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

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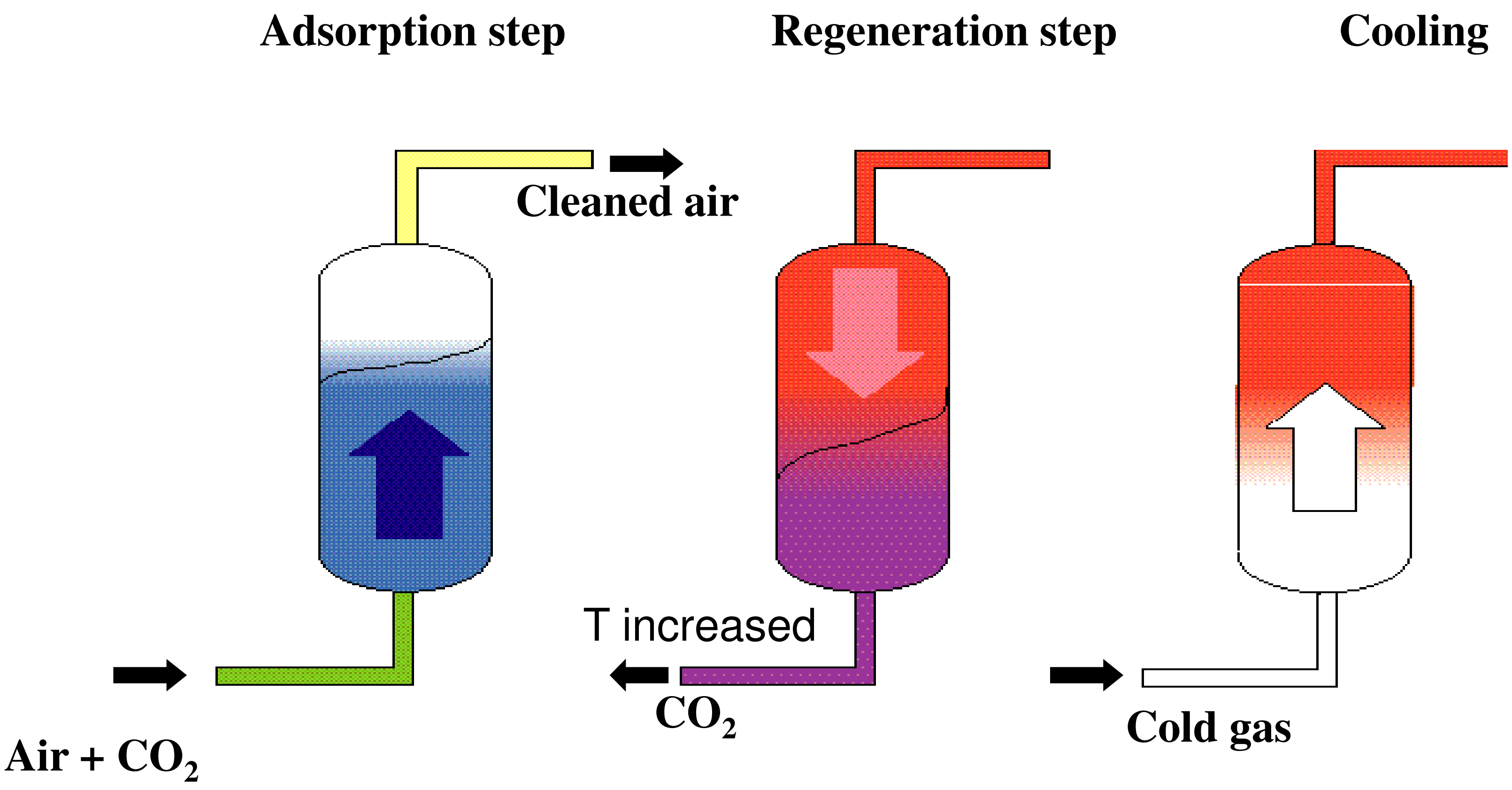
- Temperature Swing Adsorption process
- 2D modeling
  - Model equations
  - Parameter estimability
  - Parameter identification
- Results for Adsorption step
- Results for Regeneration step
- Conclusions

TEMPERATURE SWING ADSORPTION PROCESS



TWO DIMENSIONAL MODEL

Model Assumptions

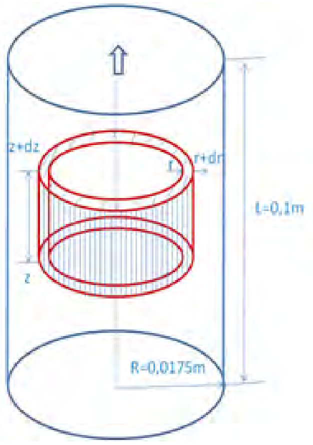
- The gaseous mixture obeys the perfect gas law
- Only CO_2 is adsorbed
- kinetics of mass transfer within a particle described by LDF model. The gas phase is in equilibrium with the adsorbent.
- Isosteric heat of adsorption ($-\Delta H$) does not change with temperature.
- The adsorbent is considered as a homogeneous phase and the porosity of the bed is 0.4
- The physical properties of adsorbent are assumed as constant .

TWO DIMENSIONAL MODEL

Model Equations

- Overall mass balance

$$\frac{\partial u}{\partial z}+\frac{\partial v}{\partial r}+\frac{v}{r}+\frac{1-\varepsilon}{\varepsilon}\frac{RT}{P}\frac{\partial q_1}{\partial t}-\frac{1}{T}\left(u\frac{\partial T}{\partial z}+v\frac{\partial T}{\partial r}\right)-\frac{1}{T}\frac{\partial T}{\partial t}$$
$$+\frac{1}{P}\left(u\frac{\partial P}{\partial z}+v\frac{\partial P}{\partial r}\right)+\frac{1}{P}\frac{\partial P}{\partial t}=0$$



- Mass balance for the adsorbed component (CO_2):

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

- LDF Model (Linear Driving Force)

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

TWO DIMENSIONAL MODEL

Model Equations

- Heat Balance

$$C_{pg}\left(u\frac{\partial T}{\partial z}+v\frac{\partial T}{\partial r}\right)+\left[C_{pg}+\frac{1-\varepsilon}{\varepsilon}\frac{RT}{P}\left(\rho_s C_{ps}+q_1 C_{pg}\right)\right]\frac{\partial T}{\partial t}$$

$$=\nabla(\lambda\nabla T)-\frac{1-\varepsilon}{\varepsilon}\frac{RT}{P}\frac{\partial q_1}{\partial t}\left(\Delta H+q_1\frac{\partial \Delta H}{\partial q_1}\right)$$

- Momentum balance (Ergun's equation)

$$-\frac{\partial P}{\partial z}=150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu_F u}{d_p^2}+1.75\frac{1-\varepsilon}{\varepsilon^3}\frac{\mu_F\sqrt{u^2+v^2}\,u}{d_p}$$

$$-\frac{\partial P}{\partial r}=150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu_F v}{d_p^2}+1.75\frac{1-\varepsilon}{\varepsilon^3}\frac{\mu_F\sqrt{u^2+v^2}\,v}{d_p}$$

TWO DIMENSIONAL MODEL

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	$\frac{\partial T}{\partial z}=0$	$\frac{\partial T}{\partial z}=0$	$\frac{\partial T}{\partial r}=0$	$-\lambda\frac{\partial T}{\partial r}=kc(T-T_{out})$
P	$\frac{\partial P}{\partial z}=0$	$P = P_1$	$\frac{\partial P}{\partial r}=0$	$\frac{\partial P}{\partial r}=0$

PARAMETER ESTIMABILITY

Parameters involved in the model :
for adsorption and regeneration steps: λ, k_1, D, k_c

Available experimental measurements :
for adsorption step : T (center of the column) and y_1 (exit of the column)
for regeneration step : T (center of the column) and Q (exit of the column)

Q1 : Do the available experimental measurements contain the necessary information to identify all the unknown parameters ?

A1 : The general answer is NO.

Q2 : Which parameters are then estimable from the available experimental measurements ?

A2. To answer the question we carried out a parameter estimability analysis.

PARAMETER ESTIMABILITY

Parameter estimability: matrix of sensitivities of the measured outputs with respect to different parameters involved in the model and at different sampling time

$$M^s = \begin{bmatrix} \left.\dfrac{\theta_1}{S_1^{exp}}\dfrac{\partial S_1}{\partial O_1}\right|_{t=t1} & \cdots & \left.\dfrac{\theta_{N^{par}}}{S_1^{exp}}\dfrac{\partial S_1}{\partial O_{N^{par}}}\right|_{t=t1} \\ \vdots & \ddots & \vdots \\ \left.\dfrac{\theta_1}{S_1^{exp}}\dfrac{\partial S_1}{\partial \theta_1}\right|_{t=tn} & \cdots & \left.\dfrac{\theta_{N^{par}}}{S_1^{exp}}\dfrac{\partial S_1}{\partial \theta_{N^{par}}}\right|_{t=tn} \\ \vdots & \cdots & \vdots \\ \left.\dfrac{\theta_1}{S_{N^{val}}^{exp}}\dfrac{\partial S_{N^{val}}}{\partial \theta_1}\right|_{t=t1} & \cdots & \left.\dfrac{\theta_{N^{par}}}{S_{N^{val}}^{exp}}\dfrac{\partial S_{N^{val}}}{\partial \theta_{N^{par}}}\right|_{t=t1} \\ \vdots & \ddots & \vdots \\ \left.\dfrac{\theta_1}{S_{N^{val}}^{exp}}\dfrac{\partial S_{N^{val}}}{\partial \theta_1}\right|_{t=tn} & \cdots & \left.\dfrac{\theta_{N^{par}}}{S_{N^{val}}^{exp}}\dfrac{\partial S_{N^{val}}}{\partial \theta_{N^{par}}}\right|_{t=tn} \end{bmatrix}_{(n*N^{val})\times N^{par}}$$

PARAMETER IDENTIFICATION

- NON estimable parameters are taken from literature
- ESTIMABLE parameters identified by NLP method
  - Objective function = least squares between model predictions and experimental measurements
  - Minimized within Matlab® using the gradient-based NLP solver « fmincon »

ADSORPTION STEP

Outputs of the model = CO_2 mole fraction at the exit and T at the center of the column.

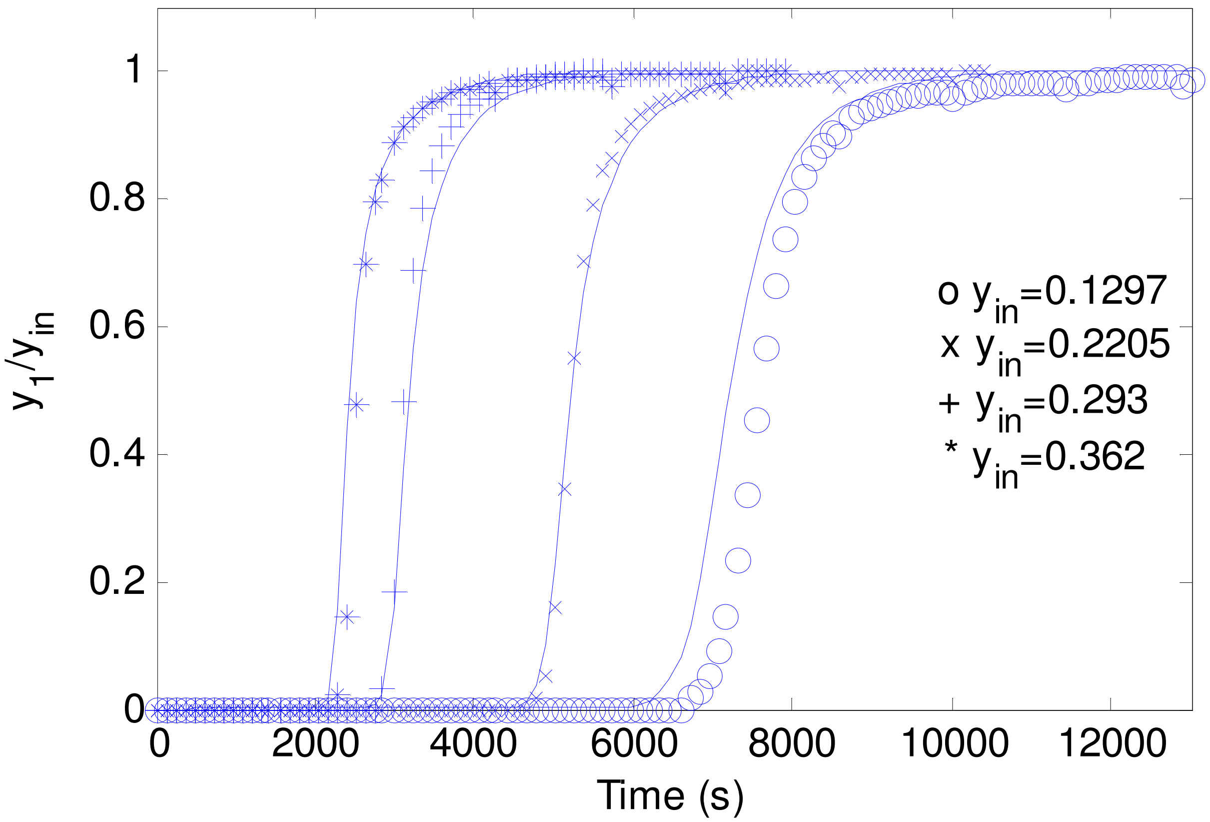
Ranking		1	2	3	4
Parameter		λ	k_1	D	k_c
Initial value		0.05	0.004	1.10^{-5}	15
Norm		5.6417	1.5265	0.9516	0.2960
Iteration	1	5.6417	1.5265	0.9516	0.2960
	2	0	1.4735	0.9512	0.2680
	3	0	0	0.8404	0.2655
	4	0	0	0	0.2650

Non estimable k_c : value fixed from literature to 10 $W.m^{-2}K^{-1}$

ADSORPTION STEP

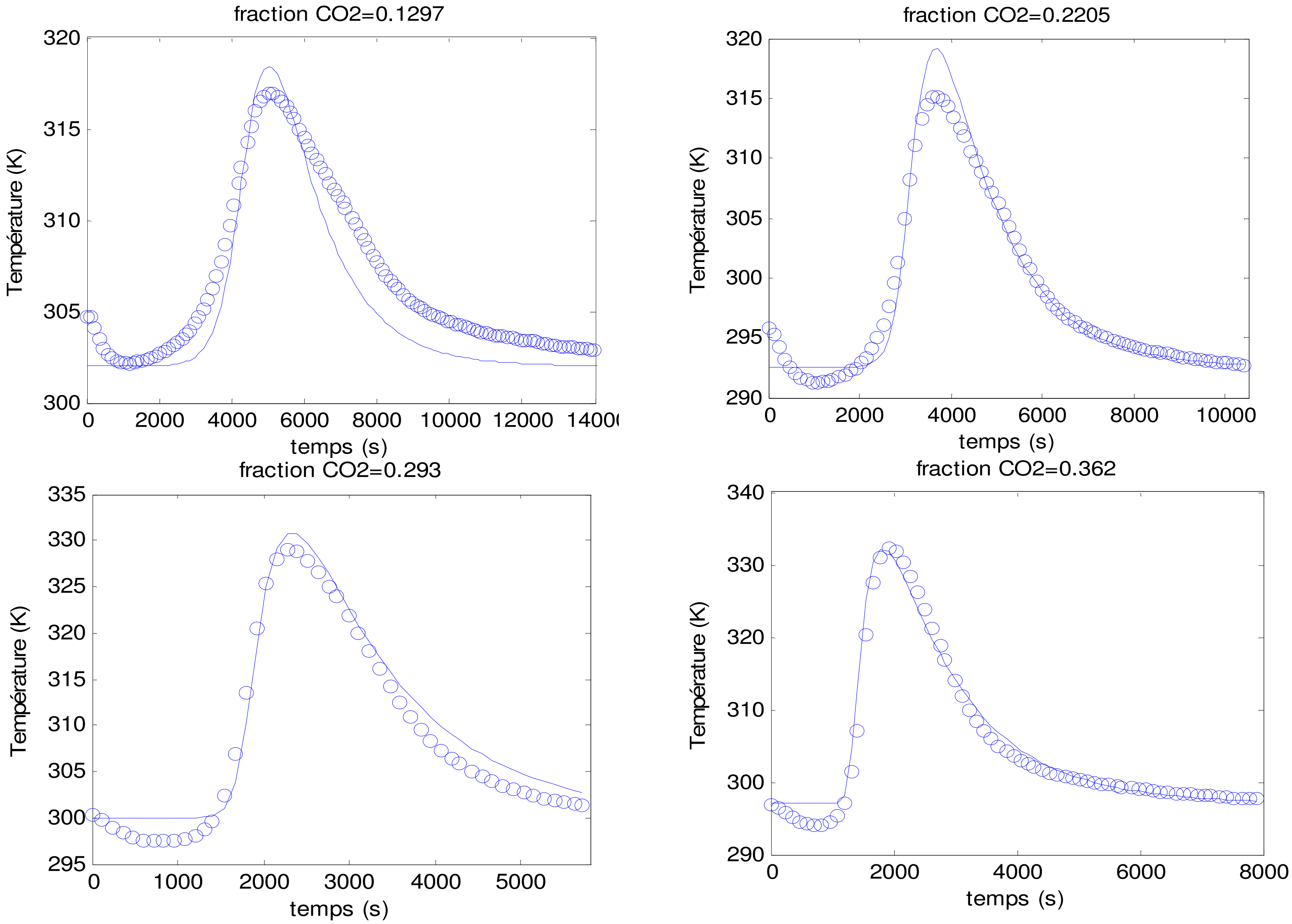
Breakthrough curves

$D*10^5$ (m^2s^{-1})	k_1 (s^{-1})	λ ($Wm^{-1}K^{-1}$)
1.9732	0.0051	0.060



ADSORPTION STEP

Temperature profiles at the center of the column



Comparison of the model predictions with the experimental measurements

REGENERATION STEP

Outputs of the model = outlet gas flow rates (Q) and T at the center of the column.

Ranking		1	2	3	4
Parameter		λ	k_1	k_c	D
Initial value		0.0228	0.0027	16.605	$2.89.10^{-5}$
Norm		1.855	0.5490	0.188	0.0038
Iteration	1	1.855	0.783	0.411	0.0038
	2	0	0.549	0.406	0.0039
	3	0	0	0.188	0.0038
	4	0	0	0	0.0038

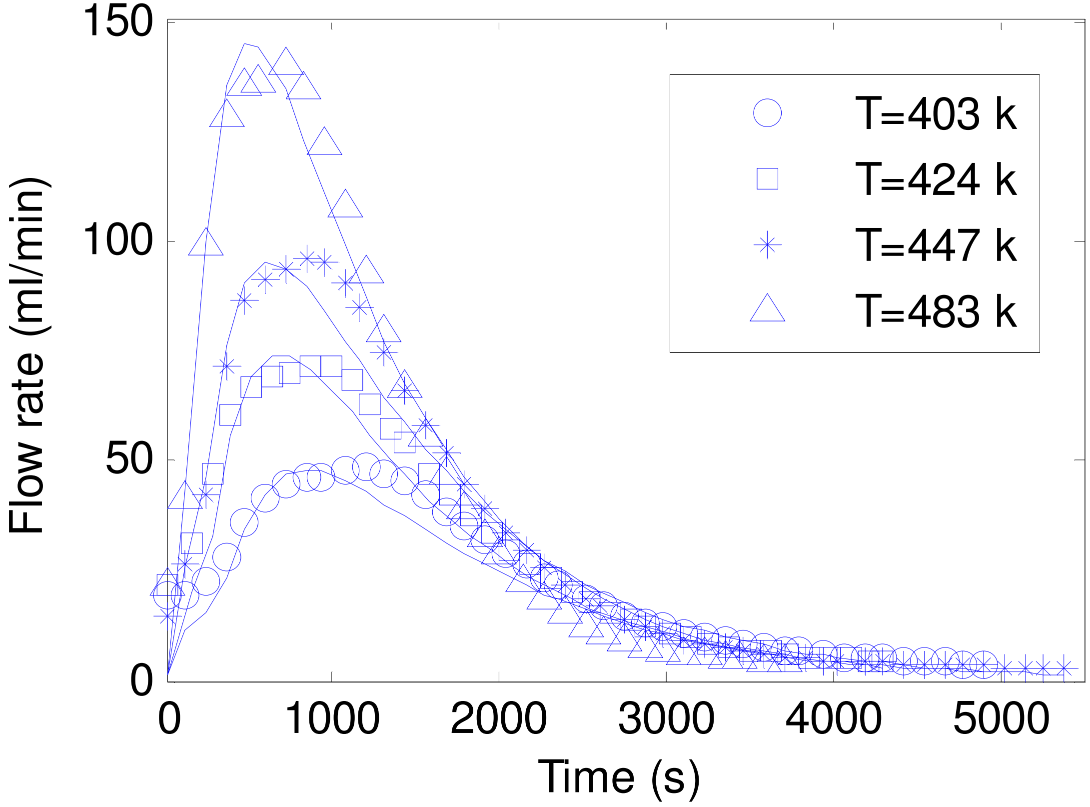
Non estimable k_c : value fixed from literature to 10 $W.m^{-2}K^{-1}$

D : value fixed from literature to 2.10^{-5} $m^2.s^{-1}$

REGENERATION STEP

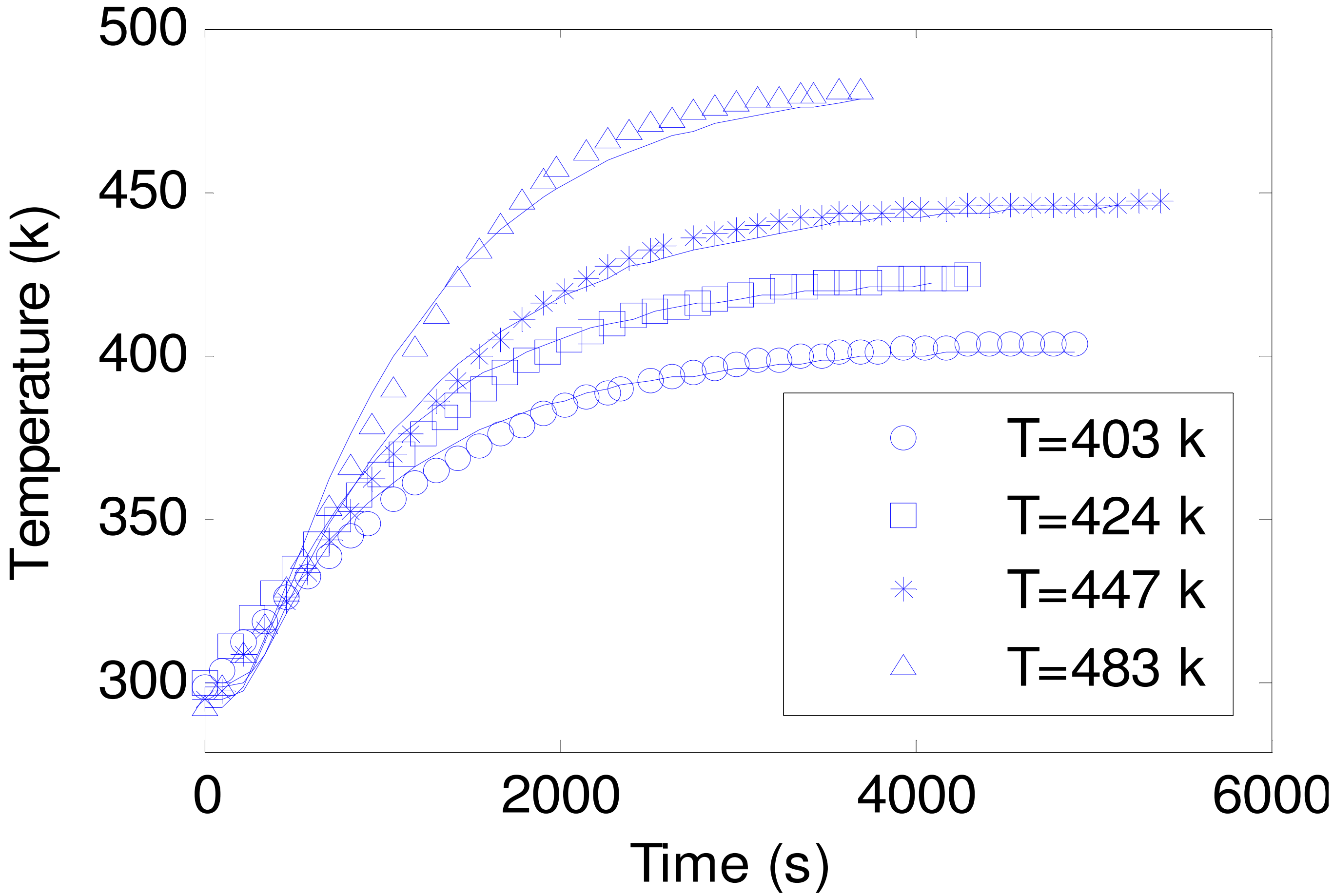
Outlet gas flow rates

T (K)	k_1 (s^{-1})	λ ($Wm^{-1}K^{-1}$)
403	0.0014	0.0654
424	0.0018	0.0685
447	0.0018	0.0609
483	0.0022	0.0650



REGENERATION STEP

Temperature profiles (center of the column)



CONCLUSIONS

- 2D non isothermal model developed to simulate a TSA process
  - temperature and concentration for adsorption step
  - temperature and flow rate for regeneration step
- Estimability analysis carried out
- Parameters identification from
  - T and CO_2 concentration for adsorption step
  - T and gas flow rate for regeneration step
- Good agreement with the experimental measurements in both adsorption and regeneration steps .

Thank you for your attention