



Assessment of TVSA Cycle Configurations for Cooperative Adsorbents with Step-Shaped Isotherms under Direct Air Capture

Introduction

Rising atmospheric CO₂ concentrations continue to drive significant changes in the global climate system, making carbon removal a critical component of climate mitigation strategies. Atmospheric CO₂ levels have increased from approximately 180 ppm during pre-industrial glacial periods to 427.87 ppm in July 2025 (Lan, 2025). Although conventional carbon capture technologies targeting point sources such as power plants and industrial facilities play an important role, they can address only a portion of total emissions. Emissions from diffuse sources and the historically accumulated CO₂ already present in the atmosphere remain largely unmitigated, highlighting the need for complementary carbon removal technologies (Nasiri-ghiri et al., 2026)

Direct Air Capture (DAC) has therefore emerged as a promising approach for removing CO₂ directly from ambient air, independent of emission source location, and enabling permanent removal when coupled with storage or utilisation pathways (Lackner et al., 1999). Several DAC technologies have been proposed, including absorption, adsorption, membrane separation, and cryogenic processes. Among these, adsorption-based DAC systems have gained increasing attention due to their relatively low energy requirements, operational simplicity, modularity, and suitability for low-concentration CO₂ streams (Aghaie et al., 2018).

The performance of adsorption-based DAC systems is strongly governed by the properties of the sorbent material and the design of the adsorption-desorption cycle. Amine-functionalised metal-organic frameworks (MOFs), particularly mmen-Mg₂(dobpdc), have been widely studied due to their cooperative CO₂ adsorption mechanism and high selectivity at ultra-dilute CO₂ concentrations (McDonald et al., 2012). However, the stepped adsorption isotherm and kinetic behaviour of this material can significantly influence process performance under realistic DAC conditions, underscoring the importance of integrated process-level evaluation rather than material-level assessment alone (Darunte et al., 2019). In this work, a one-dimensional temperature-vacuum swing adsorption (TVSA) model is developed in Aspen Adsorption V14 to investigate the effect of process cycle design on the performance of mmen-Mg₂(dobpdc)-based DAC systems. The model incorporates coupled mass, energy, and momentum balances and is validated against experimental data. Different TVSA process configurations are examined, including a single bed-heating step applied after vacuum desorption and a two-stage heating strategy applied before and after the vacuum step. Process performance is assessed in terms of CO₂ purity, recovery, and energy consumption. The results demonstrate that the single-stage heating configuration achieves higher CO₂ recovery at comparable purity while requiring lower energy input, indicating a more energy-efficient pathway for adsorption-based DAC operation.

Methodology

To evaluate the impact of process cycle design on product purity and sorbent regeneration performance, a packed-bed adsorption reactor was modelled based on experimental parameters reported by (Darunte et al., 2019), DAC conditions. The air feed was defined at 1.1013 bar and 23 °C, with a molar composition of 99.96% N₂ and 0.04% CO₂, where CO₂ was considered the only adsorbing species.

CO₂ adsorption on mmen-Mg₂(dobpdc) was described using the Sips isotherm model to capture the cooperative stepped adsorption behaviour of the sorbent. To accurately represent adsorption kinetics across different operating regimes, two pressure-dependent kinetic models were employed: a linear driving force (LDF) model for CO₂ partial pressures below the step pressure (P_{step}), and an Avrami fractional-order kinetic model for pressures above P_{step} .

The dynamic behaviour of the TVSA process was simulated using a one-dimensional, non-isothermal model incorporating coupled mass, momentum, and energy conservation equations. The model was implemented in Aspen Adsorption V14 to capture the transient adsorption-desorption behaviour of the packed bed and was validated against experimental data reported in the literature (Ghiri et al., 2025).

The base-case TVSA cycle considered in this study includes five sequential steps: (i) adsorption, during which ambient air passes through the bed and CO₂ is selectively adsorbed while CO₂-depleted air exits the column; (ii) evacuation, where system pressure is reduced to remove residual N₂; (iii) combined



heating and evacuation, in which the bed is heated via an external heat exchanger under vacuum to promote CO₂ desorption; (iv) cooling, applied to stabilise the bed temperature, mitigate amine degradation, and prepare the sorbent for the subsequent adsorption step; and (v) pressurisation, where the column is returned to atmospheric pressure by controlled air introduction to initiate the next cycle. The primary distinction between the two configurations lies in the strategy used for N₂ removal from the bed. In the base-case cycle, nitrogen and residual air are removed exclusively through vacuum evacuation. In contrast, the modified cycle employs a two-step strategy for N₂ removal. First, moderate preheating is applied to expand the gas phase and promote partial desorption of light components, primarily N₂. Subsequently, vacuum pressure is applied to remove the expanded gas mixture from the bed. Final CO₂ desorption and sorbent regeneration are then achieved at a higher temperature under vacuum conditions.

Based on this modified N₂ removal strategy, a second TVSA configuration comprising six steps was developed by introducing an additional preheating stage before vacuum application. The durations of each step for both configurations are summarised in *Table 1*. Identical initial conditions and operating parameters were applied to the base-case and modified cycles to ensure a fair and consistent comparison.

Table 1. Comparison of cycle duration in the TVSA model with and without the preheating stage

Cycles of Process	Unit	Preheat TVSA Duration(modified)	TVSA Duration (Base)
Adsorption	s	7200	7200
Preheating	s	720	0
Evacuation	s	6	6
Heating+Evacuation	s	2000	2000
Cooling	s	The temperature matched the feed temperature	The temperature matched the feed temperature
Pressurising	s	Pressure matched the atmospheric pressure	Pressure matched the atmospheric pressure

The performance of the base-case and modified TVSA cycles was evaluated using key process indicators, namely CO₂ recovery, product purity, and specific energy consumption. The definitions and calculation methods for these metrics are provided in *Table 2* and were used to enable a consistent and quantitative comparison of separation efficiency and energy requirements between the two process configurations.

Table 2. Formulas for performance indicators.

Performance Indicators	Unit	Formula
CO ₂ Purity	%	$\frac{\int_0^{t_{\text{cycle}}} F_{\text{product}} y_{\text{CO}_2} dt}{\sum_{i=1}^m \int_0^{t_{\text{cycle}}} F_{\text{product}} y_i dt}$
Recovery	%	$\frac{\int_0^{t_{\text{cycle}}} (y_{\text{product,CO}_2} F_{\text{product}} _{z=L}) dt}{\int_0^{t_{\text{cycle}}} (y_{\text{feed,CO}_2} F_{\text{feed}} _{z=0}) dt}$
SEC (vacuum)	MJ/Kg CO ₂	$\frac{\int_0^{t_{\text{cycle}}} \frac{F_{\text{vac}} P_{\text{vac}} Y}{\eta(\gamma - 1)} \left[\left(\frac{P_{\text{feed}}}{P_{\text{vac}}} \right)^{1-\frac{1}{\gamma}} - 1 \right] dt}{\int_0^{t_{\text{cycle}}} F_{\text{product}} y_{\text{product,CO}_2} dt}$

Results

Model Accuracy and Validation

Breakthrough experiments provide a direct and sensitive means of assessing the accuracy of both equilibrium and kinetic models under dynamic operating conditions. Unlike static adsorption isotherm measurements, breakthrough curves capture the transient interplay between mass transfer, adsorption



thermodynamics, and flow hydrodynamics, which is essential for the reliable simulation of TVSA processes. This is particularly important for sorbents such as mmen-Mg₂(dobpdc), which exhibit cooperative, step-shaped adsorption behaviour. In such systems, the breakthrough response directly reflects the abrupt CO₂ uptake mechanism and the propagation of the adsorption front within the packed bed. Consequently, accurate reproduction of experimental breakthrough behaviour is a critical prerequisite for establishing model reliability and predictive capability under DAC conditions.

Figure 1 presents the validation of the simulated CO₂ breakthrough performance against experimental data, obtained at 23 °C and a volumetric flow rate of 17.2 N mL/min. The predicted breakthrough time deviates from the experimental value by approximately 3%, with a coefficient of determination (R^2) of 0.9756, demonstrating good agreement between model predictions and experimental observations. These results confirm that the developed model accurately captures the dynamic adsorption behaviour of mmen-Mg₂(dobpdc) and is suitable for subsequent TVSA cycle simulations and process-level performance analysis.

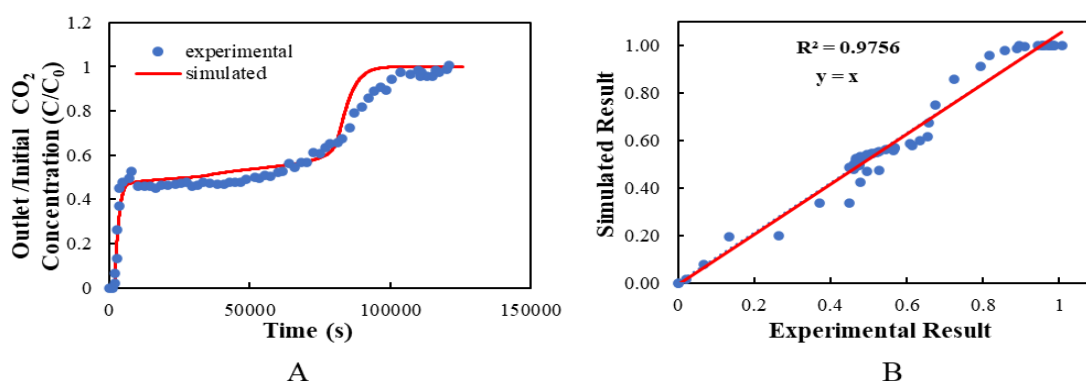


Figure 1 (A) Breakthrough curve fitting at 23 °C and flow rate of 17.2 N ml/min, (B) Error estimation between experimental and simulated breakthrough points.

Impact of Cycle Configuration on DAC Performance

The performance of the standard 5-step TVSA cycle was compared against the preheating-enhanced configuration under DAC conditions across two vacuum pressure levels. As illustrated in Figure 2, the introduction of a preheating step before the vacuum stage did not yield the anticipated improvements in CO₂ purity. Instead, the modified cycle resulted in a notable decline in recovery and a simultaneous increase in SEC.

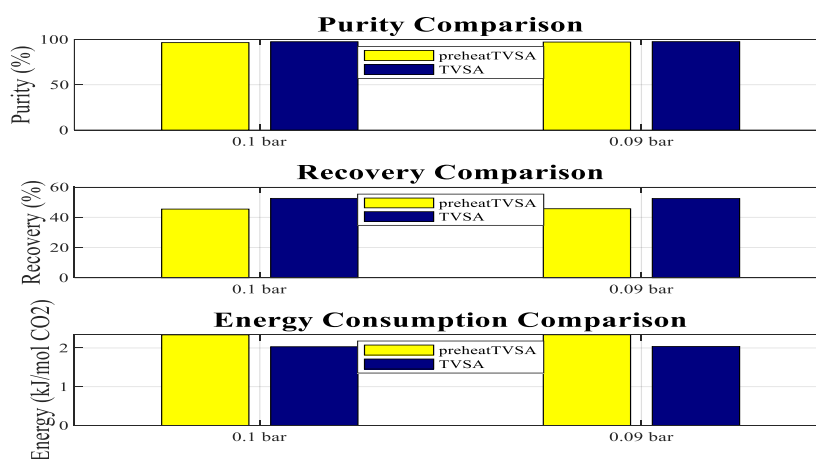


Figure 2. Comparison of two scenarios - with and without preheating - in terms of CO₂ purity, recovery, and specific energy consumption.

The rise in SEC is primarily driven by the additional thermal duty required to provide sensible heat during the preheating phase, which increases the total heat duty of the regeneration process without a corresponding gain in productivity. Furthermore, the observed reduction in recovery suggests that a



significant portion of the adsorbed CO₂ was prematurely desorbed and removed along with N₂ during the preheating stage. This observation is particularly noteworthy as it deviates from established trends for other DAC adsorbents. For instance, (Deschamps et al., 2022) successfully utilised preheating with amine-functionalised nano-fibrillated cellulose to enhance CO₂ purity by improving the removal of N₂ and O₂ from the bed in DAC conditions. The efficacy of preheating in this study relies on the typical adsorption behaviour of conventional materials, where a clear energy gap exists between N₂ physisorption and CO₂ chemisorption. In contrast, the performance degradation observed in this work is intrinsically linked to the unique cooperative, step-shaped adsorption mechanism of mmen-Mg₂(dobpdc). Unlike Langmuir-type adsorbents, this MOF undergoes a phase-change-like transition that is highly sensitive to temperature. As the bed temperature rises during the preheating phase, the threshold pressure required to maintain CO₂ on the adsorbent sites (the step position) shifts rapidly. Because this shift occurs at even moderate temperatures, the CO₂ begins to desorb at the partial pressures typical of DAC conditions before the vacuum stage is even initiated. Consequently, the CO₂ is purged from the system and lost.

Conclusion

A one-dimensional TVSA model was developed and validated to evaluate the impact of process cycle design on the performance of mmen-Mg₂(dobpdc)-based direct air capture systems. The results demonstrate that incorporating a preheating step in the TVSA cycle for this sorbent may be counterproductive, as observed through increased energy consumption and reduced CO₂ recovery. This performance decline is linked to the cooperative step-shaped mechanism, which appears to trigger premature CO₂ desorption at moderate temperatures. These findings indicate that standard cycle configurations optimised for conventional materials may not be directly transferable to phase-change MOFs. Consequently, effective DAC cycle design requires explicit consideration of the distinct thermodynamic sensitivities of these materials.

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