Supplementary Information:
Comparative Simulation Study of PSA, VSA, and TSA
Processes for Purification of Methane from CO₂ via
SAPO-34 Core-Shell Adsorbent

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1. Schematic of the experimental dynamic adsorption system

Figure S.1: Schematic of the experimental dynamic adsorption system

2. Operating steps of the introduced cyclic adsorption processes

Each cycle of the suggested process is planned to be consisting of six sequential steps as follows:

Step 1. Adsorption (ADS): The binary gas mixture of CO_2 - CH_4 enters from the bottom of the bed as the feed stream. The gas flows through the bed with inlet pressure of 5 bara and temperature of 298 K. During the adsorption step, CO_2 would be adsorbed selectively into the adsorbent micropores and the bed temperature gradually increases because of the exothermic adsorption phenomena. The gas density and pressure slightly decrease because of CO_2 adsorption and friction forces along the bed. The solid adsorbents are loaded with CO_2 along the bed during the time, hence, choosing an appropriate step time helps to separate CO_2 from CH_4 at the top of the bed.

Step 2. Depressurizing Equalization (DPE): In this stage, the feed inlet valve is closed and the gas with high pressure flows from the top of the bed to another bed for equalization. During this stage, pressure of the first bed is reduced and some of the bulk gas enters to the other bed. The bed temperature is slightly reduced due to gas pressure reduction and slightly desorption of the adsorbed CO_2 .

Step 3. Blow down (BDN): The top of the bed is closed and the remained gas is evacuated to the atmosphere counter-currently, as the off-gas. Because of pressure reduction and desorption of some of CO_2 impurities the bed temperature is reduced slightly.

4. Purge with product (PRG): The main difference of PSA, VSA and TSA is appeared in this section. In the PSA method, bed regeneration is carried out by purging with a portion of product at atmospheric pressure, whereas at VSA method bed regeneration is carried out by applying a relative evacuation under atmospheric pressure followed by purging with product at low pressure. The regeneration condition in the TSA method is applied by heating the bed by heating jacket. Therefore, an extra cooling step would be applied through the jacket to cool down the bed to the normal temperature.

Step 5. Pressurizing Equalization (PEQ): The bottom of the bed is closed and the bed is connected from the top to the other bed, working at second step, to be partially pressurized by equalization. As well in TSA approach,

temperature of the bed is reduced down by using cold water at 293 K in the jacket.

Step 6. Re-pressurization (REP): The pressure of the bed is increased to the adsorption step using the high-pressure gas feed from the bottom of the bed. The slightly increase of the bed temperature is resulted from increasing bed pressure as well as slightly adsorption of CO₂.

3. Boundary conditions for the stages of the cyclic process

Table S.1: Boundary conditions for the stages of the cyclic process

$z = 0$	$z = L$
Adsorption	
$C_i = \frac{P}{RT_f} y_{i_f}$	$\frac{\partial C_i}{\partial z} = 0$
$T = T_f$	$\frac{\partial T}{\partial z} = 0$
$u = u_f$	$P = P_{prod}$
Co-Current Depressurization (Equalization)	
$\frac{\partial C_i}{\partial z} = 0$	$\frac{\partial C_i}{\partial z} = 0$
$\frac{\partial T}{\partial z} = 0$	$\frac{\partial T}{\partial z} = 0$
$u = 0$	$\frac{\partial P}{\partial t} = -\tau_{P_{dpe}} (P - P_{dpe})^{0.85}$
Counter-Current Depressurization (Blowdown)	
$\frac{\partial C_i}{\partial z} = 0$	$\frac{\partial C_i}{\partial z} = 0$
$\frac{\partial T}{\partial z} = 0$	$\frac{\partial T}{\partial z} = 0$
$\frac{\partial P}{\partial t} = -\tau_{P_{bdn}} (P - P_{bdn})^{0.85}$	$u = 0$
Counter-Current Purge	
$\frac{\partial C_i}{\partial z} = 0$	$C_i = \frac{P}{RT} \frac{C_{i_{prod}}}{C_{prod}}$
$\frac{\partial T}{\partial z} = 0$	$T = T_{prg}$
$P = P_{prg}$	$u = -u_{prg}$
Counter-Current Pressurization (Equalization)	
$\frac{\partial C_i}{\partial z} = 0$	$C_i = \frac{P}{RT} \frac{C_{i_{dpe}}}{C_{dpe}}$
$\frac{\partial T}{\partial z} = 0$	$T = T_{dpe}$
$u = 0$	$\frac{\partial P}{\partial t} = \tau_{P_{dpe}} (P_{peq} - P)^{0.85}$
Co-Current Re-pressurization	
$C_i = \frac{P}{RT_f} y_{i_f}$	$\frac{\partial C_i}{\partial z} = 0$
$T = T_f$	$\frac{\partial T}{\partial z} = 0$
$\frac{\partial P}{\partial t} = \tau_{P_{rep}} (P_{rep} - P)^{0.85}$	$u = 0$

4. Spatial discretization of the governing PDE's via OCM

At the first step, the spatial domain should become dimensionless within 0 to 1. With respect to the boundary conditions of different stages of the process given in the previous Part (Table S.1), some of the boundary conditions are from the type of Neumann and homogeneous, that is as like as symmetric boundary condition. As shown in Table S.1 adsorption, blow down, and repressurization steps reveal this type of symmetric boundary condition at $z = L$ and in the other stages boundary conditions are observed at $z = 0$. Therefore the z variable should be converted to a new variable of ξ to keep symmetrical boundaries always at $\xi = 0$, during the model solutions in each stage. The mapped equations via $\xi = (1 - \frac{z}{L})^2$ are given in Table S.2. In the next step, the N internal collocation points are selected on the base of roots of a Jacobi orthogonal polynomial. The Jacobi polynomial parameters, α and β , are chosen regarding the type of boundary conditions in the governing equations at each stage of PSA cycle¹.

Table S.2: Mapped governing equations from (t, z) to (t, ξ) using $\xi = (1 - \frac{z}{L})^2$

<i>Partial mass balance</i>
$\varepsilon_t \alpha_p \frac{\partial C_i}{\partial t} = \frac{4\varepsilon_b D_{ax} \xi}{L^2} \frac{\partial^2 C_i}{\partial \xi^2} + \frac{2\varepsilon_b D_{ax}}{L^2} \frac{\partial C_i}{\partial \xi} + \frac{2\sqrt{\xi}}{L} \frac{\partial(u C_i)}{\partial \xi} - \rho_p(1 - \varepsilon_b) \alpha_p \frac{\partial \bar{Q}_i}{\partial t}$
<i>Overall mass balance</i>
$\varepsilon_t \alpha_p \frac{\partial C_T}{\partial t} = \frac{2\sqrt{\xi}}{L} C_T \frac{\partial u}{\partial \xi} - \rho_p(1 - \varepsilon_b) \alpha_p \sum_{i=1}^{N_{comp}} \frac{\partial \bar{Q}_i}{\partial t}$
<i>Energy balance</i>
$\begin{aligned} \psi \frac{\partial T}{\partial t} = & \frac{4\lambda \xi}{L^2} \frac{\partial^2 T}{\partial \xi^2} + \frac{2\lambda}{L^2} \frac{\partial T}{\partial \xi} + \frac{2u\sqrt{\xi}}{L} \sum_{i=1}^{N_{comp}} (C_i C_{pi}) \frac{\partial T}{\partial \xi} + \rho_p(1 - \varepsilon_b) \alpha_p \sum_{i=1}^{N_{comp}} \left(\frac{\partial \bar{Q}_i}{\partial t} (-\Delta H_i) \right) \\ & + \varepsilon_t R T \sum_{i=1}^{N_{comp}} \frac{\partial C_i}{\partial t} + U_j \frac{A}{D} (T_j - T) \end{aligned}$
<i>Momentum balance</i>
$\frac{2\sqrt{\xi}}{L} \frac{\partial P}{\partial \xi} = \frac{150\mu(1-\varepsilon_b)^2}{\epsilon_b^3 d_p^3} u + \frac{1.75(1-\varepsilon_b) \sum_{i=1}^{N_{comp}} (C_i MW_i)}{\epsilon_b^3 d_p} u u$

The roots of Jacobi polynomial are used in a Lagrange interpolating polynomial as a trial function to be substituted in the PDE of governing equations.

¹Shohreh Fatemi. Application of numerical methods in chemical engineering. University of Tehran Press, 2013.

The general formula of Lagrange polynomial is presented in Eq. (1) in which y_j is the function (e.g. C_j and T) values at the collocation points along the bed:

$$y(x) = \sum_{j=0}^{N+1} l_j(x) y_j \quad (1)$$

$$l_j(x) = \prod_{k=0, k \neq j}^{N+1} \frac{x - x_k}{x_j - x_k} \quad (2)$$

The aim of trial function is to satisfy the governing equations and boundary condition in the collocation points. The first and second derivatives of Lagrange polynomials should be replaced in the governing PDE equations as follows:

$$\frac{dy(x)}{dx} = \sum_{j=0}^{N+1} \frac{dl_j(x)}{dx} y_j = \mathbf{A} \bar{\mathbf{y}} \quad (3)$$

$$\frac{d^2 y(x)}{dx^2} = \frac{d}{dx} \frac{dy(x)}{dx} = \mathbf{A}^2 \bar{\mathbf{y}} = \mathbf{B} \bar{\mathbf{y}} \quad (4)$$

where $\bar{\mathbf{y}} = [y_0 \ y_0 \ \dots \ y_{N+1}]^T$ denotes the values of variable y estimated in the $N + 1$ collocation points and $\mathbf{A}$ and $\mathbf{B}$ are collocation matrices with the dimension of $(N + 1) \times (N + 1)$.

The governing ODE's are obtained based on the illustrated scheme. All of the variables that are function of ξ , are introduced as vectors like $\bar{\mathbf{y}}$ in Eqs. (3) and (4). The spatially discretized equations based on the mapped equations of Table S.2, corresponding to the stages with symmetry boundary condition at $z = L$, are given in Table S.3. The same as the governing equations, the boundary conditions are mapped and provided as discretized vectors in the new (t, ξ) coordinate system. For example, the boundary condition $\frac{\partial C_i}{\partial \xi} = 0$ at $z = 0$, for a stage with symmetry boundary condition at $z = L$, should be transformed to the new space of discretized equations as Eq. (5) which leads to algebraic evaluation of the function values at the boundary.

$$\begin{aligned} \mathbf{A}_{N+1,k} \bar{\mathbf{C}}_{i,k} &= 0 \quad \forall \ k = 1..N+1 \\ \Rightarrow \bar{\mathbf{C}}_{i,N+1} &= \frac{-1}{\mathbf{A}_{N+1,N+1}} \sum_{k=0}^N \mathbf{A}_{N+1,k} \bar{\mathbf{C}}_{i,k}. \end{aligned} \quad (5)$$

These ODE's are simply solved via the four-step Adams-Bashforth/Adams-Moulton method. At the start point of the solution, the initial conditions of the initial stages (here adsorption in Bed 1 and purge in Bed 2) are defined.

Table S.3: Spatially discretized governing equations for the stages with symmetry boundary condition at $z = L$

Mass balance

$$\begin{aligned}\frac{\partial \bar{C}_i}{\partial t} &= \frac{4\varepsilon_b D_{ax}}{\varepsilon_t \alpha_p L^2} \xi \odot (\mathbf{B} \bar{C}_i) + \left(\frac{2\varepsilon_b D_{ax}}{\varepsilon_t \alpha_p L^2} + \frac{2\mathbf{u}}{\varepsilon_t \alpha_p L} \odot \sqrt{\xi} \right) \odot (\mathbf{A} \bar{C}_i) - \rho_p \frac{1 - \varepsilon_b}{\varepsilon_t} \frac{\partial \bar{Q}_i}{\partial t} \\ \varepsilon_t \alpha_p \frac{\partial \bar{C}_T}{\partial t} &= \frac{2\sqrt{\xi}}{L} \odot \bar{C}_T \odot (\mathbf{A} \mathbf{u}) - \rho_p (1 - \varepsilon_b) \alpha_p \sum_{i=1}^{N_{comp}} \frac{\partial \bar{Q}_i}{\partial t} \\ \frac{\partial \bar{Q}_i}{\partial t} &= \overline{\mathbf{K}_{LDF}} \odot (\bar{Q}_i^* - \bar{Q}_i) \\ \bar{Q}_i^* &= \bar{Q}_i^{\max} \odot \bar{K}_i \odot \bar{C}_i \odot R \bar{T} \odot \left[1 - \sum_{i=1}^{N_{comp}} (\bar{Q}_i^* \oslash \bar{Q}_i^{\max}) \right]^{a_i} \\ \bar{K}_i &= \bar{K}_{0i} \odot \exp(-\overline{\Delta \mathbf{H}_i} \odot R \bar{T})\end{aligned}$$

Energy balance

$$\begin{aligned}\psi \frac{\partial \bar{T}}{\partial t} &= \frac{4\lambda}{L^2} \xi \odot (\mathbf{B} \bar{T}) + \left(\frac{2\lambda}{L^2} + \frac{2}{L} (\bar{C}_i^T \bar{C}_{pi}) \mathbf{u} \odot \sqrt{\xi} \right) \odot (\mathbf{A} \bar{T}) + \rho_p (1 - \varepsilon_b) \alpha_p \left(\frac{\partial \bar{Q}_i}{\partial t} \right)^T (-\overline{\Delta \mathbf{H}_i}) \\ &\quad + \varepsilon_t R \bar{T} \sum_{i=1}^{N_{comp}} \frac{\partial \bar{C}_i}{\partial t} + U_j \frac{4}{D} (\bar{T}_j - \bar{T}) \\ \psi &= \varepsilon_t (\bar{C}_i^T \bar{C}_{vi}) + \rho_p C_{ps} (1 - \varepsilon_b) + \rho_p (1 - \varepsilon_b) \alpha_p (\bar{\bar{Q}}_i^T \bar{C}_{vi})\end{aligned}$$

Momentum balance

$$\frac{2}{L} \sqrt{\xi} \odot (\mathbf{A} \bar{P}) = \frac{150\mu(1-\varepsilon_b)^2}{\varepsilon_b^3 d_p^3} \mathbf{u} + \frac{1.75(1-\varepsilon_b) \sum_{i=1}^{N_{comp}} (C_i MW_i)}{\varepsilon_b^3 d_p} |\mathbf{u}| \odot \mathbf{u}$$

* The operators $\odot$ and $\oslash$ denote element-by-element product and divide, respectively.

Subsequently the initial conditions of the next stages are the calculated values at the end of previous stages. At each stage of the process, the simulation would be running until it is approaching to the specified time for the stage. With respect to the location of symmetry boundary condition at $z = L$ or $z = 0$, the utilized map varies between $\xi = (\frac{z}{L})^2$ and $\xi = (1 - \frac{z}{L})^2$, hence, the (t, ξ) coordinate system varies in different stages of the process. Therefore, in the transition between the stages, the coordination system has to be changed. To this aim, the values of variables at the new collocation points in the new stage are interpolated based on the calculated values from the previous stage. Spline interpolation is used in this regard.

5. Flowchart of the steps of numerical simulation

Figure S.2: Flowchart of the steps of numerical simulation

6. More simulation results for VSA using ordinary adsorbent

Figure S.3: CH_4 (a) and CO_2 (b) concentration profiles along the bed at the end of the process stages at CSS for VSA with $P_{prg}=0.7$ bara and ordinary adsorbent

The concentration profiles of CH_4 and CO_2 at the end of each stage of the VSA process (with purging at 0.7 bara), at the CSS are shown in Fig. S.3a and b, respectively. Fig. S.3a shows the almost constant profile of CH_4 concentration which indicates the low adsorption of CH_4 on the adsorbent, while Fig. S.3b presents that the level of impurities in the bed was changed during the stages. During the first four stages, from adsorption to purge, the impurity level decreases, and then it is increased with rising pressure at the two remaining stages of equalization and re-pressurization. The impurity level is minimum at the end of the purge stage.

7. More simulation results for TSA process

Evolution of temperature along the bed from initial condition at the first cycle toward CSS is shown in Fig. S.4 for TSA with $T_J=348$ K and ordinary adsorbent, in which the profiles are captured at the end of adsorption steps. The temperature variations approach to CSS in the cycles after 5th. Temperature profile of Bed 1 during the first 5 cycles of the TSA with $T_J=348$ K and ordinary adsorbent are shown in Fig. S.4a and b, respectively. It is observed that the TSA process reached to the CSS faster than VSA process. This is due to the slow variation of the temperature in the VSA process, which is accelerated by temperature swing in TSA process. The temperature of the beds is increased during purge step and again, reduced during re-pressurizing step.

Figure S.4: Evolution of bed temperature profile with process cycles from the initial condition to the CSS for TSA case with purge at 348 K 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

The temperature and CO_2 concentration profiles of the adsorption bed in the first and fifth cycles are illustrated in Fig. S.5a-d as function of time and

bed length. Fig. S.5a and b shows the temperature profiles in the first and fifth cycles, respectively. Temperature of the bed was significantly increased in the purge step and reduced in the cooling step (PEQC). Fig. S.5c-d shows the corresponding CO₂ concentration profiles in the first and fifth cycles. Regeneration of the adsorbents was conducted properly during the process, which was resulted by temperature increase and well desorption of impurities in the purging stage.

Figure S.5: Variation of bed temperature and CO₂ concentration with dimensionless time and length of the bed for TSA with $T_J=348$ K and ordinary adsorbent; with 12 internal collocation points: (a) temperature at the 1st cycle; (b) temperature at the 5th cycle (CSS); (c) CO₂ concentration at the 1st cycle; (d) CO₂ concentration at the 5th cycle (CSS).

The concentration profiles of CO₂ along the beds with ordinary adsorbent at the end of the process stages at CSS are illustrated in Fig. S.6. In comparison to VSA with $P_{prg}=0.7$ bara, level of impurities is well reduced in purge step that affected all steps of the process.

Figure S.6: CO₂ concentration profiles along the bed at the end of the process stages at CSS for TSA process with ordinary adsorbent