How Adsorbent Thermodynamics Shape Direct Air Capture Performance: A Global Sensitivity Study

Introduction

The deployment of carbon capture technologies at scale is essential to achieving global climate targets, particularly for mitigating emissions from hard-to-abate sectors and enabling negative emissions through direct air capture (DAC). Among the available capture routes, adsorption-based processes have attracted significant attention due to their potential for low energy consumption, modularity, and compatibility with low-concentration CO_2 streams (Ben-Mansour et al., 2016). In this technology adsorbent materials play a decisive role in determining process efficiency, as their thermodynamic and kinetic properties directly influence productivity, energy requirements, and overall cyclic performance (Li et al., 2022) . Identifying which material characteristics are most critical remains a major challenge, particularly for advanced adsorbents with non-linear adsorption behaviour.

Step-shaped or cooperative adsorption materials, including diamine-functionalised metal-organic frameworks like mmen-Mg_2(dobpdc), offer exceptional promise due to their sharp uptake transitions at low CO_2 partial pressures(Mcdonald, 2015; McDonald et al., 2012). This unique behaviour can enhance working capacity and reduce regeneration energy; however, the highly non-linear nature of these isotherms complicates traditional design and optimisation approaches. Systematic understanding of how individual isotherm parameters affect process performance is still limited, constraining the rational development of next-generation adsorbents.

Global Sensitivity Analysis (GSA) provides a systematic way to quantify the influence of input parameters across their full range of uncertainty, accounting for interactions and non-linear effects. By applying GSA to the isotherm parameters of mmen-Mg_2(dobpdc) within a cyclic adsorption process, it is possible to reveal which material properties dominate performance metrics such as CO_2 capture efficiency, energy consumption, and cycle productivity. This insight supports process-informed material design, offering a pathway to optimise adsorbents not only for equilibrium capacity but for overall process effectiveness. Luukkonen and Elfving used global sensitivity analysis and dynamic temperature vacuum swing adsorption (TVSA) and steam assistant TVSA simulations to identify key parameters controlling DAC performance and cost, providing guidance for adsorbent design under atmospheric CO_2 conditions (Luukkonen & Elfving, 2024). Additionally, simulation-based approaches reduce the need for expensive and time-consuming experimental procedures.

This study applies GSA to systematically link the material properties of a step-isotherm adsorbent with process performance, based on high-fidelity TVSA process modelling under direct air capture conditions, providing guidance for targeted adsorbent development and advancing the integration of material science with process-level engineering for CO_2 capture.

Methodology

A one-dimensional TVSA process model was developed to represent a fixed-bed adsorption column operating under DAC conditions using Aspen Adsorption. The key geometric and operating specifications of the model are available in (Ghiri et al., 2025). The model predicts key process performance indicators, including CO_2 purity, CO_2 productivity, and specific energy consumption (SEC), which are commonly used metrics for evaluating DAC systems. These performance indicators are calculated by formula 1-3. The equilibrium adsorption behaviour of CO_2 on the adsorbent is described using the step-shaped Sips isotherm model proposed by (Darunte et al., 2019) , which present in Figure 1. This isotherm model captures the cooperative adsorption mechanism characteristic of diamine-functionalised metal-organic frameworks, specifically mmen-Mg_2(dobpdc). This formulation enables accurate representation of the sharp adsorption transition observed at low CO_2 partial pressures relevant to DAC. The overall modelling framework, including transport assumptions, cycle configuration, and numerical implementation, has been previously validated against experimental data, showing close agreement across a wide range of operating conditions (Ghiri et al., 2025). Therefore, the present study focuses on parametric variation and sensitivity analysis rather than further model validation. Three key isotherm parameters are selected for investigation: (i) the step pressure at

reference temperature (P_{step0}), which governs the induction region of adsorption;(ii) the enthalpy change associated with the cooperative adsorption step (ΔH_{High}), which influences the position and sharpness of the transition zone and (iii) the high-loading saturation capacity (q_H), which determines the capacity in the saturation region. These parameters define distinct regions of the step-shaped isotherm (Figure 2) and were systematically varied to quantify how changes in adsorbent thermodynamic properties propagate to process-level performance metrics. This approach enables the identification of parameter domains that offer the greatest potential for enhancing DAC process performance.

$$b_U = b_{L0}\exp\left(\frac{\Delta H_L}{RT_g}\right)$$
$$\sigma = \lambda_1 \exp[\lambda_2\left(\frac{1}{T_0}-\frac{1}{T_g}\right)]$$
$$n = n_0 \exp(\frac{\Delta H_{Ln}}{RT_g})$$
$$q_U = q_{u0}\exp\left(\frac{\Delta H_u}{RT_g}\right)$$
$$b_H = b_{H0}\exp(\frac{\Delta H_H}{RT_g})$$

- $q_{total} = q_1^* + q_2^*$
- $q_1^* = q_{low} \times (1-w) + q_{sat} \times w$
- $q_2^* = (q_{high} - q_{sat}) \times w$
- $q_{low} = \frac{q_L(b_{LP})^{n_L}}{1+(b_{LP})^{n_L}}$
- $q_{high} = \frac{q_H b_{HP}}{1+b_{HP}} + q_U p \qquad p < p_{step}$
- $q_{sat} = \frac{q_L(b_{LPstep})^n}{1+(b_{LPstep})^n} \qquad p > p_{step}$
- $w = [\frac{\exp(\frac{\log(p)-\log(p_{step})}{\sigma})}{1+\exp(\frac{\log(p)-\log(p_{step})}{\sigma})}]^\gamma$

Parameters	Unit	Value	Parameters	Unit	Values
q_L	mol/Kg	28.25	ΔH_{step}	KJ/mol	-62.49
b_{L0}	1/bar	2.51e-15	ΔH_L	KJ/mol	70.74
n_0	-	0.518	ΔH_n	KJ/mol	1.35
q_H	mol/Kg	3.46	ΔH_H	KJ/mol	67.72
b_{H0}	1/bar	2.42e-11	ΔH_u	KJ/mol	18.67
q_{u0}	mol/Kg.bar	5.27e-4	λ_1	-	1.74e-2
Y	-	4	λ_2	1/°K	6.53

Figure 1: *Sips isotherm model equations and the corresponding parameter values used in the TVSA simulations.*

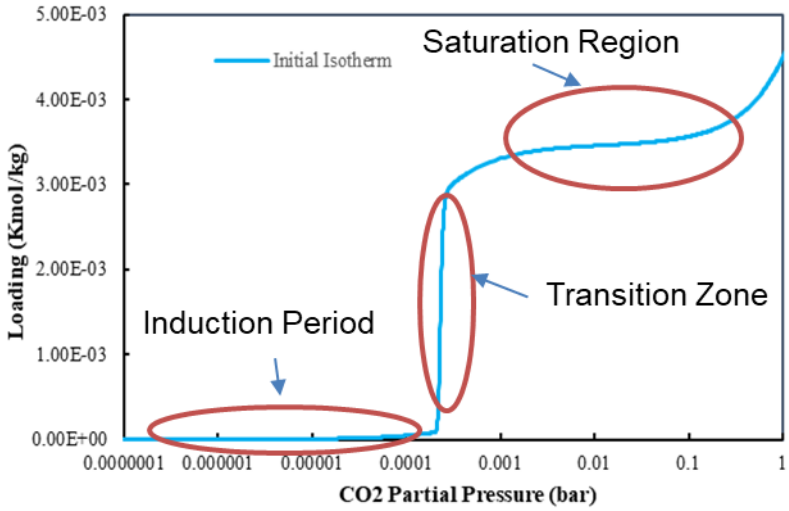

Figure 2: *Step-shaped adsorption isotherm for mmen-Mg_2(dobpdc) with distinct regions identified: induction, transition, and saturation.*

A variance-based global sensitivity analysis (GSA) was performed using the Sobol method to quantify the contribution of the selected isotherm parameters to variability in DAC process performance. The three parameters (P_{step0}, ΔH_{High}, and q_H) were treated as uncertain inputs and sampled within physically realistic ranges derived from literature data and experimental constraints (Table ---). The resulting parameter combinations were evaluated in terms of key performance indicators, including productivity and specific energy consumption (SEC), subject to a CO_2 purity constraint of ≥ 98%. The Sobol indices were then used to determine how variations in each parameter, individually and through interaction

effects, influence process performance. This analysis enabled the identification of parameter regions associated with improved performance under DAC operating conditions.

Table 1: Parameter values and ranges used for the global sensitivity analysis (GSA).

Parameters	ΔH_{High}	q_H	P_{step0}
Initial Value	67720	0.00346	8e-4
Upper Bond	74490	0.00432	12e-4
Lower Bond	60948	0.00259	4e-4

Results

The Sobol analysis quantifies the relative contribution of each parameter to performance variability. Among the three investigated parameters, ΔH_{High} exhibits the highest first-order sensitivity index for productivity and SEC, indicating that the enthalpy associated with the cooperative adsorption step is the dominant driver of process performance under DAC conditions. Table 2 summarises the second-order (interaction) effects between parameters, revealing that the strongest interaction for productivity occurs between ΔH_{High} and q_H, whereas for SEC the most significant interaction is observed between P_{step0} and ΔH_{High}. These results indicate that simultaneous variations of these parameter pairs have the largest combined impact on the corresponding performance metrics.

***Table 2**: Second-order Sobol indices for the isotherm parameters affecting DAC process performance.*

Parameters	Productivity	SEC
P_{step0}-ΔH_{High}	0.01442	0.02906
P_{step0} - q_H	0.008623	0.01293
ΔH_{High} - q_H	0.05091	0.01082

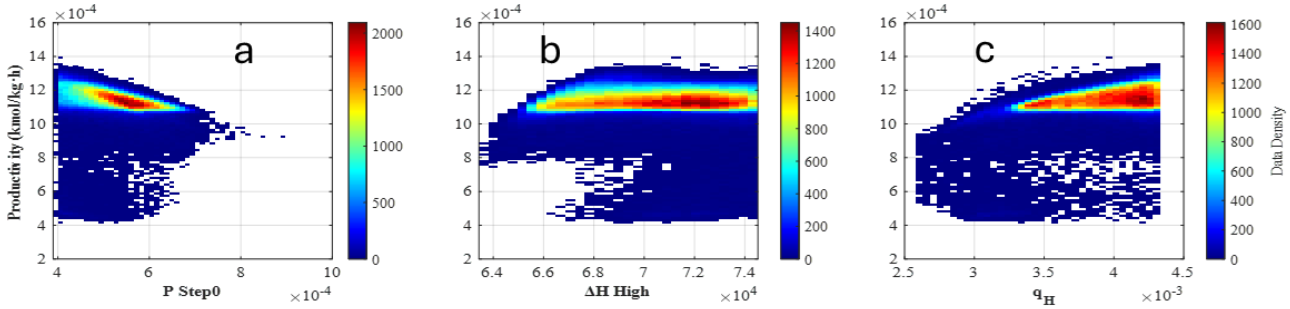

***Figure 3**. Effect of isotherm parameters on productivity under DAC conditions (CO_2 purity ≥ 98%).*

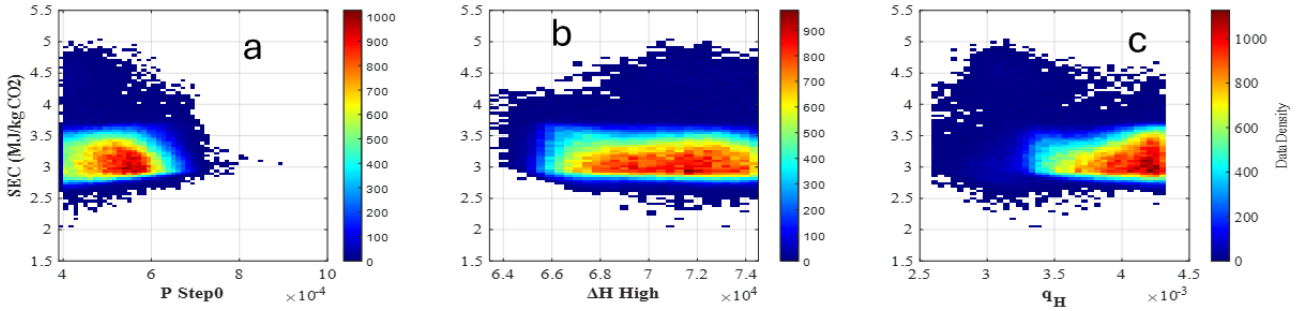

***Figure 4**. Effect of isotherm parameters on SEC under DAC conditions (CO_2 purity ≥ 98%).*

Figures 3 and 4 illustrate the dependence of both productivity and specific energy consumption (SEC) on the input parameters (P_{step0}, ΔH_{High}, and q_H) under a CO_2 purity constraint of ≥ 98%. The colour density represents the concentration of feasible solutions within the explored design space, where higher density indicates a greater number of parameter combinations satisfying the DAC process constraints. These visualisations highlight the regions of the thermodynamic parameter space where a larger number

of adsorbent configurations lead to viable operation, while also showing how variations in step position, step enthalpy, and saturation capacity affect both cyclic productivity and energy requirements.
According to Figure 3 and 4 (panel a), decreasing P_{step0} from 5×10^{-4} Pa leads to higher productivity and lower SEC. Figure 3 (panel b) shows that productivity reaches a plateau at approximately $\Delta H_{High}\approx$ 68,000 J/mol, and further increases in this parameter do not significantly affect productivity. Figure 3 and 4 (panel c) demonstrates the effect of increasing q_H: although higher saturation capacity increases productivity, it also results in higher energy consumption, indicating a trade-off between productivity and SEC.

Conclusion

This study demonstrates the critical influence of step-shaped isotherm parameters on DAC process performance using a combined TVSA modeling and Sobol global sensitivity analysis framework. Among the parameters investigated, the enthalpy of the adsorption step (ΔH_{High}) was identified as the dominant factor controlling both productivity and specific energy consumption, while significant interaction effects were observed between ΔH_{High} and q_H for productivity, and between ΔH_{High} and P_{step0} for SEC. The analysis of feasible design spaces highlights parameter regions that simultaneously enable high productivity and manageable energy consumption, providing quantitative guidance for the targeted design and optimisation of cooperative step-isotherm adsorbents. Overall, this work bridges material-level properties and process-level performance, offering a systematic approach to accelerate adsorbent development for efficient DAC implementation.

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