows.

The energy equation in the bed in radial direction (R):

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{1}{R} \frac{\partial T}{\partial R} + \frac{\partial^2 T}{\partial R^2} \right) + \frac{\Delta H}{\rho_s C_s} \cdot \frac{\partial \overline{q}}{\partial t} - \frac{1}{\rho_s C_s} \frac{\partial p}{\partial t} - \frac{h}{L \rho_s C_s} (T - T_\infty)$$

(6)

Initial and boundary conditions for this equation has been presented as follow:

$$\begin{cases} t = 0 & T = T_0 \\ R = R_i & \lambda \frac{\partial T}{\partial R}\bigg|_{R=R_i} = C_0 Cp_g u (T - T_g) \\ R = R_o & -\lambda \frac{\partial T}{\partial R}\bigg|_{R=R_o} = h(T - T_\infty) \end{cases}$$

The energy equation in the bed in axial direction (Z):

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{\Delta H}{\rho_s C_s} \cdot \frac{\partial \overline{q}}{\partial t} - \frac{2h}{R_o \rho_s C_s} (T - T_\infty) - \frac{1}{\rho_s C_s} \frac{\partial p}{\partial t}$$

(7)

Following initial and boundary conditions are used to solve this equation:

$$\begin{cases} t = 0 & T = T_0 \\ Z = 0 & T = T_i \\ Z = \text{L} & -\lambda \dfrac{\partial T}{\partial Z} = h(T - T_0) \end{cases}$$

The first term in the right-hand side of equations (6) and (7) represents the heat diffusion in the activated carbon bed, while the following three terms represent the heat of adsorption, heat lost by convection with surrounding through the vessel wall and the compressibility effect of the gas. These three terms act as a heat source term in the energy equation.

Initially, the system is considered to be at a homogeneous and uniform temperature and pressure, given by T0 and P0 respectively. In the model A, the generated heat can be removed from the bed with two surfaces, the inner surface and the outer surface. Conduction heat transfer of the inner surface raises the temperature of the entered gas during the filling time of the bed. In the model B, at the entrance of the vessel, the gas has initial temperature Ti, and heat is transferred by convection at the end of the vessel. Notation h denotes convection coefficient and λ is conductivity of the bed. T∞ denotes the ambiental temperature.

Pressure equation

Pressure is determined from gas concentration and temperature distribution by using the Peng-Robinson equation to evaluate compressibility factor that is shown by z in the following equation.

$$P = zCRT \tag{8}$$

$$z^3 - (1 - B) z^2 + (A - 3B^2 - 2B)z - (AB - B^2 - B^3) = 0 \tag{9}$$

which in A and B parameters are defined below:

$$A = \frac{a\alpha P}{R^2 T^2}, \qquad B = \frac{bP}{RT}$$

$$a = \frac{0.45724 \, R^2 T_c^2}{P_c}, \qquad b = \frac{0.0778 \, RT_c}{P_c}$$

$$\alpha = \left(1 + \left(0.37464 + 1.54226 \, \omega - 0.26992 \, \omega^2\right)\left(1 - T_r^{0.5}\right)\right)^2, \quad T_r = \frac{T}{T_c}$$

In these equations Tc, Pc and ω are critical temperature and pressure and acentric factor of methane.

3.2. Numerical solution

The previous equations have been discretized by using the implicit finite difference method. Several iterations are used to obtain the mean temperature as functions of time and uptake data. Iterative process to gain the numerical solution requires the following steps.

At first, the initial value of the variables C, T, q, P are supplied. The values of $\overline{q}$ in the bed during the adsorption process are evaluated from the Langmuir equilibrium relation instead of solving Eq (5). This route was chosen due to the lack of required parameters to solve these equations at this initial step, so initial estimation for C as a function of time and bed length is obtained without diffusion in the particles by solving Eqs (1) or (2). At the next step, by neglecting the pressure change, Eqs (6) or (7) is solved to obtain the temperature profile. The required parameters for Peng-Robinson equation are evaluated and pressure distribution is calculated from Eq (8) and Eq (9) using C and T. In this step, diffusion equation could be solved to obtain the amount of mean adsorbed gas. In this step, the Eq (5) is solved to obtain new values of $\overline{q}$. The next step is return to solving the Eqs (1) or (2), and an iterative procedure is finally required for updating the variables to get the final solution.

4. Results and discussion

In this paper activated carbon and methane are considered as adsorbent and adsorbate. Physical description of the storage system and other data used in the simulation are illustrated in Table 1.

Table 1

Data and physical properties used in the methane adsorption on activated carbon system

Bed length	10 cm
Bed diameter	5 cm
Adsorbent density	0.48 g/cm3
Inlet gas density	0.0226 g/cm3
Bed heat capacity	650 J/kg K
Adsorbent thermal diffusivity	3.3189×10-7 m2/s
Adsorbent thermal conductivity	54 W/m∘C
Inlet gas temperature	298 K
Initial bed temperature	298 K
Adsorption heat	19500 J/mol
Adsorbate velocity	0.5-2 m/s
Convection heat transfer coefficient	20 W/m2∘C

Henry's law is used as adsorption isotherm for equilibrium between gas adsorbed at the outer surface of particles and the gas phase. The rate of diffusion of methane in carbon sphere is calculated based on the diffusion coefficient given in [25].
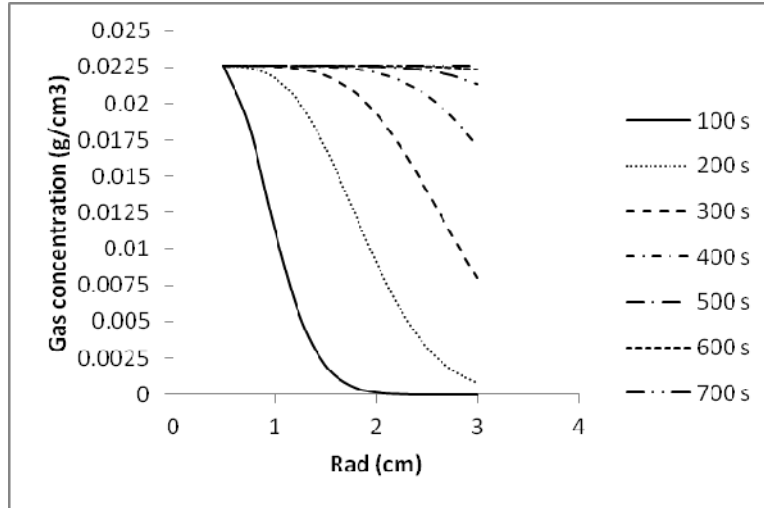

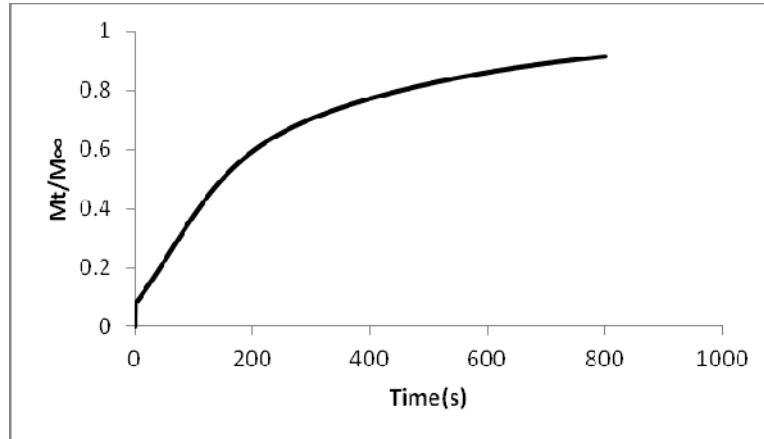Fig. 2. Gas concentration profile at radial direction in the first model

Fig. 3. Uptake curve in the first model

Fig. 2 and Fig. 3 show the gas concentration profiles along the bed radius and uptake curve for results of first model for inlet velocity equal to 0.5 m/s. At initial time of adsorption, the gas concentration at the entrance of the bed is high and decreases along the radius. The uptake curve presents a sharp slope because pores of adsorbent particles are empty, so the rate of adsorption is high. After that,

the slope of uptake curve decreases. It means that gas adsorption diminishes and gas concentration increases along the radius the bed. After about 800 s the bed is filled and gas concentration reaches its maximum over the bed length. Consequently, this time is considered as the filling time of the bed for this model.
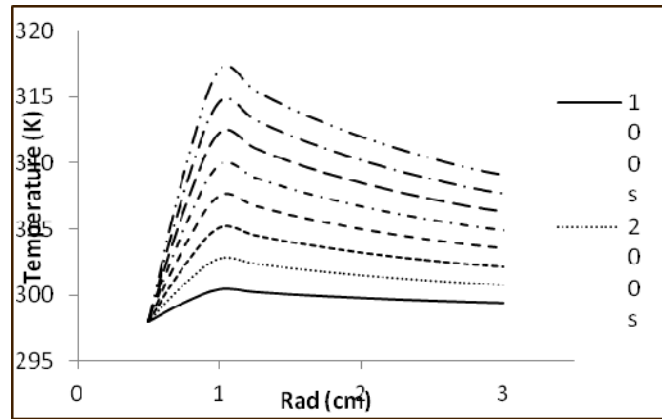

Fig. 4. Temperature profile in the radial direction in the first model

In Fig. 4 temperature profile as a function of radius at distinct points of time has been shown. It can be seen that, due to the accumulation of adsorption heat at the entrance section of bed, the temperature is increasing in this zone. At the second zone, because adsorption is an exothermic process, the amount of adsorbed gas is decreasing as it was shown in Fig. 3, so the temperature is also decreasing. According to Fig. 4, maximum temperature rising is 20 °C.

In Fig. 5 and Fig. 6 gas concentration profile as a function of bed length and uptake curve during the 1500 s are shown. It can be seen that in the second model the maximum value of adsorbed gas along the bed length is reached after 1500 s, so this time is the filling time of the bed in the second model.
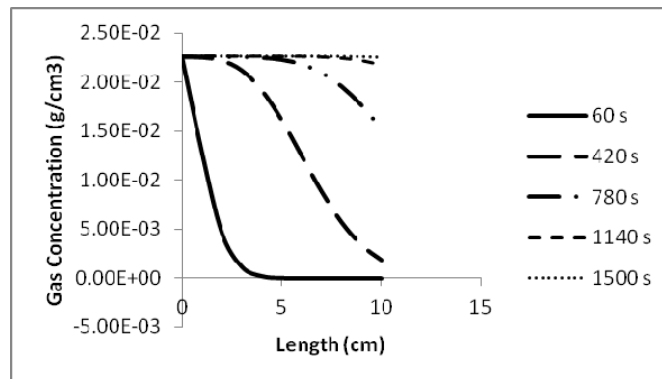

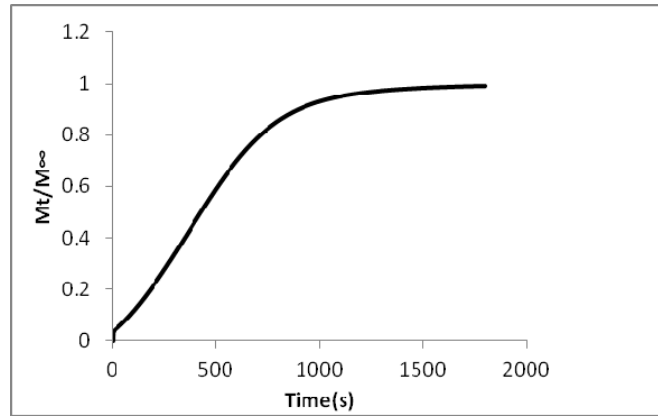Fig. 5. Gas concentration profile at axial direction in the second model

Fig. 6. Uptake curve of methane on activated carbon in the second model

Temperature profile as a function of bed length during the charging time is drawn in Fig. 7 according to the second model. At the beginning of the adsorption process, temperature rising occurs at the entrance zone of the bed length, and gas is adsorbed only in this part. After some time, more gas is adsorbed in the bed and temperature increases along the bed length. This model predicts maximum temperature rise of about 62 °C.
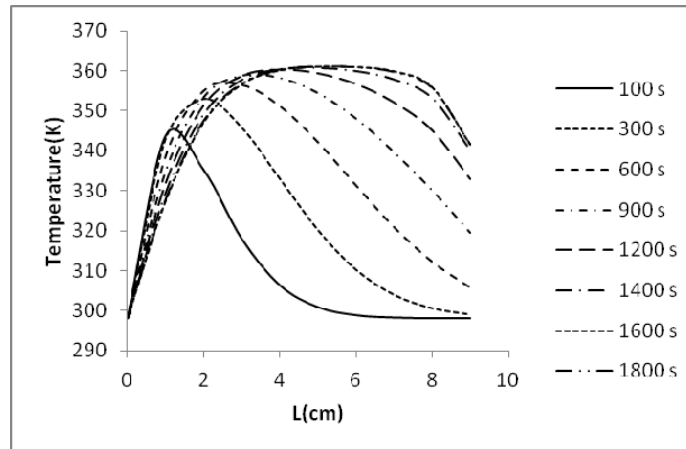

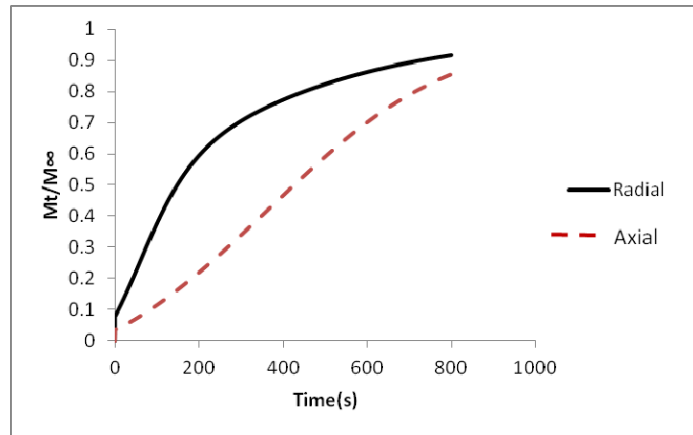Fig. 7. Temperature profile at the axial direction in the second model

Fig. 8. Comparison of uptake curve of methane on activated carbon in radial and axial models.

Comparison of Fig. 4 and Fig. 7 shows that the temperature increase is about 20∘C and 62∘C in the first and second models respectively, so gas entrance in the radius direction can decrease the adsorption heat effect on temperature rising. It is to remark that in the first model gas entrance surface is higher than that of the second model. In the second model, the gas must moves along the bed, while in the first model must move along the radius the bed, which is shorter path.

In Fig. 8 uptake curves of two models are shown. As discussed earlier, the maximum value of gas adsorbed is achieved after 800 s and 1500 s in the first and second models respectively. Fig. 7 shows that after charging time of the first model, gas adsorbed in the second model reaches only about 80% of the maximum value. It means that when the gas enters the bed in radial direction adsorption rate is higher than the axial entrance of the gas to the bed.

Effect of gas velocity

In order to test the influence of gas velocity in the amount of adsorbed gas, three distinct gas velocities were used: 0.3, 0.5 and 0.8 m/s.
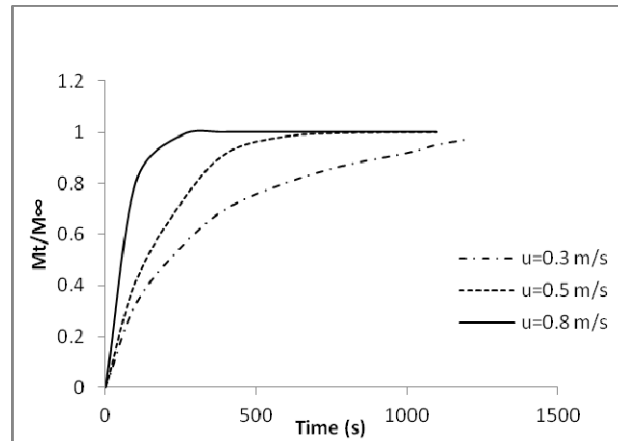
Fig. 9. Effect of gas velocity on uptake curve in the first model

Fig. 9 and Fig. 10 present the results in term of uptake curve in first and second models. It can be seen that in the two models a progressive increase in gas velocity causes a progressive reduction of the filling time of the bed and increase the rate of adsorption. In the first model the filling time of the bed decreased from 1200 s to 250 s for velocities from 0.3 to 0.8 m/s. In the second model the filling time changes from 1800 s to 1200s for velocities from 0.3 to 0.8 m/s. As a result, the effect of velocity in the first model is more important than in the second model.
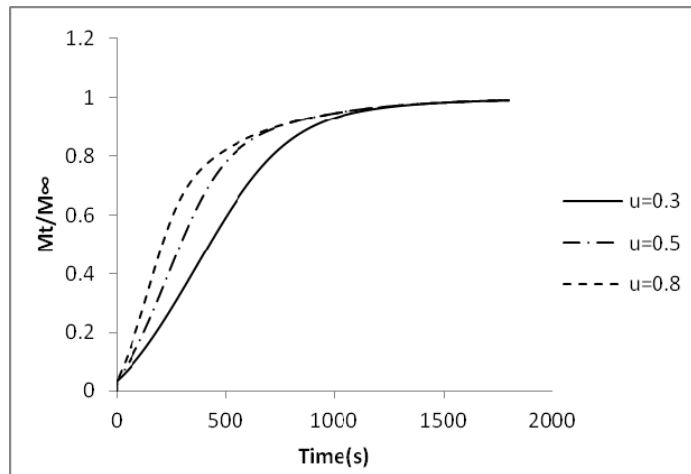

Fig. 10. Effect of gas velocity on uptake curve in the second model

5. Conclusions

In this work two models are studied for methane adsorption on activated carbon. The gas enters into the cylindrical vessel at radial and axial directions in the first model and second model, respectively. Gas concentration, adsorbed mass and temperature distributions in the bed are obtained from the numerical solution of the model equations. Comparison of the gas concentration, temperature and uptake profiles show that the rate of temperature rising and the filling time in the first model are smaller than of the second model. The filling time of the vessel in the first model is 800 s and in the second model is 1500 s. After the filling time, the temperature maximum increases to 20 ◦C and 62 ◦C in the first and the second models, respectively. Influence of the gas velocity on the filling time of the bed has been investigated and results proved that in the first model the increase in velocity has more effect on reduction of charging time of the bed than in the second model. As a result, radial gas flow through the bed seems to be more advantageous than the axial admission of the gas.

Nomenclature

rp	Particle radius(cm)	C	Gas density(g/cm3)
t	Time(s)	co	Inlet concentration(g/cm3)
T	Temperature(K)	Deff	Effective diffusivity(cm2/s)
To	Initial Temperature(K)	ΔH	Adsorption heat(j/g)
Ti	Inlet Temperature(K)	h	Convection coefficient (W/m2C)
u	Gas velocity(cm/s)	K	Henry constant
λ	Thermal conductivity(W/m C)	L	Length of vessel(cm)
z	Compressibility factor	P	pressure (Pa)
α	Thermal Diffusivity(cm2/s)	q	Adsorbed gas (g methane/g activated carbon(-)
ε	Porosity(-)	$\bar{q}$	Mean gas adsorbed over the time (g/g)

R E F E R E N C E S

[1] *L.L. Vasiliev*, L.E. Kanonchik, D.A. Mishkinis, M.I. Rabetsky, Adsorbed natural gas storage and transportation vessels, porous Media Laboratory, Luikov Heat and Mass Transfer Institute, 2007.

[2] *J. Alca˜niz-Monge, M.A. De la Casa-Lillo, D. Cazorla-Amor´os, S. Linares*, Methane Storage in Activated Carbon Fibres, Carbon, vol. 35, 1997, pp.291–297.

[3] *T.L. Cook, C. Komodromos, D.F. Quinn, S. Ragan*, Carbon Materials for Advanced Technologies, 1999, pp.269–302.

[4] *R.F. Cracknell, , P. Gordon, K.E. Gubbins*, Influence of Pore Geometry on the Design of Micro porous Materials for Methane Storage, J. Physical Chemistry, vol. 97, 1993, pp.494–499 .

[5] *V.C. Menon, and S. Komarneni*, Porous Adsorbents for Vehicular Natural Gas Storage: A Review, J. Porous Materials, vol. 5, 1998, pp. 43–58.

[6] *N.D. Parkyns, D.F. Quinn, J.W. Patrick*, Porosity in Carbons, London, 1995, pp.293–325.

[7] *D. Lozano-Castello, D. Cazorla-Amoros*, A. Linares-Solano, D.F. Quinn, Activated carbon monoliths for methane storage: influence of binder, Carbon, vol. 40, 2002, pp. 2817–2825.

[8] *C. Almansa, M. Molina-Sabio, F. Rodr guez-Reinoso*, Adsorption of ethane into ZnCl2-activated carbon derived discs, Microporous and Mesoporous Materials vol. 76, 2004, pp.185–191.

[9] *A. Celzard, A. Albiniak, M. Jasienko-Halat, J.F. Mareˆche, G. Furdin*, Methane storage capacities and pore textures of active carbons undergoing mechanical densification, Carbon, vol. 43, 2005, pp.1990–1999.

[10] *A.M. Rubel, J.M. Stencel*, CH4 storage on compressed carbons, Fuel, vol. 79, 2000, pp. 1095–1100.

[11] *A. Perrin , A. Celzard, A. Albiniak, M. Jasienko-Halat, J.F. MareˆcheˊFurdin*, NaOH activation of anthracites: effect of hydroxide content on pore textures and methane storage ability, Microporous and Mesoporous Materials, vol. 81, 2005, pp.31–40.

[12] *A. Celzard, A. Perrin, E. Albiniak, J.F. Broniek*, The effect of wetting on pore texture and methane storage ability of NaOH activated anthracite, Fuel, vol. 86, 2007, pp.287–293.

[13] *F. Rodrˊiguez-Reinoso, M. Molina-Sabio*, Role of chemical activation in the development of carbon porosity, Colloids and Surfaces A: Physicochem. Eng. Aspects, vol. 241,2004, pp. 15–25.

[14] *M.M. Dubinin*, The potential theory of adsorption of gases and vapors for sorbents with energetically nonuniform surfaces, Chem. Rev, vol. 60, 1960, pp.235–241.

[15] *V.T. Paveliev*, Methane sorption by the active carbons at high pressures, Proc. Acad. Sci. USSR 1948, pp. 779–782.

[16] *K.J. Chang, O. Talu*, Behavior and performance of adsorptive natural gas storage cylinders during discharge, Appl. Therm. Eng, vol. 3, 1996, pp. 475–374.

[17] *X.D. Yang , Q.R. Zheng, A.Z. Gu, X.S. Lu*, () Experimental studies of the performance of adsorbed natural gas storage system during discharge, Applied Thermal Engineering, vol. 25, 2005, pp. 591–601.

[18] *N. Firas, M. Rosli, R.Mohamad*, Dynamic delivery analysis of adsorptive natural gas storages at room temperature, Fuel Processing Technology, vol. 88, 2007, pp. 349–357.

[19] *S. Biloˊe, V. Goetz, S. Mauran*, Dynamic Discharge and Performance of a New Adsorbent for Natural Gas Storage, AIChE J., vol. 47, 2001, pp. 2819–2830.

[20] *J.P.B. Mota*, Impact of Gas Composition on Natural Gas Storage by Adsorption, AIChE J., vol. 45, 1999, pp. 986–996.

[21] *J.P.B. M ota, A.E. Rodrigues, E. Saatdjian, D. Tondeur*, Charge Dynamics of a Methane Adsorption Storage System: Intraparticle Diffusional Effects, Adsorption, vol. 3, 1997a, pp.117–125.

[22] *J.P.B. Mota, A.E. Rodrigues, E. Saatdjian, D. Tondeur*, Dynamics of Natural Gas Adsorption Storage Systems Employing Activated Carbon, Carbon, vol. 35,1997b, pp. 1259–1270.

[23] *J.P.B. Mota, E. Saatdjian, D. Tondeur, A.E. Rodrigues*, A Simulation Model of a High-Capacity Methane Adsorptive Storage System, Adsorption,vol. 1, 1995, pp.17–27.

[24] *O. Pupier, V. Goetz, R. Fiscal*, Effect of Cycling Operations on an Adsorbed Natural Gas Storage, Chemical Engineering and Processing, vol.44, no. 2005, pp.71–79.

[25] *R.D. Cess*, Handbook of Heat Transfer, McGraw-Hill, New York, 1973.