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

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Summary

As Direct Air Capture (DAC) becomes essential for climate mitigation, optimising process-level performance for advanced adsorbents is critical. This study investigates the impact of cycle configuration on the performance of mmen-Mg2(dobpdc), a metal-organic framework with a unique cooperative, step-shaped adsorption mechanism. A one-dimensional temperature-vacuum swing adsorption (TVSA) model was developed in Aspen Adsorption V14 and validated against experimental breakthrough data (R2 = 0.9756). The study compares a standard 5-step TVSA cycle with a modified configuration incorporating a preheating stage before the vacuum stage to enhance product purity.

Contrary to established trends for conventional adsorbents, results indicate that preheating is counterproductive for this phase-change MOF. The modified cycle resulted in significantly lower CO2 recovery and higher specific energy consumption (SEC) without improving purity. This degradation is attributed to the material's steep temperature sensitivity; heating before evacuation triggers a rapid shift in the step position, causing premature CO2 desorption and loss at atmospheric pressure. These findings suggest the need for specialised cycle strategies tailored to the unique thermodynamic characteristics of phase-change materials.

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Introduction

Rising atmospheric CO_2 concentrations continue to drive significant changes in the global climate system, making carbon removal a critical component of climate mitigation strategies. Atmospheric CO_2 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 CO_2 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 CO_2 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 CO_2 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-Mg_2(dobpdc), have been widely studied due to their cooperative CO_2 adsorption mechanism and high selectivity at ultra-dilute CO_2 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-Mg_2(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 CO_2 purity, recovery, and energy consumption. The results demonstrate that the single-stage heating configuration achieves higher CO_2 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 ºC, with a molar composition of 99.96% N_2 and 0.04% CO_2, where CO_2 was considered the only adsorbing species.

CO_2 adsorption on mmen-Mg_2(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 CO_2 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 CO_2 is selectively adsorbed while CO_2-depleted air exits the column; (ii) evacuation, where system pressure is reduced to remove residual N_2; (iii) combined

heating and evacuation, in which the bed is heated via an external heat exchanger under vacuum to promote CO_2 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 N_2 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 N_2 removal. First, moderate preheating is applied to expand the gas phase and promote partial desorption of light components, primarily N_2. Subsequently, vacuum pressure is applied to remove the expanded gas mixture from the bed. Final CO_2 desorption and sorbent regeneration are then achieved at a higher temperature under vacuum conditions.
Based on this modified N_2 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 CO_2 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	%	$\frac{\int_0^{t_{cycle}} F_{product}\, y_{CO_2} dt}{\sum_{i=1}^{m} \int_0^{t_{cycle}} F_{product}\, y_i dt}$
Recovery	%	$\frac{\int_0^{tcycle} (y_{product,CO_2} F_{product}\big\vert_{z=L}) dt}{\int_0^{tcycle} (y_{feed,CO_2} F_{feed}\big\vert_{z=0}) dt}$
SEC (vacuum)	MJ/Kg CO_2	$\frac{\int_0^{t_{cycle}} \frac{F_{vac} P_{vac} \gamma}{\eta(\gamma-1)} \left[(\frac{P_{feed}}{P_{vac}})^{1-\frac{1}{\gamma}} - 1 \right] dt}{\int_0^{t_{cycle}} F_{product}\, y_{product,CO_2} dt}$

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-Mg_2(dobpdc), which exhibit cooperative, step-shaped adsorption behaviour. In such systems, the breakthrough response directly reflects the abrupt CO_2 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 CO_2 breakthrough performance against experimental data, obtained at 23 ºC 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-Mg_2(dobpdc) and is suitable for subsequent TVSA cycle simulations and process-level performance analysis.

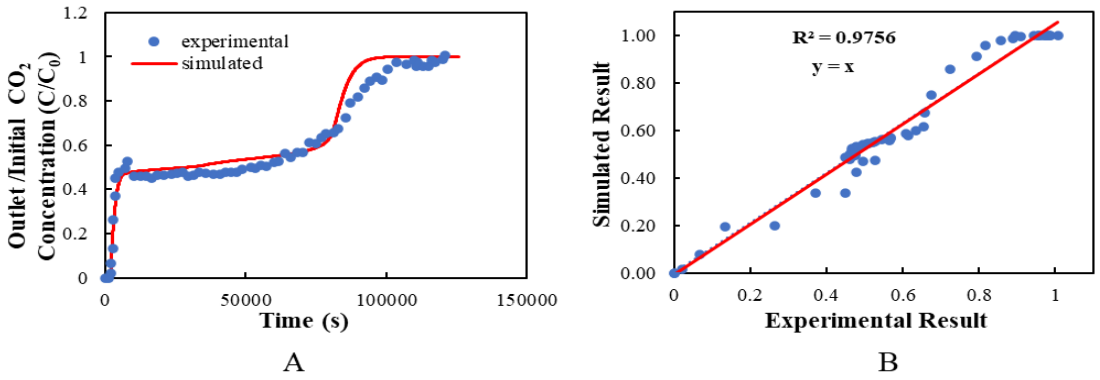

Figure 1 (A) Breakthrough curve fitting at 23 ºC and flow rate of 17.2 N ml/min, (B) Error estimation between experimental and simulated breakthrough points.

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 CO_2 purity. Instead, the modified cycle resulted in a notable decline in recovery and a simultaneous increase in SEC.

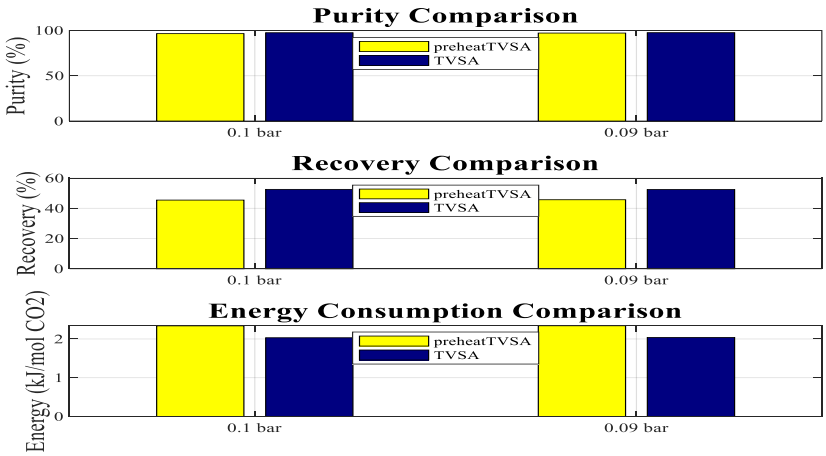

Figure 2. Comparison of two scenarios - with and without preheating - in terms of CO_2 purity, recovery, and specific energy consumption.

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 CO_2 was prematurely desorbed and removed along with N_2 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 CO_2 purity by improving the removal of N_2 and O_2 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 N_2 physisorption and CO_2 chemisorption. In contrast, the performance degradation observed in this work is intrinsically linked to the unique cooperative, step-shaped adsorption mechanism of mmen-Mg_2(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 CO_2 on the adsorbent sites (the step position) shifts rapidly. Because this shift occurs at even moderate temperatures, the CO_2 begins to desorb at the partial pressures typical of DAC conditions before the vacuum stage is even initiated. Consequently, the CO_2 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-Mg_2(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 CO_2 recovery. This performance decline is linked to the cooperative step-shaped mechanism, which appears to trigger premature CO_2 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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