Comparative simulation study of PSA, VSA, and TSA processes for purification of methane from CO$_2$ via SAPO-34 core-shell adsorbent

Mohammad Fakhroleslam and Shohreh Fatemi
School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

ABSTRACT
Cyclic adsorption processes of PSA, VSA, and TSA were modeled and numerically simulated using SAPO-34 core-shell adsorbent. The results were compared with ordinary SAPO-34 to achieve a more efficient process for CO$_2$–CH$_4$ separation. OCM coupled with method of lines was used for numerical solution of the mechanistic model. The simulation results revealed higher efficiency of core-shell adsorbent with less usage of SAPO rather than the ordinary adsorbent to achieve the same degree of purification and recovery. VSA and TSA processes against PSA resulted in CH$_4$ purification capability more than 99% with more than 73% recovery. However, VSA process has revealed higher productivity rather than TSA.

INTRODUCTION
Separation of carbon dioxide from pre-combusted and post-combusted natural gas is important regarding energy, natural gas storage, and transportation. The presence of CO$_2$ reduces the heat content of natural gas and is corrosive in the presence of moisture. Regarding gas transport pipeline standards, the strict limit for CO$_2$ concentration is as low as 2%.\cite{1} Nowadays, development of effective CO$_2$-capturing technologies has received more attention. These studies are also important in fossil-fuel power plants and recovering CH$_4$ from coalmine or landfill gas.\cite{2,3,4} Adsorption, absorption, cryogenic distillation, and membrane technologies are the processes employed for separation of CO$_2$–CH$_4$ mixtures. Adsorption is an easy and economic technique compared to the other techniques.\cite{5,6} Cyclic adsorption processes generally include pressure or vacuum swing adsorption (PSA/VSA)\cite{7,8} and temperature swing adsorption (TSA).\cite{9} Selection of the adsorbent is the most important part in design of a cyclic adsorption process.\cite{10,11} A suitable adsorbent has a high CO$_2$ adsorption capacity, high selectivity, and high thermal, chemical, and mechanical stability as well as the capability of easy regeneration. There are many porous solid materials which have been studied as CO$_2$ adsorbents in the recent works\cite{12,13} specially different types of zeolites.\cite{13}

SAPO-34 has found to be more interesting among various types of zeolites due to its high selectivity of CO$_2$ against CH$_4$ compared with other zeolitic adsorbents and activated carbon, especially at lower and moderate pressures.\cite{13,14}

The aim of this article is to propose and investigate the quality and performance of SAPO-34 in core-shell particle configuration, as a more effective material for separation of CO$_2$ from CH$_4$ in the cyclic adsorption process. VSA and TSA are suggested as the alternative processes for separation and they are investigated comparatively to figure out the highest purity, recovery, and productivity. SAPO-34 in two different forms of ordinary particles and core-shell particles are studied as the adsorbent material. In the core-shell adsorbent, it is assumed that a thin layer of SAPO-34 synthesized on the inert porous particles of ceramic can be operated as a more effective adsorbent on the base of kinetic and diffusion mass transfer rate and improve adsorption/desorption efficiency. The core-shell particles have been synthesized by the previous work of the present research group.\cite{15}

On the other hand, precise dynamic modeling and rapid simulation of cyclic adsorption processes (PSA, VSA, and TSA) is the key step of our study in these dynamic systems. Dynamic models of cyclic adsorption processes include conservation of heat, mass, and momentum distributed over space and time, augmented
by mass transport and gas–solid equilibrium models. Such a large set of nonlinear and stiff partial differential-algebraic equations presents significant computational challenges in simulation of these kinds of processes.\textsuperscript{[16, 17]} Hence, the design and optimization of cyclic adsorption systems still largely remain as an experimental effort.\textsuperscript{[17]} To overcome this challenge, method of lines (MOL) and spatial discretization by orthogonal collocation method (OCM)\textsuperscript{[18]} is employed for numerical calculations. MOL is a two-step method\textsuperscript{[19]} such that the discretization in spatial and temporal domains would be implemented separately. First, the governing PDEs are discretized in space by using OCM. The OCM is a well-known method that significantly reduces the number of discretized equations due to the less number of internal points rather than the other methods, e.g., finite difference method. Significant reduction of computational cost and rapid convergence are the advantages of OCM. Afterward, the obtained ordinary differential equation (ODE) equations are solved employing the predictor–corrector four-step Adams–Bashforth/Adams–Moulton method with one-correction step. The simulation results of the mentioned adsorption processes are investigated and compared with each other in the cyclic steady state (CSS) conditions.

Finally, a numerical package is prepared for cyclic adsorption processes to simulate different PSA, VSA, and TSA cyclic processes for separation of CO\textsubscript{2} from CH\textsubscript{4} by SAPO-34 core-shell adsorbents against ordinary pelleted ones. The impact of shell thickness of the core-shell adsorbent would be investigated by the simulated processes to achieve higher separation efficiency.

The detailed synthesis procedure of ordinary and core-shell adsorbents is provided in the previous works.\textsuperscript{[15, 20]}

**Equilibrium isotherms**

The adsorption isotherms of CO\textsubscript{2} and CH\textsubscript{4} were predicted by an IUPAC Type I rigorous model of multisite Langmuir, as shown in Eq. (0.1).\textsuperscript{[21]} The isotherm parameters of each gas have been predicted using experiments at three different temperatures and the results were extended to the multi-site Langmuir equation for binary mixture of CO\textsubscript{2} and CH\textsubscript{4}.\textsuperscript{[22]} The multi-site Langmuir isotherm is given by Eq. (0.1):

\[
\frac{Q^*_i}{Q^\text{max}_i} = K_i C_i R T \left[1 - \sum_{i=1}^{N_{\text{comp}}} \frac{Q^*_i}{Q^\text{max}_i} \right]^{-\frac{1}{a_i}}
\]

\[
K_i = K_{0i} \exp \left(\frac{-\Delta H_i}{RT}\right)
\]

Volumetric method was used for measurement of adsorption capacity of the adsorbent at different gas pressures.\textsuperscript{[23]} A static adsorption setup was used for contacting each gas with a specific amount of adsorbent at any constant temperature. The gas pressure was determined by a pressure sensor equipped to adsorption cell, at initial and final conditions. The equilibrium adsorbed amount was calculated using the gas state equation of Pitzer. At any constant temperature, the initial gas pressure was changed to obtain different points of the isotherm as the equilibrium adsorbed amount versus equilibrium pressure for each gas.

The experimental data of the pure components on pure SAPO-34 were captured at three operating temperatures of 278, 288, and 298 K.\textsuperscript{[20]} The experimental single-component isotherms were properly fitted with the multi-site Langmuir model (Fig. 1) and the parameters are presented in Table 1. The presented isotherm parameters have been used in the adsorption model of SAPO-34 for both ordinary and core-shell adsorbent. In the core-shell adsorbent, mullite was used as the inert core with no adsorption tendency and a thin layer of SAPO-34 was covered with the active shell of SAPO-34 and this material was used as core-shell SAPO-34 adsorbent.

**Experimental**

**Adsorbents**

Two types of SAPO-34 particles—ordinary and core-shell type—were prepared and they were used comparatively to investigate their separation efficiency in adsorption process. The ordinary SAPO-34 pellets were prepared from the SAPO powder, which were previously synthesized by hydrothermal method using a gel with molar composition of Al\textsubscript{2}O\textsubscript{3}: 0.4SiO\textsubscript{2}: P\textsubscript{2}O\textsubscript{5}: 57H\textsubscript{2}O: 1.8TEAOH.\textsuperscript{[20]} The powders were compressed under 0.2 MPa pressure and they were meshed to an average diameter of 3 mm. This material was named as ordinary SAPO-34 particle. The core-shell adsorbents were fabricated by synthesizing SAPO-34 crystals, with the same molar composition, on the outer surface of mullite particles with average diameter of 3 mm. Therefore inert core material of mullite was covered with the active shell of SAPO-34 and this material was used as core-shell SAPO-34 adsorbent.
adsorption pressure more than 10 bar, in adsorption process.

**Dynamic breakthrough curves**

Dynamic breakthrough curves of CH$_4$ and CO$_2$ associated with the aforementioned SAPO-34 adsorbents are established employing an experimental setup, shown in Part 1 of the Supplementary Information. Dynamic adsorption experiments were conducted with binary gas mixture of CH$_4$ and CO$_2$ and the breakthrough curves of CH$_4$ and CO$_2$ were determined by measuring molar fractions of the outgoing gas. The operating conditions and the characteristics of the adsorption bed and adsorbents are given in Table 2. The molar fraction of the outlet product was measured by an online gas chromatograph (GC) versus time, to obtain the experimental breakthrough curves of CH$_4$ and CO$_2$.

**Cyclic adsorption process**

**Process description**

Three methods of cyclic adsorption process, PSA, VSA, and TSA, were proposed and designed for purification of CH$_4$ from gas mixture of CH$_4$ and CO$_2$ by the ordinary and core-shell SAPO-34 adsorbents. In all methods, six steps were considered in each cyclic process. The PSA and VSA cycle times are the same but different from TSA process, since regeneration of the bed in TSA is taking place by a heating jacket and the regeneration step needs more time for the bed heating up and cooling down. The considered stages of PSA, VSA, and TSA processes are illustrated in Figs. 2a–c and 3a–c, respectively. Each cycle consists of six sequential steps as follows: adsorption (ADS), depressurizing equalization (DPE), blow down (BDN), purge with product (PRG), pressurizing equalization (PEQ), and re-pressurization (REP). The mentioned steps are described with details in Part 2 of the Supplementary Information.

**Cyclic adsorption model**

The mathematical model of the process was performed by total and partial mass balances in the gas and solid phases and energy balances. Isotherm adsorption models were
Figure 2. Step transition of the two-bed, six-step PSA/VSA process. (a) Schematic; (b) averaged pressure and temperature variations with time, at CSS; (c) the scheduled step times and pressure conditions.

| Stage | ADS  | DPE  | BDN  | PRG  | PEQ  | REP  |
|-------|------|------|------|------|------|------|
| duration (sec) | 200  | 75   | 75   | 200  | 75   | 75   |
| Pressure (bara)  | 5.0  | 0.4  |      |      |      |      |

Figure 3. Step transition of the two-bed, six-step TSA process. (a) Schematic; (b) averaged pressure and temperature variations with time, at CSS; (c) the scheduled step times and pressure–temperature conditions.

| Stage | ADS  | DPE  | BDN  | PRG  | PEQC | REP  |
|-------|------|------|------|------|------|------|
| duration (sec) | 300  | 120  | 75   | 300  | 120  | 75   |
| Pressure (bara)  | 5.0  | 1.0  |      |      | 348  | 293  |
used to relate the saturated adsorbed amount with the gas phase concentration. The pressure drop along the bed was considered with Ergun equation. Ideal gas law was considered for the CO$_2$-CH$_4$ gas mixture over all operating pressures and temperatures. The radial variations of concentration and temperature inside the bed were ignored and the flow pattern was described by axial dispersed plug flow. The beds were uniformly packed with spherical particles with same size. The partial mass balance equation is given in Eq. (0.3):

$$
\varepsilon_i \frac{\partial C_i}{\partial t} = \varepsilon_b D_{ax} \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (\mu C_i)}{\partial z} - \rho_p (1 - \varepsilon_b) \alpha_p \frac{\partial Q_i}{\partial t},
$$

(3)

where $\varepsilon_i = (\varepsilon_b + (1 - \varepsilon_b) \varepsilon_p)$ denotes total porosity, and $\alpha_p = \left(1 - \frac{\varepsilon_b}{\varepsilon_p}\right)^3$ indicates the volume fraction of the adsorbent particles that is composed of active adsorbent rather than inert core. Variation of velocity along the bed ($u$) was evaluated based on the overall mass balance equation, which is given in Eq. (0.4):

$$
\varepsilon_i \frac{\partial C_r}{\partial t} = -C_r \frac{\partial u}{\partial z} - \rho_p (1 - \varepsilon_b) \alpha_p \sum_{i=1}^{N_{comp}} \frac{\partial Q_i}{\partial t},
$$

(4)

The adsorption process was considered non-isothermal and non-adiabatic. The wall thickness was assumed negligible and the bed including the solid–gas system and the bed’s wall was assumed to be in thermal equilibrium. The energy balance equation of the bed was given in Eq. (0.5):

$$
\psi \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial z^2} - u \sum_{i=1}^{N_{comp}} (C_i C_{pi}) \frac{\partial T}{\partial z} + \rho_p (1 - \varepsilon_b) \alpha_p \sum_{i=1}^{N_{comp}} \frac{\partial Q_i}{\partial t} (-\Delta H_i)
$$

$$
+ \varepsilon_i RT \sum_{i=1}^{N_{comp}} \frac{\partial C_i}{\partial t} + U_j \frac{4}{D} (T_j - T),
$$

(5)

where

$$
\psi = \varepsilon_i \sum_{i=1}^{N_{comp}} (C_i C_{vi}) + \rho_p C_{ps} (1 - \varepsilon_b)
$$

$$
+ \rho_p (1 - \varepsilon_b) \alpha_p \sum_{i=1}^{N_{comp}} (C_i C_{vi}).
$$

(6)

The velocity dependency of the axial mass and heat-transfer dispersion coefficients, i.e., $D_{ax}$ and $\lambda$, is neglected and the coefficients are assumed to be constant. $^{[24, 25]}$ The physical properties $\rho, \mu, C_{pi}, C_{vi}$, and $C_{ps}$ are calculated at the feed condition and assumed to be constant during the operation, as well as the parameters $\varepsilon_b$ and $\varepsilon_p$.

Since the time constant for momentum equation is very small compared with that for either mass or heat transfer, $^{[16]}$ the axial velocity–pressure equation inside the bed is described by steady state Ergun equation as shown in Eq. (0.7):

$$
- \frac{\partial P}{\partial z} = \frac{150 \mu (1 - \varepsilon_b)^2}{\varepsilon_b^3 d_p^3} u + \frac{1.75 (1 - \varepsilon_b) \sum_{i=1}^{N_{comp}} (C_i MW_i)}{\varepsilon_p d_p^3} |u| u.
$$

(7)

The particle mass balance is assumed as lumped kinetic model with linear driving force (LDF) model for the mass transfer between gas and solid phases as shown by Eq. (0.8).$^{[11, 26, 27]}$ The LDF model with carefully selected parameters, is adequate in most adsorption applications. $^{[11]}$

$$
\frac{\partial Q_i}{\partial t} = K_{LDF} (Q^i - \bar{Q}_i).
$$

(8)

In the steps of cyclic adsorption with transient pressure, the variation of the pressure at the boundaries of the adsorption beds follows Eq. (0.9) which is proposed based on valve operations:

$$
\frac{\partial P}{\partial t} = \pm \tau_p (P_{High} - P_{Low})^{0.85},
$$

(9)

where $P_{High}$ and $P_{Low}$ represent the higher and lower pressures on both sides of the bed’s boundaries. The variation of pressure is negative in depressurizing steps and positive in pressurizing steps. The concentration, temperature, and velocity–pressure boundary conditions for the steps of the cyclic process are given in Part 3 of the Supplementary Information.

**Numerical programming and simulation**

As it was provided, the cyclic process is governed by partial differential equations (PDEs) which are distributed in space and time. It is obvious that the analytical solution of such a highly coupled PDE set is almost impossible. However, such large-scale systems have to be simulated numerically. In the aim of numerical simulation, MOL was employed. MOL is a two-step approach $^{[19]}$ in which the discretization in spatial and temporal domains would be implemented, separately.

In the first step, the governing PDEs are discretized in space and converted to ordinary differential equations by employing OCM. $N$ internal
collocation points are selected on the base of roots of a Jacobi orthogonal polynomial, which are used in a Lagrange interpolating polynomial as a trial function to be substituted in the PDE of governing equations. The number of considered collocation points along the bed is considered $N = 12$ internal points. One of the advantages of OCM is reduction of the number of ODEs which should be solved in comparison with the other methods such as finite difference method. The OCM is a kind of reliable numerical method, which converges rapidly and is easy to program. The obtained ODEs are solved via a multiple-step predictor-corrector method of integration. The four-step Adams–Bashforth/Adams–Moulton method is employed with one-correction step. This method uses the four-step Adams–Bashforth and three-step Adams–Moulton methods together, as predictor and corrector equations, respectively. The detail numerical solution by OCM is explained in Part 4 of the Supplementary Information. Flowchart of the steps of numerical simulation is illustrated in Part 5 of the Supplementary Information.

After solution of the obtained ODE equations, the compositions, loadings, total concentration, temperature, and velocity and pressure profiles along the bed are calculated versus the time until one cycle would be completed and the other cycles would be replicated to approach to CSS condition.

Performance of the three processes of PSA, VSA, and TSA was evaluated by simulation based on the methane purity, methane recovery, and productivity of the process, as defined in Eqs. (0.10), (0.11), and (0.12), respectively. The results were compared with each other for different adsorbents and processes.

\[
Purity = \frac{\int_{0}^{t_{ads}} C_{CH_{4}} u_{z=L} dt}{\sum_{i=1}^{m} \int_{0}^{t_{ads}} C_{i} u_{z=L} dt}
\]

(10)

\[
Recovery = \frac{\int_{0}^{t_{ads}} C_{CH_{4}} u_{z=L} dt - \int_{0}^{t_{top}} C_{CH_{4}} u_{z=L} dt - \int_{0}^{t_{top}} C_{CH_{4}} u_{z=0} dt}{\int_{0}^{t_{ads}} C_{CH_{4}} u_{z=0} dt}
\]

(11)

\[
Productivity = \frac{\int_{0}^{t_{ads}} C_{CH_{4}} u_{z=L} dt - \int_{0}^{t_{top}} C_{CH_{4}} u_{z=L} dt - \int_{0}^{t_{top}} C_{CH_{4}} u_{z=0} dt}{w_{adsorbent} t_{cycle}}
\]

(12)

**Results and discussion**

The results of simulation are presented first by the breakthrough curves, and then by cyclic adsorption process in three modes of PSA, VSA, and TSA. Methane purity, recovery, and productivity are the responses which are reported and discussed in cyclic adsorption model at CSS condition. Finally, the behavior of the core-shell adsorbent would be compared with the base ordinary SAPO-34 in each process.

**Dynamic breakthrough curves**

The performance of the mathematical model was verified by comparison of the results of numerical simulation by the experimental breakthrough curves. Figure 4 shows the breakthrough curves of CH$_4$ and CO$_2$ on both aforementioned SAPO-34-based solid adsorbents. The high breakthrough time of carbon dioxide indicates high tendency of SAPO adsorbent toward CO$_2$ adsorption rather than CH$_4$, and this leads to the efficient CO$_2$-CH$_4$ separation by adsorption process. Figure 4 shows satisfactory performance of the proposed adsorption model for adsorption of the binary mixture of CO$_2$–CH$_4$ on both ordinary and core-shell adsorbents.

As can be seen, the associated breakthrough curve with core-shell adsorbent is appeared with higher breakthrough time and with a sharper S-shape curve. The sharper breakthrough curve reveals shorter mass transfer zone inside the adsorption bed, and this is because of lower mass transfer resistance of the thin layer of SAPO-34 where the adsorption is taking place. The mass transfer coefficients ($K_{LDF}$) in the breakthrough simulations of Fig. 4 were selected such that the simulation results accommodate the experimental data. However, for the remaining parts of this research, the $K_{LDF}$ for various particles with different shell thicknesses ($r_{sh}$) was estimated by Eq. (0.13)[11]:

\[
\frac{1}{K_{LDF}} = \frac{r_{p}}{3k_{f, i}} \frac{Q_{i} \rho_{p}}{C_{i}} + \frac{r_{sh}^{2}}{15\varepsilon p D_{p, i}} \frac{Q_{i} \rho_{p}}{C_{i}} + \frac{r_{c}^{2}}{15D_{ci}}
\]

(13)

in which the terms are film, macro-pore, and micro-pore resistances, respectively. The film resistance remains constant while the particle diameter is unchanged. The micro-pore resistance corresponds to size and structure of the adsorbent crystals and remains constant since the SAPO crystals are the same as ordinary adsorbent. The macro-pore resistance is the only term that changes by variation of shell thickness which can be changed from very low values (for very thin shells) to $r_{p}$ (for ordinary adsorbent particles). The estimated $K_{LDF}$’s for five dif-
Different shell thicknesses are summarized in Table 3. Among the tested items, acceptable agreement can be observed between the experimental and calculated values. It can be seen that the $K_{LDF}$ is increased by decreasing shell thickness.

**Simulation results of the cyclic processes**

The verified adsorption model was employed in the cyclic processes. The bed dimensions, operating conditions, and feed properties are observed in Table 4 for PSA, VSA, and TSA processes. In the simulation studies, the feed flow rate and the bed length are scaled up from the experimental conditions by keeping the same space velocity. Length of the bed was indicated at 20 cm, while the feed flow rate and pressure were increased to 135 NmL/min and 5 bara, respectively. The characteristics of the simulated cyclic adsorption system are given in Table 4.

PSA, VSA, and TSA were considered at equal operating conditions at the adsorption step, whereas they were differed in the regeneration step. In the numerical simulations, initially both beds were saturated with pure CH$_4$ at feed temperature of 298K and at the initial pressures of 5 and 1 bara, respectively, in which the beds would be ready to start the adsorption and purge steps. In CSS condition, all variables were remained unchanged along the bed and at the outlet (regarding a specific tolerance) by evolution of the consequent cycles; i.e., $x(t + t_{cycle}) = x(t)$ for all $x$'s.

PSA was simulated with a cycle time of 700 s, as shown in Fig. 2. The bed regeneration was carried out by a fraction of methane product at 298K and atmospheric pressure during 200s at adiabatic condition.

VSA was simulated with the same cycle time as PSA, presented in Fig. 2. The bed regeneration was carried out by a fraction of methane product at 298K and lower pressure than the atmospheric condition during 200s at adiabatic conditions. Two cases of relative vacuum of 0.4 and 0.7 bara were examined in VSA simulation to be compared from the point of process efficiency.

### Table 3. The estimated values of $K_{LDF}$ at feed condition for different shell thicknesses.

| Particle diameter (mm) | Core diameter (mm) | Shell thickness (mm) | $K_{LDF}$ (1/s) |
|------------------------|-------------------|---------------------|-----------------|
|                         |                   |                     | Experimental    | Estimated (Eq. (0.13)) |
| CH$_4$                 | CO$_2$            | CH$_4$              | CO$_2$         |
| 3.000                  | 2.852             | 0.074               | 0.105          | 0.069 | 0.1382 | 0.0770 |
| 3.000                  | 2.500             | 0.250               |                 | – – | 0.1342 | 0.0749 |
| 3.000                  | 2.000             | 0.500               |                 | – – | 0.1225 | 0.0686 |
| 3.000                  | 1.500             | 0.750               |                 | – – | 0.1070 | 0.0603 |
| 3.500                  | 0.000             | 1.750               | 0.49           | 0.034 | 0.0636 | 0.0362 |

### Table 4. Characteristics of the cyclic processes.

| Parameter                  | Value |
|----------------------------|-------|
| Adsorption bed             |       |
| Bed length (cm)            | 20    |
| Bed diameter (cm)          | 1.27  |
| Bed porosity (-)           | 0.45  |
| Average particle diameter (mm) | 3   |
| Adsorbent porosity         | 0.55  |
| SAPO-34 solid density (kg/m$^3$) | 2260 |
| Operational               |       |
| Volumetric feed flow rate (NmL/min) | 135 |
| Feed molar fraction of CO$_2$ | 0.1 |
| Feed temperature (K)       | 298   |
| Adsorption pressure (bara)  | 5.0   |
TSA process was simulated with the cycle time of 990 s, as shown in Fig. 3. The regeneration condition was carried out by a heating jacket during 300 s and purging with a fraction of product. The purge stream was entered with normal temperature and pressure. Two cases of heating jacket temperature of 348 and 373K were considered comparatively, to achieve a better regeneration performance.

Figure 5a and b shows CO$_2$ concentration in gas and solid phases versus time at the top of the bed, at CSS. One case of PSA, two cases of VSA, and two cases of TSA are presented in this figure. The most important task is the capabilities of the process for desorption of CO$_2$ from the adsorbent pores, and this fact can be found in the regeneration step of the process. It is revealed that the order of regeneration efficiency of the studied processes would rely as the following:

PSA < VSA0.7 < VSA0.4 < TSA75 < TSA100

It was revealed that PSA is the poorest method from the point of bed regeneration, and the adsorbed CO$_2$ would cause problems in methane purification at the further cycles. In the present PSA method, a product stream with 0.9671% methane purity, 0.6849% methane recovery, and 0.001251 mol kg$^{-1}$ productivity can be obtained from a feed stream with 10% CO$_2$; this is not a satisfactory result for CO$_2$ separation purposes. Therefore, VSA and TSA methods were proposed for higher separation efficiency to approach the best conditions from the point of purification, recovery, and productivity. At the following sections, VSA and TSA processes are investigated.

**Vacuum swing adsorption**

The design and operational parameters of the implemented VSA process are given in Table 4. Two cases with the purging pressure of 0.4 and 0.7 bara were investigated in the regeneration step. The performance of both ordinary and core-shell adsorbents was evaluated in the same feed flow rate and bed dimensions. The simulated results are illustrated in Figs. 6–8.

Considering adiabatic bed assumption, temperature profile along the bed is presented from the first cycle up to the CSS conditions in Fig. 6a–b, for the VSA process with the purge pressure of 0.7 bara using ordinary adsorbent. The temperature variation is significant at the earlier cycles, but it approaches to a constant profile after 25 cycles. The temperature profiles of the bed in

![Figure 5](image-url)

**Figure 5.** (a) Mole fraction and (b) Loading of CO$_2$ at CSS at the top of adsorption bed in five different cyclic processes: PSA, VSA with $P_{prg} = 0.7$ bara, VSA with $P_{prg} = 0.4$ bara, TSA with $T_{prg} = 348$ K, and TSA with $T_{prg} = 373$ K. The black time axis is associated with PSA and VSA, and the red one is for TSA.
Figure 6. Evolution of bed temperature with process cycles from the initial condition toward CSS for VSA with $P_{prg} = 0.7$ bara and ordinary adsorbent: (a) temperature profiles at the end of adsorption steps (the numbers on the curves denote the number of cycles); (b) variation of temperature at the top of Bed 1 during time in the first 15 cycles.

Figure 7. Variation of bed temperature and CO$_2$ concentration with time and length of the bed for VSA with $P_{prg} = 0.7$ bara and ordinary adsorbent, with 12 internal collocation points: (a) temperature at the 1st cycle; (b) temperature at the 25th cycle (CSS); (c) CO$_2$ concentration at the 1st cycle; (d) CO$_2$ concentration at the 25th cycle (CSS).
the 1st and 25th cycles are illustrated in Fig. 7a and b, respectively, as function of time and length in a three-dimensional diagram. It is obvious that the temperature increases in the adsorption zone and reduces in the desorption stage. The corresponding CO$_2$ concentration profiles in the 1st and 25th cycles are observed in Fig. 7c and d. Figure 7c shows that CO$_2$ impurities are well-desorbed from the bed in the first cycle, since the bed is full of fresh adsorbent at the first cycle; whereas at the 25th cycle shown in Fig. 7d, the performance of the bed is reduced due to insufficient regeneration of the bed in the previous cycles. Asymmetrical distribution of the collocation points and change of coordination in transitions between the stages are obvious in Fig. 7a–d.

Purity and recovery of methane are shown in Fig. 8 during the first cycle up to the steady cycle at CSS. Product purity, recovery, and productivity of the VSA system at CSS are 97.94 %, 69.29 %, and 0.001407 mol kg$^{-1}$s, respectively, which are not satisfactory results for CO$_2$ separation purposes. More results are given in Part 6 of the Supplementary Information.

However, performance of VSA process at a lower pressure of 0.4 bara using both ordinary and core-shell adsorbents was evaluated in the same feed flow rate and bed dimensions. The simulation results are illustrated in Fig. 9. As expected, the performance of the VSA system is promoted by reduction of purge pressure from 0.7 down to 0.4 bara. The reducing purge pressure leads to better desorption of impurities with less product consumption, in which product purity increases by more efficient bed desorption and the recovery increases because of less consumption of the purified product. Simulation results of the core-shell adsorbent with shell thickness of 0.75 mm compared with ordinary adsorbent show almost similar results, whereas the required amount of the adsorbent is reduced by 12.5 % and the productivity is increased by 11.49 %. It is resulted that the problem of high diffusion resistance of SAPO-34 is solved by the use of core-shell adsorbent in which more efficient adsorption and desorption is occurred. It is obvious that the performance of a longer adsorption bed with the adsorbent weight equal to the ordinary adsorbent case is significantly higher. With
lower thickness of shell in core-shell adsorbent, simultaneous reduction of product purity and recovery was achieved, while the productivity was increased.

**Temperature swing adsorption**

The bed and operational properties of TSA process are presented in Table 4, and the purge step is occurred at atmospheric pressure, the beds are non-adiabatic, and the time scheduling of the cycles is arranged as illustrated in Fig. 3c. The temperature of the bed in the purge step is increased by the hot water in the bed’s jacket and reduced to a lower temperature by cold water during re-pressurization step. The higher temperature in the purge step leads to better desorption of accumulated impurities. Since variation (swing) of the temperature is much slower than the pressure change (swing), TSA requires extended step time in cyclic process rather than PSA. The overall heat transfer coefficients of the jacket-bed system are considered to be 20 and 4 W m⁻² K⁻¹ for the stages with and without fluid flow in jacket, respectively. In purge and equalization steps, the fluid flows in jacket, and in the other steps, the fluid resides within the jacket (Fig. 3a). Performance of both ordinary and core-shell adsorbents is evaluated in described TSA process with the same feed flow rate and bed dimensions at purging temperatures of 348 and 373K, respectively. The simulation results are illustrated in Part 7 of the Supplementary Information.

The simulation results of VSA and TSA processes with ordinary and core-shell adsorbents (using two shell thicknesses of 0.75 and 0.50 mm) are summarized in Fig. 10. It is concluded that the purity of CH₄ in TSA process is higher than that of VSA, while the recovery and productivity is reduced due to the longer cycle times of the TSA processes. As it is expected, variation of shell thickness in TSA processes shows similar pattern to that of VSA processes. However, in the operational scales, it needs an optimized thickness value to approach high purity with acceptable productivity. From the point of productivity and cost-effectiveness, it is proposed to work with thin-layer SAPO-34 adsorbent in a process of VSA rather than TSA.

**Conclusions**

Separation of carbon dioxide from natural gas was numerically simulated by PSA, VSA, and TSA processes for a binary gas mixture of CO₂–CH₄. SAPO-34 was considered as the active phase of the adsorbents with two types of ordinary and mulite/SAPO-34 core shell. The core-shell adsorbent in comparison with the ordinary SAPO-34 particle has shown lower mass transfer resistance into the pores, and therefore shorter mass transfer zone, latter and sharper breakthrough, lower bed temperature rise and higher degree of column utilization. It is concluded that the problem of high diffusion resistance of SAPO-34 particles could be solved by the use of core-shell adsorbent particles in which faster mass transfer rates are occurred and the adsorption process efficiency is improved. However, a longer adsorption bed with the same SAPO-34 adsorbent weight would be required for the core-shell adsorbent rather than ordinary particles. In the cyclic process, the efficiency of core-shell adsorbent is higher than ordinary particles of SAOP-34 and less amount of active phase is required to achieve the same degree of purification and recovery. It was concluded that PSA process is the least efficient process for methane purification and recovery, compared with VSA and TSA processes used for CH₄–CO₂ separation by SAPO-34. However, TSA process can separate CH₄ from CO₂ with higher degree of purification, VSA is more efficient from the point of recovery, productivity and economic cost.
Nomenclature

\[ C \] gas phase molar concentration (mol/m\(^3\))
\[ C_p \] gas phase molar specific heat at constant pressure (J/mol K)
\[ D \] bed diameter (m)
\[ D_{ax} \] axial mass transfer coefficient (m\(^2\)/s)
\[ D_c \] crystal (micro-pore) mass transfer coefficient (m\(^2\)/s)
\[ \Delta H \] heat of adsorption (J/mol)
\[ K \] equilibrium constant in the multi-site Langmuir isotherm (1/mol)
\[ K_{LDF} \] LDF rate constant (1/s)
\[ L \] bed length (m)
\[ MW \] molecular weight (kg/mol)
\[ P \] bed pressure (Pa)
\[ Q \] volume averaged loading in adsorbed phase (mol/kg)
\[ Q^* \] loading in equilibrium with bulk gas (mol/kg)
\[ Q_{max} \] maximum saturation loading (mol/kg)
\[ R \] ideal gas constant (J/mol K)
\[ t \] time (s)
\[ T \] gas or solid phase temperature (K)
\[ u \] superficial velocity (m/s)
\[ U \] overall heat transfer coefficient (W/m\(^2\) K)
\[ z \] axial position (m)
\[ \xi \] transformed axial position (-)
\[ A \] first-order collocation matrix (-)
\[ B \] second-order collocation matrix (-)

Greek letters

\[ \varepsilon \] porosity
\[ \lambda \] axial heat transfer coefficient (W/m K)
\[ \mu \] gas phase viscosity (kg/m s)
\[ \rho \] density (kg/m\(^3\))

Subscripts

\[ b \] bulk phase
\[ c \] particle core
\[ i \] gaseous species
\[ T \] total gas phase
\[ j \] jacket
\[ p \] particle phase
\[ s \] solid phase
\[ sh \] shell
\[ ads \] adsorption step
\[ dpe \] depressurize–equalization step
\[ bdn \] blowdown step
\[ prg \] purge step
\[ peq \] pressurize–equalization step
\[ peqc \] pressurize–equalization with cooling step
\[ rep \] re-pressurization step

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