

Thermal management in vacuum pressure swing adsorption processes using phase change materials

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ABSTRACT

Vacuum pressure swing adsorption (VPSA) is a mature separation process; however, given the current energy situation, further improvements in terms of process operations are required. To this end, the use of a thermal energy storage system during VPSA cycles appears promising, as the exothermic heat and endothermic heat generated by adsorption and desorption are known to reduce the working capacity. In this study, we investigated thermal management by using a commercial phase change material (PCM) composed of phenolic resin and microencapsulated paraffin wax in the VPSA process to purify an equimolar CH_4/CO_2 gas mixture using zeolite 13X. Here, VPSA processes were simulated using our one-dimensional nonisothermal column model considering the melting and solidification of the PCM. The influence of the PCM mixing ratios was evaluated based on the specifications of CO_2 products and the column length, wherein the VPSA processes were designed, such that the purity and recovery of CH_4 products met the prescribed criteria to achieve a reasonable comparison. The temperature variation (270–351 K) in the cyclic steady state owing to the exothermic and endothermic heat produced during the adsorption and blowdown steps, respectively, was suppressed to 276–344 K by the latent heat of the PCM, resulting in low CH_4 co-adsorption and improved purity of the CO_2 product. Finally, we proposed a method involving the intensive installation of a PCM in the central part of the column and demonstrated that the advantages of improved adsorbent performance realized by mixing the PCM outweighed the disadvantages of increased PCM volume, resulting in a shorter column length than that in the case without the PCM. These results demonstrate the superiority of PCM-installed VPSA systems.

1. Introduction

Pressure swing adsorption (PSA) has been widely used for many years in air separation [1-3], hydrogen purification [4-6], and CO₂ separation [7-10] systems. To achieve carbon neutrality, it is desirable to take advantage of PSA processes that do not require large amounts of energy for gas separation. However, PSA is a separation process that favors small-scale applications. To extend the applicability of PSA, there is a need to ensure processing at larger flow rates, which can be accomplished by improving the adsorbent and further optimizing the operation of PSA from an engineering perspective. Many factors must be determined in PSA processes in addition to adsorbent selection, starting with the regeneration method of the adsorbent, such as pressure reduction, sweeping, and temperature increase, followed by the time for each cycle operation process, column size, flow rate, and so on. While the flexibility of PSA makes it difficult to optimize the process, there is room for improvement beyond the adsorbent. Therefore, several advanced approaches that evolved from the primitive Skarstrom PSA cycle have been considered, including a combination of vacuum and temperature swing [11, 12], operations specific to multi-column systems [13-16], reuse of off-gas from the rinse process [14], optimization of pressure equalization steps [13-16], dual reflux method for two columns [17-19], and operation with short cycle times (rapid PSA) [20-22].

An important factor to improve PSA processes is thermal management. Because PSA processes tend to be near adiabatic, which becomes more significant when enlarging the column to achieve high throughput, the exothermic heat generated during the adsorption step and endothermic heat during the desorption step cannot be ignored [23-26]. Temperature increase due to exothermic heat reduces the amount adsorbed during the adsorption step and temperature drop due to endothermic heat increases the amount

of adsorbate remaining during the desorption step, resulting in a smaller working capacity or the amount of adsorptive gas obtained during a single cyclic operation. To suppress the reduction in the working capacity, heat exchangers are considered to be installed in adsorption columns. For example, Yang and Cen examined PSA processes under isothermal and adiabatic operations and evaluated the separation performances with the same cycle time [25]. They showed that the recovery of adsorbed components under adiabatic conditions is 25.5% lower than that under isothermal conditions because of a decrease in the equilibrium adsorption capacity due to temperature increase and that the recovery under adiabatic conditions can be improved by adding a shell-and-tube type heat exchanger or inert dummy additives.

Latent heat-type storage systems using phase change materials (PCMs) [27-29] are more effective than sensible heat-type mediums and are commonly used in various fields, including building materials [30] and agricultural food drying [31]. Moreover, the use of PCMs in adsorption processes has also been explored in several studies [32-38]. Choi *et al.* developed a method to insert PCMs directly into the pores of mesoporous silica SBA-15 [33] and mesoporous zeolite SSZ-13 [32] aiming to efficiently transfer the heat of adsorption to PCMs. In their observation, the temperature increase during adsorption was suppressed by latent heat and the melted PCM was retained in the pores by surface tension. Lively *et al.* created dual-layer hollow fibers comprising zeolite NaY and cellulose acetate coated with poly(vinyl-alcohol) [37]. Further, CO₂/He (as surrogate for H₂) breakthrough curve analyses were performed on these fibers with and without paraffin wax; consequently, the breakthrough time was found to be extended in the fibers with paraffin wax. Dewitt *et al.* prepared cellulose acetate fibers loaded with microencapsulated PCM and UiO-66, a type of MOF [34]. They measured the

breakthrough curve near the melting temperature of PCM and found that the shape of the breakthrough curve became sharp and the adsorption capacity per adsorbent weight increased. As a practical example, phenolic resin pellets developed by Osaka Gas Chemical Ltd containing microencapsulated paraffin wax, as the PCM, have been used in charcoal canisters of cars [38].

As detailed above, almost all previous studies on the use of PCMs in adsorption processes are related to new material development, and only limited studies have explored the functions of PCMs in PSA processes based on experimentation or numerical simulations [35]. Perhaps, this can be attributed to the fact that the use of PCMs usually increases the working capacity of the adsorbent, i.e., the suppression in the temperature variation resulting from the latent heat of the PCM produces a positive effect in both the adsorption and desorption steps. However, irrespective of the method adopted, the installation of a PCM in the adsorption column reduces the amount of adsorbent loading. In other words, although the working capacity per weight of the adsorbent increases upon PCM mixing, the adsorption performance per volume of the column is not necessarily improved. Furthermore, the latent heat of the PCM is useful only when the temperature fluctuates from a low to high (and vice versa) value, crossing the melting point of the PCM during the PSA cycle. Considering that a temperature difference of several tens of degrees typically exists between the bottom and the top of the column when the PSA approaches a cyclic steady state [39], certain situations wherein the PCM is not effectively utilized may be encountered. To the best of our knowledge, these engineering issues related to PCMs still remain to be addressed.

To address these prevalent issues, we recently developed a nonisothermal column model that successfully reproduced the actual adsorption behavior in a column

loaded with activated carbon pellets and commercial PCM pellets developed by Osaka Gas Chemicals Ltd, phenolic resin pellets in which PCM microcapsules were dispersed [40]. To represent the melting and freezing of the PCM, the temperature of the paraffin wax in the PCM microcapsules and that of the bed consisting of the gas phase, adsorbent, and phenolic resin were separately calculated in our model. Despite the simple approximation, the process simulation was accurate enough for engineering applications. The advantage of mixing a PCM in a single adsorption operation under adiabatic conditions was confirmed using this model. However, the role of the PCM in the PSA process, wherein the adsorption and desorption steps were repeatedly executed while influencing each other, is yet to be examined.

This study investigated thermal management in vacuum pressure swing adsorption (VPSA) processes for the purification of CH_4/CO_2 using commercial zeolite 13X pellets and PCM pellets as a model case. The one-dimensional, multiphase, nonisothermal column model developed in our previous study was used for the calculations. The kinetic parameters of mass and heat were estimated from the fitting to the breakthrough curves of CH_4 and CO_2 measured under several conditions. VPSAs under adiabatic conditions were simulated to evaluate the effect of the heat of adsorption/desorption on the separation performance. PCM-installed VPSAs with various mixing ratios were then calculated to evaluate how the latent heat of PCM acts and analyze situations where PCM pellets were effective.

This paper is organized as follows. Section 2 provides experimental details on adsorption isotherms, breakthrough measurements, and computational details on transfer coefficient estimation and VPSA simulations using our column model. In Section 3, we estimate the Sips equation for zeolite 13X and parameters of the mass and heat transfer

coefficients of the VPSA process, establish rules for determining the optimal column length and purge step time to achieve a fair comparison of systems with and without PCM, and discuss the effect of PCM mixing on adsorption performance, including the optimal location for the PCM. Finally, we conclude the results in Section 4.

2. Methods

2.1. Materials

Zeolite 13X pellets with an average length of 3.2 mm and a diameter of 2 mm were purchased from FUJIFILM Wako Pure Chemical Corporation. The PCM pellets assumed in the following VPSA simulations were modeled based on the PCM36G-AC product developed by Osaka Gas Chemicals Ltd [38]; this product was experimentally characterized in our previous study [40]. PCM36G-AC is schematically illustrated in Fig. 1. Here, inside a phenolic resin-based pellet with a length of 3 mm and a diameter of 2 mm, 72 wt% of microcapsules filled with paraffin wax are dispersed. The melting temperature of the PCM pellets can be varied by changing the type of paraffin wax; however, we selected a PCM melting at 305 K based on the following finding of our previous study: a PCM melting at a slightly higher temperature than room temperature is more effective during the adsorption step. Other parameters including the particle density, heat capacity, and latent heat are summarized in Table S1, Supporting Information. Note that PCM36G-AC is non-porous.

binary gas flowed through the bypass flow path. Then, the gas flow path was switched to the adsorption column side, and the gas composition downstream of the adsorption column was measured using QMS. The adsorbent temperatures at 4 cm, 7 cm, and 10 cm from the inlet of the adsorption column were also measured. The ambient temperature was controlled at 304 K during the breakthrough measurement using a thermostatic oven. Three breakthrough curves were measured by varying the feed gas flow rate and feed gas mixture composition, which provided sufficient data for estimating the mass and heat transfer coefficients, as summarized in Table 1. A series of measurements was conducted on the same sample, where the adsorbent was activated by heating to 573 K for 12 h under vacuum before each measurement.

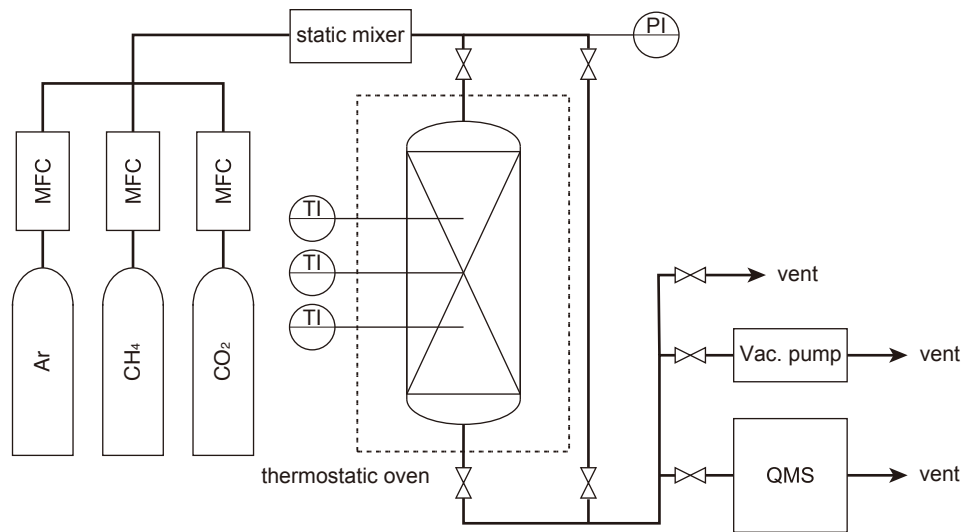


Fig. 2 Flowchart of the lab-made apparatus for breakthrough curve measurements.

Table 1 Conditions of breakthrough experiments

Condition	Flow rate of feed gas ^a [sccm ^b]	CH ₄ /CO ₂ ratio of feed gas
A	200 (0.014)	50/50

B	400 (0.028)	50/50
C	200 (0.014)	75/25

^aThe values in parentheses are the estimated superficial velocities [$\text{m}\cdot\text{s}^{-1}$] of the column at 304 K.

^bsccm: standard $\text{cm}^3\cdot\text{min}^{-1}$.

2.3. Simulation Methods

2.3.1. Column Model

We used the one-dimensional nonisothermal column model developed in our previous study [40]. In this model, the following assumptions were made:

- Radial direction profiles are neglected.
- The mass transfer rate is described using a linear driving force model.
- The temperature dependence of mass transfer coefficient, heat of adsorption, and heat capacity are neglected.
- The equilibrium adsorption of the binary gas mixture is estimated based on the ideal adsorbed solution theory (IAST) [41].
- The temperatures of the gas phase, adsorbent, and phenolic resin of PCM36G-AC are uniform as the bed temperature T_B , whereas the temperature of the paraffin wax inside PCM36G-AC is described using a separate variable T_{PW} . The heat transfer rate between the PCM and bed is defined such that the difference between the temperatures acts as the driving force.

The governing equations of the model, including the material/heat balance and adsorption

isotherm model, are summarized in Table 2, and the variables are described in the notation table. Note that the validities of these governing equations and assumptions have been thoroughly examined in our previous experimental study [40]. The position derivative of the partial differential equation in the model was discretized by dividing it equally into 50 finite volumes. Upwind approximation was applied to simplify the computation of the flux limiter. Time integration was performed using the Sundials CVODE solver [42].

Table 2 Material and heat balances

Material balance of species i

$$\varepsilon_T \frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial z} - \rho_B(1 - \phi_{PCM}) \frac{\partial n_i}{\partial t}$$

Mole flux of species i

$$J_i = uc_i - \varepsilon_B c D_L \frac{\partial y_i}{\partial z}$$

Axial dispersion coefficient

$$D_L = 0.7D_m + 0.5d_p \frac{u}{\varepsilon_T}$$

Adsorption rate

$$\frac{\partial n_i}{\partial t} = k_i(n_i^* - n_i)$$

Energy balance for the gas phase, adsorbent, and phenolic resin of the PCM pellet

$$\begin{aligned} & \left[\varepsilon_T \sum_i c_i C_{p,i} + \rho_B(1 - \phi_{PCM}) C_{p,Z} + \rho_B \phi_{PCM} (1 - \theta_{PW}) C_{p,PR} + \rho_B(1 - \phi_{PCM}) \sum_i n_i C_{p,i} \right] \frac{\partial T_B}{\partial t} - \varepsilon_T \frac{\partial p}{\partial t} \\ &= - \sum_i J_i C_{p,i} \frac{\partial T_B}{\partial z} + \rho_B(1 - \phi_{PCM}) \sum_i (-\Delta H_{ads,i}) \frac{\partial n_i}{\partial t} + \varepsilon_B \lambda_B \frac{\partial^2 T_B}{\partial z^2} \\ &+ \rho_B \phi_{PCM} U_{BPW} (T_{PW} - T_B) + \frac{2}{r_i} h_{BW} (T_W - T_B) \end{aligned}$$

Energy balance for the PCM paraffin wax

$$\theta_{PW} \frac{\partial H_{PW}}{\partial t} = U_{BPW} (T_B - T_{PW})$$

Sips equation for the adsorption isotherm model

$$n_i^* = n_{s,i} \frac{(b_i p)^{1/s_i}}{1 + (b_i p)^{1/s_i}}$$

Temperature dependence

$$n_{s,i} = n_{sref,i} \exp \left[\chi_i \left(1 - \frac{T_B}{T_{ref}} \right) \right]$$

$$b_i = b_{ref,i} \exp \left[\frac{Q_i}{RT_{ref}} \left(\frac{T_{ref}}{T_B} - 1 \right) \right]$$

$$\frac{1}{s_i} = \frac{1}{s_{ref,i}} + a_i \left(1 - \frac{T_{ref}}{T_B} \right)$$

Pressure drop

$$\frac{\partial p}{\partial z} = - \frac{150\mu(1 - \varepsilon_B)^2}{\varepsilon_B^3 d_p^2} u - \frac{1.75(1 - \varepsilon_B)\rho}{\varepsilon_B^3 d_p} |u|u$$

Temperature dependence of the paraffin wax

$$H_{PW} = \begin{cases} H_{ref,PW} + C_{p,PW}^s(T_{PW} - T_{ref}) & (T_{PW} \leq T_m) \\ H_{ref,PW} + C_{p,PW}^s(T_m - T_{ref}) + \frac{\Delta H_{PW}}{\Delta T_m}(T_{PW} - T_m) & (T_m < T_{PW} \leq T_m + \Delta T_m) \\ H_{ref,PW} + C_{p,PW}^s(T_m - T_{ref}) + \Delta H_{PW} + C_{p,PW}^l[T_{PW} - (T_m + \Delta T_m)] & (T_m + \Delta T_m < T_{PW}) \end{cases}$$

Equation of state

$$c_i = \frac{y_i p}{RT_B}$$

2.3.2. Parameter Estimation

The parameters representing the adsorption rates of CH₄ and CO₂, k_{CH_4} and k_{CO_2} , respectively and the heat transfer coefficients of the bed and walls, h_{BW} were estimated so that the calculated breakthrough curves and temperature distributions fit the experimental results. The other parameters used in the breakthrough calculations are summarized in Table 3. Following the procedure reported in [40], we first determined the mass transfer coefficients, k_{CH_4} and k_{CO_2} and the heat transfer coefficient, h_{BW} so that the simulated breakthrough curve and temperature in the column matched the experimental data obtained under condition **A** in Table 1. The estimated parameters were used to

calculate the breakthrough curve and temperature distributions for conditions **B** and **C** and compared with their experimental results. The heat transfer coefficient between the wall and the environment, h_{WA} was set to the same value ($h_{WA} = 34 \text{ J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$) as that in the previous study because the experimental setup is identical. We also used the value of the overall heat transfer coefficient between the bed and the paraffin wax encapsulated in the PCM pellets, $U_{BPW} = 60 \text{ J}\cdot\text{kg-PCM}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ used in the previous study based on the assumption that the effect of the difference in adsorbents on U_{BPW} is not significant.

Table 3 Parameters of the column model

L	column length	0.14 m
r_i	column inner radius	0.00875 m
r_o	column outer radius	0.01085 m
$C_{p,W}$	heat capacity of column wall	$4.7 \times 10^6 \text{ J}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$
λ_W	axial thermal conductivity of column wall	$16.7 \text{ J}\cdot\text{m}^{-3}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$
$\rho_{P,Z}$	particle density of zeolite 13X	$1085 \text{ kg-ads.}\cdot\text{m}^{-3}$
$\rho_{M,Z}$	material density of zeolite 13X	$2359 \text{ kg-ads.}\cdot\text{m}^{-3}$
$C_{p,Z}$	heat capacity of zeolite 13X	$900 \text{ J}\cdot\text{K}^{-1}\cdot\text{kg-ads.}^{-1}$
C_{p,CH_4}	heat capacity of methane	$35.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
C_{p,CO_2}	heat capacity of carbon dioxide	$37.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$C_{p,Ar}$	heat capacity of argon	$20.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
D_m	molecular diffusion coefficient	$9.5 \times 10^{-5} \text{ m}^2\cdot\text{s}^{-1}$
λ_B	axial thermal conductivity of packed bed	$0.3 \text{ J}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$

2.3.3. Vacuum Pressure Swing Adsorption (VPSA) Simulation

We assumed the primitive two-column Skarstrom cycle consisting of four steps, namely, pressurization of the column with feed gas, adsorption on the column while opening the column outlet, blowdown of the column and recovery of adsorbed components, and purging with non-adsorbed gas, as shown in Fig. 3. The direction of gas flow in the blowdown and purge steps was countercurrent toward the feed gas, and part of the CH₄ product gas was distributed in the purge step. The Robin and Neumann boundary conditions were appropriately applied as boundary conditions at both sides of the column model for component concentration, temperature, and pressure, as listed in Table S2, Supporting Information. In the blowdown step, we assumed the following relationship describing the pressure change at the column outlet ($z = 0$):

$$p = p_L + (p_H - p_L) \exp(-\xi t) \quad (1)$$

where p is the pressure at $z = 0$, p_L and p_H are operation pressures for adsorption and desorption, respectively, ξ is a parameter that expresses the rate of pressure decrease, and t is the time. In this study, ξ was set to 0.2 with reference to a previous experimental study [43].

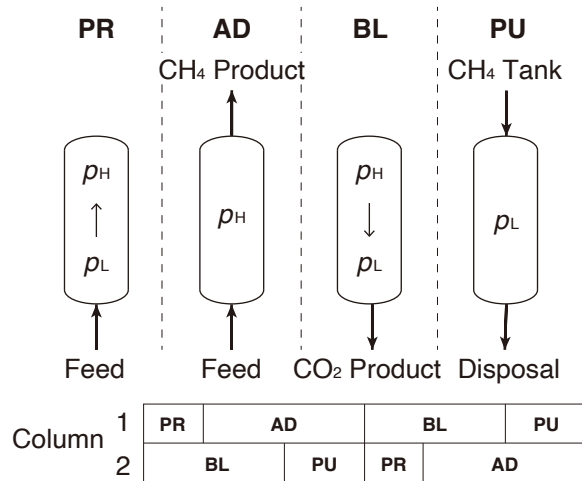


Fig. 3 VPSA cycle for purification of CH₄ and CO₂. **PR**, **AD**, **BL**, and **PU** denote the pressurization, adsorption, blowdown, and purge steps, respectively.

2.3.4. Process Design

To evaluate the effect of PCM on thermal management, we calculated the VPSAs under adiabatic conditions ($h_{BW} = h_{WA} = 0$). As the feed gas, we assumed an equimolar gas mixture of CO₂ and CH₄, which is a model case of landfill gas. The operation pressures for adsorption and desorption were set to $p_H = 500$ kPa and $p_L = 15$ kPa, respectively. The desorption pressure was apparently slightly high; however, this indicated that deep vacuum levels are not practical for large-scale processes [44]. The flow rate of feed gas was set to 333 slm (standard liter per minute) and its temperature was set to 298 K. We assumed a column with a length of L and inner radius of 0.1 m, and the total bed density of zeolite 13X and PCM pellets was set to 650 kg-(ads.&PCM)·m⁻³. In the purge step, we used pure CH₄ gas as the sweeping fluid, and its flow rate was set to 167 slm, which is equivalent to half of that of the feed gas. Before the cyclic operations, the column was purged with pure Ar gas to 100 kPa, and the VPSA cycle, depicted in Fig. 3, was then calculated until the column reached a cyclic steady state. The melting temperature of paraffin wax inside the PCM pellets was set to 305 K. Other properties of the PCM pellets are provided in Table S1, Supporting Information.

To correctly quantify the effect of PCM mixing, the columns with and without the PCM had to be suitably compared. In the present study, this was achieved by comparing the VPSA cycles that could produce CH₄ with the prescribed specifications for use as a fuel gas (purity: 0.98, recovery: 0.8) under the same operating conditions. The

purity, recovery, and productivity of the product were calculated as follows:

$$purity_{CH_4} = \frac{\int_0^{t_{AD}} F_{CH_4}(t, L) dt}{\int_0^{t_{AD}} (F_{CH_4}(t, L) + F_{CO_2}(t, L)) dt}, \quad (2)$$

$$purity_{CO_2} = \frac{\int_0^{t_{BL}} F_{CO_2}(t, 0) dt}{\int_0^{t_{BL}} (F_{CH_4}(t, 0) + F_{CO_2}(t, 0)) dt}, \quad (3)$$

$$recovery_{CH_4} = \frac{\int_0^{t_{AD}} F_{CH_4}(t, L) dt - \int_0^{t_{PU}} F_{CH_4}(t, L) dt}{\int_0^{t_{PR}} F_{CH_4}(t, 0) dt + \int_0^{t_{AD}} F_{CH_4}(t, 0) dt}, \quad (4)$$

$$recovery_{CO_2} = \frac{\int_0^{t_{BL}} F_{CO_2}(t, 0) dt}{\int_0^{t_{PR}} F_{CO_2}(t, 0) dt + \int_0^{t_{AD}} F_{CO_2}(t, 0) dt}, \quad (5)$$

$$productivity_{CH_4} = \frac{1}{m_{ads} t_{cycle}} \left(\int_0^{t_{AD}} F_{CH_4}(t, L) dt - \int_0^{t_{PU}} F_{CH_4}(t, L) dt \right), \quad (6)$$

$$productivity_{CO_2} = \frac{1}{m_{ads} t_{cycle}} \int_0^{t_{BL}} F_{CO_2}(t, 0) dt, \quad (7)$$

where F_i denotes the mole flow rate of species i ; m_{ads} denotes the weight of the adsorbent filled in the column; and t_{PR} , t_{AD} , t_{BL} , and t_{PU} denote the durations of the pressurization, adsorption, blowdown, and purge steps, respectively. Note that the unit of productivity is $\text{mol} \cdot \text{kg-ads.}^{-1} \cdot \text{h}^{-1}$. Considering the setup described in the paragraph above, the remaining design variables include the total cycle time t_{cycle} , column length L , and purge time t_{PU} . Because the operating times are limited by the following equation, only t_{PU} , instead of all the four operating times, can be varied.

$$\frac{t_{cycle}}{2} = t_{PR} + t_{AD} = t_{BL} + t_{PU}. \quad (8)$$

This equation implies that the total duration of the pressurization and adsorption steps must be equal to the sum of the time required for the blowdown and purge steps because the feed gas must flow continuously through one of the two columns. Here, t_{PR} is not a settable value because it denotes the time when the pressure inside the column approaches

the adsorption pressure ($p(z = L) = p_H$), and thus, t_{AD} is also determined by the outcome for a given t_{cycle} . Therefore, t_{PU} (or t_{BL}) is the only variable. Correspondingly, the determination of the three design variables and the subsequent comparison of columns with and without the PCM were accomplished as follows. First, t_{cycle} was set to 500 s as a case study because t_{cycle} determines the number of cycles in annual operating hours, and it is strongly correlated with the sample degradation and replacement frequency; thus, it should be equal for all VPSA cycles for a reasonable comparison. Second, the optimal t_{PU} and L based on which the VPSA cycle can produce the CH_4 product with a purity of 0.98 and a recovery of 0.8 were determined based on a series of calculations for VPSA by varying t_{PU} and L . Finally, the optimized VPSA cycles with different weight fractions of the PCM, ϕ_{PCM} , were compared in terms of the specifications of the CO_2 product, productivity, and column length. In Sections 3.3 and 3.4, details regarding the determination of the optimal t_{PU} and L are presented considering a column without the PCM as an example. Sections 3.5 and 3.6 include the main discussion of this study regarding the effect of PCM mixing.

3. Results and Discussion

3.1. Adsorption isotherms and the Sips model

Fig. 4 shows the obtained adsorption isotherms of CH_4 and CO_2 on zeolite 13X at 263 K, 283 K, and 303 K. The amount of CH_4 adsorbed was approximately 10–20% of that of CO_2 , indicating that most CH_4 flowing into the fixed bed will be recovered as a product. The amount of CO_2 adsorbed at 100 kPa decreased by 19% as the temperature increased by 40 K, suggesting that a considerable loss of work capacity will occur in the adiabatic

VPSA process. To model these adsorption isotherms, we applied the Sips equation owing to its applicability to the IAST. The solid lines in Fig. 4 show the Sips equation fitted to the experimental results, and the parameters are listed in Table 4. The Sips equation accurately describes the pressure and temperature dependence of the adsorption isotherm. Therefore, we used this equation and its parameter Q to calculate the equilibrium adsorbed amount and isosteric heat of adsorption in VPSA simulations. Note that in VPSA simulations, the amount adsorbed at high temperatures and high pressures can be extrapolated, as indicated by the gray lines in Fig. 4, which was validated based on a comparison with other reports [15, 45-49].

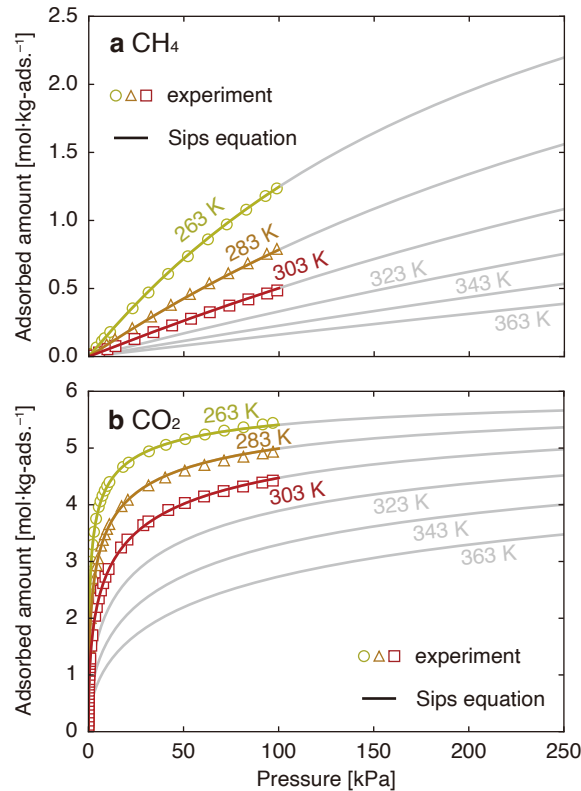


Fig. 4 Adsorption isotherms of (a) CH₄ and (b) CO₂ on zeolite 13X at 263 K, 283 K, and 303 K.

Table 4 Parameters of the Sips equation for CH₄ and CO₂ adsorption on zeolite 13X

		CH ₄	CO ₂
n_{s0}	mol·kg-ads. ⁻¹	4.35	6.2
b_0	Pa ⁻¹	2.26×10^{-6}	1.88×10^{-4}
s_0	-	0.983	2.07
χ	-	0.0	0.012
Q	kJ·mol ⁻¹	18.6	36.0
α	-	0.0	0.202
T_{ref}	K	283	283

3.2. Breakthrough curve measurements and parameter estimation

Fig. 5a,b shows the breakthrough curve and temperature inside the column measured under condition **A**. Immediately after introducing the gas mixture, only Ar, which was filled as an inert gas, flowed out. Next, the mass transfer zone of CH₄ moved faster than that of CO₂ because of the smaller amount of adsorbed CH₄, and CH₄ broke through the column at 128 s. This was also confirmed by the slight increase in temperature by 5 K. On the contrary, the mass transfer zone of CO₂ moved slower accompanied by a significant temperature increase (50 K), which is attributed to a large amount of adsorption and heat of adsorption. After the CO₂ broke through at 926 s, the mole fraction of CO₂ slowly reached 0.5.

The solid lines in Fig. 5a,b shows the calculated breakthrough curves and temperature distributions in condition **A** using the column model. The obtained mass and

heat transfer coefficients are summarized in Table 5. The calculated results accurately reproduced the breakthrough behavior of CH₄ and CO₂ and the temperature trend. In addition, the calculations for conditions **B** and **C** using the parameters obtained from condition **A** and the good agreement achieved with experimental data verified the validity of our model, as shown in Fig. 5c–f. Note that the reproducibility of the melting behavior of PCM was confirmed in our previous study.

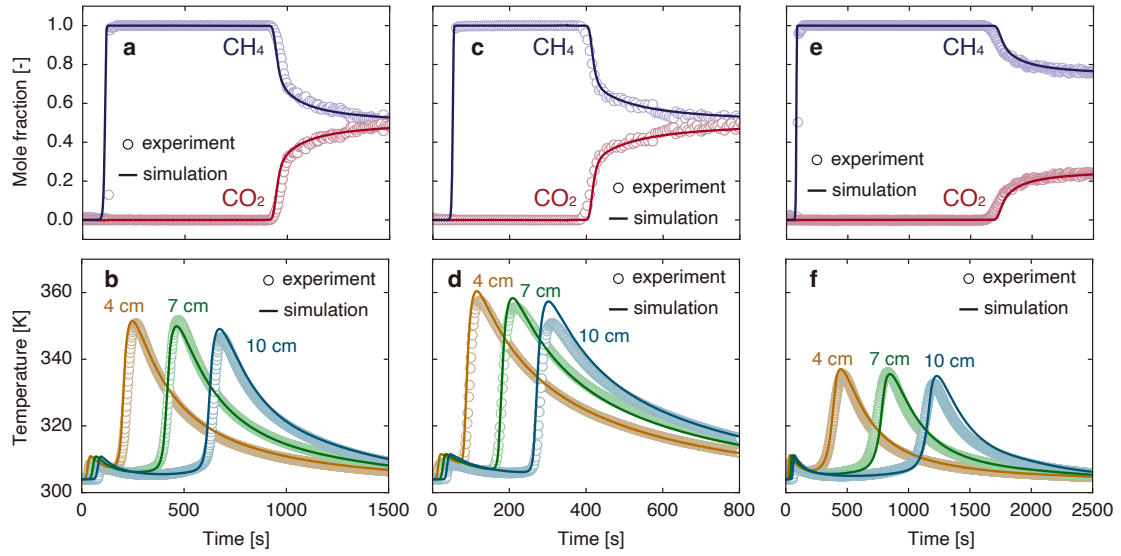


Fig. 5 Experimental and computational results of breakthrough measurements of a CH₄/CO₂ gas mixture on a column packed with zeolite 13X. (a), (c), and (e) are the mole fractions of CO₂ and CH₄ under conditions **A**, **B**, and **C**, respectively; (b), (d), and (f) are the corresponding bed temperatures measured at 4 cm, 7 cm, and 10 cm from the column inlet. Symbols are experimental values and solid lines are calculated values.

Table 5 Estimated mass and heat transfer coefficients

k_{CH_4}	s^{-1}	0.1
k_{CO_2}	s^{-1}	0.4

h_{BW}	$\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$	32
h_{WA}	$\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$	34

3.3. Amount adsorbed and temperature profiles in the column under adiabatic VPSA cycle

In Sections 3.3 and 3.4, we evaluated the adiabatic VPSA processes to examine the effects of the purge time t_{PU} and column length L and establish rules to determine the optimal t_{PU} and L for a reasonable comparison. Note that although only data for VPSA without the PCM are presented here as an example, the optimizations are performed for all VPSA cycles with varying ϕ_{PCM} . This section describes the t_{PU} dependence of the VPSA performance for a fixed L . Fig. 6a–c shows the distributions of the amount of adsorbed CH_4 and CO_2 and the bed temperatures at the end of each step when $L = 1.2$ m and $t_{\text{PU}} = 21.5$ s in which the cyclic steady state was established. The mole fractions of the gas phase in the corresponding states are also depicted in Fig. S1, Supporting Information. In the pressurization step, where the state of the column changed from blue lines to red lines, CO_2 was mainly adsorbed near the column inlet. On the other hand, CH_4 was adsorbed near the outlet of the column rather than the inlet because CO_2 adsorption at the inlet resulted in a higher CH_4 fraction in the gas stream passing through the rear of the column. However, most of the adsorbed CH_4 in the column was released during the adsorption step, which is the state change from red lines to orange lines. Considering the increase in CO_2 adsorption at the rear of the column (orange line in Fig. 6b), the release of CH_4 was caused by the competitive adsorption between CO_2 and CH_4 on zeolite 13X. The adsorption step was terminated just before the CO_2 breakthrough, and hence the purity of the CH_4 product was as high as 0.98. The same could be said for the purity of the CO_2

product recovered in the blowdown step (0.88) as very little CH₄ remained in the column at the end of the adsorption step. However, a considerable amount of CO₂ remained in the column even after the blowdown step, particularly near the inlet, as shown by the blue line in Fig. 6b. This result indicates that the affinity of zeolite 13X to CO₂ is too high to desorb guest molecules and that the temperature near the inlet decreases owing to the endothermic heat of desorption, as shown in Fig. 6c. The purge step (green lines → blue lines) enhanced CO₂ desorption throughout the column, but the state change during this step was less significant than at other steps. Over the entire operation, the temperature near the inlet was less than that of the feed gas, whereas the temperature near the outlet tended to be higher, as shown in Fig. 6c. This temperature fluctuation, which varies from 270 K to 350 K, decreases the working capacity compared with isothermal conditions.

Fig. 6d–f shows the results when t_{PU} is extended from 21.5 s to 50 s. The longer purge step enhanced CO₂ desorption and slowed the movement of the mass transfer zone of CO₂ in the subsequent pressurization and adsorption steps. This enabled us to obtain CH₄ product with a significantly higher purity (0.99). However, a large amount of CH₄ was also adsorbed at the rear of the column after completing the adsorption step as the adsorbent near the outlet was not involved in CO₂ adsorption. Therefore, the remaining CH₄ mixed with the CO₂ product during the blowdown step, thereby decreasing the CO₂ product purity (0.75) and CH₄ product recovery (0.75), failing to satisfy the prescribed criterion.

Fig. 7a,b shows the dependence of t_{PU} on purity and recovery of CH₄ and CO₂. As mentioned above, increasing t_{PU} at a fixed column length enhanced CO₂ desorption, thereby and hence, improved the CH₄ product purity but degraded the CH₄ product recovery and CO₂ product purity. In contrast, a different trend was observed for the

recovery of the CO₂ product, which was convex upward. The trend in the case of a large t_{PU} only reflects the fact that a longer purge time results in a higher amount of CO₂ off-gas generated in the purging process. Contrarily, if the purge time is too short to desorb enough CO₂, CO₂ breaks through the column in the subsequent adsorption process and is mixed with the CH₄ product, resulting in a loss of the CO₂ to be recovered as a product.

For a reasonable comparison in the following discussions, we selected a t_{PU} value that results in CH₄ product purity of 0.98 (21.5 s in this case).

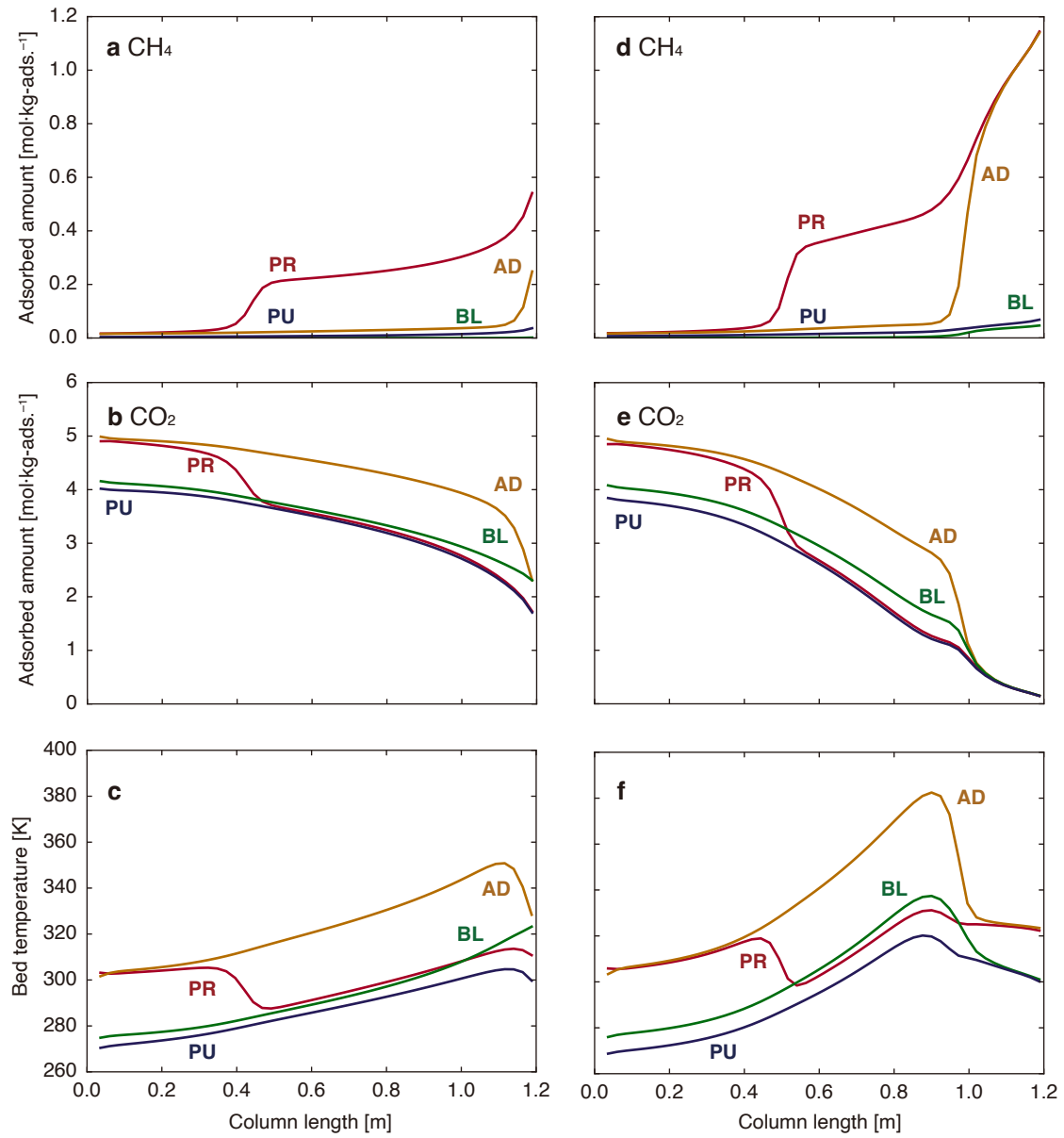


Fig. 6 (a) Adsorbed amount of CH_4 , (b) adsorbed amount of CO_2 , and (c) bed temperature in the column after completing the pressurization (**PR**; red), adsorption (**AD**; orange), blowdown (**BL**; green), and purge (**PU**; blue) steps at a purge time of 21.5 s. (d)–(f) are the results at a purge time of 50 s.

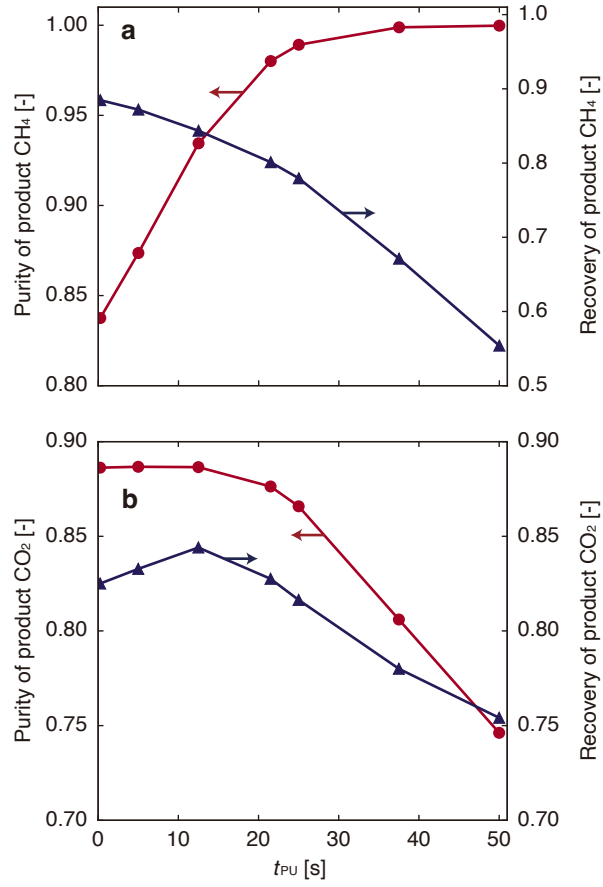


Fig. 7 Separation performances at varying t_{PU} for (a) CH_4 and (b) CO_2 under adiabatic conditions without PCM pellets. Purity (red circle) and recovery (blue triangle).

3.4. Column length optimization

In this section, the optimal L value is determined to meet the other criterion, i.e., the CH_4 product recovery of 0.8. Fig. 8a,b shows changes in the purity and recovery of CH_4 and CO_2 at a varying L . As stated in Section 3.3, the purge time was tuned to achieve CH_4 product purity of 0.98. While the CH_4 product recovery shows a parabolic profile, a trade-off exists between the purity and recovery of the CO_2 product. If the column length is short, that is, the amount of adsorbent packed in the column is low, the CO_2 working capacity per adsorbent must be increased to prevent the CH_4 purity from decreasing below

0.98 owing to CO₂ slipping off the column. This requires a longer purge time to enhance CO₂ desorption, which results in a lower CH₄ product recovery due to the consumption of the CH₄ product and lower recovery of the CO₂ product. Conversely, the purge time can be reduced if the column length is longer. However, there was an area at the rear of the column that mainly adsorbed CH₄ (e.g., Fig. 6d), and these CH₄ molecules contaminated the CO₂ product, decreasing the amount of CH₄ that could be recovered and CO₂ product purity.

In the following discussions, all the VPSA processes are designed to achieve CH₄ product recovery of 0.8. Note that when two conditions satisfy the CH₄ product recovery of 0.8 as shown in Fig. 8, a shorter column was selected in which the purity of the CO₂ product takes precedence over the recovery of the CO₂ product.

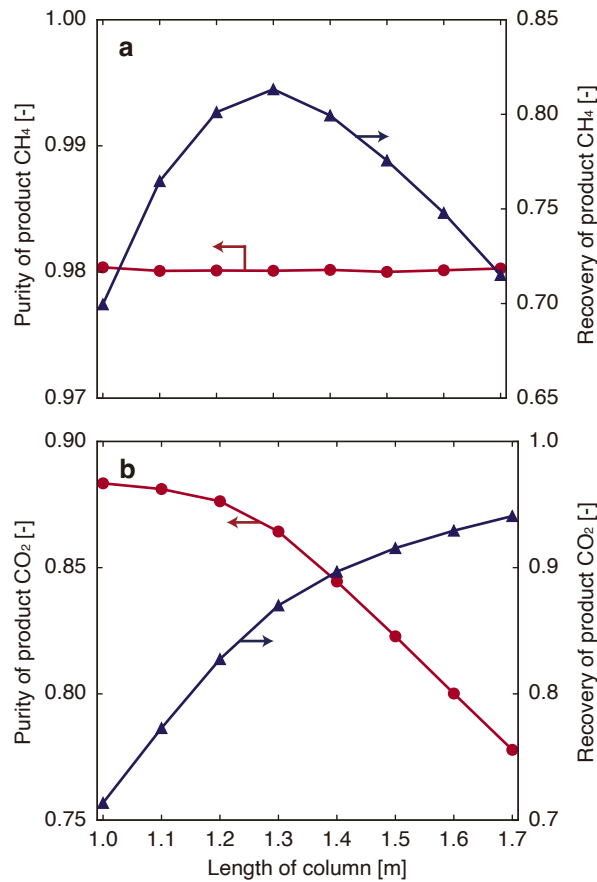


Fig. 8 Purity (red) and recovery (blue) of (a) CH₄ and (b) CO₂ products at varying column lengths under adiabatic conditions without PCM pellets.

3.5. Evaluation of PCM-installed VPSA

Using the developed optimization scheme for t_{PU} and L , we optimized all the VPSA cycles with varying weight fractions of PCM pellets, ϕ_{PCM} . The optimal t_{PU} and L for ϕ_{PCM} satisfying the target specifications for the CH₄ product (purity: 0.98, recovery: 0.80) are illustrated in Fig. 9 and are discussed below. Fig. 10a–c shows the distributions of the adsorbed amount of CH₄ and CO₂ and the bed temperature at $\phi_{PCM} = 0.3$, as a typical example. The major difference in the condition without PCM pellets (Fig. 6) is an abrupt change in the profiles around a column length of 0.8 m caused by melting of PCM. While the adsorbed amount of CH₄ (Fig. 10a), which was originally low, remained almost unchanged, the adsorbed amount of CO₂ (Fig. 10b) increased compared with that without PCM pellets, particularly in the central part of the column. The bed temperature at the center of the column (Fig. 10c) was kept lower than that in the column without PCM pellets (Fig. 6c). The temperature of PCM at this position was 305 K, which is the melting point of PCM, indicating that PCM suppressed the temperature increase due to the heat of adsorption by latent heat. This increase in the adsorbed amount improved the adsorption performance per weight of adsorbent, and the column length increased by only 0.1 m despite a 30 wt% decrease in the amount of adsorbent due to the PCM pellet volume. If we assume that the same amount of adsorbent as in the condition without PCM pellets was packed, the column length would increase by 0.51 m. Furthermore, the productivity, which is the unit adsorbent weight per unit time, increased by 2.2 mol·kg⁻¹·h⁻¹ (see Table

S3, Supporting Information).

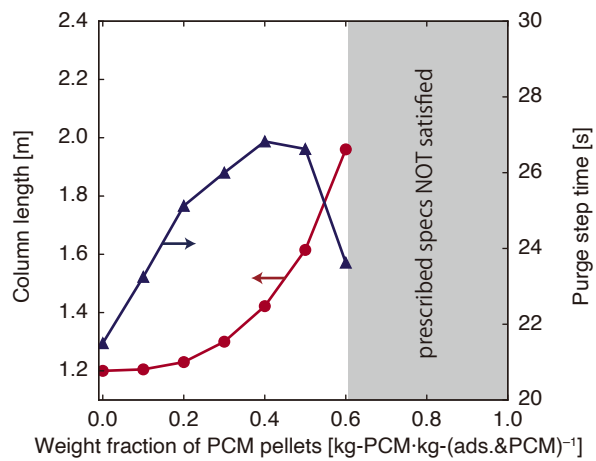


Fig. 9 Column length and purge step time satisfying the CH₄ product specifications.

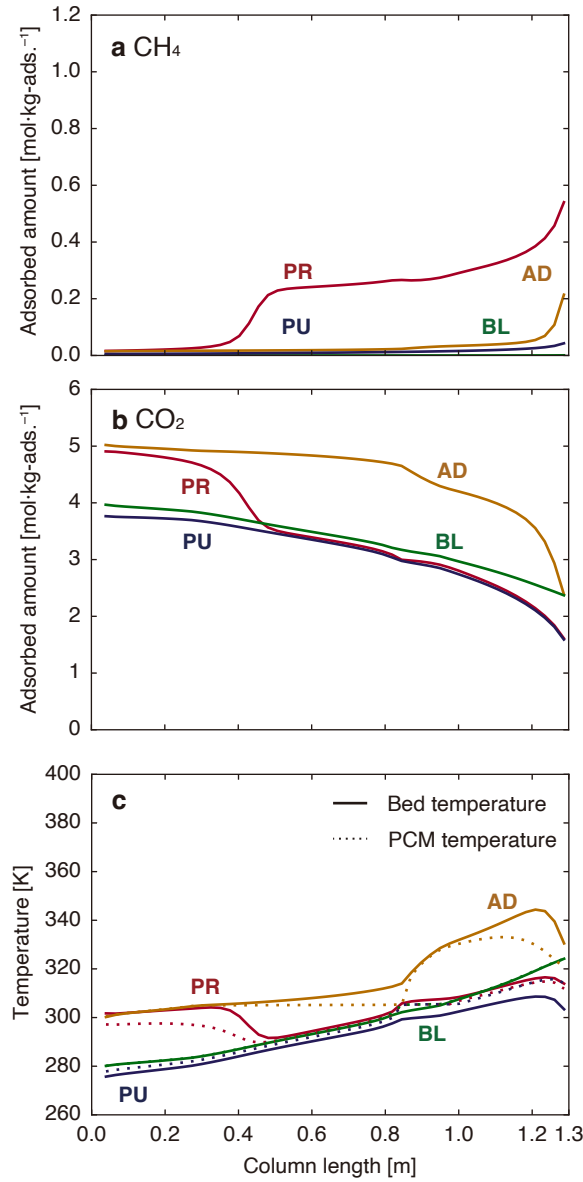


Fig. 10 Adsorbed amount inside the column of (a) CH₄, (b) CO₂, and (c) bed temperature under the condition with PCM pellets at $\phi_{\text{PCM}} = 0.3$ after pressurization (PR; red), adsorption (AD; orange), blowdown (BL; green), and purge (PU; blue) steps.

Fig. 11a,b shows the effects of ϕ_{PCM} on CO₂ product purity, recovery, and productivity for both components. When $\phi_{\text{PCM}} > 0.6$, there were no conditions that satisfied the CH₄ product specifications, that is, purity of 0.98 and recovery of 0.8. Mixing

PCM pellets decreased the amount of adsorbent by bringing the system closer to isothermal condition; however, in most cases, it increased the column length because the increase in the bed volume due to PCM installation exceeded the decrease in the adsorbent. Therefore, the column length at $\phi_{\text{PCM}} > 0.6$ was too long, as shown in Fig. 9, and a large amount of CH_4 remained in the gas phase at the end of the adsorption step, resulting in a significant decrease in the recovery of CH_4 . As shown by the red line in Fig. 11a, the purity of the CO_2 product was improved by increasing ϕ_{PCM} up to 0.4. Because the CO_2 product depends on both components adsorbed at the end of the adsorption step, the purity is influenced by the CO_2 selectivity. In general, the selectivity becomes higher at lower temperatures as the entropy term becomes less important than the energy term, which leads to the improvement. The decrease in the CO_2 purity when $\phi_{\text{PCM}} > 0.4$ was caused by the same factor responsible for the failure in the product specifications when $\phi_{\text{PCM}} > 0.6$; the large amount of CH_4 that remained in the gas phase at the end of the adsorption step contaminated the CO_2 product. At feasible ϕ_{PCM} conditions, the purity of CO_2 product was higher than that in the condition without PCM pellets (at $\phi_{\text{PCM}} = 0$ in Fig. 11), indicating that PCM has a significant effect on the suppression of temperature changes. On the other hand, the trend in the recovery of CO_2 product is slightly complicated, but the key point here is that the CH_4 product specifications, namely purity of 0.98 and recovery of 0.8, regulate the amount of CH_4 flowing out from the column outlet. Therefore, according to material balance, CH_4 must be contained in the off-gas stream in the purge step or in the CO_2 product. As mentioned above, the CO_2 product purity was improved by mixing PCM, which indicates that the amount of CH_4 contaminating the CO_2 product decreased. Therefore, the amount of CH_4 used as the sweeping gas should be higher, as shown by the increased the purge time in Fig. 9, enhancing CO_2 desorption

in the purge step and consequently reducing CO₂ recovery. However, this cannot explain the increase observed when $\phi_{\text{PCM}} > 0.2$, which suggests that another factor should be considered. By carefully analyzing the column, we found that this increase is as a result of mitigating the effect of temperature increase by PCM. That is, the amount of CO₂ recovered in the blowdown step simply increased owing to lower temperatures in the adsorption step and higher temperatures in the blowdown step, thereby improving the CO₂ working capacity per adsorbent weight.

Fig. 11b demonstrates that the productivity of both components increased monotonically as the mixing ratio of PCM increased. From this figure, one may conclude that the more PCM installed, the better the column performance. However, as mentioned earlier, mixing an excessive amount of PCM lengthens the column, and hence, the amount of adsorbent and PCM pellets increases. The best operating condition should be determined through a detailed cost balance including the price of the CH₄ product, which is constant in this comparison, price of the CO₂ product (or carbon tax imposed for the off-gas emission), adsorbent and PCM cost, and duty cost as electric power for vacuum; however, given that the difference between power requirements in this comparison is negligible because the total cycle time and operating pressures are the same, the adsorbent and PCM cost would be dominant in most cases. Therefore, the optimal ϕ_{PCM} value should largely depend on the ratio of adsorbent cost to PCM cost. In the case of zeolite 13X, which is relatively cheaper than PCM, considering that even a small value of $\phi_{\text{PCM}} = 0.1$ can improve the specifications of the CO₂ product with almost no change in the column length, the optimal value will be found to be about a small ϕ_{PCM} . In contrast, if relatively expensive adsorbents such as metal-organic frameworks are used in the future, mixing a large amount of PCM can be expected to provide a cost advantage.

Although the desorption pressure is typically set at 15 kPa for practical use in large-scale processes [44], the effect of the PCM under high-vacuum conditions is also worth investigating. Therefore, we simulated VPSA cycles for $\phi_{\text{PCM}} = 0$ and 0.3 by setting the desorption pressure to 5 kPa. Compared with the results obtained for $p_L = 15$ kPa, in this case, the column length was shortened by 23%, and the purity and recovery of the CO₂ product were improved by 5% because the working capacity increased owing to the high-vacuum level. However, the energy requirement of a vacuum pump at $p_L = 5$ kPa is almost twice that at $p_L = 15$ kPa, considering the work required for the adiabatic expansion of gas. Furthermore, the degree of improvement in the VPSA process resulting from PCM mixing is almost the same, regardless of the desorption pressure (see Fig. S2 and Table S3, Supporting Information). This partially indicates that the above results can be universal, regardless of the operating pressures.

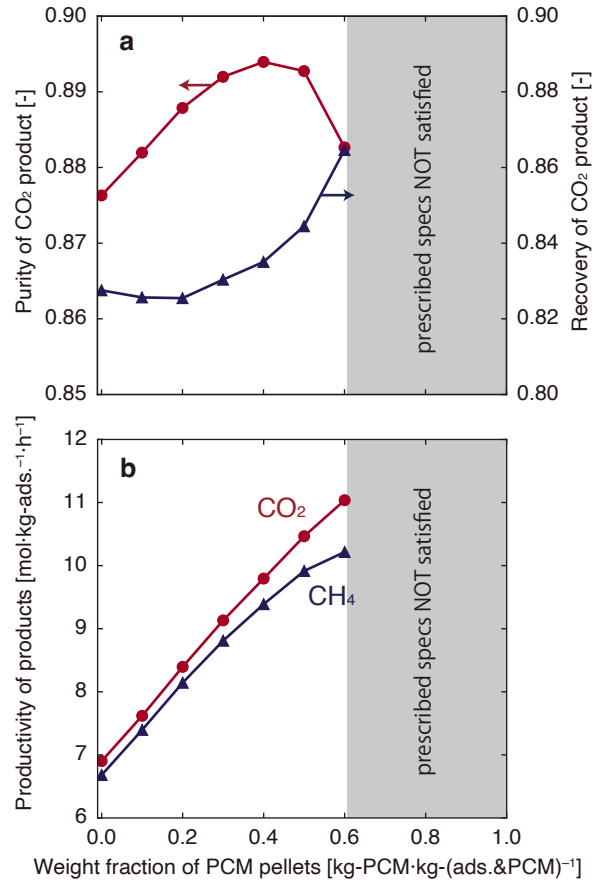


Fig. 11 Effect of the weight fraction of PCM pellets on (a) purity and recovery of CO₂ product and (b) productivities of CO₂ (red circle) and CH₄ products (blue triangle).

3.6. Further improvement of PCM-installed VPSA

As shown in Fig. 10c, the latent heat of PCM works mainly in the center of the column, which leads to two contradictory hypotheses. One is that if the PCM only works near the center of the column, then the PCM should be concentrated only in this area. The other is that the PCM should be concentrated at the front and back of the column to improve performance in ineffective areas. Therefore, we simulated VPSAs in which PCM pellets were mixed locally at the front, center, and rear of the column. Here, the PCM installation area corresponded to 40% of the column length, and ϕ_{PCM} was set to 0.3. Fig. 10a shows

the column length and separation performance, where red bars represent the result when the same amount of PCM was uniformly installed in the entire column ($\phi_{\text{PCM}} = 0.1$) as a benchmark. Compared with the condition without PCM (gray bars), the uniform installation system showed a slightly larger L because the advantages of improved adsorbent performance did not outweigh the disadvantages of increased PCM volume. However, the column length of the center installation system can be reduced by 0.04 m. The separation performance was also higher than that of the uniform installation system. In contrast, neither the front nor the rear installation system can shorten the column, and the separation performance was equal to or slightly inferior to that of the uniform installation system. To determine the reason for this result, we examined the temperature distribution at the end of each step, as shown in Fig. 12b–d. In the case of the front installation system, the PCM temperature fluctuation near the front of the column during one cycle was smaller than that of the system without PCM; however, the temperature did not fluctuate from below to above the melting point of the PCM, indicating that the latent heat of the PCM was hardly utilized. These results demonstrate that to utilize the effect of PCM, that is, to improve the performance of the adsorbent using a minimum amount of PCM, the PCM should be placed only in the center of the column where the PCM temperature fluctuation exceeds the melting point, and hence, latent heat can be effectively used.

This study clarified the function of PCM in VPSA from rigorous process simulations, and in particular, a new fact that the PCM should be concentrated in the center of the column was discovered. However, it should be mentioned that the degree of improvement by adding PCM was not so significant. We believe that this is a result specific to the CH_4/CO_2 separation by zeolite 13X, which adsorbs a large amount of CO_2

even at low pressure and high temperature, and thus, shows a high CO₂ selectivity even when the temperature was increased due to the heat of adsorption. Specifically, the CO₂ selectivity in the entire column at the end of the adsorption step was as high as 133 even without PCM, and a 13% increase to 150 with mixing 40 wt% of PCM had only a trivial effect on the overall process. In addition, the fact that the primary product in the CH₄/CO₂ separation was CH₄, a non-adsorbed gas, and that no restrictions were imposed on the specification of the adsorbed gas product may have obscured the work of PCM. Namely, the latent heat of PCM is considered more effective in processes where the original selectivity is not very high and deterioration of selectivity due to temperature increase is fatal, or those where adsorption gas is the main product and high purity is required.

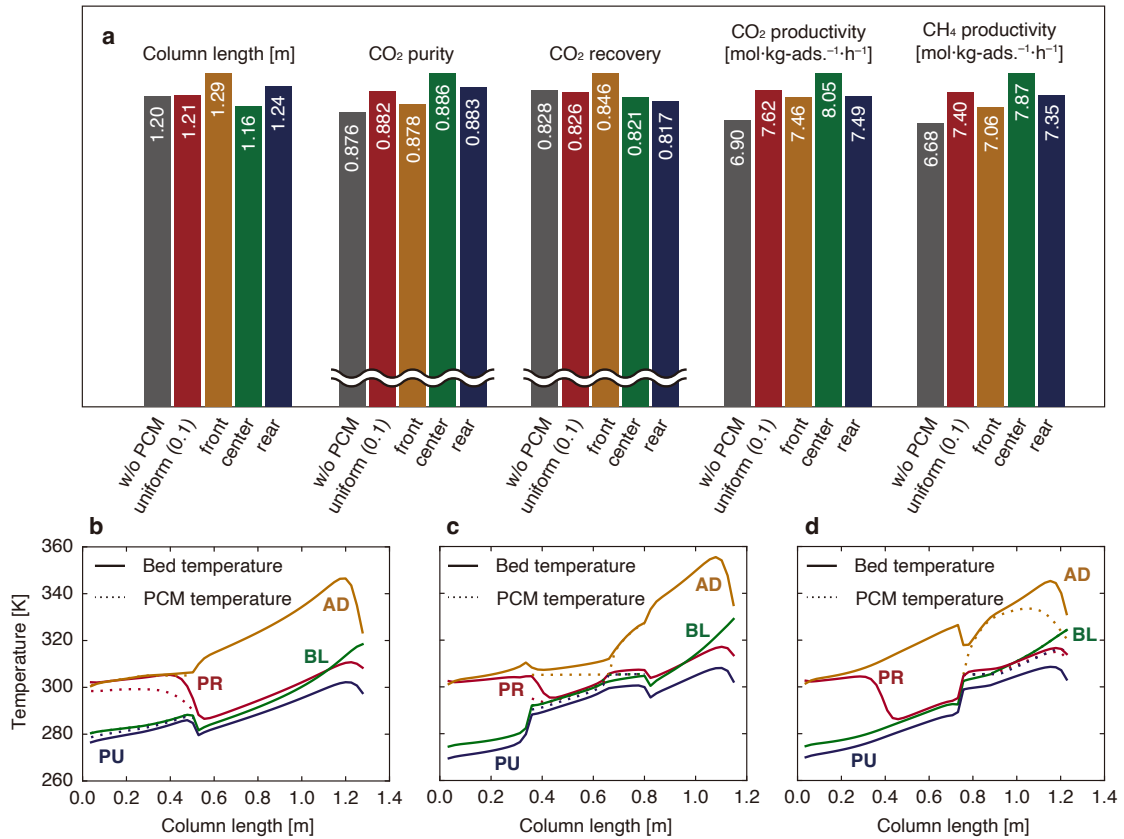


Fig. 12 (a) Separation performances, (b)–(d) temperature distribution under PCM

locally installed conditions after pressurization (**PR**; red), adsorption (**AD**; orange),
blowdown (**BL**; green), and purge (**PU**; blue) steps.

4. Conclusions

We investigated the effect of the latent heat of a PCM on the cyclic operation of VPSA processes used to purify CH_4 and CO_2 from a CH_4/CO_2 mixture using zeolite 13X based on our column model. In this regard, the mass and heat transfer parameters used in the column model were determined by fitting the results obtained from breakthrough curve experiments; accordingly, the model based on these parameters successfully reproduced the breakthrough curves and temperature distributions under three different conditions. In the VPSA simulations, the purge time and column length for each VPSA cycle were first optimized to meet the prescribed specifications of the CH_4 product (purity: 0.98, recovery: 0.8), which was assumed to be used as a fuel gas, and subsequently, VPSA cycles with varying mixing ratios of the PCM were compared. We found that the PCM installed in the center of the column mainly suppressed the temperature increase due to the heat of adsorption during the adsorption step. As the PCM mixing ratio increased, the purity of the CO_2 product increased because the system was closer to isothermal; however, it began to decrease when the PCM mixing ratio exceeded 0.4. This is a result of the column being too long and consequently increasing the amount of CH_4 in the gas phase. That is, the addition of PCM improves the productivity per adsorbent, but the increase in the column length owing to the amount of PCM could be a drawback. To solve this, we proposed a novel method involving the mixing of a PCM in a biased manner. As expected

from the uniform installation system, the system in which the PCM was placed only at the column center worked effectively. As a result, the productivity was improved even in terms of per column volume. Another feasible effective method involves the packing of PCMs with different melting points, such that the PCMs with lower melting points are at the column inlet; relevant research in this direction is currently underway.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Notation

a_w	cross-sectional area of column	$[m^2]$
b_i	affinity constant	$[Pa^{-1}]$
$b_{ref,i}$	reference values of b_i at T_{ref}	$[Pa^{-1}]$
$C_{p,i}$	heat capacity of gas species i	$[J \cdot mol^{-1} \cdot kg^{-1}]$
$C_{p,PW}^l$	heat capacity of paraffin wax in liquid phase	$[J \cdot K^{-1} \cdot kg^{-1}]$
$C_{p,PW}^s$	heat capacity of paraffin wax in solid phase	$[J \cdot K^{-1} \cdot kg^{-1}]$
$C_{p,PR}$	heat capacity of phenolic resin	$[J \cdot K^{-1} \cdot kg^{-1}]$
$C_{p,W}$	heat capacity of column wall	$[J \cdot K^{-1} \cdot kg^{-1}]$

$C_{p,Z}$	heat capacity of zeolite 13X	$[\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}]$
c	total concentration of gas phase	$[\text{mol}/\text{m}^3]$
c_i	gas phase concentration of species i	$[\text{mol}/\text{m}^3]$
c_i^{Feed}	feed gas phase concentration of species i	$[\text{mol}/\text{m}^3]$
c_i^{Purge}	purge gas phase concentration of species i	$[\text{mol}/\text{m}^3]$
D_L	axial dispersion coefficient	$[\text{m}^2/\text{s}]$
D_m	molecular diffusion coefficient	$[\text{m}^2/\text{s}]$
d_p	Sauter mean diameter	$[\text{m}]$
F_i	mole flow rate of species i	$[\text{mol}/\text{s}]$
$\Delta H_{\text{ads},i}$	isosteric heat of adsorption	$[\text{J}/\text{mol}]$
H_i	enthalpy of gas phase of species i	$[\text{J}/\text{mol}]$
H_i^{Feed}	enthalpy of feed gas phase of species i	$[\text{J}/\text{mol}]$
H_i^{Purge}	enthalpy of purge gas phase of species i	$[\text{J}/\text{mol}]$
H_{PW}	enthalpy of paraffin wax	$[\text{J}/\text{kg}]$
$H_{\text{ref,PW}}$	enthalpy of paraffin wax at T_{ref}	$[\text{J}/\text{kg}]$
ΔH_{PW}	latent heat of paraffin wax	$[\text{J}/\text{kg}]$
h_{BW}	heat transfer coefficient between packed bed and column wall	$[\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{K}^{-1}]$
h_{WA}	heat transfer coefficient between column wall and environment	$[\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{K}^{-1}]$
J_i	mole flux of species i	$[\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}]$
k_i	adsorption rate constant	$[\text{s}^{-1}]$
L	column length	$[\text{m}]$
m_{ads}	adsorbent weight	$[\text{kg}]$
n_i	amount adsorbed of species i	$[\text{mol}/\text{kg}]$

n_i^*	equilibrium adsorbed amount of species i	[mol/kg]
$n_{sref,i}$	reference values of $n_{s,i}$ at T_{ref}	[mol/kg]
$n_{s,i}$	saturation capacity of species i	[mol/kg]
p	pressure	[Pa]
p_H	operation pressure in the adsorption step	[Pa]
p_L	operation pressure in the desorption step	[Pa]
Q_i	isosteric heat when fractional loading is 0.5	[J/mol]
R	gas constant	[J·mol ⁻¹ ·K ⁻¹]
r_i	inner radius of column	[m]
r_o	outer radius of column	[m]
s_i	Sips constant characterizing heterogeneity of adsorbent surface	[–]
$s_{ref,i}$	reference values of s_i at T_{ref}	[–]
T_A	ambient temperature	[K]
T_B	bed temperature	[K]
T_m	melting temperature of paraffin wax	[K]
ΔT_m	melting temperature range of paraffin wax	[K]
T_{ref}	reference temperature in Sips equation	[K]
T_{PW}	temperature of paraffin wax	[K]
T_W	temperature of column wall	[K]
t	time	[s]
t_{AD}	operation time in the adsorption step	[s]
t_{BL}	operation time in the blowdown step	[s]
t_{cycle}	total operation time	[s]

t_{PR}	operation time in the pressurization step	[s]
t_{PU}	operation time in the purge step	[s]
U_{BPW}	overall heat transfer coefficient between packed bed and paraffin wax	[J·kg ⁻¹ ·s ⁻¹ ·K ⁻¹]
u	superficial gas velocity	[m/s]
u^{Feed}	superficial gas velocity of feed gas	[m/s]
u^{Purge}	superficial gas velocity of purge gas	[m/s]
y_i	mole fraction of species i	[-]
z	space coordinates	[m]

Greek Letters

α_i	constant parameter of species i	[-]
ε_B	bed void fraction	[-]
ε_T	overall void fraction	[-]
θ_{PW}	weight fraction of paraffin wax	[-]
λ_B	axial thermal conductivity of packed bed	[J·m ⁻¹ ·s ⁻¹ ·K ⁻¹]
λ_W	axial thermal conductivity of column wall	[J·m ⁻¹ ·s ⁻¹ ·K ⁻¹]
μ	dynamic viscosity of fluid	[Pa·s]
ξ	pressure decreasing rate parameter in the blowdown step	[-]
ρ	density of fluid	[kg/m ³]
ρ_B	bed density	[kg/m ³]
$\rho_{P,Z}$	particle density of activated carbon	[kg/m ³]
$\rho_{M,Z}$	material density of activated carbon	[kg/m ³]

$\rho_{P,PCM}$	particle density of PCM	[kg/m ³]
ϕ_{PCM}	weight fraction of PCM	[–]
χ_i	constant parameter of species i	[–]

Appendix A. Supplementary data

The following is the Supplementary data to this article:

link

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