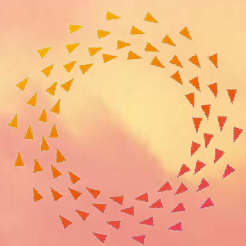


MODELLING OF FIXED-BED CO₂ ADSORPTION COLUMN FOR
DIRECT AIR CAPTURE

Jere Elfving, VTT



**NEO
CARBON
ENERGY**

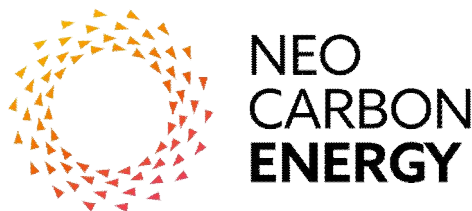
Neo-Carbon Energy 9th Researcher's seminar
11.-13.12.2017 Lappeenranta

Introduction

- Equilibrium working capacity (EWC) modelling can be used for sorbent comparison or preliminary process comparison analysis*
- However, EWC analysis does not assess dynamics → cannot be used for reliable specific energy requirement analysis

→ Modelling of fixed-bed dynamics required

- Assumption: TSA process with a long bed approximated well by 1-D model**
 - Previous results utilized in the model: T-dependent Toth parameters and adsorbent characteristics



*See: J. Elfving, C. Bajamundi, J. Kauppinen, T. Sainio, Modelling of equilibrium working capacity of PSA, TSA and TVSA processes for CO₂ adsorption under direct air capture conditions, J. CO₂ Util. 2017; 22: 270–277.

And

J. Elfving, C. Bajamundi, J. Kauppinen, Characterization and performance of direct air capture sorbent, Energy Procedia. 2017; 114: 6087 – 6101.

**S. Farooq, D.M. Ruthven, Heat effects in adsorption column dynamics. 1. Comparison of one- and two-Dimensional models, Ind. Eng. Chem. Res. 1990; 29: 1076–1084.

And

S. Farooq, D.M. Ruthven, Heat effects in adsorption column dynamics. 2. Experimental validation of the one-dimensional model, Ind. Eng. Chem. Res. 1990; 29: 1084–1090.

Modelling goals

- Model CO₂ capture in a fixed bed in cyclic operation
 - Fitting to experimental dynamic data → dynamic parameters → use fitted parameters for simulation of fixed bed in various conditions
 - CO₂ concentration and temperature profiles in adsorption/desorption
 - CO₂ production during desorption (working capacity)
 - Specific energy requirement estimate
 - Scale-up
 - Testing different sorbent and process options
- **Minimize the specific energy requirement of DAC**

Model balances: 1-D fixed-bed adsorption

- Mass and energy balances modelled by widely used equations*:

Adsorption rate equation approximated by linear driving force (LDF) model

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - v_i \frac{\partial c}{\partial z} - \left(\frac{1-\varepsilon}{\varepsilon} \right) \rho_s \frac{\partial q}{\partial t}$$

- Axially dispersed plug-flow
- Constant total pressure
→ constant velocity

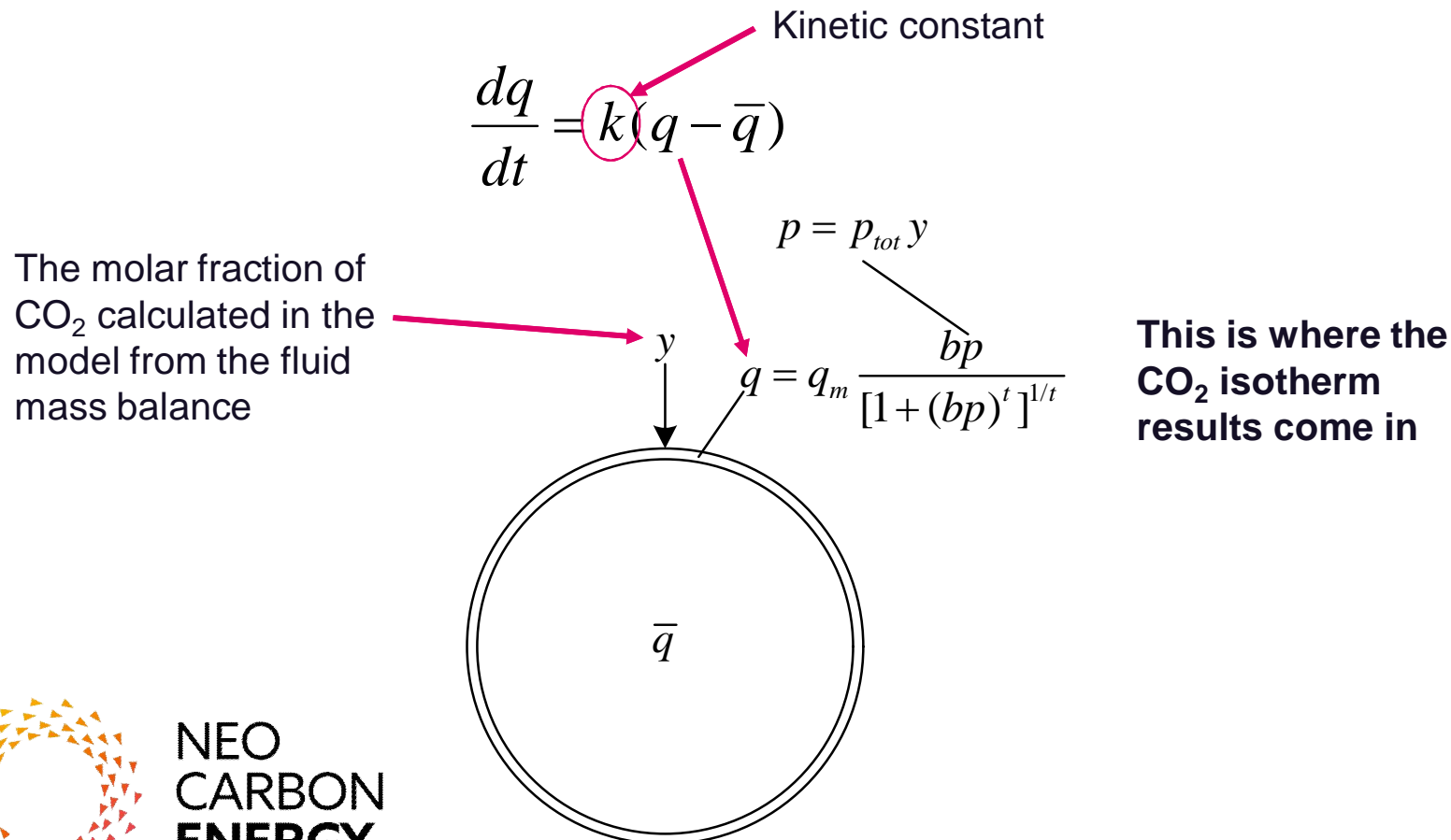
Overall heat transfer coefficient

$$\frac{\partial T}{\partial t} = \frac{K_z \frac{\partial^2 T}{\partial z^2} - v_i \varepsilon \rho_g c_g \frac{\partial T}{\partial z} - (-\Delta H) \rho_B (1-\varepsilon) \frac{\partial q}{\partial t} - \frac{2h}{R} (T - T_{wall})}{\varepsilon \rho_g c_g + (1-\varepsilon) \rho_s c_s}$$

- Gas temperature = adsorbent temperature

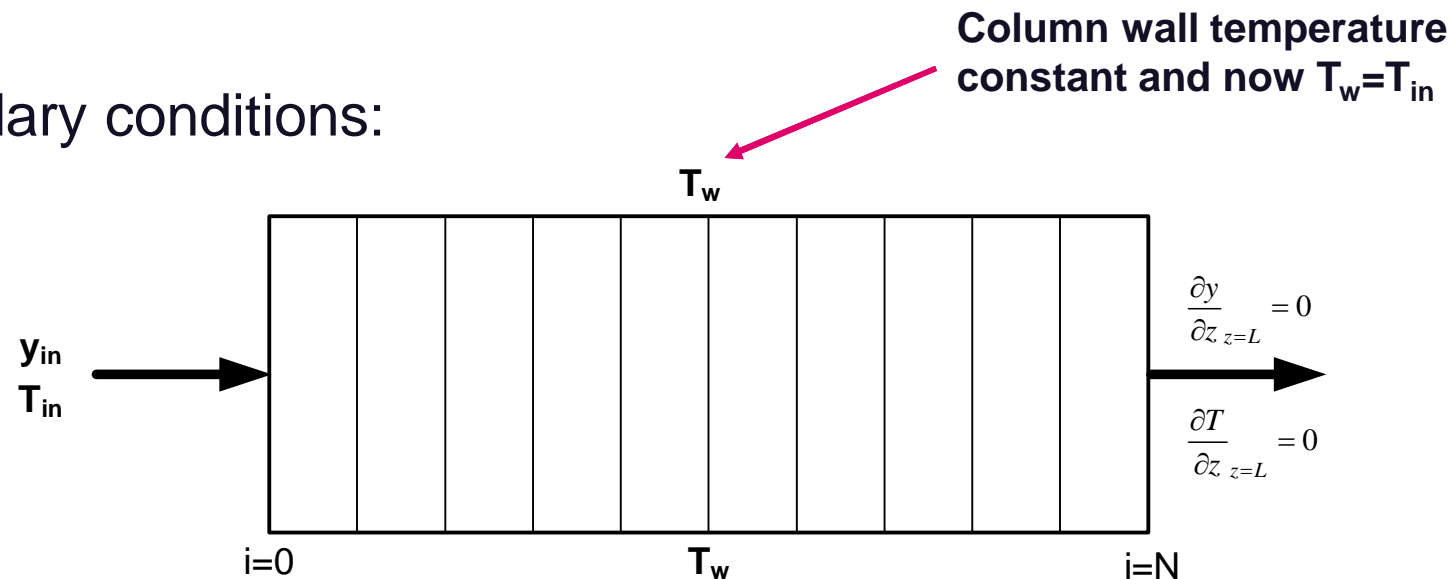
Adsorption in the particle

- LDF model determines the adsorption rate:



Boundary & initial conditions

- Boundary conditions:



- Initial conditions:

- Adsorption from fresh sorbent: $y=0$, $q=0$, $T=T_{in}$
- Otherwise: column state preserved from the previous phase

Numerical methods

- Method of lines:
 - Spatial discretization in a separate function
 - Built-in Matlab solver used to integrate ODEs
 - Here “ODE15s” or “ODE23t”

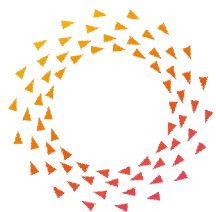
- Discretization method: Finite difference

- 1st order backward for convective terms:

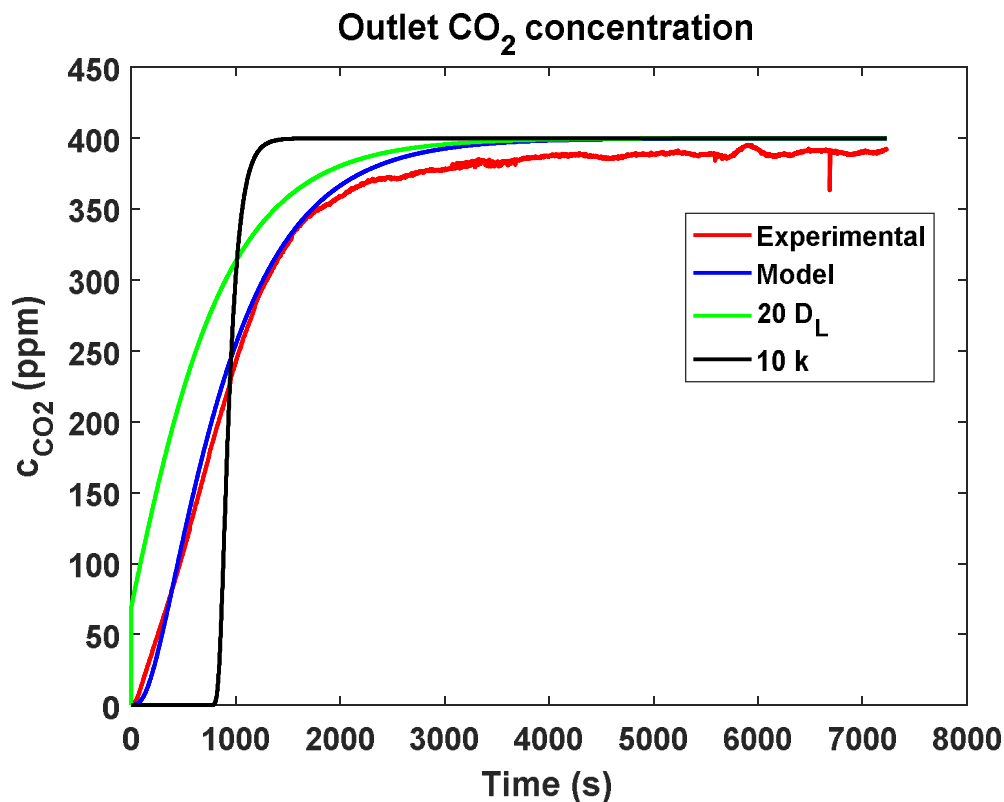
$$\frac{\partial X}{\partial z} \approx \frac{X(i) - X(i-1)}{\Delta z}$$

- 2nd order central for dispersion/conduction terms:

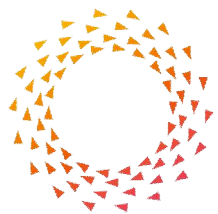
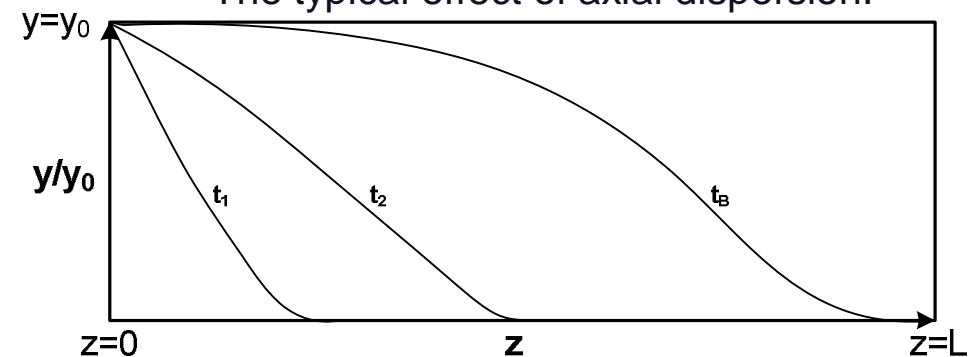
$$\frac{\partial^2 X}{\partial z^2} \approx \frac{X(i+1) - 2X(i) + X(i-1)}{\Delta z^2}$$



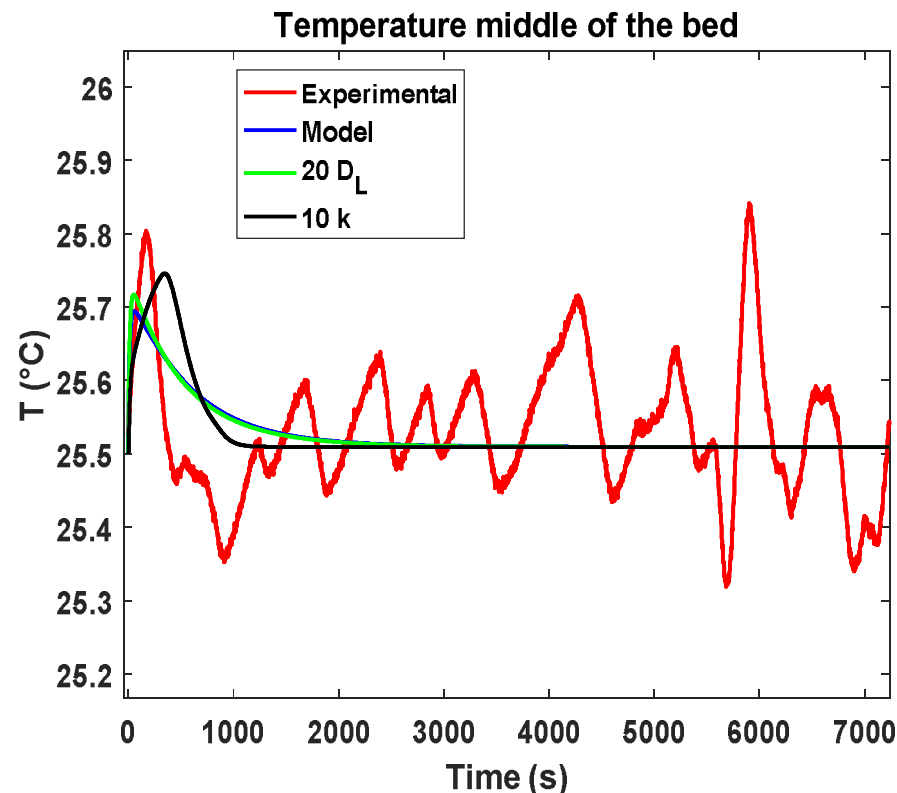
Fitting of dynamic experimental data



- Difference between the model and the experiment when reaching saturation, possible reasons:
 - Underpredicting the equilibrium capacity
 - Inadequate kinetic model
 - Nonideal outlet measurement
- Increasing $k \rightarrow$ ideal behaviour
 - Faster adsorption
- Increasing $D_L \rightarrow$ prolonged adsorption step
 - The typical effect of axial dispersion:

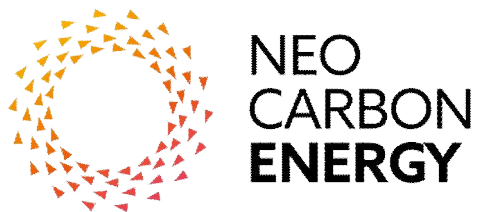
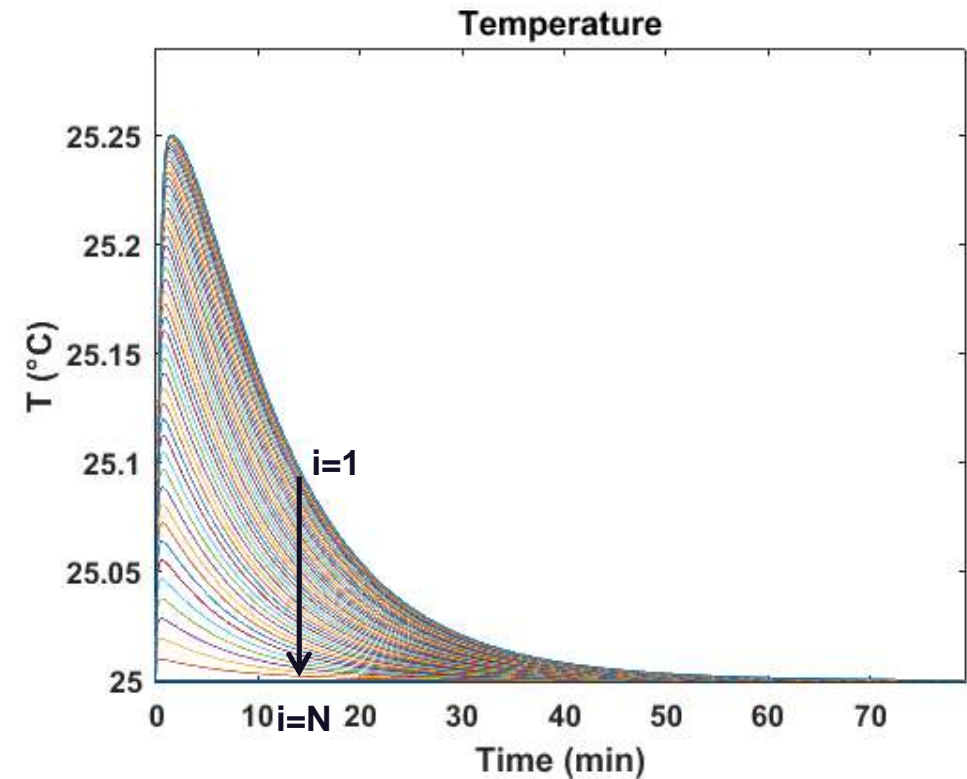
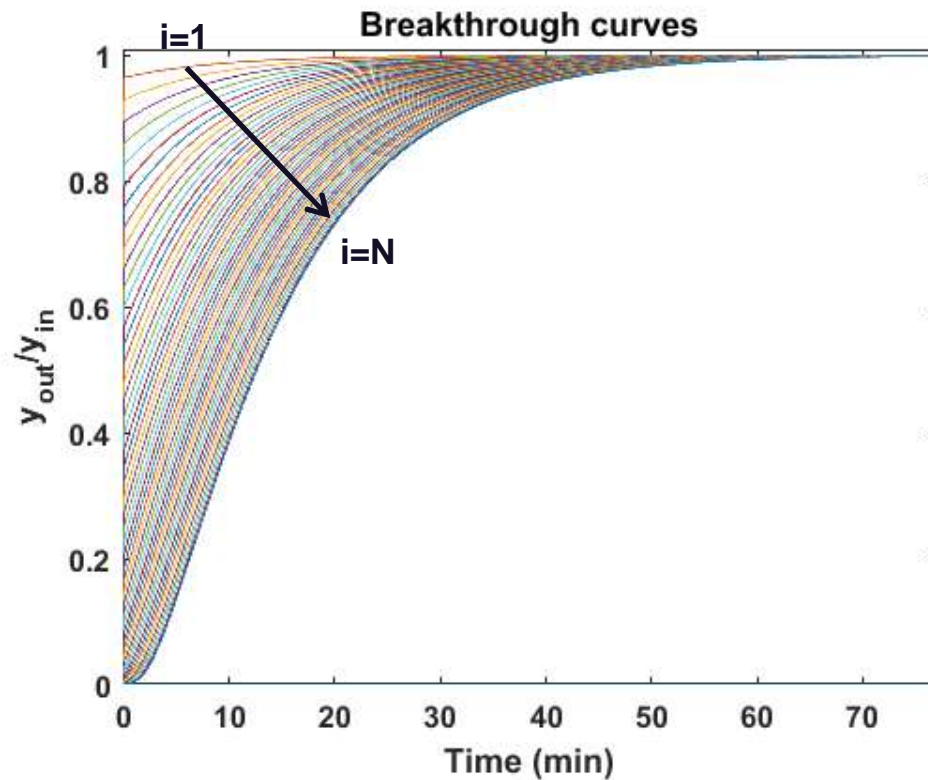


Fitting of dynamic experimental data



- Very small adsorption temperature peak
 - Lost in the noise
 - more accurate temperature control & measurement system required
- Increasing k or D_L also affect the shape and size of the temperature peak

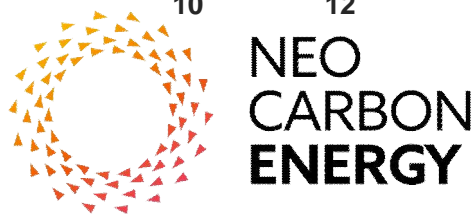
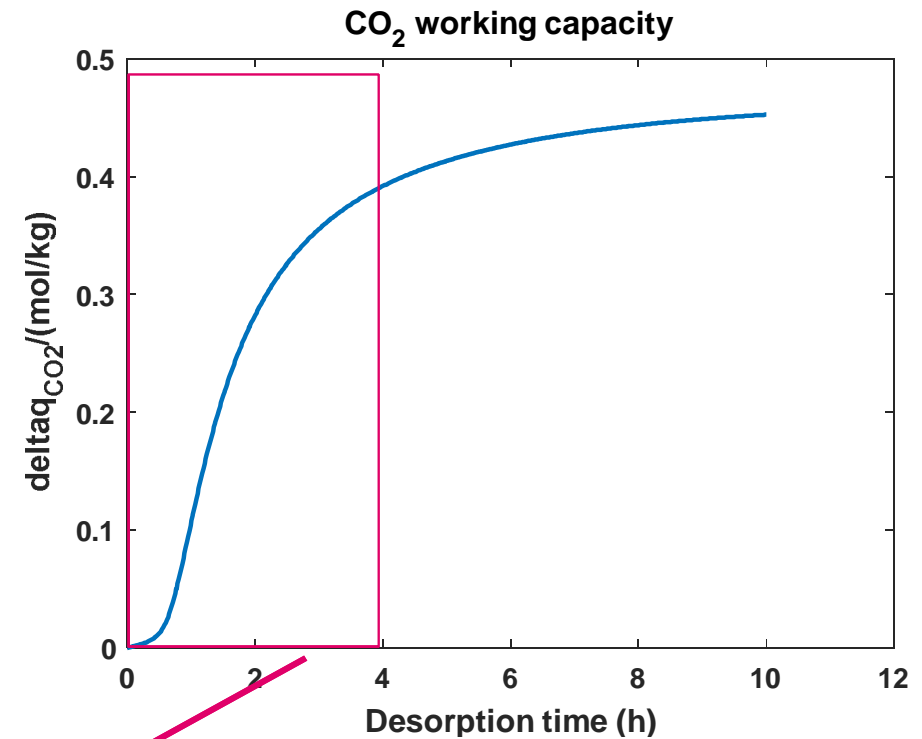
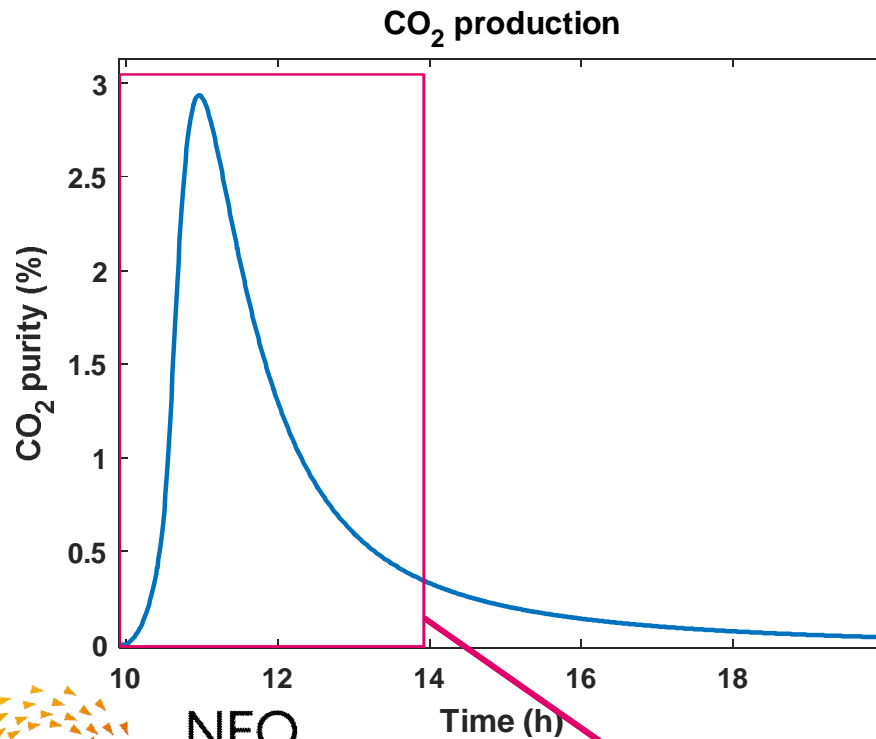
Lab-scale column adsorption dynamics



- Similar conditions as in the experimental:
 - 0.5 g adsorbent in fixed-bed
 - 1 l/min total flow rate
 - 400 ppm CO₂

Bench-scale column desorption dynamics

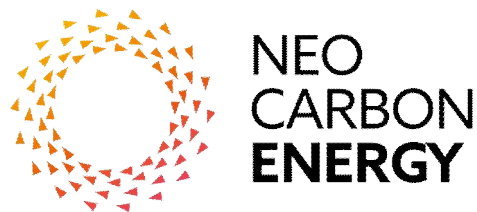
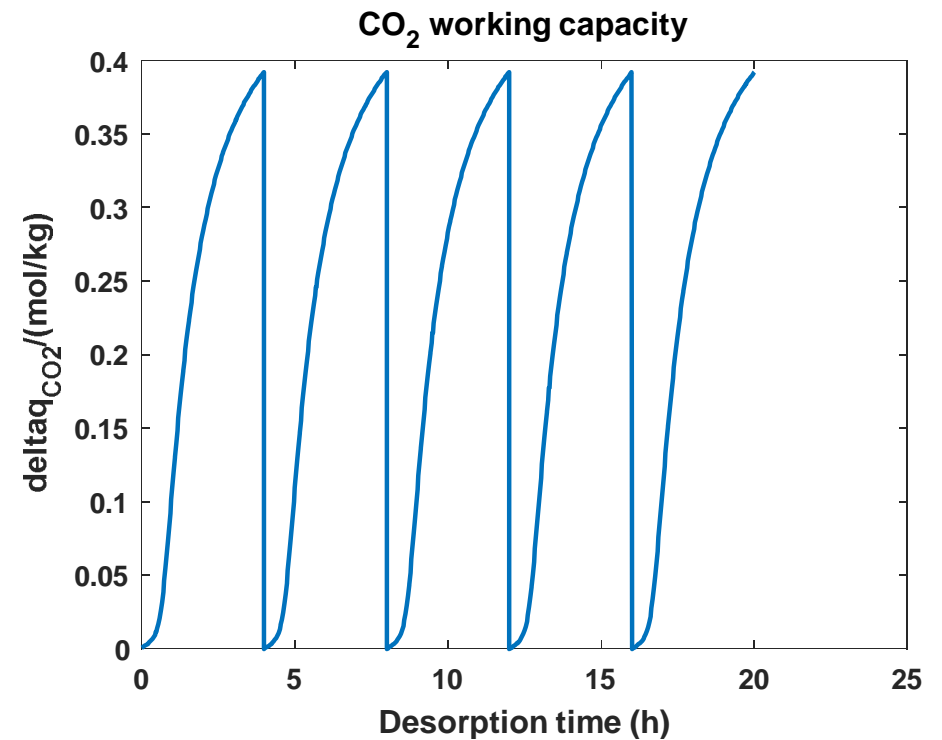
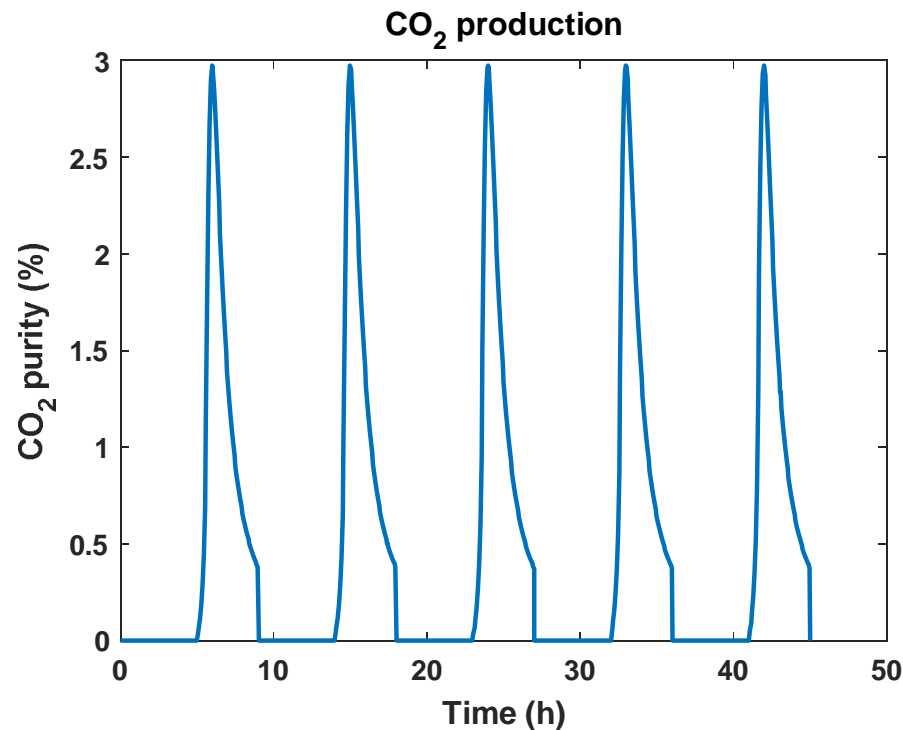
- Case: Producing low-purity CO₂ in bench-scale
 - Sample size 500 grams in the model
 - Using the same fitted dynamic parameters (k , D_L , K_z , h)
 - Temperature-swing adsorption



Bulk of the production takes place during the first 4 h
 → After this the purity decreases too low even for this case
 → **Too long desorption step**

Bench-scale column desorption dynamics

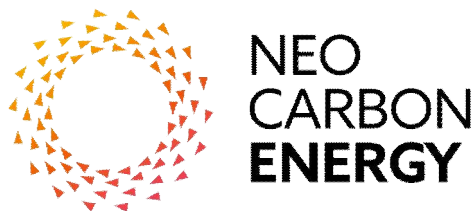
- Cyclic CO₂ purity and working capacity in 5 cycles
- Shortened cycles



- Almost 90% of working capacity preserved with 60% shorter desorption cycles
- Parallel columns required to supply concentrated CO₂ continuously
- Specific energy requirement of regeneration 0.67 MJ/kg_{CO₂}
 - **Ideal value: no heat losses**

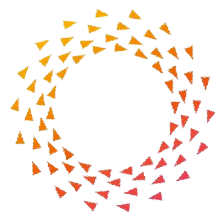
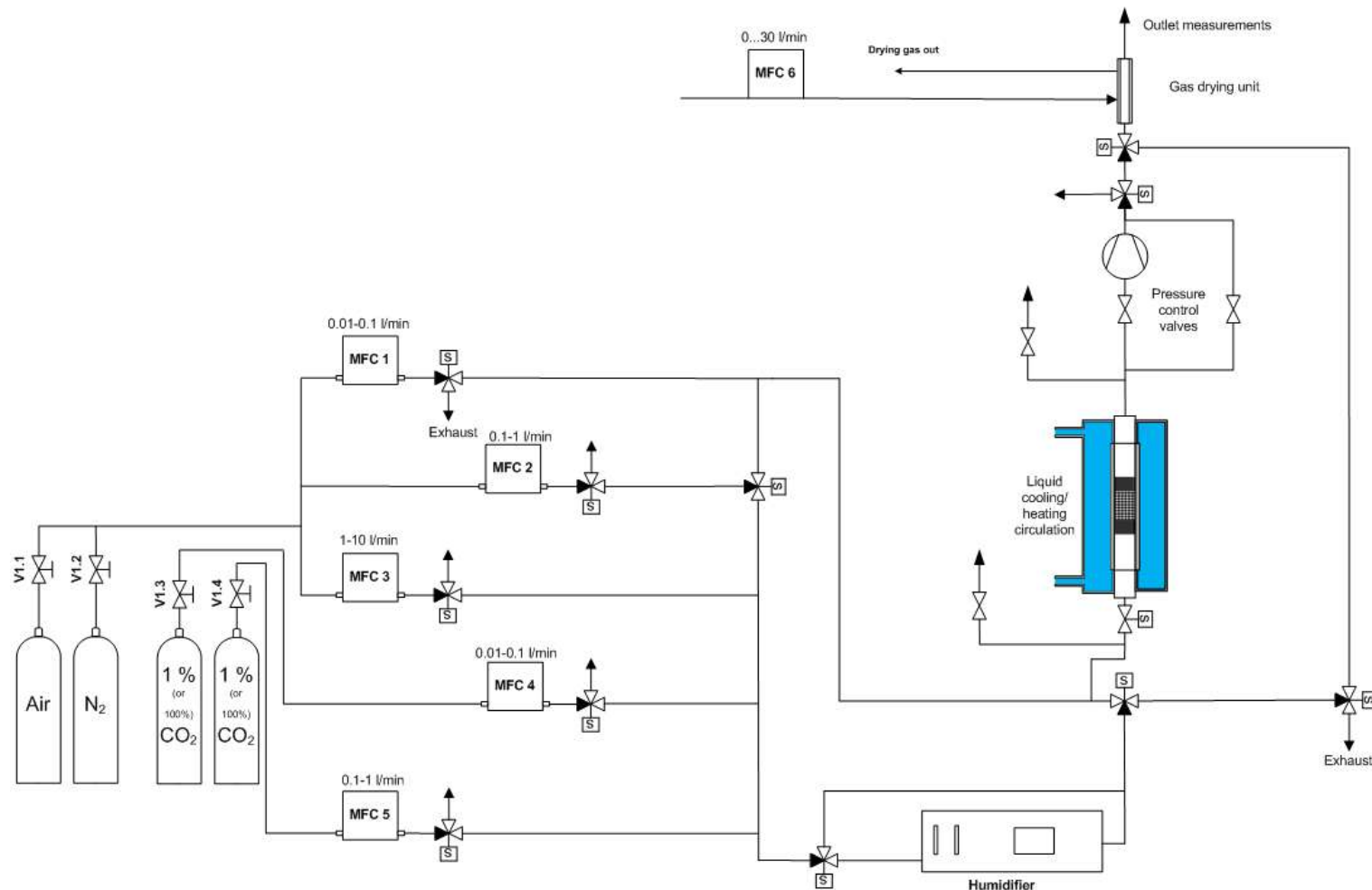
Points of improvement

- Fitting better experimental data
 - Acquired from new experimental setup which is underway
 - Other adsorbents
- Adding momentum balance
 - Variable total pressure and velocity
- Taking humidity into account
 - Rigorous way: Using a semi-empirical isotherm model for CO₂+H₂O adsorption CO₂+H₂O and H₂O isotherms in multiple CO₂ and H₂O partial pressures
 - Easier way:
 - Toth model for CO₂ adsorption
 - Separate model for H₂O
 - Assume insignificant effect of CO₂ on H₂O adsorption
 - Use an enhancing factor* for effect of H₂O on CO₂
- More accurate energy balance modelling
 - May require 2-D modelling
- Coupling Matlab-model with Apros
 - modelling of the whole process → better specific energy analysis



*See: Wurzbacher et al., Heat and mass transfer of temperature-vacuum swing desorption for CO₂ capture from air, Chemical Engineering Journal, 283, (2016), 1329-1338

New experimental setup



**NEO
CARBON
ENERGY**

- Sorbent CO₂ Adsorption/desorption performance testing
- Cyclic runs
- Improved measurements and temperature control
- CO₂ production using different process options (TSA, TVSA, PSA...)



NEO-CARBON Energy project is one of the Tekes strategic research openings and the project is carried out in cooperation with Technical Research Centre of Finland VTT Ltd, Lappeenranta University of Technology LUT and University of Turku, Finland Futures Research Centre FFRC.