Modeling and Simulation of a Thermal Swing Adsorption Process for CO_2 Capture and Recovery

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Abstract: The present study deals with a two-dimensional modeling and simulation of a thermal swing adsorption (TSA) process used for the capture of CO_2 from CO_2/N_2 mixture. The models are described by partial differential equations (PDEs) including conservation equations, models for equation of state, equilibrium, thermodynamic and transport properties. The resulting models involve different unknown parameters to be estimated from the available experimental measurements. An estimability analysis was carried out in order to determine which parameters are able to be estimated from experimental results. The most estimable parameters are then identified and the less estimable parameters are fixed from the literature. The resulting models are implemented and solved using the software Comsol Multiphysics®. The results obtained show that the model predictions fit quite well with the experimental results.

Keywords: thermal swing adsorption (TSA), mathematical modeling, simulation ,optimization

1. Introduction

Adsorption processes such as thermal swing adsorption (TSA) and pressure swing adsorption (PSA) are widely used in industry for purification and separation. In TSA processes, the gas mixture is percolated through the fixed bed of adsorbent, and then the adsorbent is regenerated by raising its temperature. Pressure swing adsorption (PSA) processes work between a high pressure level during adsorption and a low pressure level for desorption.

In one of our previous studies [1], a TSA process was used to capture carbon dioxide from a gas mixture of carbon dioxide and nitrogen. The mixture feeds an adsorption column (length: 10cm, diameter: 3.5cm) filled with zeolite 5A particles on which CO_2 is adsorbed. The adsorbent is then regenerated by heating the fixed bed at the wall. Experimental studies of the adsorbent (adsorption isotherm) have also been carried out in [1].

As the column is not adiabatic, the radial temperature is not uniform, especially for desorption step. So it is necessary to take into account the influence of radial temperature difference in the bed. Even though many studies on TSA have been done, little has been published about the cyclic simulation with two dimensions and about how to determine the unknown parameters by means of a numerical method. In this work, a two-dimension model was established and solved using the software Comsol Multiphysics®. The model consists of partial differential equations representing heat balance, mass balance of CO_2, overall mass balance and momentum balance. Heat transfer to the wall of the column is taken into account. Since the model involves many unknown parameters whose values cannot be obtained accurately from literature, an estimability analysis method was used in order to determine those which are estimable from the available experimental measurements. The resulting set of estimable parameters was then identified by the combination of Matlab® and Comsol Multiphysics. With the optimized parameters, the TSA processes (adsorption and regeneration steps) were simulated and compared to the experimental measurements.

2. Process model

A process model describing the TSA process which contains both the adsorption and regeneration steps is established. The main differences between the models of the two steps are the initial and boundary conditions which define the operation conditions.

2.1 Model assumptions

The process model developed is based on the following assumptions:

- The gaseous mixture obeys the perfect gas law.
- Only carbon dioxide is adsorbed.

- The resistance of mass transfer in the gas phase is negligible, the kinetics of mass transfer within a particle was described by the linear driving force (LDF) approximation model [2].
- The gas phase is in equilibrium with the adsorbent.
- Isosteric heat of adsorption (-? H) does not change with temperature.
- The adsorbent is considered as a homogeneous phase and the porosity of the bed is 0.4.
- The physical properties of adsorbent are assumed as constants.

2.2 Model equations

According to the aforementioned assumptions, the balance equations may be written as:

Mass balance for the adsorbed component (CO_2):

$$\frac{\partial y_1}{\partial t}+(1-y_1)\frac{1-e}{e}\frac{RT}{P}\frac{\partial q_1}{\partial t}+u\frac{\partial y_1}{\partial z}+v\frac{\partial y_1}{\partial r}=\nabla(D\nabla y_1) +2D\left[\frac{1}{P}\left(\frac{\partial y_1}{\partial z}\frac{\partial P}{\partial z}+\frac{\partial y_1}{\partial r}\frac{\partial P}{\partial r}\right)-\frac{1}{T}\left(\frac{\partial y_1}{\partial z}\frac{\partial T}{\partial z}+\frac{\partial y_1}{\partial r}\frac{\partial T}{\partial r}\right)\right] \quad (1)$$

Where y_1 is the mole fraction of CO_2, D the dispersion coefficient (m^2/s), e the bed porosity, q_1 adsorbed phase concentration averaged over the adsorbent particle (mol/m^3), u the interstitial bulk fluid axial velocity (m/s), v the interstitial bulk fluid radial velocity (m/s), P the total pressure (Pa).

Overall mass balance:

$$\frac{\partial u}{\partial z}+\frac{\partial v}{\partial r}+\frac{v}{r}+\frac{1-e}{e}\frac{RT}{P}\frac{\partial q_1}{\partial t}-\frac{1}{T}\left(u\frac{\partial T}{\partial z}+v\frac{\partial T}{\partial r}\right) -\frac{1}{T}\frac{\partial T}{\partial t}+\frac{1}{P}\left(u\frac{\partial P}{\partial z}+v\frac{\partial P}{\partial r}\right)+\frac{1}{P}\frac{\partial P}{\partial t} =\frac{D}{T}\left\{\frac{T}{P}\nabla(\nabla P)-\frac{2}{P}\left(\frac{\partial T}{\partial z}\frac{\partial P}{\partial z}+\frac{\partial T}{\partial r}\frac{\partial P}{\partial r}\right) -\nabla(\nabla T)+\frac{2}{T}\left[\left(\frac{\partial T}{\partial z}\right)^2+\left(\frac{\partial T}{\partial r}\right)^2\right]\right\} \quad (2)$$

Heat Balance:

$$C_{pg}\left(u\frac{\partial T}{\partial z}+v\frac{\partial T}{\partial r}\right)+\left[C_{pg}+\frac{1-e}{e}\frac{RT}{P}\left(r_s C_{ps}+q_1 C_{pg}\right)\right]\frac{\partial T}{\partial t} =\nabla\left(l\nabla T\right)-\frac{1-e}{e}\frac{RT}{P}\frac{\partial q_1}{\partial t}\left(\Delta H+q_1\frac{\partial \Delta H}{\partial q_1}\right) \quad (3)$$

Where –? H is the isosteric heat of adsorption (J/mol), and is defined by a Clausius-Clapeyron equation type as [3]:

$$-\frac{\Delta H}{RT^2}=\frac{\partial(\ln P)}{\partial T} \quad (4)$$

Where p is the adsorbate partial pressure.

?H is then calculated for different values of adsorbed phase concentration q, and fitted by means of a 3rd order polynomial as:

$$-?H = 842.3q^3 - 447.2q^2 + 1577q + 17847 \quad (5)$$

C_{ps} is the heat capacity of the solid (J/kg/K), and C_{pg} (J/mol/K) the heat capacity of the gas.

Mass transfer kinetics (LDF model):

The kinetics of mass transfer within a particle was approximated by the linear driving force (LDF) model as [2]:

$$\frac{\partial q_1}{\partial t}=k_1(q_e-q_1) \quad (6)$$

With $k_1=\frac{15D_e}{R_P^2}$, where R_p is the radius of the particle, D_e is the effective diffusivity in the particle.

Adsorption isotherm:

The adsorption isotherm is represented using the Langmuir isotherm [1] as :

$$q_e=\frac{q_m KP}{1+KP} \quad (7)$$

Where

$$q_m=(-0.0145T+7.531)r_s \quad (8)$$

$$K=6.53.10^{-7}\exp\left(\frac{13904}{RT}\right) \quad (9)$$

Momentum balance:

The momentum balance equations were simplified and reduced to the following two Ergun equations [4, 5]:

$$-\frac{\partial P}{\partial z}=150\frac{(1-e)^2}{e^3}\frac{m_F u}{d_P^2}+1.75\frac{1-e}{e^3}\frac{r_F\sqrt{u^2+v^2}u}{d_P} \quad (10)$$

$$-\frac{\partial P}{\partial r}=150\frac{(1-e)^2}{e^3}\frac{m_F v}{d_P^2}+1.75\frac{1-e}{e^3}\frac{r_F\sqrt{u^2+v^2}v}{d_P} \quad (11)$$

2.3 Boundary conditions and initial conditions

The boundary conditions for both adsorption

Table 1: Boundary conditions

	z=0	z=L	r=0	r=Rc
y_1	$-D\frac{\partial y_1}{\partial z} = (y_{in} - y_1)u_{in}$	$\frac{\partial y_1}{\partial z} = 0$	$\frac{\partial y_1}{\partial r} = 0$	$\frac{\partial y_1}{\partial r} = 0$
u	$u = u_{in}$	$\frac{\partial u}{\partial z} = 0$	$\frac{\partial u}{\partial r} = 0$	$\frac{\partial u}{\partial r} = 0$
v	$\frac{\partial v}{\partial z} = 0$	$\frac{\partial v}{\partial z} = 0$	$v = 0$	$v = 0$
q_1	$\frac{\partial q_1}{\partial z} = 0$	$\frac{\partial q_1}{\partial z} = 0$	$\frac{\partial q_1}{\partial r} = 0$	$\frac{\partial q_1}{\partial r} = 0$
T	$\frac{\partial T}{\partial z} = 0$	$\frac{\partial T}{\partial z} = 0$	$\frac{\partial T}{\partial r} = 0$	$-l\frac{\partial T}{\partial r} = kc(T - T_{out})$
P	$\frac{\partial P}{\partial z} = 0$	$P = P_1$	$\frac{\partial P}{\partial r} = 0$	$\frac{\partial P}{\partial r} = 0$

and regeneration steps are summarized in Table 1, where P_1 is the final pressure defined as a boundary condition at the exit of the column.

For the regeneration step, $u_{in}=0$, $y_{in}=0$, the time-varying experimental data of the temperature outside the wall of the column are assumed to be described by the following expression:

$$T_{out} = \left(T_{regen} - T_0\right)\exp\left(\frac{-120}{t^{1.5}}\right) + T_0 \quad (12)$$

Here T_{regen} is the regeneration temperature, T_0 is the initial temperature, t is the elapsed time from the starting time point of the regeneration step.

For the adsorption step, the outside temperature is the room temperature.

The initial conditions are as follows:

$$y_1(r,z)\big|_{t=0} = y_0$$
$$u(r,z)\big|_{t=0} = 0$$
$$v(r,z)\big|_{t=0} = 0$$
$$q_1(r,z)\big|_{t=0} = q_0$$
$$T(r,z)\big|_{t=0} = T_0$$
$$P(r,z)\big|_{t=0} = P_0$$

All the above initial conditions are defined for:

$$0 = z = L \text{ and } 0 = r = Rc.$$

The basic parameters values used for numerical computation are given in Table 2.

Table 2: Basic parameters for numerical computation

Parameter	Unit	Value
e	----	0.4
R	J $mol^{-1}K^{-1}$	8.314
Cps[6]	J $kg^{-1}K^{-1}$	1046
Rc	m	0.0175
?s	kg m^{-3}	1212

3. Parameter estimability and identification

The TSA process model developed involves many unknown parameters and strongly influence the predictions. On the other hand, only some experimental measurements carried out in the center and at the exit of the column and at limited time samples are available. The question is whether or not the measurements contain the necessary information to identify all the unknown parameters. If not, which ones are the most estimable and in which order. To answer these questions, an estimability analysis was carried out and followed by a parameter identification study.

3.1 Parameter estimability

The estimability analysis method used is based on the matrix of sensitivities of the measured outputs with respect to different parameters and at different sampling times. A row is formed by the sensitivity of an output with respect to all parameters at a sampling time, whereas a column is formed by the sensitivities of an output with respect to a parameter at all sampling times. The sensitivities are normalized using values of variables and parameters taken from the literature or measured or previously computed in order to give to the matrix elements the same order of magnitude.

The estimability of a parameter is evaluated through the norm of the corresponding column in the normalized matrix of sensitivities. A threshold value of the norm is a priori fixed from the experience and knowledge of the process. The parameters with the norms higher than the threshold value are estimable and the others are not. Moreover, the comparison of the norms of the estimable parameters enables to rank the parameters from the most to the less estimable.

The higher the norm of a parameter, the higher its influence on the considered output, and the higher its estimability. Finally, an orthogonalization process of the columns of the normalized matrix is carried out in order to cancel the effects of the most influencing parameter on the other parameters [7].

Table 3: Operating conditions for the adsorption step

Parameter	Exp 1	Exp 2	Exp 3	Exp 4
y_0	0	0	0	0
y_{in} (%)	12.97	22.05	29.3	36.2
P_0 (P_a)	111102	108691	110142	112419
Feeding flow rate (ml/min)	218	210.5	252	268.5
T_0(K)	302	292.5	300	297
T_{out} (K)	302	292.5	300	297

3.2 Parameter identification

The values of parameters considered as non estimable are taken from literature or from previous studies. The estimable parameters are then identified from the available experimental measurements by means of a non linear programming (NLP) method. An objective function is thus defined as the least squares between the model predictions and the experimental measurements. This function is then minimized within Matlab using the gradient-based NLP solver "fmincon".

4. Results and discussion

4.1 Adsorption step

The operating conditions for the adsorption step are presented in Table 3 [1].

a) Parameter estimability

For the adsorption step, the temperature in the center of column (T) and the mole fraction of CO_2 at the exit (y_1) were measured. Their experimental values were compared to the corresponding model predictions. The unknown parameters are ?= [D, k_1, kc, ?].

The results of estimability analysis are presented in Table 4.

It can be seen that the order of estimability of parameters in the adsorption step is ?>k1>D>kc. On the other hand, since the threshold value of the norm was fixed to 0.4 the last parameter, i.e. kc, is considered as non estimable from the available experimental measurements. Its value was fixed from literature to 10 W $m^{-2}K^{-1}$.

Table 4: Estimability analysis in the adsorption step

Ranking		1	2	3	4
Parameters		?	k_2	D	kc
Initial values		0.05	0.004	1.10^{-5}	15
Norm		5.6417	1.5265	0.9516	0.2960
Iteration	1	5.6417	1.5265	0.9516	0.2960
	2	0	1.4735	0.9512	0.2680
	3	0	0	0.8404	0.2655
	4	0	0	0	0.2650

Table 5: Optimized values of parameters in the adsorption step

	$Dx10^5$(m^2s^{-1})	k_1(s^{-1})	? (W/m/K)
Optimized value	1.9732	0.0051	0.060

b) Parameter identification and validation

The data used for parameter identification correspond to a set of measurements with four different concentrations of CO_2.

The values of optimized parameters are presented in Table 5. The results are in a quite good agreement with the common values for the process under consideration.

The computed predictions of the mole fraction of CO_2 at the exit and temperature at the center of column were compared to the experimental measurement using the optimized values of the estimable parameters. The temperature measurements were collected at the centre of the column and at 7 cm from the inlet for all experimental runs. Figs. 1 and 2 show the breakthrough curves and the bed temperature respectively for different feed concentrations. Both numerical (solid lines) and experimental (symbols) results are reported. It can be seen that for breakthrough curves (Fig.1) the agreement is quite good except for the experiment with y_{in}= 0.1297 where the model appear earlier than the measurements. This is probably due to the inaccuracy of the adsorption isotherm at low concentrations. For the bed temperatures (Fig.2) of the simulations agree well with the

experimental measurements for all feed concentrations analyzed.

4.2 Regeneration step

Table 6: Operating conditions in the regeneration step

Parameter	Exp 5	Exp 6	Exp 7	Exp 8
y_0 (%)	12.87	13.03	13.0	12.79
P_0 (P_a)	109473	109961	111621	111816
P_1(P_a)	99414	98733	100879	102246
T_0(K)	299	300	295.5	293
T_{regen} (K)	403	424.2	447	483

Table 7: Estimability analysis in the regeneration step

ranking		1	2	3
Parameter		λ	k1	kc
Initial values		0.0278	0.0065	13.7501
Norm		2.2526	0.5626	0.0717
Iterations	1	2.2526	0.6415	0.1448
	2	0	0.5626	0.0719
	3	0	0	0.0717

In the regeneration step, the operating conditions are presented in Table 6 [1].

a) Parameter estimability

Here the outputs of the model are the outlet gas flow rates (Q) and the temperature at the center of the column. On the other hand, in the model equations of this step, the dispersion term is neglected. The unknown parameters are therefore ?= [k_1, kc, ?].

The results of estimability analysis are presented in Table 7. It can be seen that the order of estimability of parameters in the regeneration step is ? > k1 > kc.

On the other hand, since the threshold value of the norm was fixed here also to 0.4 the last parameter, i.e. kc, is considered as non estimable from the available experimental measurements.

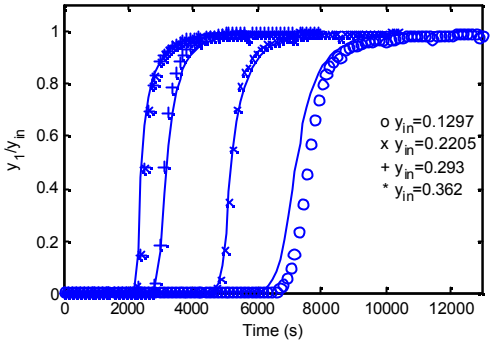
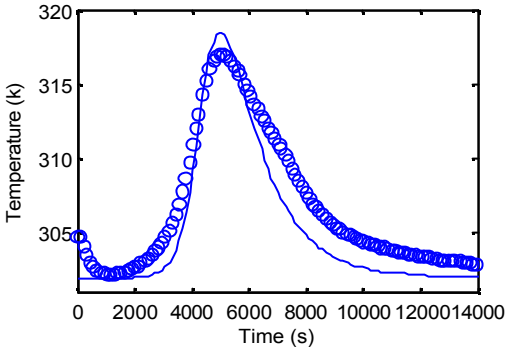
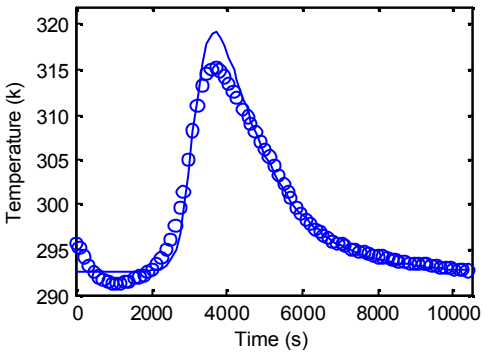


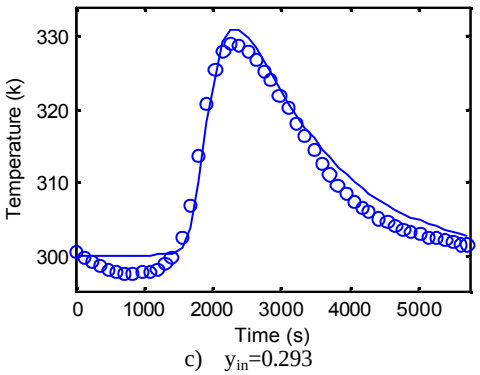
Figure 1: Comparison of predicted breakthrough curves with experimental data.



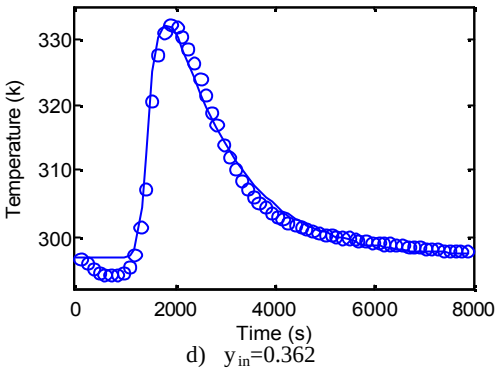
a) y_{in}=0.1297



b) y_{in}=0.2205



c) y_{in}=0.293



d) y_{in}=0.362

Figure 2: Comparison of predicted temperature profiles with experimental results

Table 8: Optimized values of parameters in the regeneration step

	Optimized values	
T (°C)	k_1	?
130	0.0015	0.0664
150	0.0019	0.0687
170	0.0018	0.0608
210	0.0022	0.0649

Its value was fixed from literature to10 W $m^{-2}K^{-1}$.

b) Parameter identification and validation

The values of optimized parameters are presented in Table 8. It can be seen that ? seems to be constant when the operating temperature increases. However k1 shows a substantial increase.

Figs.3 and 4 represent the comparison of the numerical and experimental results; it shows the variation of the gas flow rate and the temperatures. We see that the simulations result agree well with those of the experiments. Therefore, the optimization result and the model

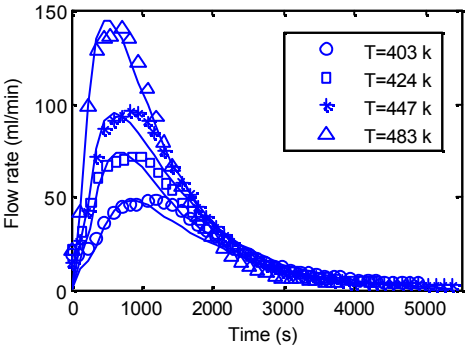


Figure 3: Comparison of predictions and measurements of the gas flow rate in the regeneration step.

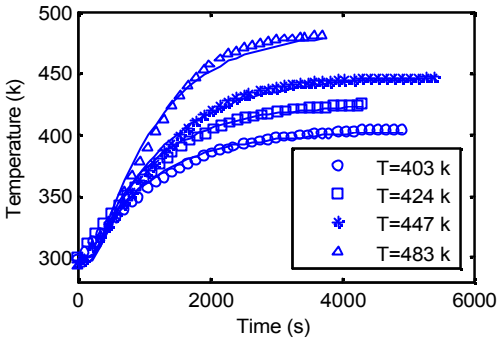


Figure 4: Comparison of computed and measured temperature profiles rate in the regeneration step.

are feasible.

The computed predictions of the gas flow rate and temperature were compared to the experimental measurement using the optimized values of the estimable parameters. Figs. 3 and 4 show the gas flow rate curves and the bed temperature respectively for different temperatures. Both numerical (solid lines) and experimental (symbols) results are reported. It can be seen that the agreement is quite good for the two variables.

5. Conclusions

A two dimensional non-adiabatic model was developed to simulate a temperature swing adsorption (TSA) process (temperature and concentration for adsorption step, temperature and flow rate for regeneration step). Since many unknown parameters are involved in the model, prior to their identification, an estimability analysis was carried out in order to determine the set of the most estimable parameters from the available experimental measurements.

The resulting estimable parameters are then identified from the measurements of temperature and CO2 concentration in the adsorption step, and from the measurements of temperature and gas flow rate in the regeneration step.

The model predictions computed using the optimized parameters exhibit a quite good agreement with the experimental measurements in both adsorption and regeneration steps.

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Nomenclature

Cpg	Heat capacity of gas, J/mol/K
Cps	Heat capacity of solid, J/mol/K
D	Dispersion coefficient (m^2s^{-1})
De	Effective diffusivity. (m^2s^{-1})
d_P	Particle diameter (m)
-? H	Isosteric heat of adsorption (J/mol)
K_1	Overall mass transfer rate coefficient (LDF), (s^{-1})
Kc	Heat transfer coefficient (Wm^2K^{-1})
L	Adsorbent bed length (m)
P	Pressure (Pa)
P_0	Initial total pressure (Pa)
P_1	Export pressure (Pa)
Q	Outlet gas flow rates (ml/min)
q_1	Average amount adsorbed of CO_2 in a pellet or particle(mol/m^3)
q_e	Equilibrium amount adsorbed of CO_2 (mol/m^3)
q_m	Saturated amount adsorbed (mol/m^3)
R	Gas constant
Rc	Radius of the column (m)
R_p	Radius of particle (m)
S	A set of the output of the model
T	Temperature (K)
T_0	Initial Temperature (K)
T_{out}	Temperature outside the wall of the column (K)
T_{regen}	Regeneration temperature (K)
u	Axial interstitial bulk fluid velocity (m/s)
u_{in}	Inlet axial interstitial bulk fluid velocity of the feeding gas (m/s)
v	Radial interstitial bulk fluid velocity (m/s)
y_0	Initial mole fraction of CO_2
y_1	Mole fraction of CO_2
y_{in}	Mole fraction of CO_2 of the feeding gas
e	Bed porosity
$?_s$	Solid density (kg/m^3)
$?_F$	Fluid density(kg/m3)
μ_F	Fluid viscosity (Pa·s)
?	Heat conductivity (W/m/K)
?	A set of unknown parameters