Supporting Information for Superstructure model for the simultaneous design and optimization of the PVSA process cycle

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Adsorbent properties			
Density of the solid particle	ρ_s	kg m^{-3}	1130
Adsorbent specific heat capacity	$C_{p,s}$	J kg^{-1} K^{-1}	1070
Adsorption saturation capacity	q_{sat}	mol m^{-3}	3489
Adsorption saturation capacity	q_{sat}	mol m^{-3}	2872
Adsorption equilibrium constant of CO2	b_0	m3 mol^{-1}	8.64×10^{-07}
Adsorption equilibrium constant of N2	b_0	m3 mol^{-1}	2.50×10^{-06}
Adsorption equilibrium constant of CO2	b_0	m3 mol^{-1}	2.62×10^{-08}
Adsorption equilibrium constant of N2	b_0	m3 mol^{-1}	2.50×10^{-06}
Heat of adsorption of CO2	ΔU_{CO_2}	kJ mol^{-1}	-36.64
Heat of adsorption of N2	ΔU_{N_2}	kJ mol^{-1}	-15.8
Heat of adsorption of CO2	ΔU_{CO_2}	kJ mol^{-1}	-35.7
Heat of adsorption of N2	ΔU_{N_2}	kJ mol^{-1}	-15.8

Table S1 The simulation parameters used in this study.

Optimization Decision Variables			
Time of Adsorption step	t_{ADS}	s	10-500
Time of Light Reflux step	t_{LR}	s	0-100
Time of Heavy Reflux -1 step	t_{HR1}	s	0-100
Heavy Reflux-2 ratio	Θ	-	0-0.7
Intermediate Pressure	P_{INT}	bar	0.08-PH
Evacuation Pressure	P_{EVAC}	bar	0.01-PINT
Feed Velocity	v_{Feed}	m/s	0.1-3

Table S2 Optimization Decision variables and their range

Details of process models and boundary conditions; the isotherm and simulation parameters are shown.

Step	z=0	z=L
OPEN-OPEN (ADS LR HR)	$v\|_{z=0} = v_{\text{Step}}$ $D_L \left.\frac{\partial y_i}{\partial z}\right\|_{z=0} = -v\|_{z=0}\left(y_{i,\text{F}} - y_i\|_{z=0}\right)$ $\left.\frac{\partial,T}{\partial z}\right\|_{z=0} = -\epsilon\, v\|_{z=0}\,\rho_g C_{p,\text{g}}(T_F - T\|_{z=0})$	$P\|_{z=\text{L}} = P_{\text{Step}}$ $\left.\frac{\partial y_i}{\partial z}\right\|_{z=\text{L}} = 0$ $\left.\frac{\partial T}{\partial z}\right\|_{z=\text{L}} = 0$
OPEN-CLOSED (LPP PED FP)	$\left.\frac{\partial y_i}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial P}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial T}{\partial z}\right\|_{z=0} = 0$	$v\|_{z=\text{L}} = \frac{v_{\text{Step}} P_{\text{Step}}\|_{z=\text{L}}}{P\|_{z=\text{L}}}$ $D_L \left.\frac{\partial y_i}{\partial z}\right\|_{z=\text{L}} = -v\|_{z=\text{L}}\left(y_{i,\text{F}} - y_i\|_{z=\text{L}}\right)$ $\left.\frac{\partial \text{T}}{\partial z}\right\|_{\text{z}} = \text{L} = -\epsilon\, v\|_{\text{z}} = \text{L}\rho_{\text{g}} C_{\text{p,g}}(T_{\text{F}} - T\|_{\text{z}} = \text{L})$
CLOSED-OPEN (BLO EVAC PED)	$v\|_{z=0} = 0$ $\left.\frac{\partial y_i}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial T}{\partial z}\right\|_{z=0} = 0$ $\left.\frac{\partial P}{\partial z}\right\|_{z=0} = 0$	$v\|_{z=\text{L}} = v_{\text{Step}}$ $\left.\frac{\partial y_i}{\partial z}\right\|_{z=\text{L}} = 0$ $\left.\frac{\partial T}{\partial z}\right\|_{z=\text{L}} = 0$

Table S3 Boundary conditions for the typical steps in a cyclic adsorption process.

Model equations	
Overall mass balance	$\frac{1}{P}\frac{\partial P}{\partial t} - \frac{1}{T}\frac{\partial T}{\partial t} = -\frac{T}{P}\frac{\partial}{\partial z}\left(\frac{P}{T}v\right) - \frac{1-\epsilon}{\epsilon}\frac{RT}{P}\sum_{i=1}^{n_{\text{comp}}}\frac{\partial q_i}{\partial t}$
Component mass balance	$\frac{\partial y_i}{\partial t} + \frac{y_i}{P}\frac{\partial P}{\partial t} - \frac{y_i}{T}\frac{\partial T}{\partial t} = \frac{T}{P}D_L\frac{\partial}{\partial z}\left(\frac{P}{T}\frac{\partial y_i}{\partial z}\right) - \frac{T}{P}\frac{\partial}{\partial z}\left(\frac{y_i P}{T}v\right) - \frac{RT}{P}\frac{1-\epsilon}{\epsilon}\frac{\partial q_i}{\partial t}$
Mass transfer rate	$\frac{\partial q_i}{\partial t} = k_i\left(q_i^* - q_i\right); k_i = \frac{C_i}{q_i^*}\frac{15\epsilon_{\text{P}} D_{\text{P}}}{r_{\text{P}}^2}; D_{\text{P}} = \frac{D_{\text{M}}}{\tau}$
Pressure drop	$-\frac{\partial P}{\partial z} = \frac{150}{4}\frac{1}{r_{\text{p}}^2}\left(\frac{1-\epsilon}{\epsilon}\right)^2\mu v$
Column energy balance	$\left[\frac{1-\epsilon}{\epsilon}\left(\rho_{\text{s}} C_{\text{p,s}} + \sum_{i=1}^{n_{\text{comp}}} C_{\text{p,a,i}} q_i\right)\right]\frac{\partial T}{\partial t} = \frac{K_z}{\epsilon}\frac{\partial^2 T}{\partial z^2} - \frac{\sum_{i=1}^{n_{\text{comp}}} y_i C_{\text{p,g,i}}}{R}\frac{\partial}{\partial z}(vP) - \frac{\sum_{i=1}^{n_{\text{comp}}} y_i C_{\text{p,g,i}} - R}{R}\frac{\partial P}{\partial t} -$ $\frac{1-\epsilon}{\epsilon}T\sum_{i=1}^{n_{\text{comp}}} C_{\text{p,a,i}}\frac{\partial q_i}{\partial t} + \frac{1-\epsilon}{\epsilon}\sum_{i=1}^{n_{\text{comp}}}\left(\left(-\Delta H_i\right)\frac{\partial q_i}{\partial t}\right); C_{\text{p,g,i}} = C_{\text{p,a,i}}$

Table S4 Equations for modeling adsorption column dynamics.