

Mathematical Modeling of Gas Adsorption Processes in Packed Bed: The Role of Numerical Methods on Computation Time

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Abstract: Rigorous mathematical modeling of adsorption processes in packed beds involves time-consuming computations which are considered as the fundamental weakness of such thorough mathematical models. Thus, reducing the computation time was a key factor in improving adsorption mathematical models. In order to achieve this goal, an attempt was made to know how much using different numerical methods influenced the accuracy and time of these computations. For this purpose, the adsorption process of gas mixture consisting of H₂O, CO₂, CH₄ and N₂ in a tower packed with Zeolite 5A was considered to be modeled. The mathematical model was simplified based on the fact that neglecting the variations of pressure and temperature had no significant effect on the results of the model. This fact has been confirmed through previous research (M. Gholami & Talaie, 2009). The main objective of this study was to compare the capabilities of two important numerical methods in terms of their computation time and stability. Finite difference and orthogonal collocation were the numerical methods that were taken into account to be examined in solving the governing equations. The results obtained in this study revealed that orthogonal collocation was the best to solve pellet equations, while finite difference was more appropriate for bed equations. As a result, a combined method was suggested to be proper, i.e. orthogonal collocation for solving pellet equations and finite difference for solving bed equations. The results demonstrated that the combined method required half as much computation time as the one in which finite difference method was employed to solve the whole equations.

Keywords: Simulation, Natural Gas, Zeolite 5A, Adsorption, Orthogonal Collocation, Finite Difference

Introduction

Natural gas has attracted more attention nowadays as an important energy resource for responding to industrial, transportation and domestic demands.

The natural gas produced from wells is saturated with water, and it contains the detrimental components such as H₂O and CO₂. Since the presence of these components causes corrosion and hydrate problems in pipelines,

fittings and equipment, various processes have been developed to remove harmful components from natural gas. Adsorption is an efficient process by which undesirable components of natural gas such as water vapor can be adsorbed through the beds packed with adsorbents such as activated carbon, silica gel or Zeolites. Zeolites are crystalline microporous structures containing pores of uniform and molecular-size pores. The major advantages of

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using zeolites are their high ability for successive regeneration and high selectivity for adsorbing specific materials.

The mathematical modeling of adsorption processes comprises solving conservation equations of mass, energy and momentum to describe the dynamics of adsorption on a fixed bed packed with commercial adsorbents. Usually, these equations are solved numerically, and the computation is time-consuming. Therefore, it is necessary to find an appropriate and accurate numerical method leading to less computation time.

Different numerical methods such as finite difference, finite volume, orthogonal collocation and orthogonal collocation on finite elements have been used to solve the governing equations of adsorption and other similar process (Afshar Ebrahimi, 2007; Ahmed & Theydan, 2014; Carmo Coimbra, Sereno, & Rodrigues, 2000; Cavenati, Grande, & Rodrigues, 2006; Cen & Yang, 1986; M. Gholami & Talaie, 2009; Kaczmarski, Mazzotti, Storti, & Morbidelli, 1997; Park, 2002; Rambabu, Muruganandam, & Velu, 2014; Ribeiro, Grande, Lopes, Loureiro, & Rodrigues, 2008; Tefera, Hashisho, Philips, Anderson, & Nichols, 2014).

The method choice can influence the precision of the results. Finite difference method is widely used to solve the governing equations of adsorption mathematical model because of its simplicity. However, it has been reported in literature that orthogonal collocation is a successful method especially for solving nonlinear differential equations and takes less computation time compared with finite difference (1990; Finlayson, 1972, 1980; Mehdizadeh, 2001).

The collocation method was initially used by Slater and Barta to solve differential equations. Based on the Tchebychev's polynomial expansion, Lanczos has introduced a mathematical function whose roots were used as the collocation points. Then, the method has been developed further, and finally was called as orthogonal collocation. It has been employed to solve nonlinear partial differential equations in chemical engineering problems in which it has showed better results compared with other methods (Finlayson, 2013).

Lin (1990) has compared the results of orthogonal collocation with the method of lines in solving the governing equations of oxygen-nitrogen adsorption process. The results of this study revealed that using orthogonal collocation resulted in less calculation time than the method of lines with the same accuracy. Park (Park, 2002) has applied this method to solve the equations associated with

the model of single-component gas adsorption in a fixed bed. He has come to the same conclusion as Lin. Following to Lin and Park, Cruz (Cruz, Mendes, & Magalhaes, 2004) has solved the equations related to the model of single-component gas adsorption into an adsorbent pellet using orthogonal collocation and sub-domain method. He has reached the conclusion that orthogonal collocation converged well. Sankararao and Gupta (Sankararao & Gupta, 2007) investigated multi-component adsorption on fixed bed by considering non-isothermal effects, pressure variations, axial dispersion of components inside the gas (macro-void) phase as well as the diffusion of components inside the particles (micro-void). The partial differential equations for the gas in the axial direction were solved by using the finite difference technique. The method of orthogonal collocation is used to solve the diffusion equation for particles.

Delgado et al. (Delgado, Uguina, Sotelo, & Ruiz, 2006) studied an adsorption of methane and nitrogen on a fixed-bed packed with silicalite pellets. They use the LDF approximation for the adsorption kinetics to simulate the breakthrough curves of nitrogen and methane. The complete model was solved numerically using the PDECOL program, which uses orthogonal collocation on finite elements technique.

A dynamic behavior of 2-methyl thiophene adsorption from mixtures in hexane on a fixed bed of NiY, CeY and CeNiY zeolite adsorbents is studied experimentally and mathematically by Dasgupta et al. (Dasgupta et al., 2009). The fixed bed is simulated by applying an axial dispersed plug flow model utilizing Langmuir isotherm. Mass conservation equation along the fixed bed, is discretized using the method of orthogonal collocation using shifted Legendre polynomials.

Muthanna et al. (Ahmed, Mohammed, & Kadhun, 2011) studied adsorption of propane, n-butane, and iso-butane mixture on 5A molecular sieve zeolite experimentally and theoretically at a constant temperature. The equilibrium model along with linear driving force model was used to predict the experimental breakthrough curves for this multicomponent mixture. The model equations were solved numerically by using backward finite difference technique.

Dantas et al. experimentally and mathematically studied adsorption of carbon dioxide and nitrogen on activated carbon (Dantas et al., 2011) and CO₂ on commercial activated carbon (Dantas et al., 2009). The model consists of mass, energy and momentum balances employing LDF model for the mass

transfer rate in pellets. The governing equations were solved numerically by the orthogonal collocation method on finite elements using the commercial software gPROMS.

In this study, the process of natural gas adsorption on a fixed bed packed with 5A Zeolite adsorbents is simulated numerically. It was assumed that the natural gas is a mixture of H_2O , CO_2 , CH_4 and N_2 . The multi-component adsorption on fixed bed is investigated by considering axial dispersion of components inside the gas (macro-void) phase as well as the diffusion of components inside the particles (micro-void).

Since dehydration is a time-consuming process, the objective of this study is to find a numerical approach which needs less computation time. For this purpose, two numerical methods of finite difference and orthogonal collocation are compared in terms of computation time.

The best numerical approach which provided the best fit with experimental data and had less computational time was selected for simulating the packed bed adsorption process.

Mathematical Model

The process of gas adsorption in a fixed bed packed with 5A zeolite is simulated. The fixed bed is modeled based on mass conservation equations over the macro-voids (the voids between particles) as well as mass balances over the micro-voids (the voids inside the pellet). The mass transfer rate in crystals (very fine particles inside the pellets which are mainly responsible for capturing) is represented by a Linear Driving Force (LDF) model. The LDF model is frequently used for this purpose because it is analytically simple and physically consistent.

Gholami and Talaie (M. Gholami & Talaie, 2009) have demonstrated that isothermal assumption is a valid assumption in the process of natural gas dehydration. As a result, the energy balances were eliminated from the governing equations.

The following assumptions were made in the developed mathematical model:

1. The flow pattern is described by the plug-flow pattern (Delgado et al., 2006).
2. Temperature and pressure are constant along the bed.
3. The external mass transfer resistance (the resistance between gas bulk and the surface of pellets) is negligible (M. Gholami & Talaie, 2009).

4. The bed operates in adiabatic condition.

5. Adsorbent pellets are sphere and in the same size, and they are distributed uniformly through the bed.

It is also assumed that the bed is saturated initially with pure nitrogen.

Governing Equations

The differential gas phase mass balance for the component i yields the following equation (Ruthven, 1984):

$$\frac{\partial C_{b,i}}{\partial t} = D_{ax,i} \frac{\partial^2 C_{b,i}}{\partial z^2} - u \frac{\partial C_{b,i}}{\partial z} - \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial \bar{q}_{pi}}{\partial t} \quad (1)$$

In the above relation D_{ax} is the axial dispersion, $C_{b,i}$ is the gas-phase concentration of component i , u is the interstitial velocity, ε_b was the bed porosity and $\frac{\partial \bar{q}_{pi}}{\partial t}$ is the rate of loading of component i into a pellet. This equation is used to find the gas composition distribution, $C_{b,i}$, along the bed.

The value of D_{ax} is calculated using the following equation (Ruthven, 1984):

$$D_{ax,i} = \gamma_1 D_{mi} + \gamma_2 d_p u \quad (2)$$

In the above equation $\gamma_1=0.7$, $\gamma_2=0.5$, D_{mi} is the molecular diffusivity and d_p is the particle diameter. D_{mi} is calculated using a suitable correlation.

By assuming that the bed is initially saturated with some gases (see table 2) as a result of previous regeneration stage, the initial and boundary conditions of equation 1 are as follow:

$$\begin{aligned} C_{b,i} \big|_{z=0,t} &= C_{in,i} \\ \frac{\partial C_{b,i}}{\partial z} \bigg|_{z=l,t} &= 0 \\ C_{b,i} \big|_{z,t=0} &= C_{b,i}^0 \end{aligned} \quad (3)$$

The mass transfer rate of the component i into a pellet $\frac{\partial \bar{q}_{pi}}{\partial t}$ is calculated by integrating the term $\frac{\partial \bar{q}_{ci}}{\partial t}$, which is the loading rate of component i into micro-pore volumes, over whole spherical pellets:

$$\frac{\partial \bar{q}_{pi}}{\partial t} = \frac{3}{R_p^3} \int_0^{R_p} r^2 \frac{\partial \bar{q}_{ci}}{\partial t} dr \quad (4)$$

In the above equation R_p is the pellet radius. The mass balances for penetrating of gas component i into the macropore volume is expressed by (Delgado et al., 2006; M. Gholami & Talaie, 2009):

$$\frac{\partial C_{p,i}}{\partial t} = \frac{D_{eff,i}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{p,i}}{\partial r} \right) - \frac{1 - \varepsilon_p}{\varepsilon_p} \frac{\partial \bar{q}_{ci}}{\partial t} \quad (5)$$

Where $C_{p,i}$ is the gas-phase concentration of component i in the pellet, ε_p is the pellet porosity and $D_{eff,i}$ is the effective diffusivity in the pellet. The following equation is used to calculate the value of $D_{eff,i}$ (Poling, Prausnitz, John Paul, & Reid, 2001):

$$D_{eff,i} = \left(\frac{1}{D_{mi}} + \frac{1}{D_{ki}} \right)^{-1} \quad (6)$$

In this equation D_{ki} is the Knudsen diffusivity in the particle and calculated by using a suitable correlation.

By ignoring the external resistance (M. Gholami & Talaie, 2009), the concentrations of component i at the surface of pellets and those at bulk gas phase will be equal. It is also assumed that the initial concentration of the gaseous components in micro-void is equal to that in macro-void. As a result of these assumptions, the initial and boundary conditions of equation 5 are obtained as:

$$\begin{aligned} C_{p,i}|_{r=R_p,t} &= C_{b,i} \\ \frac{\partial C_{p,i}}{\partial r} \Big|_{r=0,t} &= 0 \\ C_{p,i}|_{r,t=0} &= C_{b,i}^0 \end{aligned} \quad (7)$$

The mass transfer rate of the component i through micropore volumes (crystals) by considering Glueckauf (Glueckauf, 1955) linear driving force model, is described by following equation:

$$\frac{\partial \bar{q}_{c,i}}{\partial t} = \frac{15D_{c,i}}{R_c^2} (q_{c,i}^* - \bar{q}_{c,i}) \quad (8)$$

Where $q_{c,i}^*$ is the equilibrium concentration of component i in the micro-pore volume, $D_{c,i}$ is the diffusivity in the crystal and R_c is the crystal radius.

The initial condition needed for this equation, is as follows:

$$\bar{q}_{c,i}|_{t=0} = q_{c,i}^* (C_{b,i}^0) \quad (9)$$

The crystalline diffusivity coefficient of component i , D_{ci} , is obtained by (Poling et al., 2001):

$$D_{ci} = D_{0i} \exp \left(-\frac{E_i}{R_g T} \right) \quad (10)$$

The values of the parameters D_{0i} and E_i are listed in Table 1 (M. Gholami & Talaie, 2009). In order to evaluate $q_{c,i}^*$, one needed an equilibrium relation. Gholami et al. (M. T. Gholami, M.R.; Roodpeyma, Sh., 2009) presented that the dual site Langmuir model was more accurate than Langmuir, Langmuir-Freundlich, and Toth models for predicting adsorption equilibrium of binary and ternary mixtures of light gases on A and X Zeolites. Therefore, in this study the extended dual site Langmuir isotherm for multi-component adsorption is utilized to find equilibrium concentrations:

$$\begin{aligned} q_{c,i}^* &= q_{si,1} \frac{b_{i,1} P_i}{1 + \sum_{j=1}^{noc} b_{j,1} P_j} \\ &+ q_{si,2} \frac{b_{i,2} P_i}{1 + \sum_{j=1}^{noc} b_{j,2} P_j} \end{aligned} \quad (11)$$

In the above equation P_i is the partial pressure, b_i and q_{si} are the i th component constant coefficients and q_{si} is the maximum adsorbed amount; $b_{i,j}$ and $q_{si,j}$ are functions of temperature as:

$$\begin{aligned} b_{i,j} &= b_{0,j} \exp \left(\frac{E_j}{RT} \right) \quad j \\ &= 1,2 \end{aligned} \quad (12)$$

$$\begin{aligned} q_{si,j} &= \frac{A_{j,1}}{T} + A_{j,2} \quad j \\ &= 1,2 \end{aligned} \quad (13)$$

Where $b_{0,j}$ and E_j are constants, and they are different for each component. These adsorption equilibrium parameters for methane, carbon dioxide, nitrogen and water vapor in Zeolite 5A are tabulated in Table 2.

Table 1. Kinetic Parameters of Water Vapor, Methane, Carbon Dioxide, and Nitrogen in Zeolite 5A Crystal (Micropore Volume) (M. Gholami & Talaie, 2009)

Component	$D_0 (m^2/s)$	$E (J/mol)$
H ₂ O	2.39×10^{-8}	17 288.47
CO ₂	5.9×10^{-11}	26 334
CH ₄	7.20×10^{-12}	12 551.94
N ₂	5.20×10^{-13}	6 275.97

Table 1. Adsorption equilibrium constants of Water, Methane, Carbon Dioxide and Nitrogen in Zeolite 5A (M. T. Gholami, M.R.; Roodpeyma, Sh., 2009).

Component	$A_{11} (mol K/kg)$	$A_{12} (mol/kg)$	$b_{01} (1/kPa)$	$E_1 (J/mol)$
H ₂ O	-3799.940	18.711	3.580×10^{-7}	44140.040
CO ₂	516.743	-0.794	3.320×10^{-7}	41077.100
CH ₄	348.971	0.542	6.770×10^{-6}	13672.210
N ₂	605.423	-0.582	3.730×10^{-5}	7528.091
Component	$A_{21} (mol K/kg)$	$A_{22} (mol/kg)$	$b_{02} (1/kPa)$	$E_2 (J/mol)$
H ₂ O	3684.491	-4.450	1.620×10^{-5}	45 199.990
CO ₂	-932.131	6.083	6.430×10^{-7}	29 812.290
CH ₄	348.971	0.542	6.130×10^{-7}	20 307.220
N ₂	605.423	-0.582	3.180×10^{-5}	7 941.248

Orthogonal Collocation Method

As mentioned before, in this study, orthogonal collocation method is used as a one numerical method to solve governing equations. In this method, the gradient and Laplacian operator in equations 1 and 4 are replaced as follows:

$$\begin{aligned}\frac{\partial C_{b,i}}{\partial Z} &= \sum_{j=1}^{nz+2} A'_{ij} C_{b,i,j} \\ \frac{\partial^2 C_{b,i}}{\partial Z^2} &= \sum_{j=1}^{nz+2} B'_{ij} C_{b,i,j} \\ \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial C_{p,i}}{\partial R} \right) &= \sum_{j=1}^{nz+2} B''_{ij} C_{p,i,k,j}\end{aligned}\quad (14)$$

As it is clear, by using this numerical method the original PDEs are converted to a set of ODEs, and then the complete set of differential-algebraic equations is solved by convenient standard methods. In orthogonal collocation method the collocation points are the roots of the orthogonal polynomials. In the non-symmetric systems these points are the roots of shifted Legendre polynomials or the Chebyshev Polynomials but for symmetric systems they are the roots of Jacobi polynomials. The detailed description of the method is available in (Finlayson, 1972, 1980). By discretizing conservation equations of bed and pellet, the following relations are obtained. Discretizing mass conservation of component i in the packed bed (equation 1) led to below equation. Since, the collocation points are between 0 and 1, the equation should be locally dimensionless. By defining $Z = \frac{z}{l}$:

$$\begin{aligned}\frac{\partial C_{b,i}}{\partial t} &= \frac{D_{ax,i}}{l^2} \frac{\partial^2 C_{b,i}}{\partial Z^2} - \frac{u}{l} \frac{\partial C_{b,i}}{\partial Z} \\ &\quad - \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial \bar{q}_{pi}}{\partial t}\end{aligned}\quad (15)$$

By replacing $\frac{\partial^2 C_{b,i}}{\partial Z^2}$ and $\frac{\partial C_{b,i}}{\partial Z}$ from equation 14 the following algebraic equation is obtained:

$$\begin{aligned}\frac{\partial C_{b,i,k}}{\partial t} &= \frac{D_{ax,i}}{l^2} \sum_{j=1}^{nz+2} B'_{ij} C_{b,i,j} - \frac{u}{l} \sum_{j=1}^{nz+2} A'_{ij} C_{b,i,j} \\ &\quad - \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial \bar{q}_{p,i,k}}{\partial t}\end{aligned}\quad (16)$$

$i = 1, \dots, noc$ $k = 2, \dots, nz + 1$

In the above equation, nz is the number of interior collocation points for the axial domain and noc is the number of gas components. The initial and boundary conditions of equation 3 are converted to following equation:

$$\begin{aligned}z = 0 & \quad C_{b,i,1} = C_{b,i,in} \\ z = 1 & \quad \sum_{j=1}^{nz+2} A'_{nz+2,j} C_{b,i,j} \\ &= 0 \\ t = 0 & \quad C_{b,i} = C_{b,i}^0\end{aligned}\quad (17)$$

Since the system is non-symmetric the roots of shifted Legendre polynomials is used to calculating A'_{ij} and B'_{ij} .

By defining $R = \frac{r}{R_p}$, equation 5 is locally dimensionless as follow.

$$\begin{aligned}\frac{\partial C_{p,i}}{\partial t} &= \frac{D_{eff,i}}{R_p^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial C_{p,i}}{\partial R} \right) \\ &\quad - \frac{1 - \varepsilon_p}{\varepsilon_p} \frac{\partial \bar{q}_{c,i}}{\partial t}\end{aligned}\quad (18)$$

Then by substituting from equation 14, the PDEs describing the mass conservation law of component i (micro-void) are converted to ODEs by using the method of orthogonal collocation in the radial direction, r , at any z and t is written by following form:

$$\begin{aligned}\frac{\partial C_{p,i,k,m}}{\partial t} &= \frac{D_{eff,i}}{R_p^2} \sum_{j=1}^{nr+1} B''_{ij} C_{p,i,k,j} - \frac{1 - \varepsilon_p}{\varepsilon_p} \frac{\partial \bar{q}_{c,i,k,m}}{\partial t} \\ i &= 1, \dots, noc \quad m = 1, \dots, nr \quad k = 2, \dots, nz + 1\end{aligned}\quad (19)$$

The boundary and initial conditions of equation 7 are summarized as:

$$\begin{aligned}r = 1 & \quad C_{p,i,k,nr+1} = C_{b,i,k} \\ t = 0 & \quad C_{p,i,k} = C_{p,i,k}^0\end{aligned}$$

In these equations nr is a number of interior collocation points for the radial domain of each pellet. These points are the roots of Jacobi polynomial. Matrix B''_{ij} is obtained by these points. At first glance, maybe it seemed that the Neumann boundary condition (derivative of the function equal to zero) is not used but, it is applied by using Jacobi polynomials.

Finite Difference Method

Equations 1, 4 and their boundary conditions are also discretize by using implicit form of finite difference method. For first order derivative with respect to length simple backward and for the second order one central scheme are applied. Through this discretizing, PDEs converted to a set of ODEs. The obtained ODEs are solved by using Newton Raphson numerical method. Since this method is a usual method for solving PDEs, the detailed explanation of it, is avoided to report in this paper.

Results and Discussion

The experimental data of Mohamadinejad et al. (Mohamadinejad, 1999), for adsorption of three components (N_2 , CO_2 and H_2O) on a packed bed of Zeolite 5A, are used to evaluate the presented model. The governing equations are solved by two numerical solution, orthogonal collocation and finite difference.

Figure 1 demonstrates the comparison of the calculated results obtained by finite difference method with the experimental breakthrough curves of CO_2 and H_2O at the outlet of the bed. There is a good agreement between the calculated results and the experimental data. As can be seen, finite difference method predicated the experimental data fairly well.

As it is mentioned before, equations are also solved by Orthogonal Collocation method. Unfortunately, this method converged poorly in solving the bed equation; In case of having a sharp-gradient solution, Orthogonal Collocation is not an appropriate choice because it requires employing high-degree polynomial (Finlayson, 2003). Thus, similar to the work of Sankararao et al. (Sankararao & Gupta, 2007), the finite difference technique is used to solve governing equations in macro-void, and the method of orthogonal collocation is applied for micro-void equation. The result of

this method, which is called as combined method, is shown in Figure 2.

According to table 3, nine interior nodes in finite difference method and five points in orthogonal collocation method are used to solve the pellet equations. In each method, using more nodes did not change the results significantly anymore.

Obviously, comparison of figures 1 and 2 indicates that the combined method produces more accurate results than finite difference method.

The results of figure 2 are in good agreement with the experimental data. A small deviation appeared can be attributed to the error created by Glueckauf LDF equation and isotherms for multicomponent adsorption (Sankararao & Gupta, 2007), and also the assumption of isothermal condition (M. Gholami & Talaie, 2009).

CPU Time for Experimental Data

The CPU time required for the combined method, as shown in Table 3, is remarkably less than the one used by finite difference method. This reduction in CPU time is achieved because of the different number of collocation nodes applied in these methods.

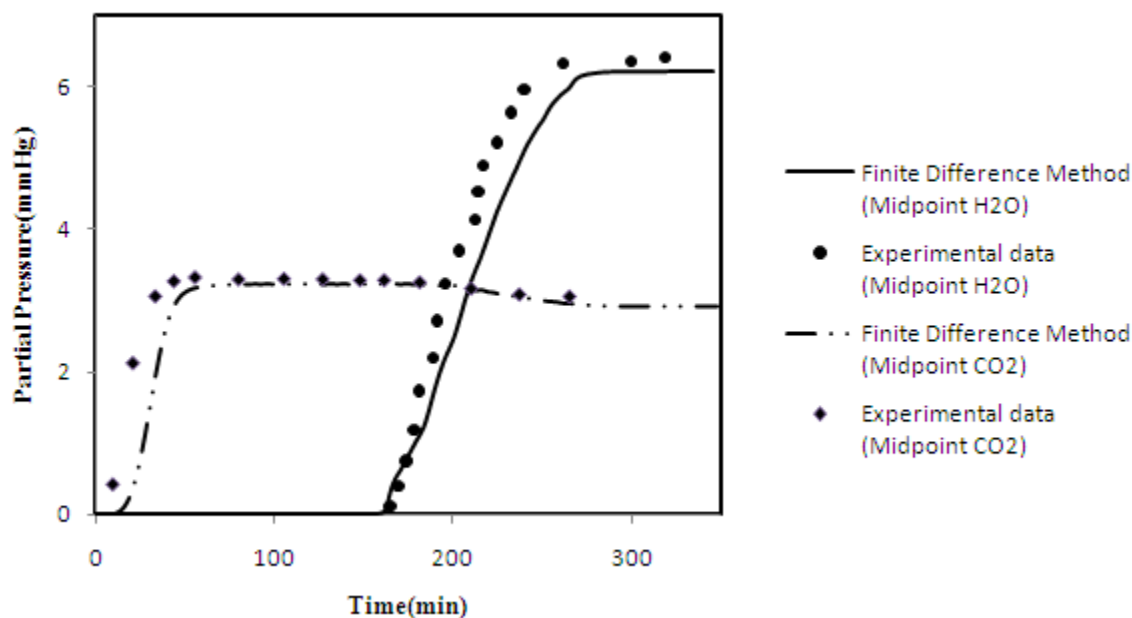


Figure 1. The comparison between the experimental data of Mohamadinejad et al (Mohamadinejad, 1999) and the obtained results based on Finite Difference Method.

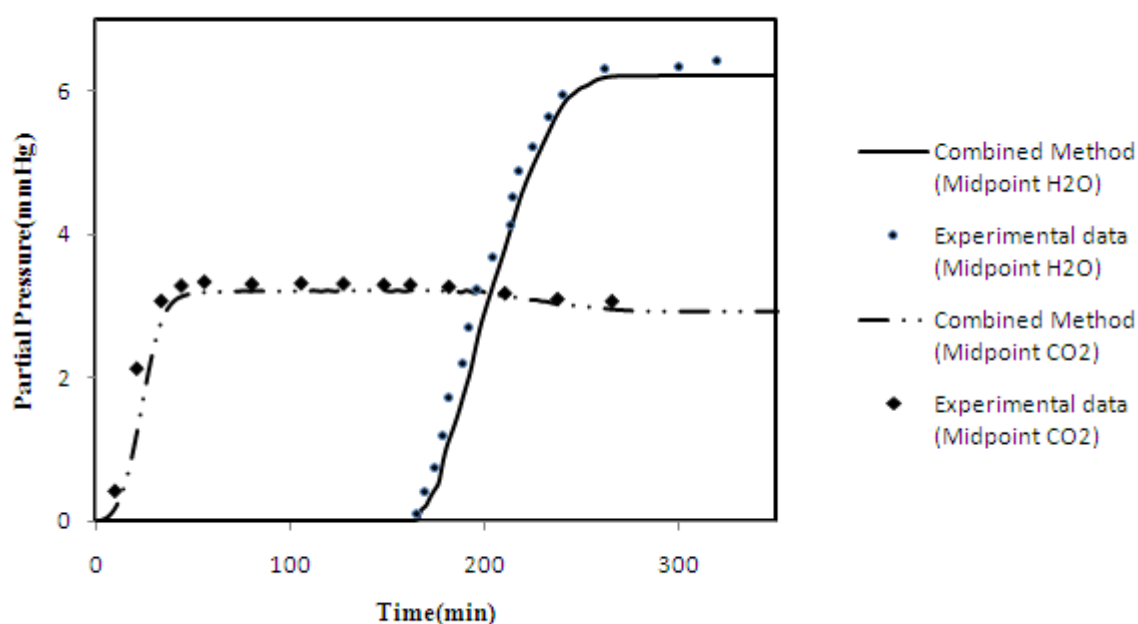


Figure 2. The comparison between the experimental data of Mohamadinejad et al. (Mohamadinejad, 1999) and the obtained results based on the Combined Method.

Table 3. Comparison between the CPU times of combined method and finite difference method for experimental data of Mohamadinejad et al (Mohamadinejad, 1999).

Numerical Method	CPU Time(min)	Number of collocation points	
		Pellet	Bed
Combined Method	16.90	5	50
Finite Difference	31.130	9	50

Industrial Operating Condition

In order to examine the performance of both numerical methods in industrial operating conditions, dehydration of a gas stream containing CH_4 , CO_2 , H_2O , and N_2 in a packed bed of zeolite 5A operating under a real-world condition are simulated. The characteristics of the adsorption bed and sorbent, and the value of gas flow rate are listed in table 3. The data belongs to the gas refinery located in fifth phase of Iran South Pars gas field.

Natural gas fed to the dehydration process is usually saturated with water vapor at high

pressure. Water vapor content cannot exceed the natural gas dew point, which is maximum 200 ppm (0.2 mol%) at industrial operating conditions. Thus, the maximum value of 200 ppm for water content of wet natural gas was applied in these calculations. The computations are stopped when the concentration of water vapor in the gas stream leaving the bed rise to 5 ppm at its breakthrough point (M. Gholami & Talaie, 2009).

Table 4. Characteristics of Adsorption Bed, Sorbent Pellet, and Gas flow

Inlet Gas Composition	
H_2O	0.00184
CO_2	0.00098
CH_4	0.953
N_2	0.03518
Initial Values of Gas Composition in the Bed	
H_2O	0.0
CO_2	0.0
CH_4	0.9644
N_2	0.0356
Inlet Gas Characteristics	
gas pressure (bar)	64
gas temperature (K)	295.5
molar gas flow rate (kmol/h)	23929
Bed Characteristics	
bed diameter (m)	3.5
bed length (m)	5.5
bed porosity	0.34
Pellet Characteristics	
pellet porosity	0.36
pellet-solid density (kg/m ³)	1812.5
pellet diameter (m)	0.0026
mean crystal diameter (m)	1×10^{-6}
mean macropore diameter (m)	1.7×10^{-7}

Table 5. Comparison between the CPU time of the combined and finite difference methods for the gas adsorption process characterized by the data of Table 4.

Numerical Method	CPU Time(min)	Number of collocation points	
		Pellet	Bed
Combined Method	9.5271	5	60
Finite Difference	22.0974	9	60

Results of solving the governing equations, employing three methods including finite difference, orthogonal collocation and combined method could be observed in Figures 3 to 5. In these figures, the breakthrough curves of H_2O in the center of the bed, using all the aforementioned methods, are presented.

As it is observed in Figure 3, oscillations are appeared by applying orthogonal collocation as a numerical solution to solve both bed and pellet equations. The oscillations are led to gross errors. Increasing the collocation points does not improve the accuracy of the results. In order to make the results converge, several numerical methods such as Newton-Raphson, Gauss-Seidel and relaxation factor are applied. Nevertheless, no significant improvement is obtained. Therefore, orthogonal collocation is considered as an unreliable method for solving the bed governing equation (Sankararao & Gupta, 2007). However, as it is illustrated in Figures 4 and 5, solving equations by finite difference and combined method demonstrate stable results.

In order to solve the pellet equation, the pellet radius is discretized by 5 and 9 nodes for combined and finite difference method,

respectively. Number of nodes used in axial direction to solve bed equation for both methods is 60. No more improvement is observed by further increasing the number of nodes. In Table 5, the CPU time is compared for these methods.

In order to further evaluation of combined method, the results obtained by this method is discussed in the following.

Figures 6 and 7 show breakthrough curves of H_2O and CO_2 , respectively. The concentration profile is displayed in four parts of bed (inlet $Z = 0.0325$, center $Z = 0.5$ and outlet $Z = 0.983$) and as expected, the concentration increases with time until the adsorption saturation point is reached. As it can be seen from these figures the concentration of CO_2 in gas bulk reaches a saturation point with a higher velocity because H_2O is adsorbed more than other existing components.

Figures 8 through 11 show the variation of the adsorption amount of each component in the pellets at different positions (inlet $Z = 0.0325$, center $Z = 0.5$ and outlet $Z = 0.983$) versus time.

Figure 12 illustrates the variations of the adsorption amount of existing components in the bed versus time at the outlet of the bed.

As an initial condition, it was supposed that packed bed was saturated with only CH_4 and N_2 as a result of preceding regeneration stage. At adsorption stage, when wet natural gas fed to the bed, H_2O as the strongest adsorbent was adsorbed in the first layers of the bed and forced CH_4 and N_2 to be desorbed as can be seen in figures 10 and 11. As the gas flows

through the bed H_2O is depleted in gas and it is CO_2 turn to be adsorbed as the second-rank strongest adsorbent. The same trends will emerge for CH_4 and N_2 , respectively.

As the time goes by, and the first layers are saturated by H_2O , and hence the wet gas reaches the regions where is saturated by CO_2 . The H_2O substitutes for CO_2 in these regions by sweeping it off. This scenario will repeat for CH_4 and N_2 , respectively as can be seen in figure 12.

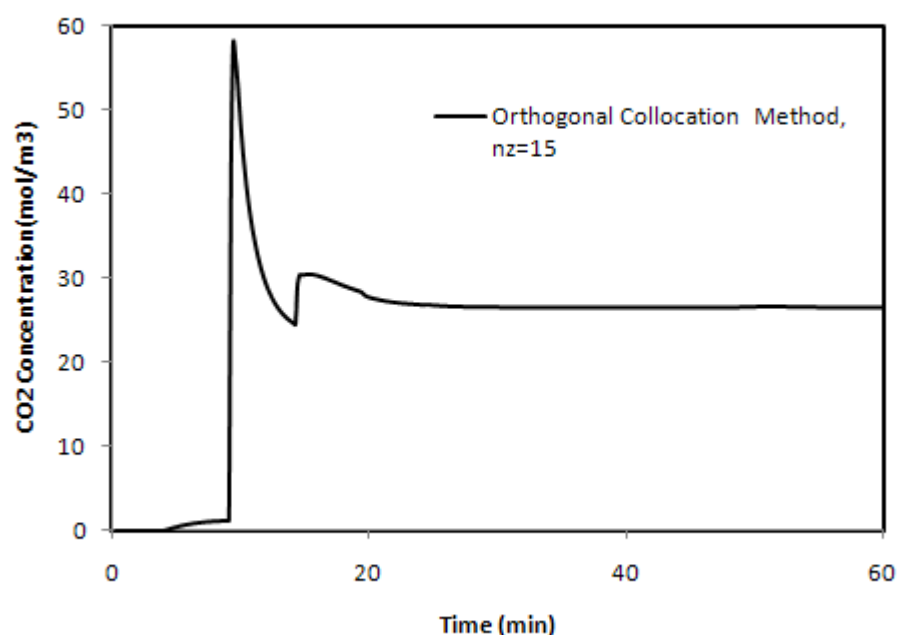


Figure 3. Breakthrough curve of CO_2 in the center of the bed by using Orthogonal Collocation Method.

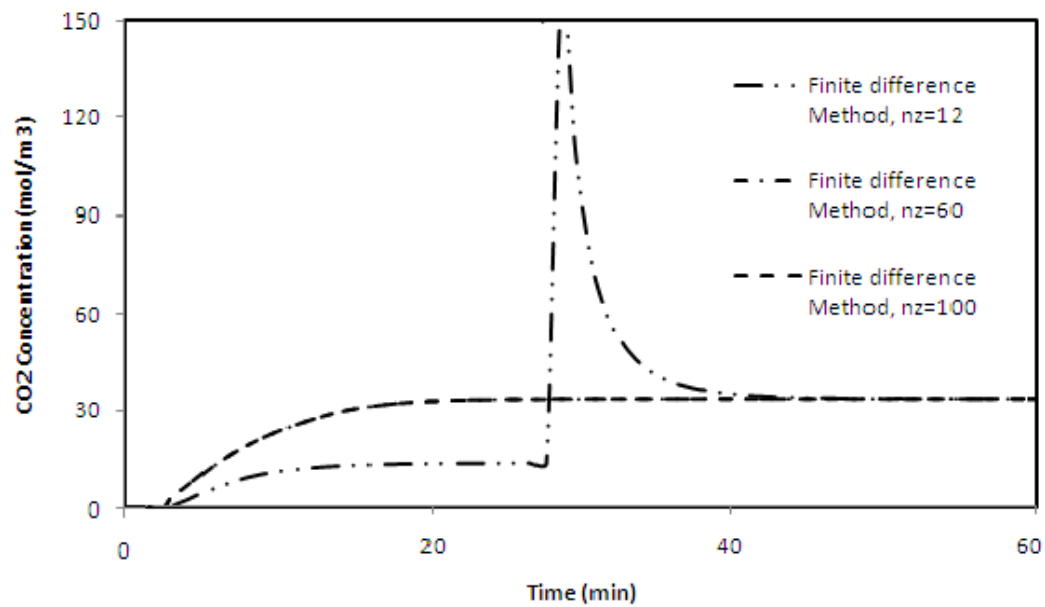


Figure 4. Breakthrough curve of CO₂ in the center of the bed by using Finite Difference Method.

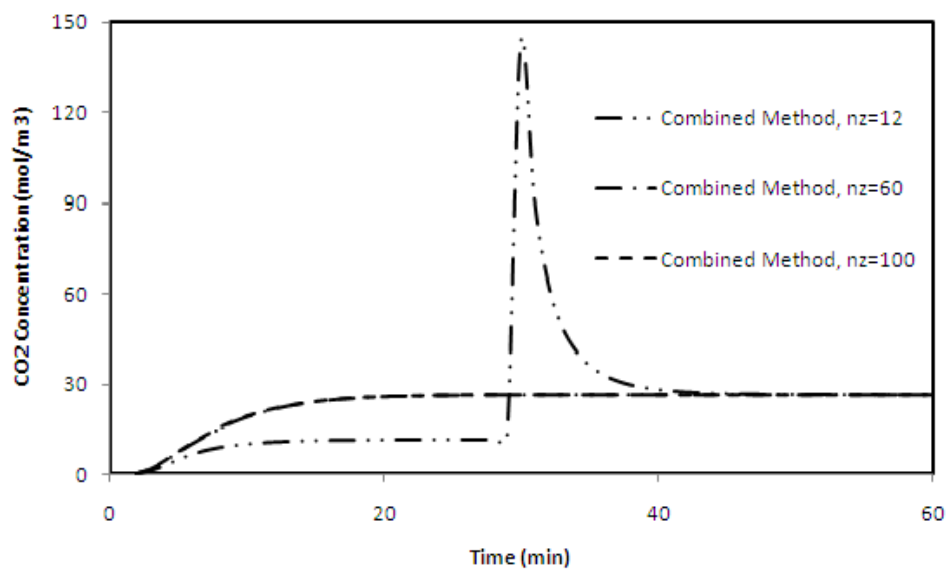


Figure 5. Breakthrough curve of CO₂ in the center of the bed by using Combined Method.

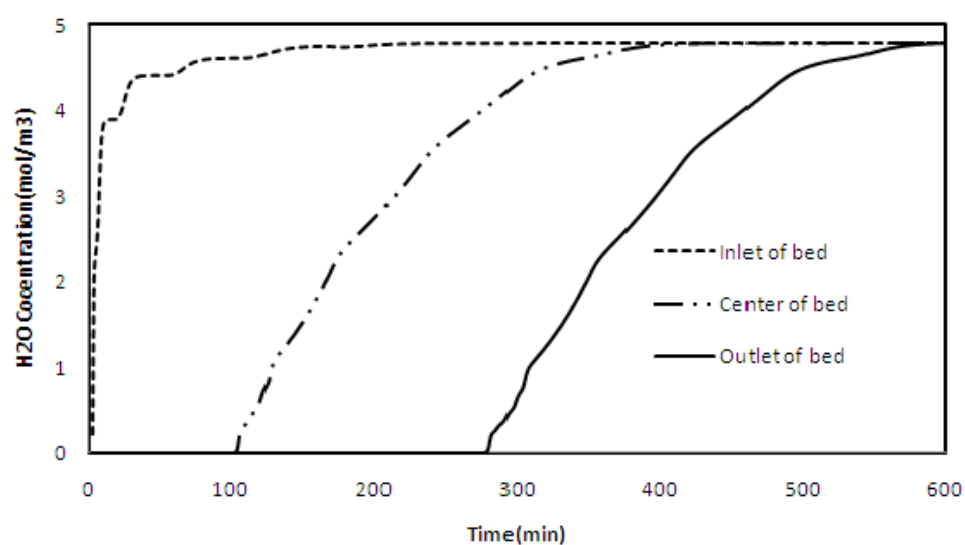


Figure 6. Breakthrough curve of H₂O in the inlet, center and outlet of the bed.

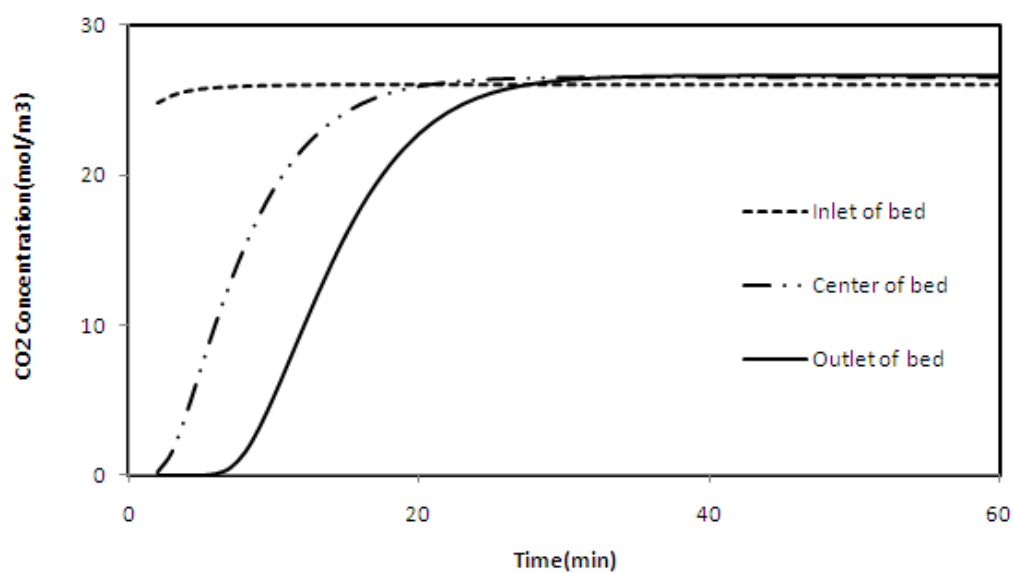


Figure 7. Breakthrough curve of CO₂ in the inlet, center and outlet of the bed.

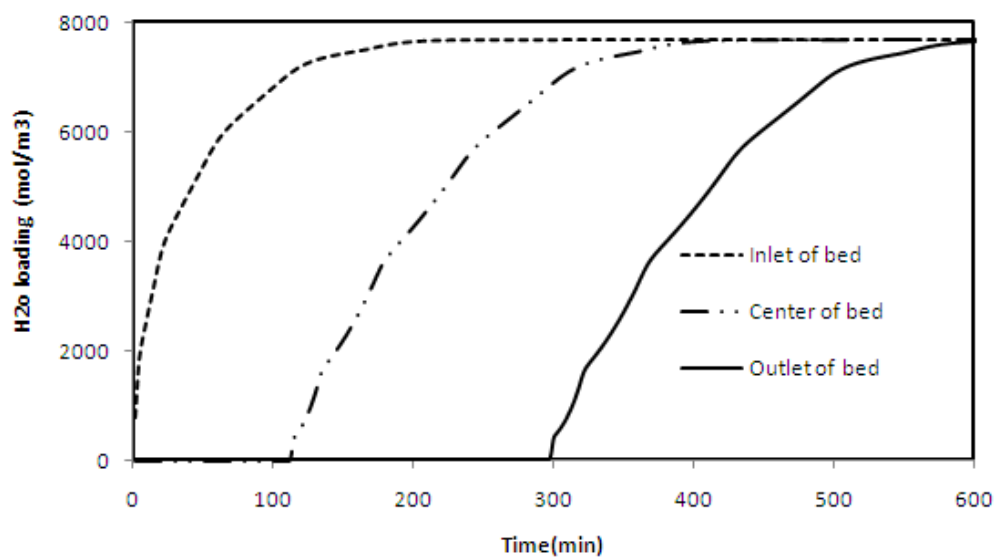


Figure 8. The variation of adsorption amount of H_2O versus time in the inlet, Center and outlet of the bed.

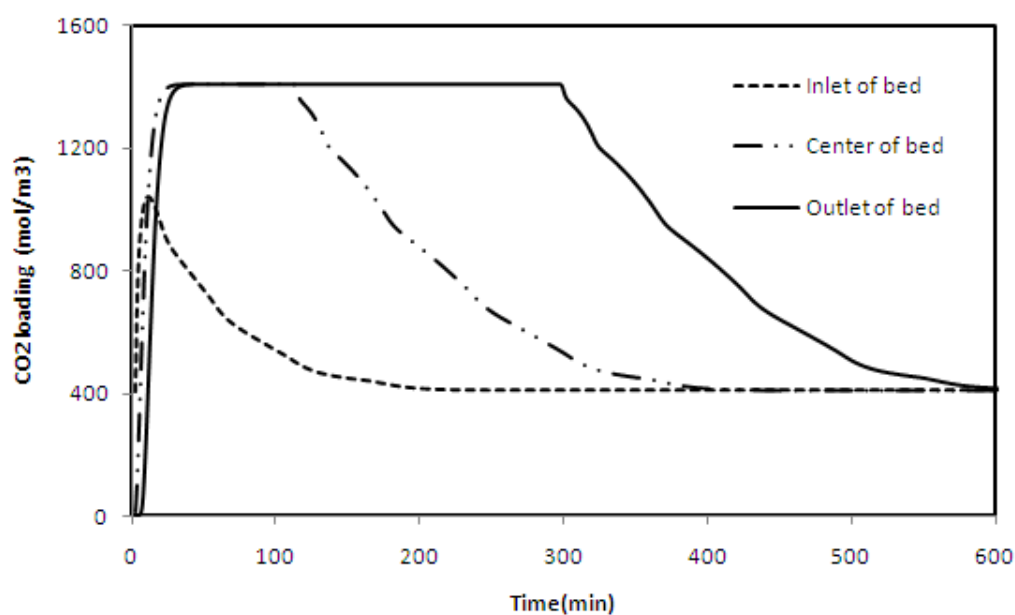


Figure 9. The variation of adsorption amount of CO_2 versus time in the inlet, Center and outlet of the bed.

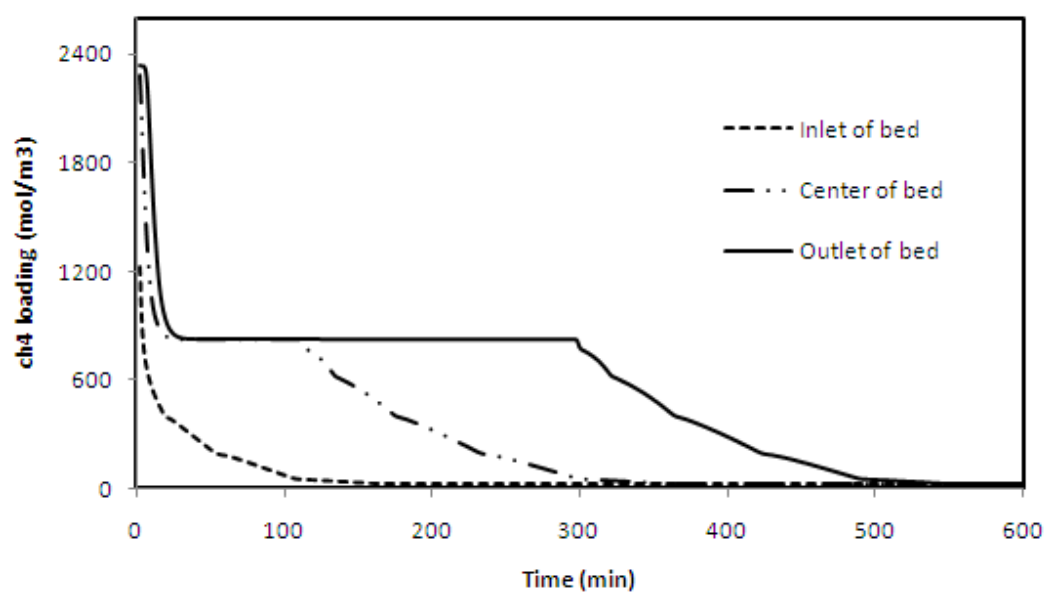


Figure 10. The variation of adsorption amount of CH_4 versus time in the inlet, Center and outlet of the bed.

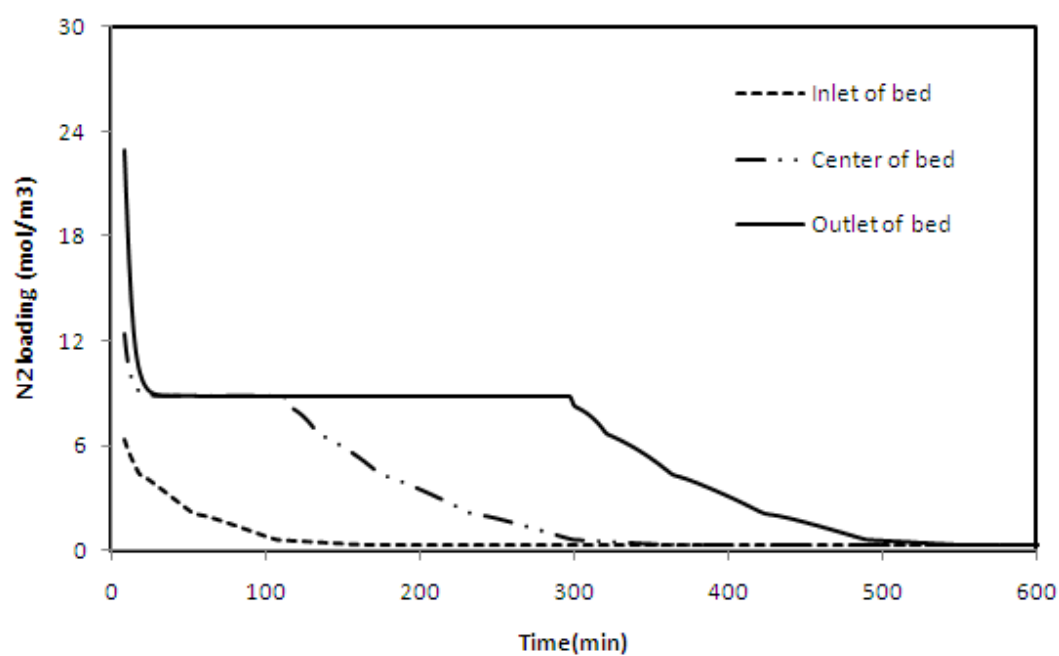


Figure 11. The variation of adsorption amount of N_2 versus time in the inlet, Center and outlet of the bed.

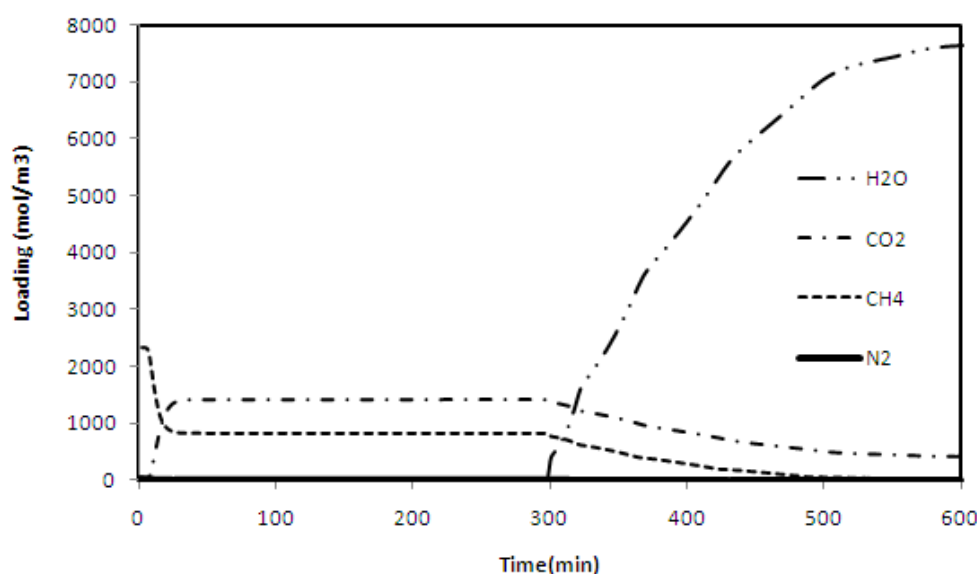


Figure 12. Comparison between profiles of the adsorption amounts of H₂O, CO₂, CH₄ and N₂ in the center of the bed.

Conclusions

In this study, the performances of finite difference, orthogonal collocation and combined numerical methods in simulating the performance of a fixed-bed packed with 5A zeolite in dehydration of the natural gas stream containing CH₄, CO₂, H₂O, and N₂ was studied. The isothermal and isobar conditions were assumed to be valid. The axial dispersion of components inside the macro-voids, the diffusion of components inside the particles (macro-voids) and linear driving force inside the crystals were taken into account in the presented model.

Equations were solved by using two numerical methods, orthogonal collocation and finite difference. The results revealed that orthogonal collocation did not provide appropriate results when it was used for the bed equation. Therefore, to solve the bed equation, finite difference method was employed. It has been shown that applying the combined method to solve governing equations of the four components gas adsorption process was reduced the CPU time 50 percent as much as finite difference method.

As a result, the combined method (the orthogonal collocation for pellet and the finite difference method for bed equations) was used as a superior numerical approach. The good agreement between the results and the experimental data was obtained.

Nomenclature

$A_{i,j}$	parameters in isotherm model (mol/kg)
A'_{ij}	orthogonal collocation parameter in equation 14
$b_{i,j}$	adsorption affinity parameter of component i (1/kPa)
B'_{ij}	orthogonal collocation parameter in equation 14
B''_{ij}	orthogonal collocation parameter in equation 14
C_{bi}	concentration of component i in gas phase (bed) (mol/m ³)
C_{bi}^0	initial concentration of component i in gas phase (bed) (mol/m ³)
$C_{in,i}$	Inlet concentration of component i in gas phase (bed) (mol/m ³)
C_{pi}	concentration of component i in gas phase (voidage of particle) (mol/m ³)
$D_{ax,i}$	axial dispersion of component i (m ² /s)
$D_{eff,i}$	effective diffusivity in particle applied in eq 6 (m ² /s)
D_{ci}	crystalline diffusivity (m ² /s)
D_{ki}	Knudsen diffusivity
D_{mi}	molecular diffusivity
D_{oi}	corrected crystalline diffusivity (m ² /s)

d_p	particle's diameter
E_i	affinity constant activation energy of component i (J/mol)
l	bed length (m)
noc	Number of components of the gas mixture
nr	Number of collocation points in radial direction
nz	Number of collocation points in axial direction
P	total pressure (Pa)
P_i	Partial pressure of component I (pa)
$\bar{q}_{c,i}$	Average concentration of component i in micro-pore volume (mol/m ³)
$\bar{q}_{p,i}$	Average loading of component i into a pellet (mol/m ³)
$q_{c,i}^*$	equilibrium concentration of component i in the micro-pore volume (mol/m ³)
r	Radial position (m)
RP	sorbent particle radius (m)
Rc	sorbent crystal radius (m)
R	dimensionless radial coordinate
RR_g	gas constant (8.314 J/mol K)
T	Temperature (k)
t	time (s)
Uu	interstitial velocity (m/s)
z	Axial position along the bed (m)
Z	dimensionless axial coordinante

Greek symbols

γ	constant parameter in equation 2
ϵ_b	bed porosity
ϵ_p	particle porosity

Subscripts

I	component index
J	collocation point index(and also transition index)
M	collocation point index
K	collocation point index

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