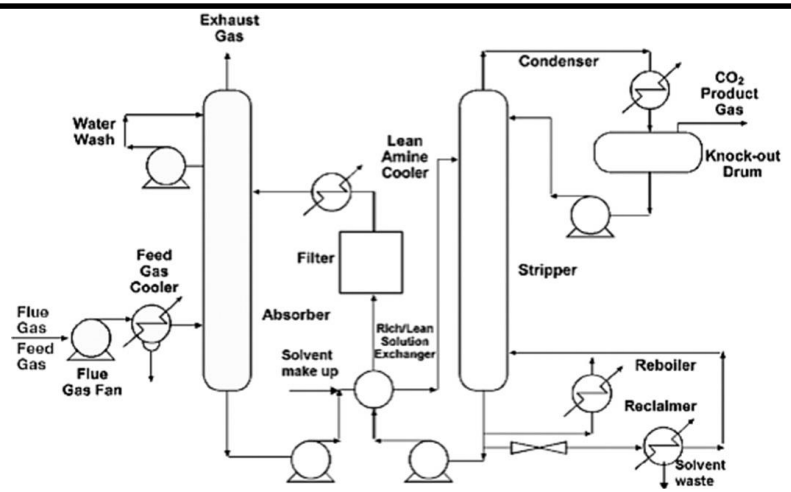
ETH zürich

Innovative TSA processes for post-combustion CO_2 capture

Max Hefti, Stefano E. Zanco, and Marco Mazzotti

SPL, Institute of Process Engineering – ETH Zürich

Introduction

ABS	 Amines (1)		
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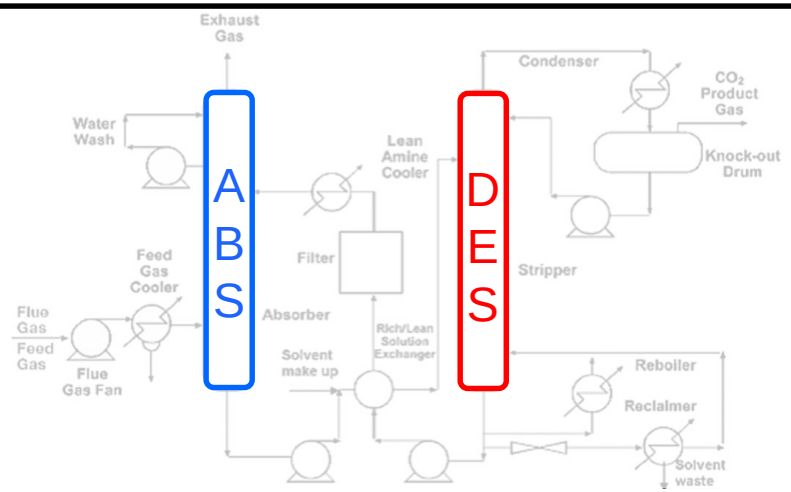
ABS	 Amines (1)		• high desorption enthalpy
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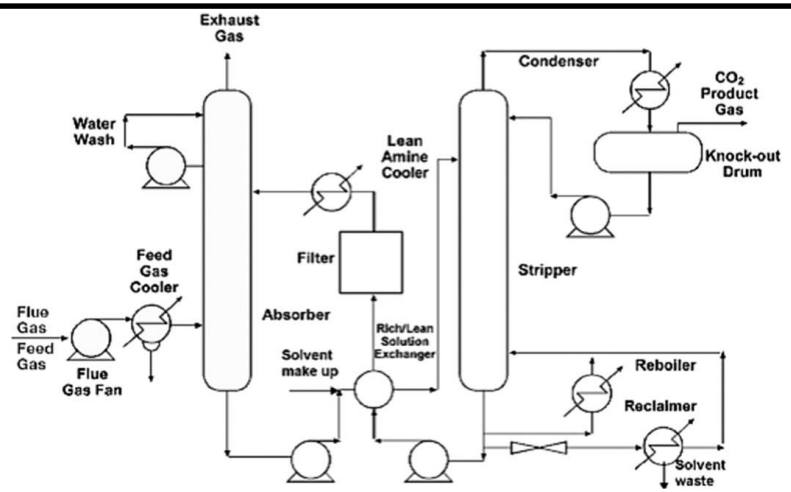
ABS	 Amines (1)		• high desorption enthalpy
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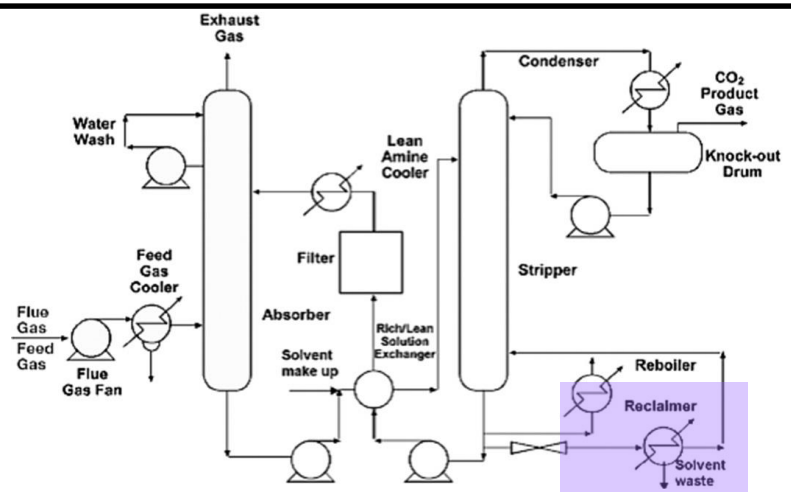
ABS	 Amines (1)		• solvent degradation • high desorption enthalpy
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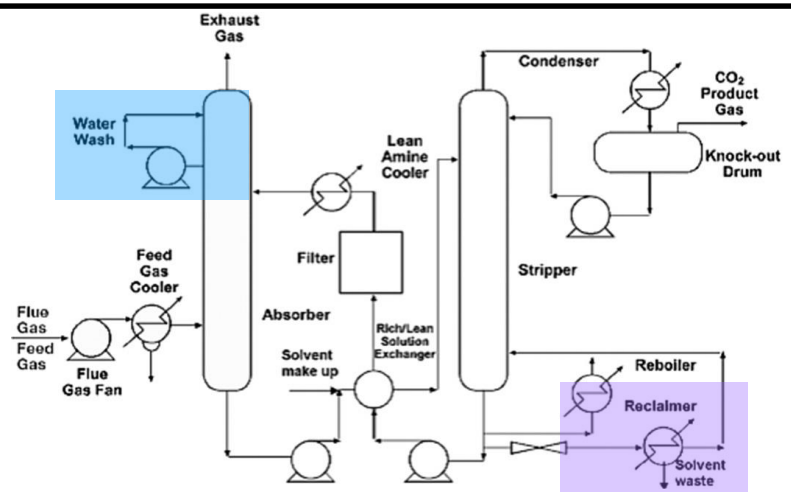
ABS	 Amines (1)		• solvent degradation • solvent slip • high desorption enthalpy
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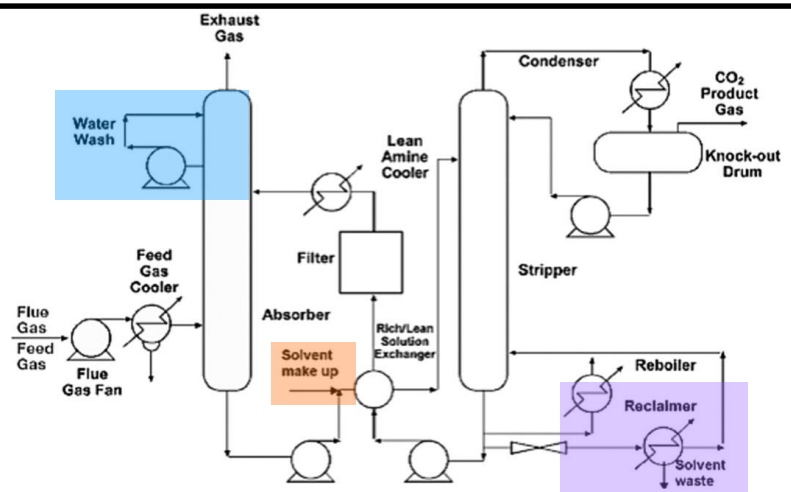
ABS	 Amines (1)		• solvent degradation • solvent slip • solvent loss • high desorption enthalpy
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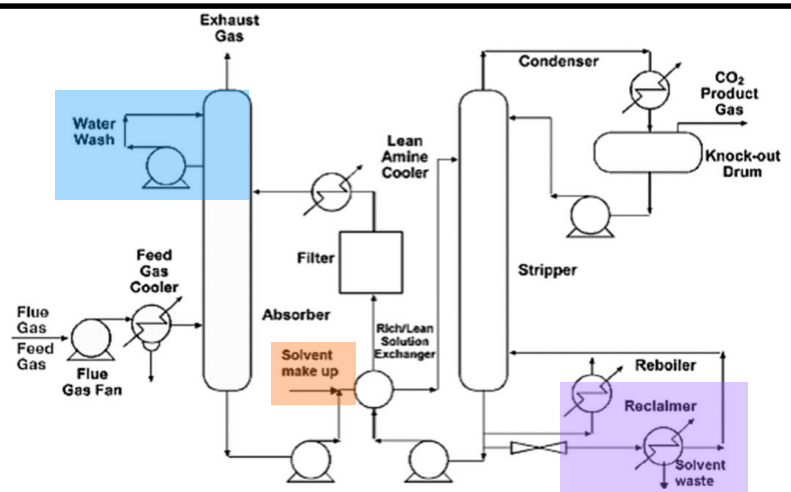

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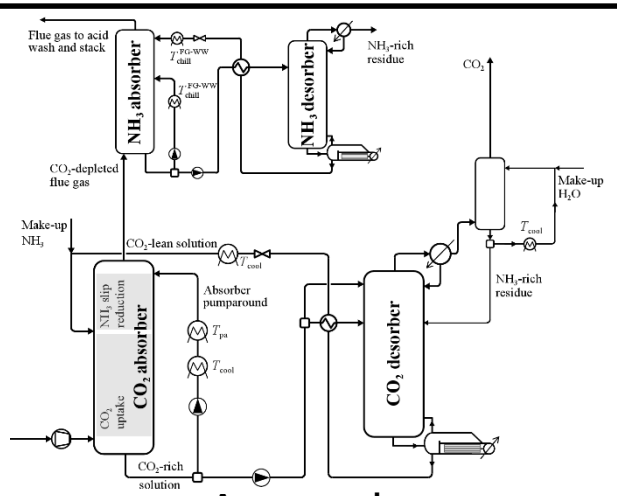

Ammonia (2)

- solvent degradation
- solvent slip
- solvent loss
- high desorption enthalpy

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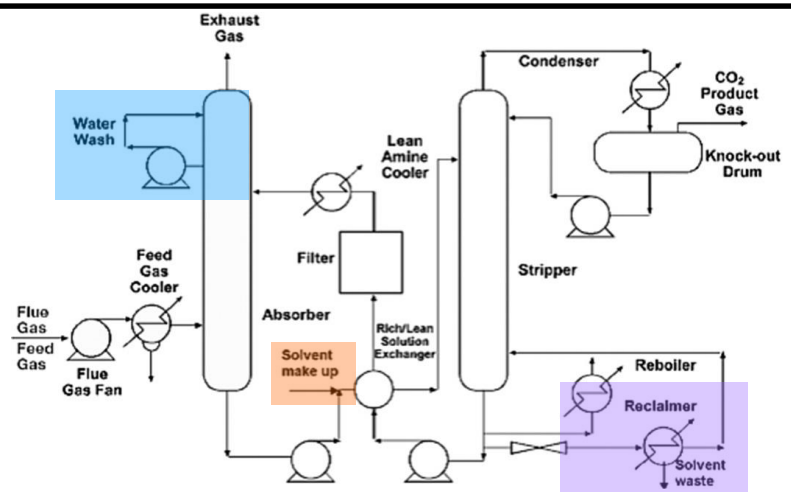

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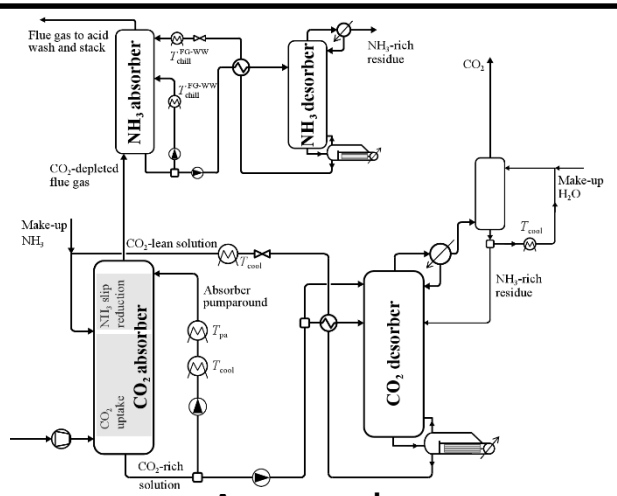

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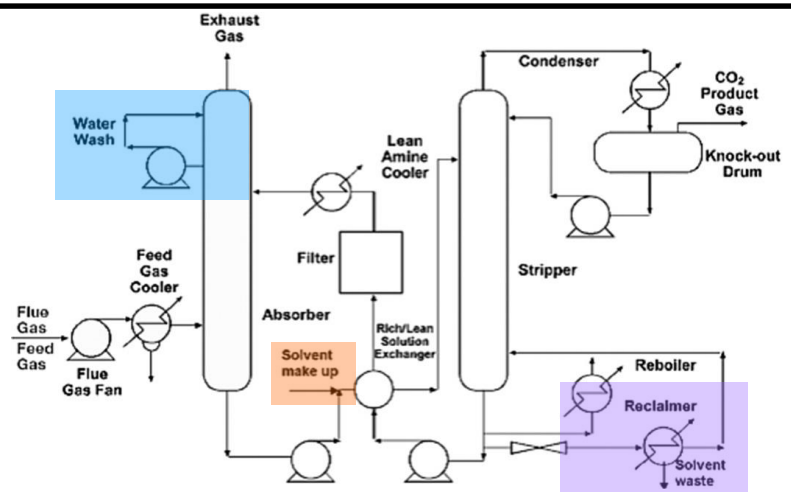

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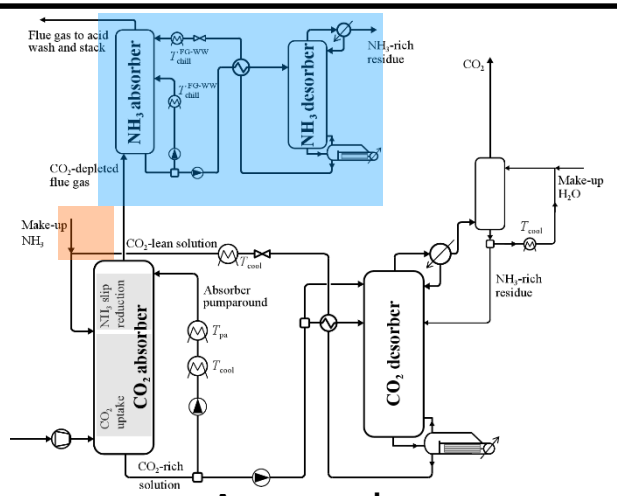

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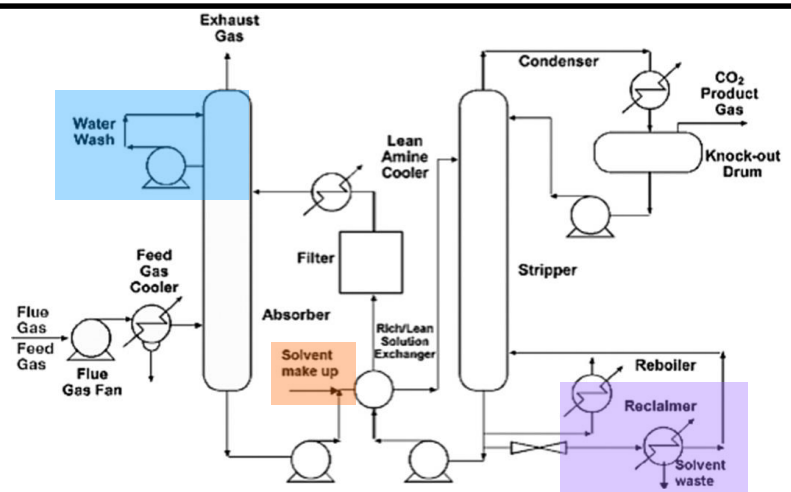

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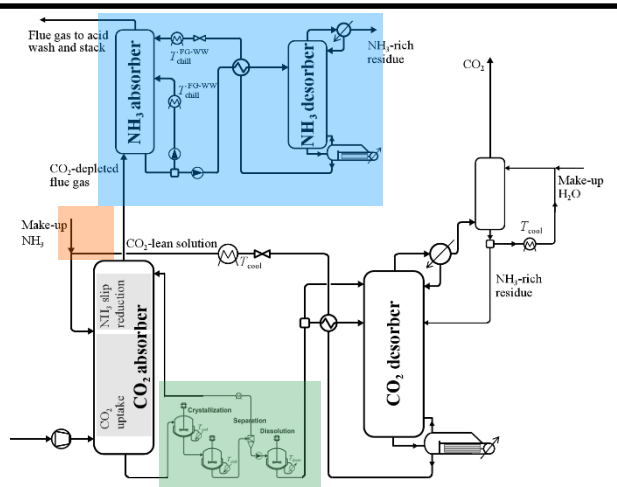

Ammonia (2)

- solid handling
- solvent slip
- solvent loss
- high desorption enthalpy

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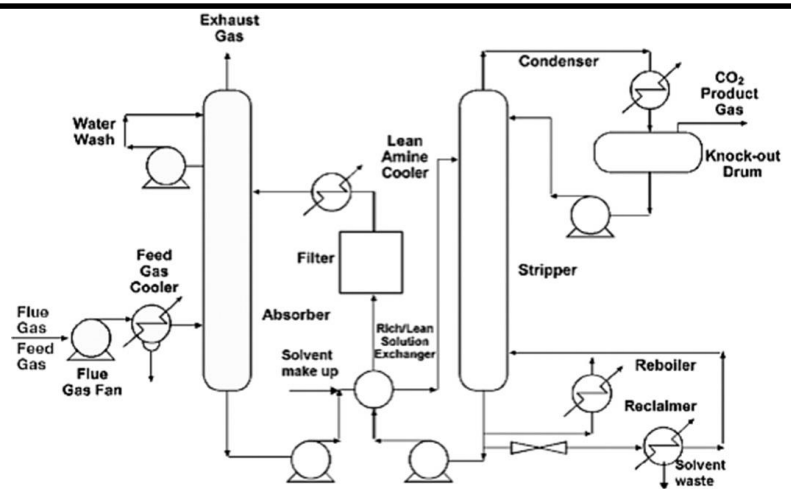

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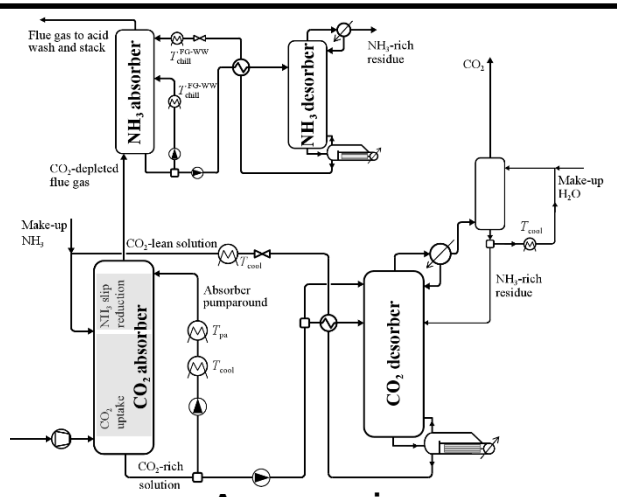

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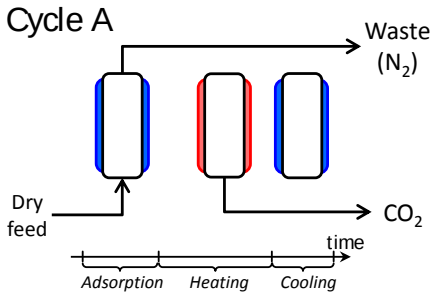

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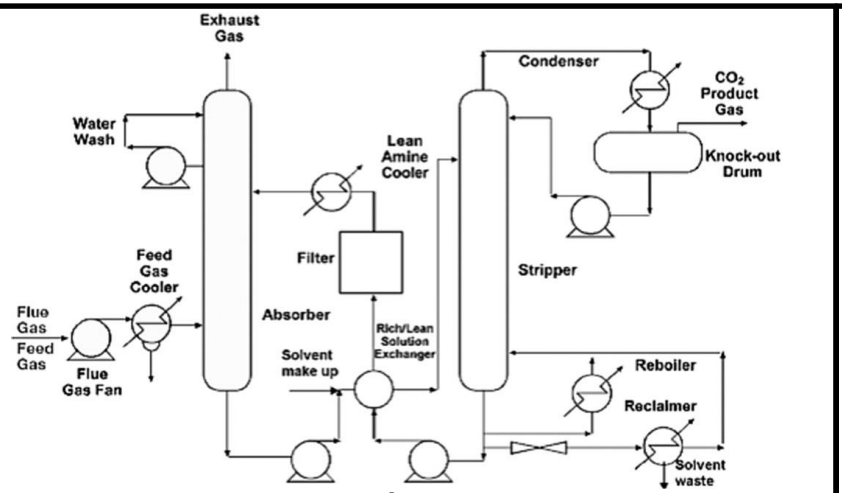

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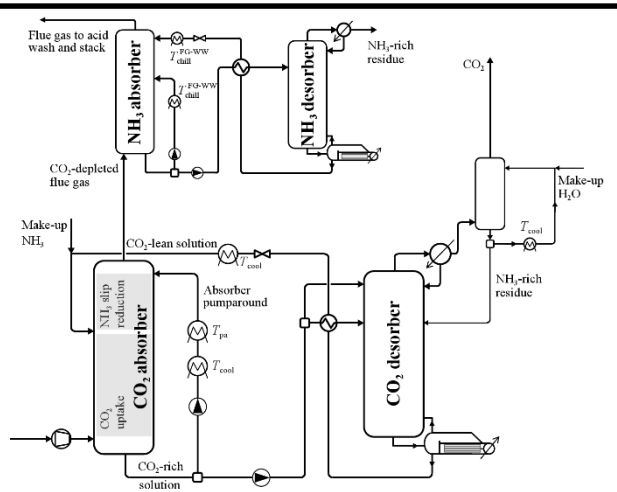

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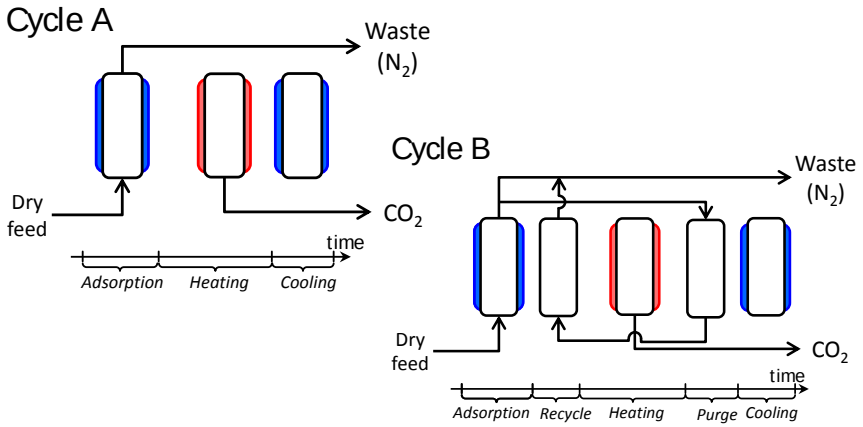

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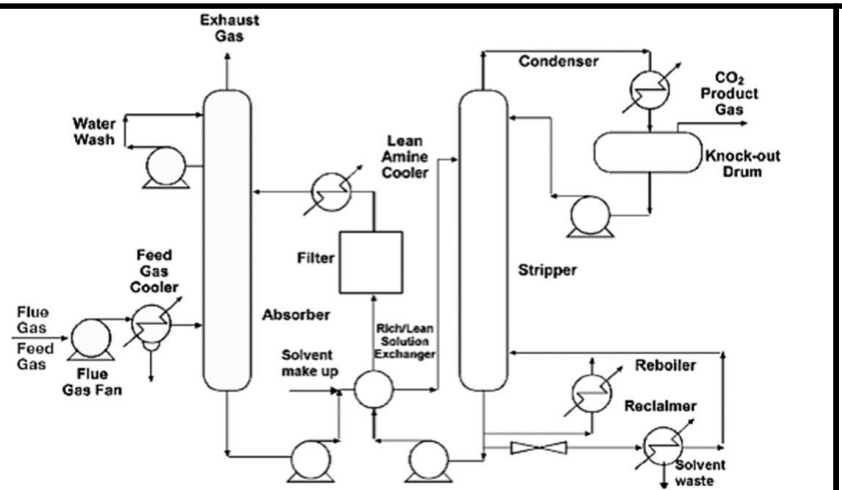

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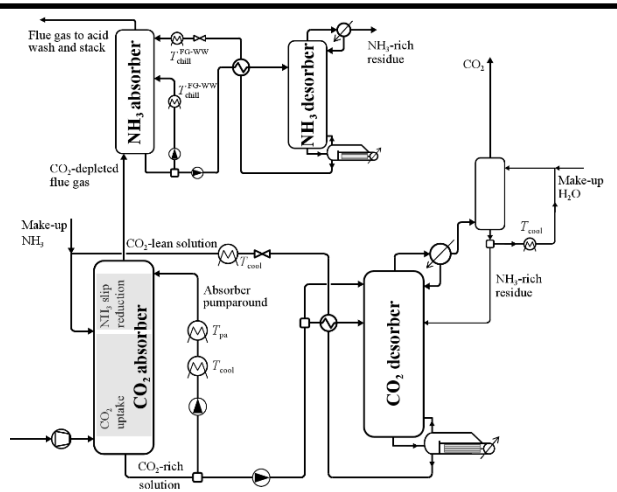

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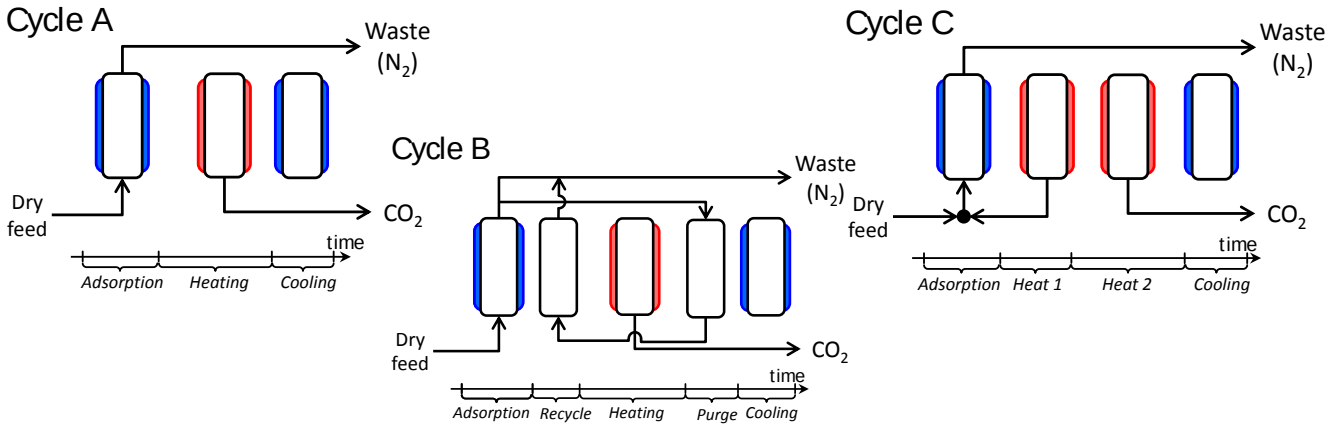

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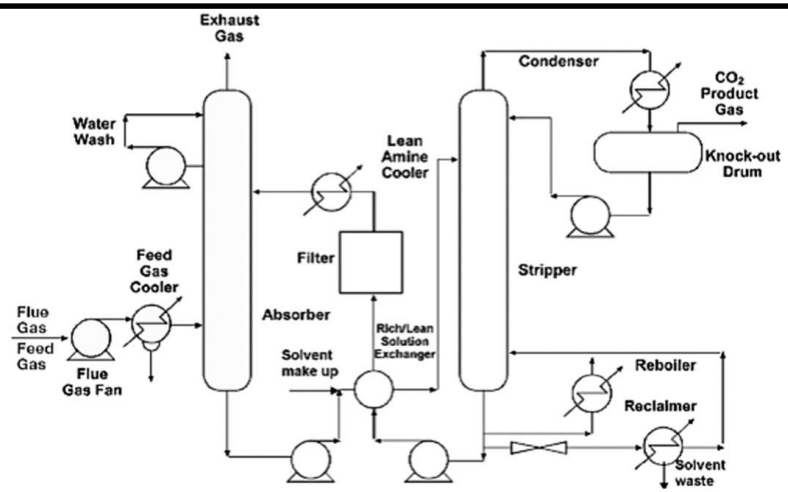

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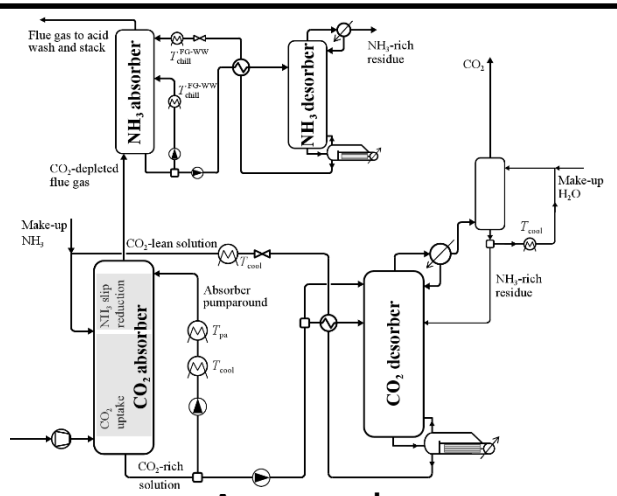

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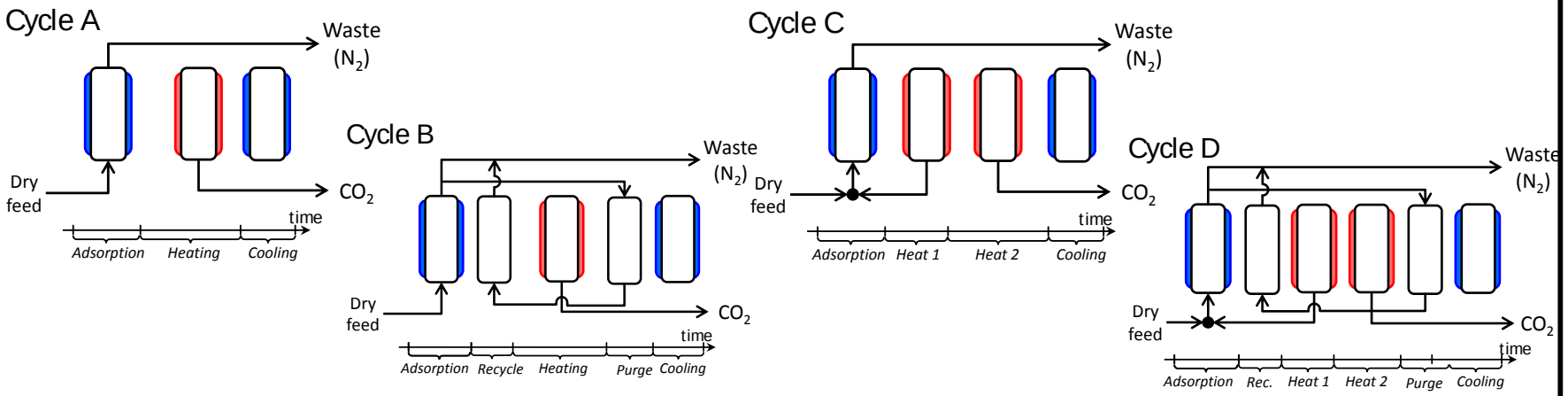

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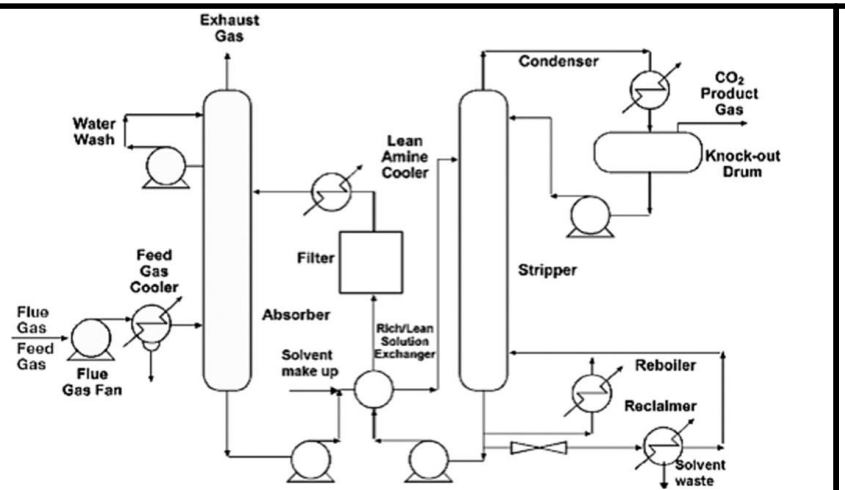

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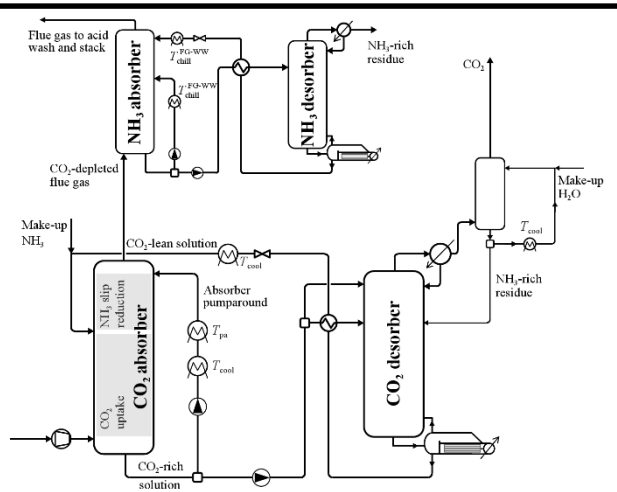

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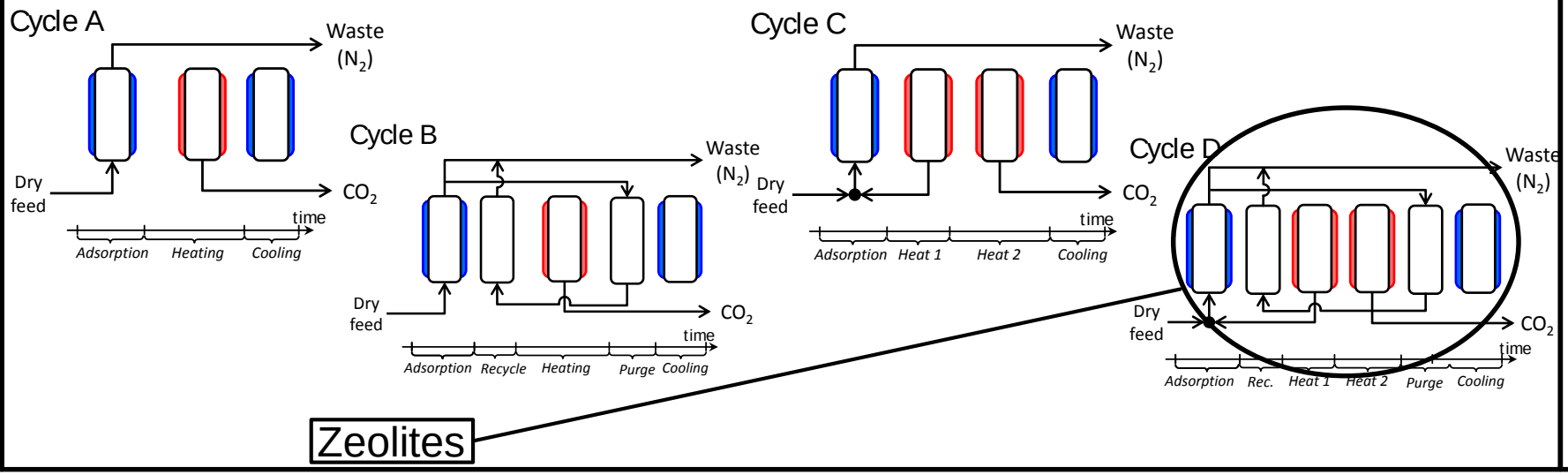

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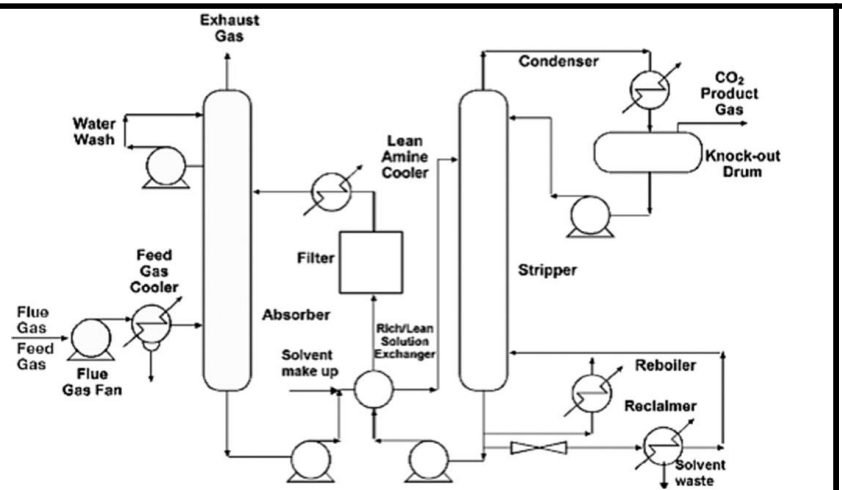

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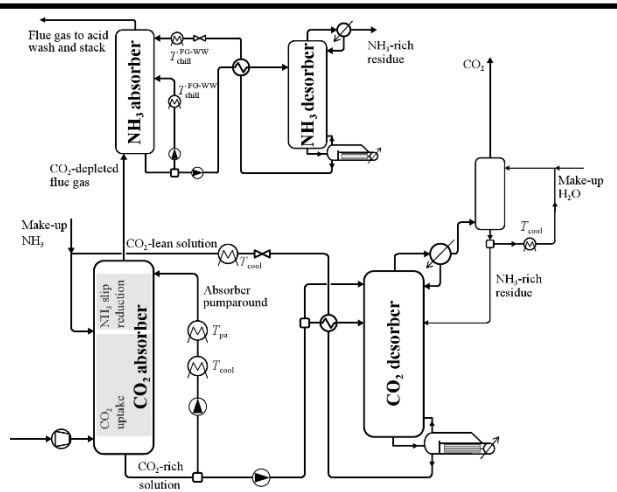

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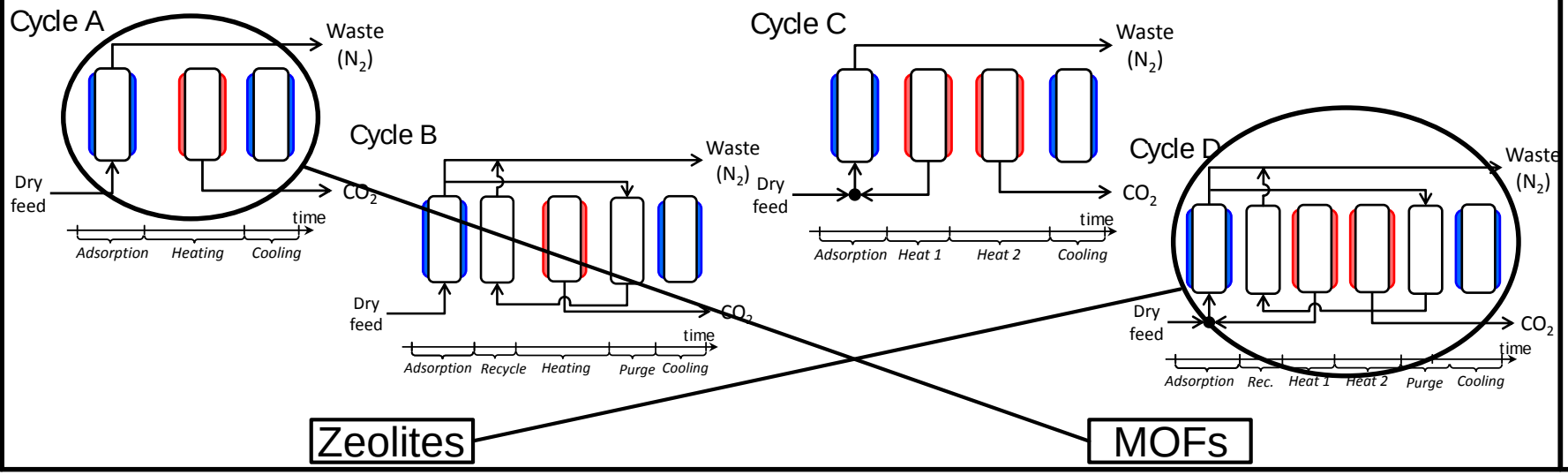

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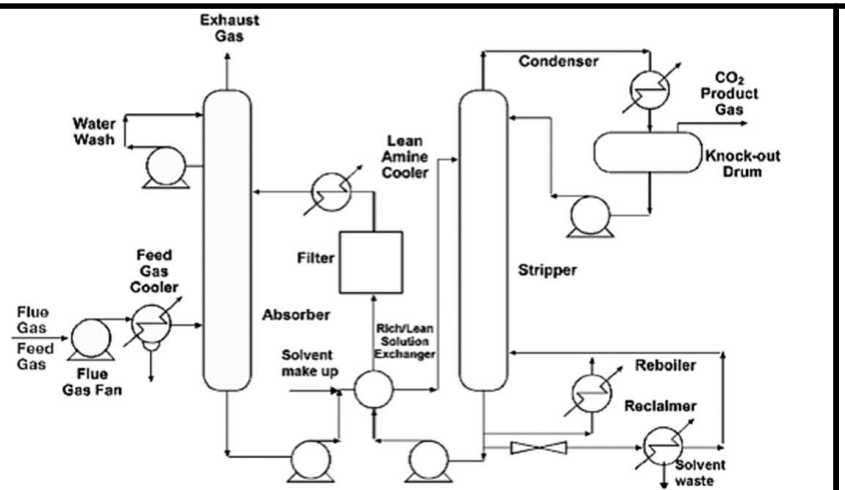

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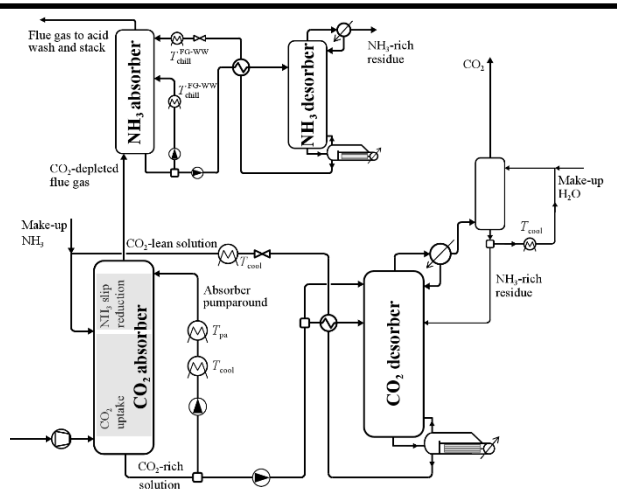

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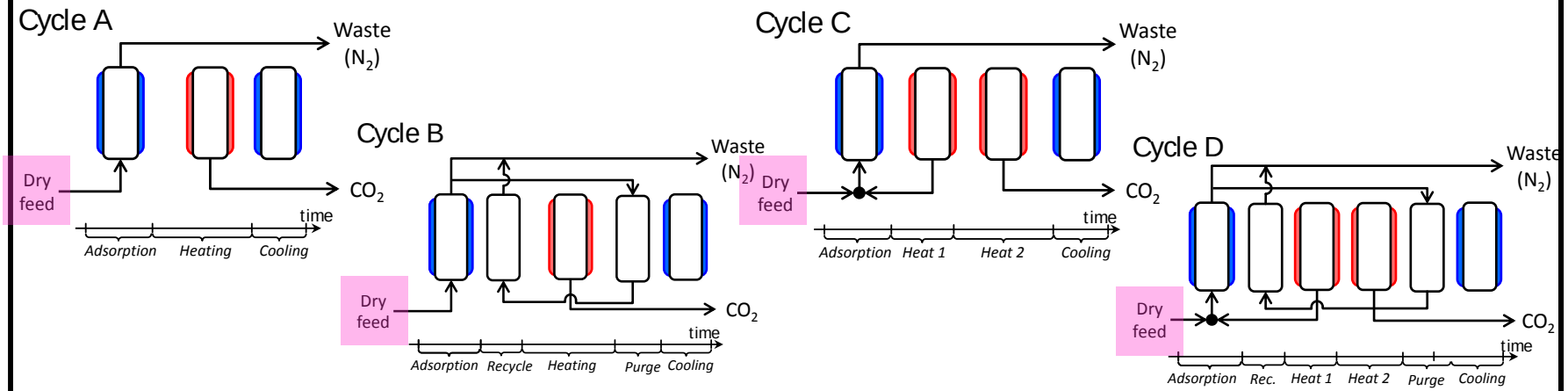

Zeolites

MOFs

- adsorbent performance degradation with water

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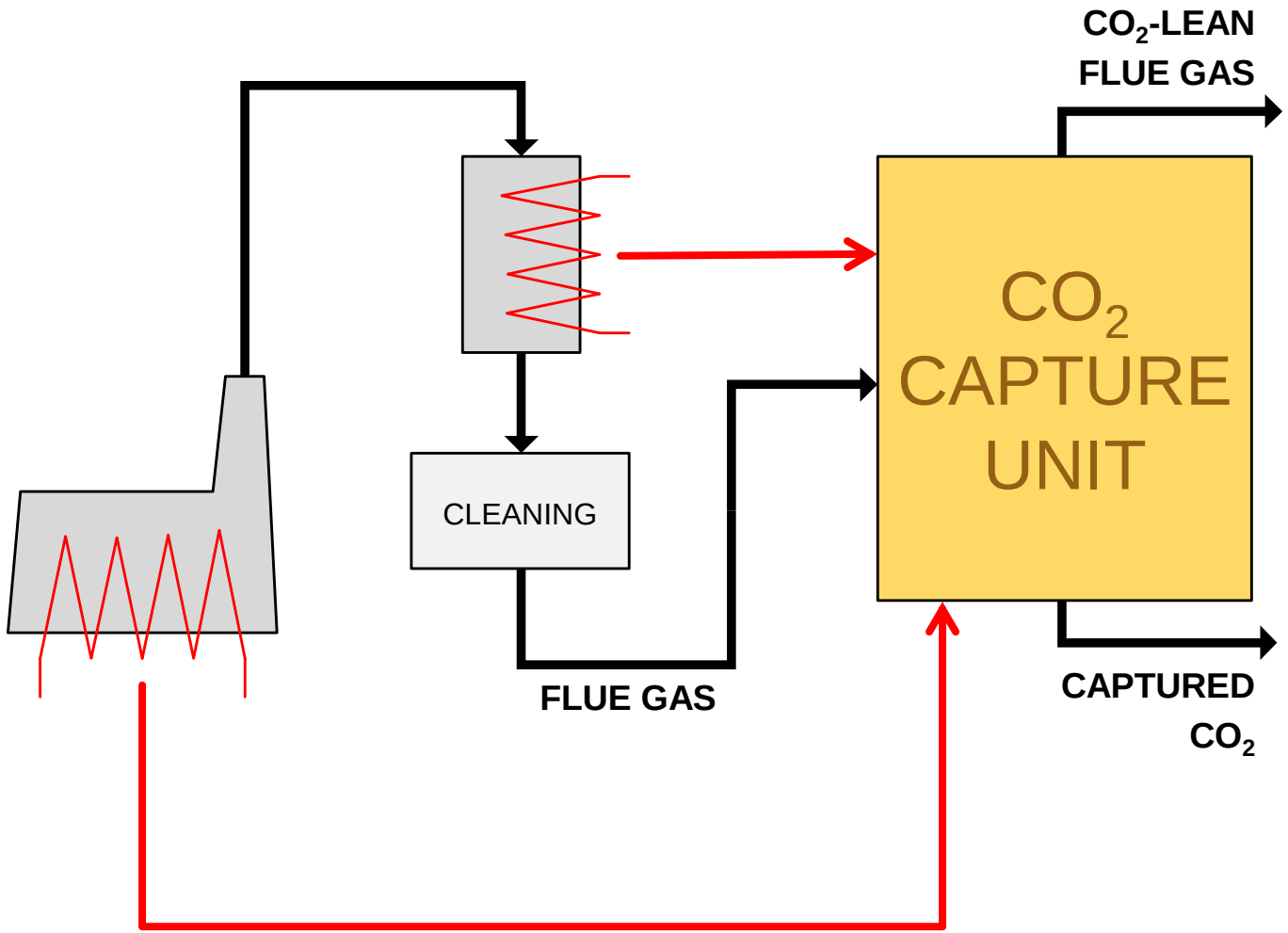
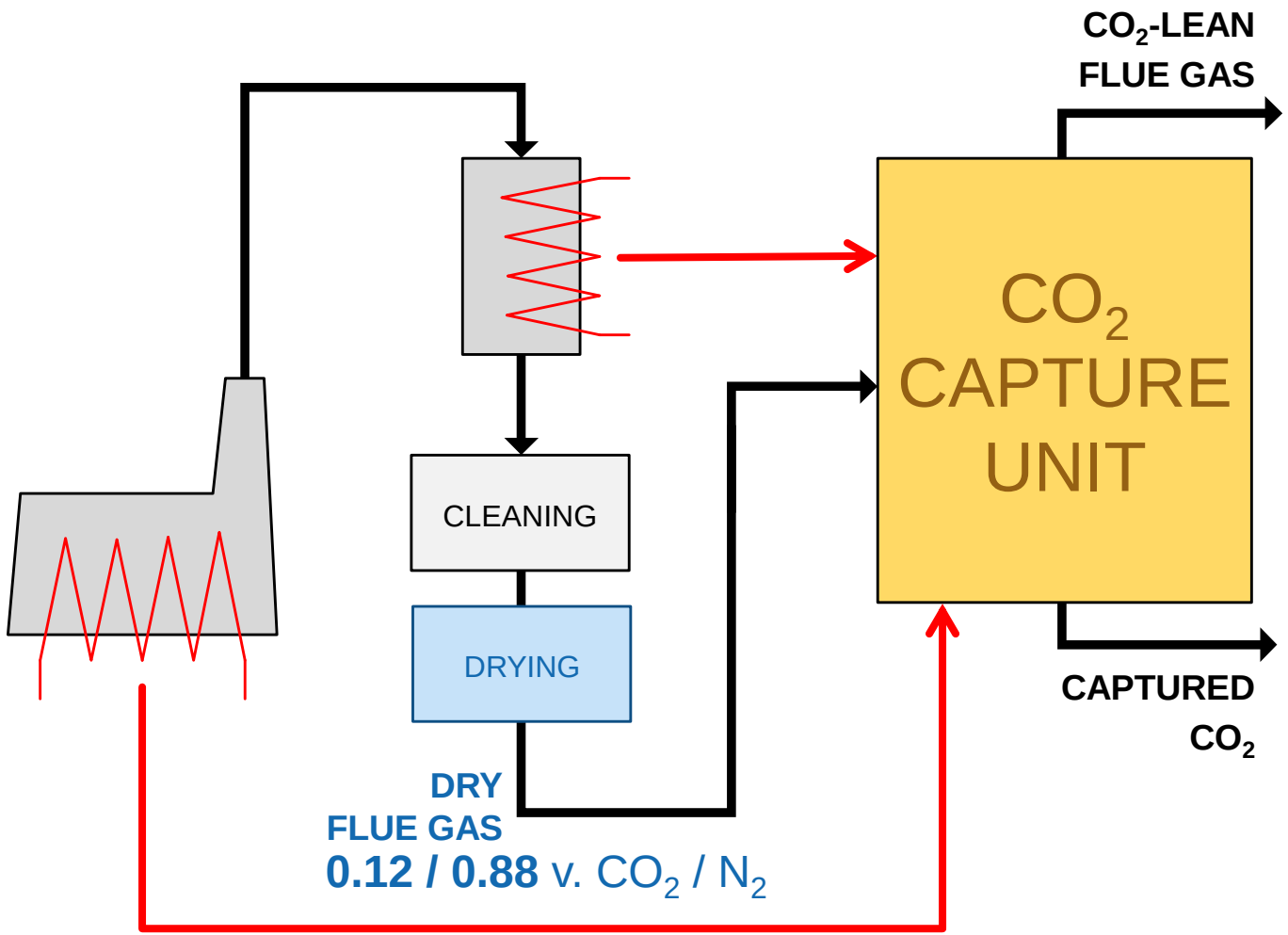
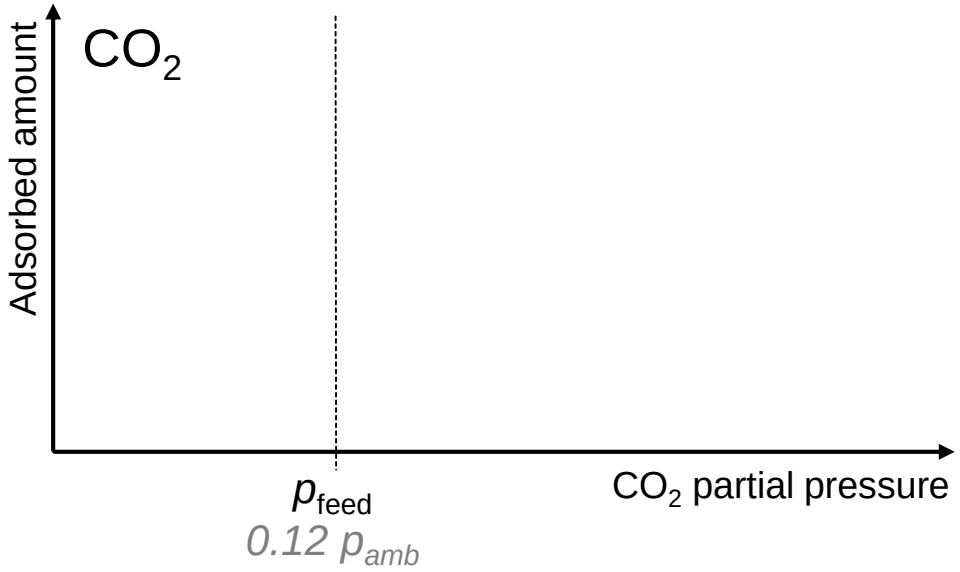
Post-combustion CO_2 capture

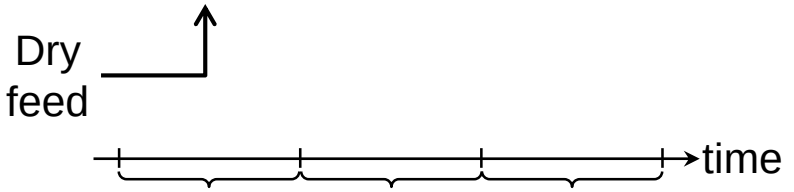


Post-combustion CO_2 capture via adsorption



TSA processes for CO_2 capture





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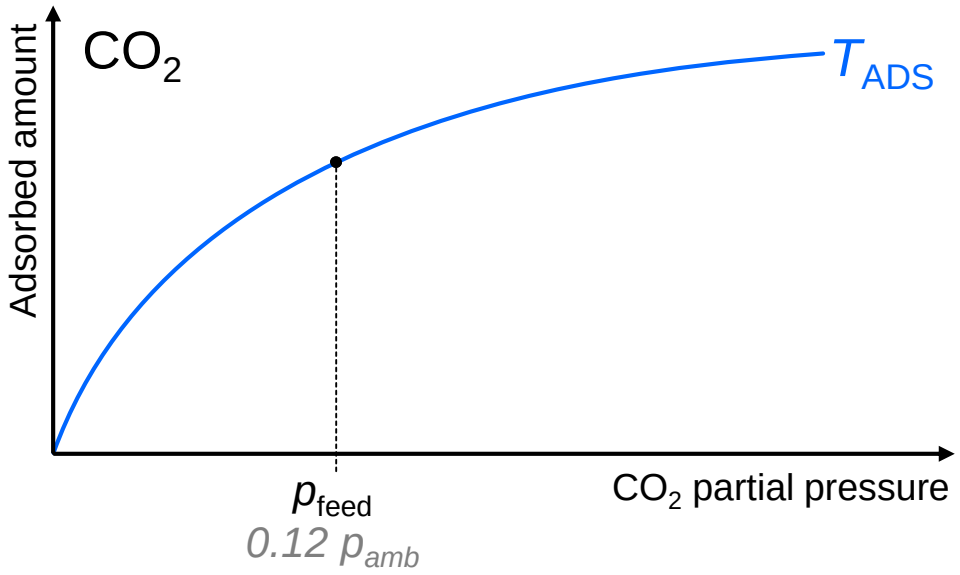

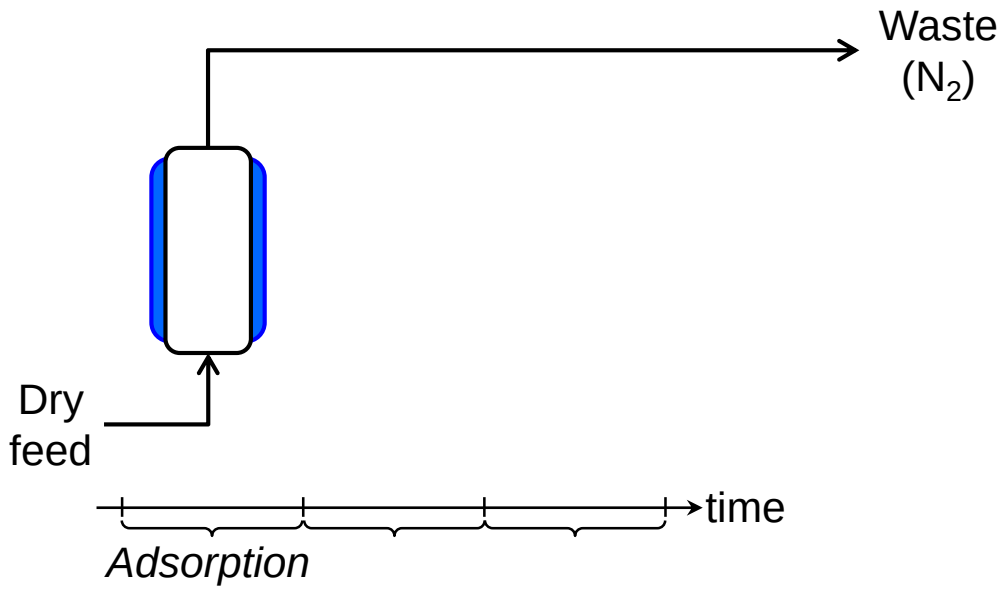

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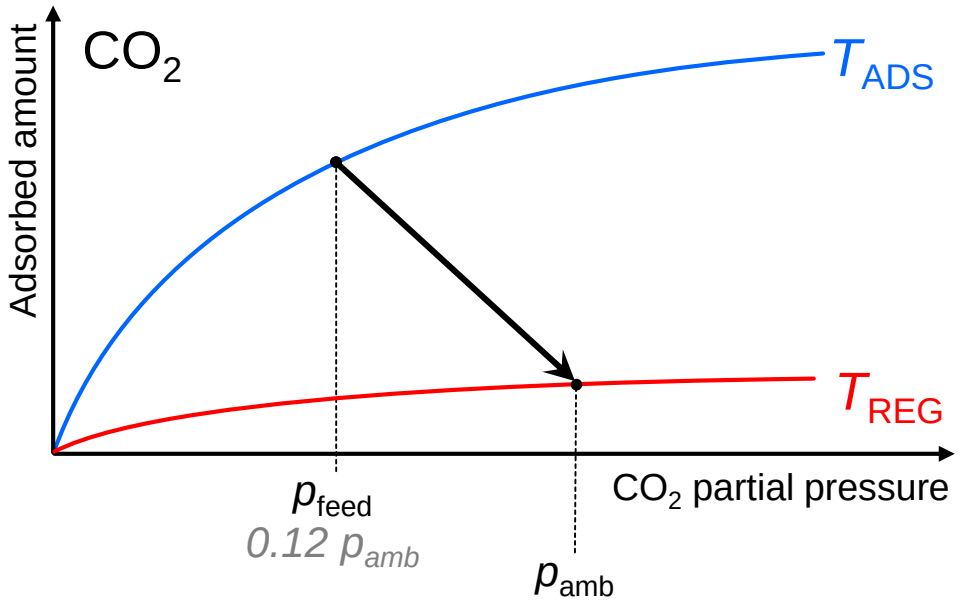

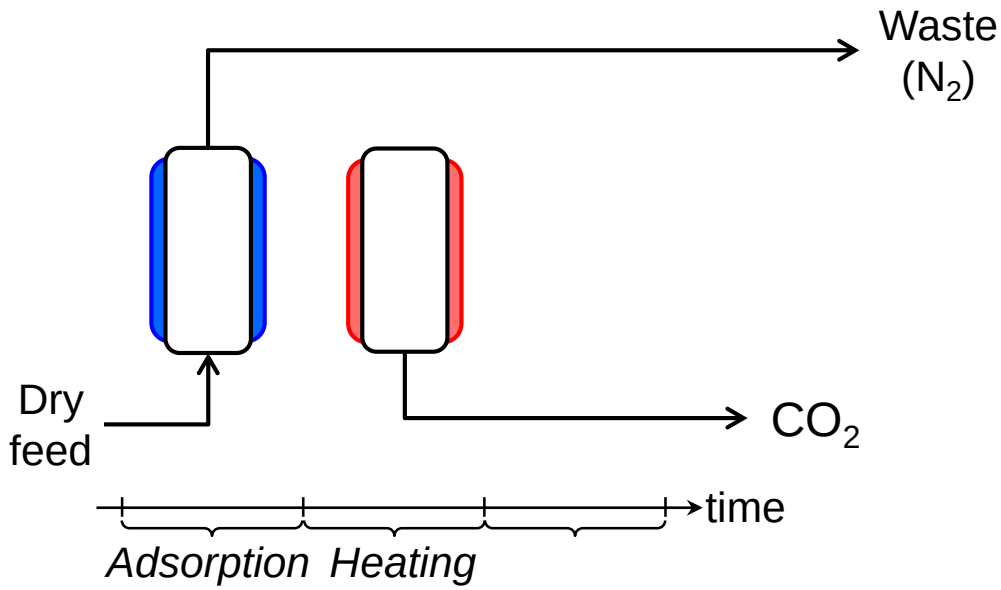

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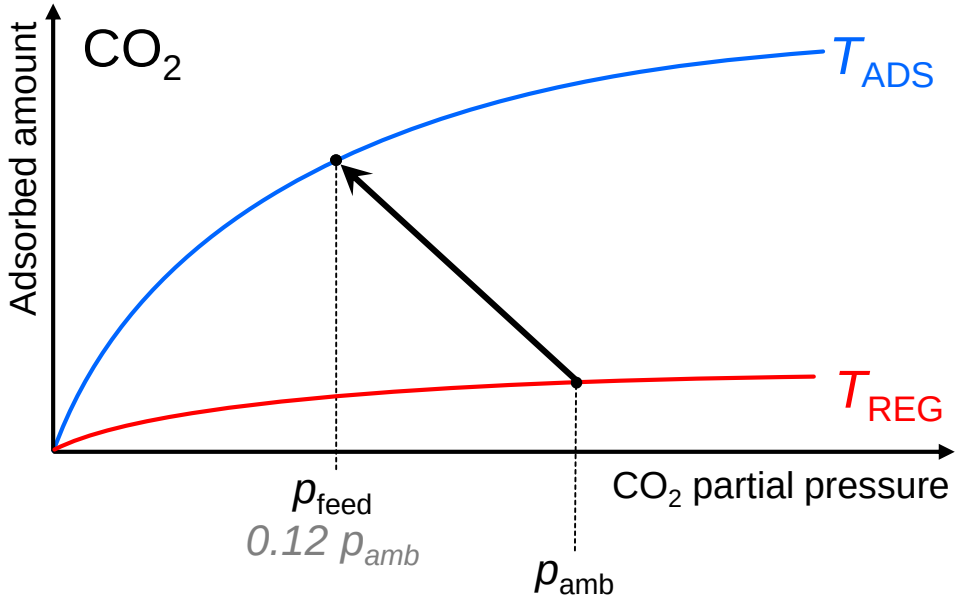

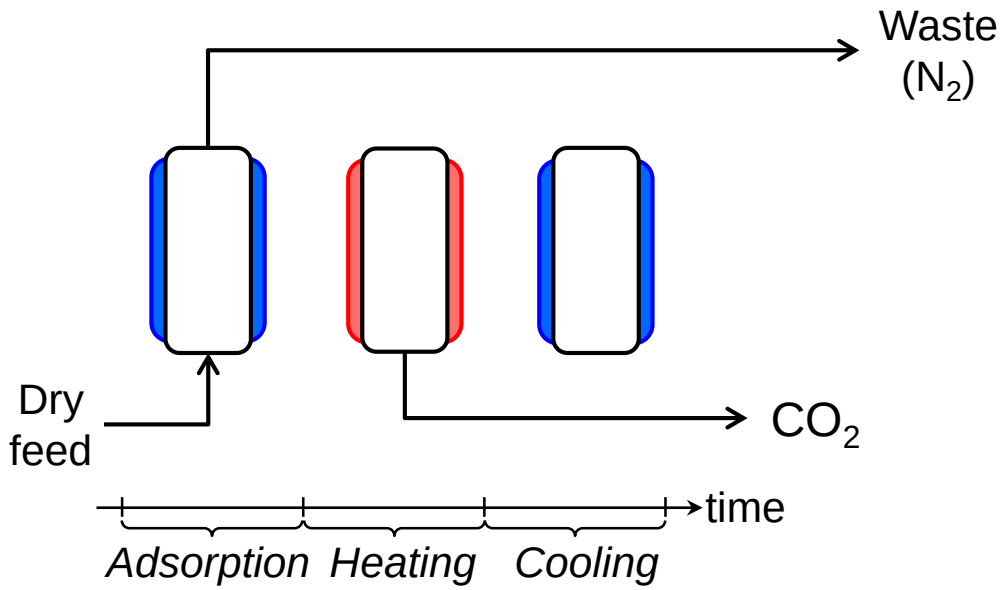

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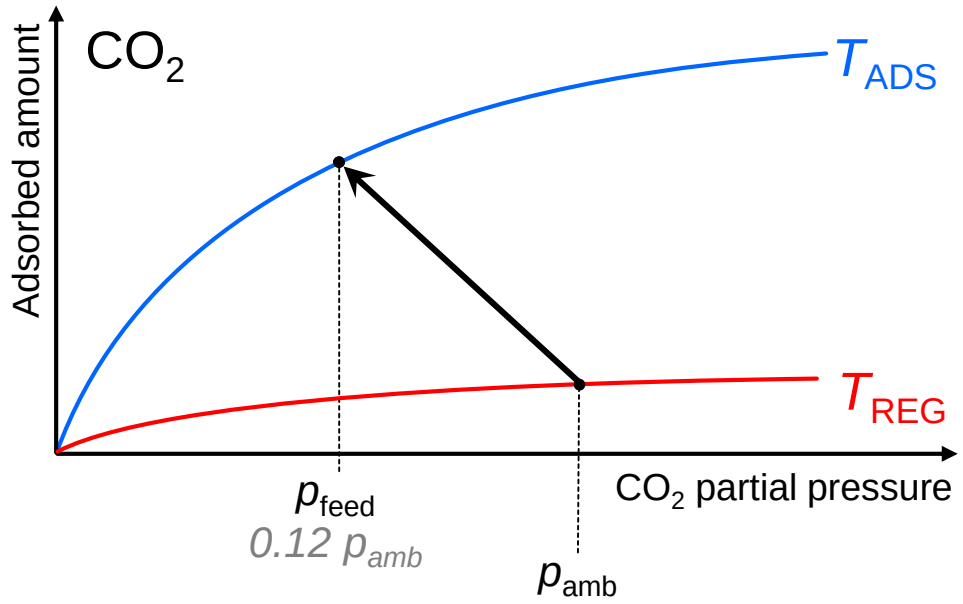
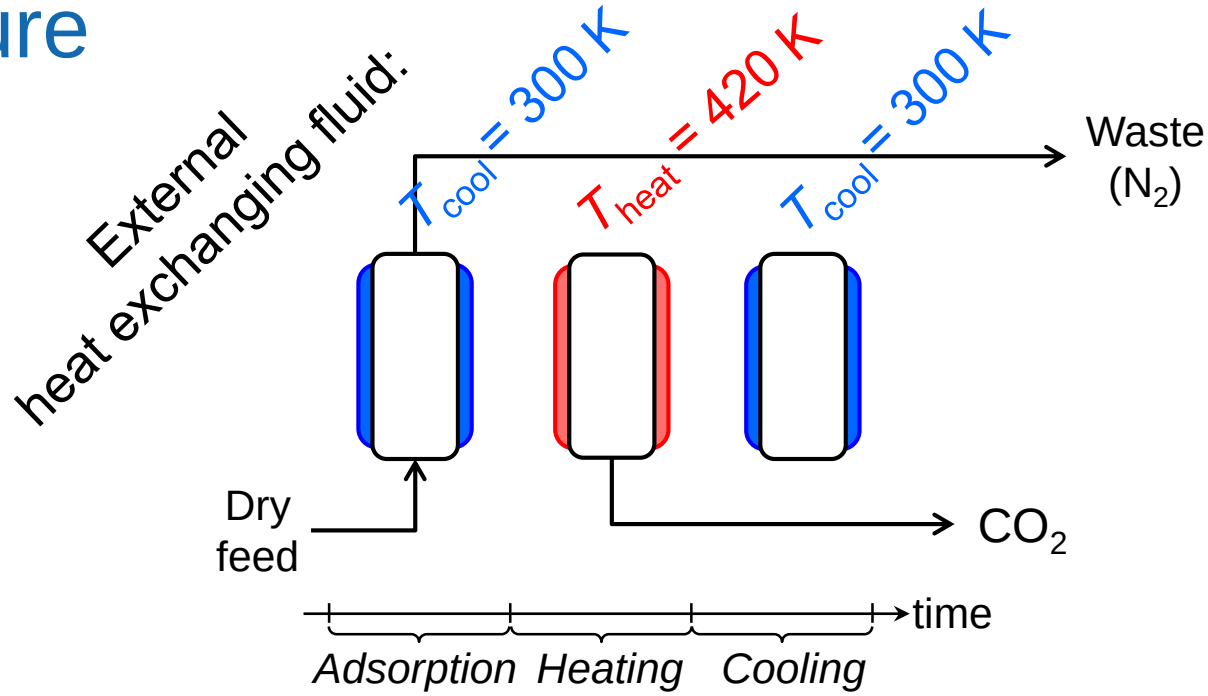
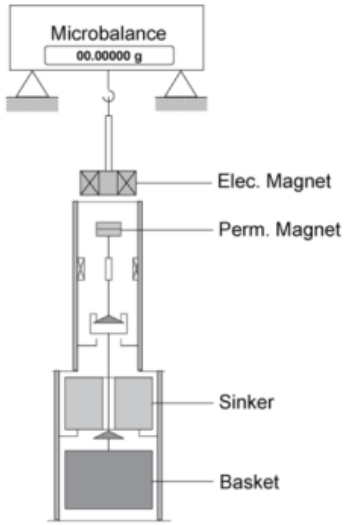
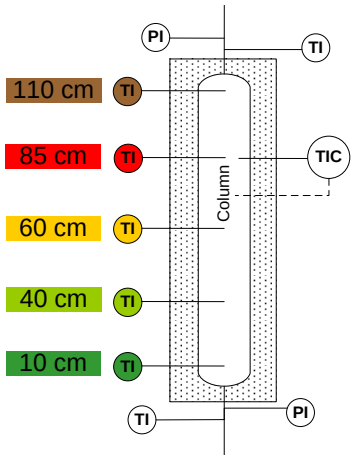
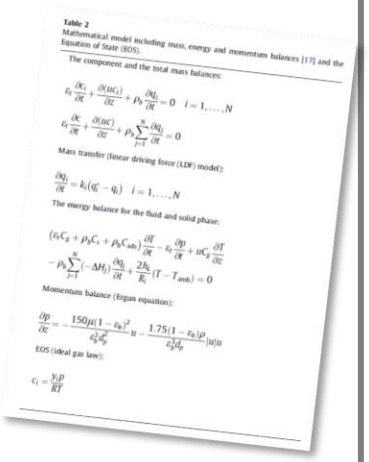
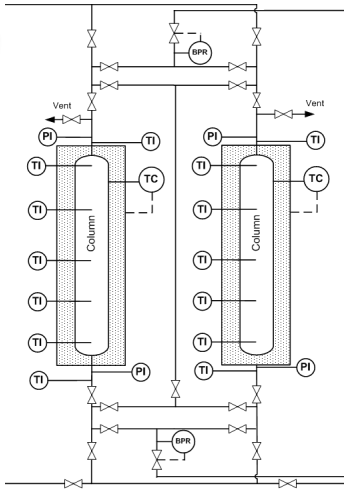
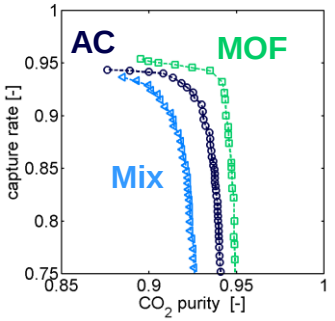
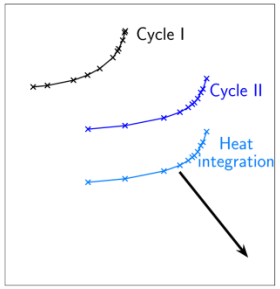




Development of TSA processes

Equilibria	Fixed bed	Modeling	Lab pilot	Process design & Optimization
				 
Rubotherm MSB *adsorption isotherms*	Breakthrough experiments *transport parameters*	Mass and energy balances Isotherms EOS	Experimental validation	

Equilibria

Schell et al., *Adsorption* **2012**, 18, 49-65
Hefti et al., *Adsorption* **2014,** 20, 359-371

Fixed Bed

Casas et al., *Adsorption* **2012**, 12, 143-161
Marx et al., *Ind. Eng. Chem. Res.* **2015,** 54, 6035-6045

Modeling

Marx et al., Adsorption **2014,** 20, 493-510

Lab pilot

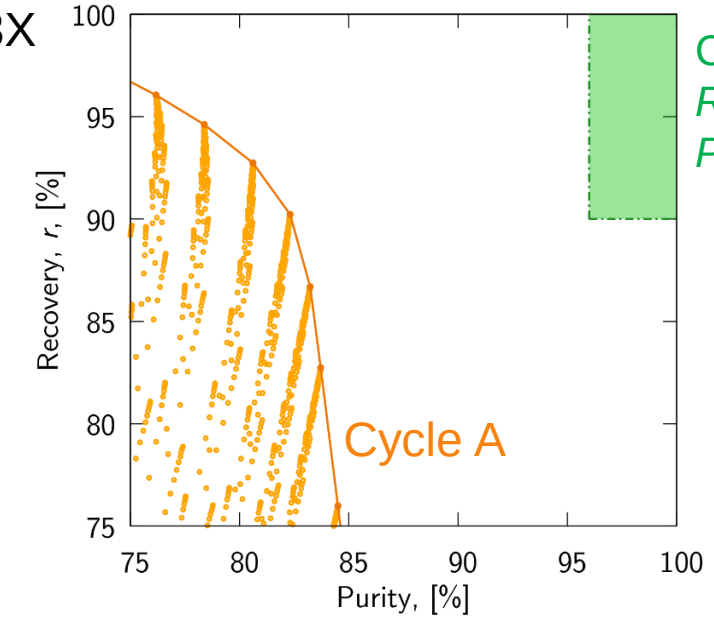
Schell et al., *Ind. Eng. Chem. Res.* **2013**, 52, 8311-8322
Marx et al., *Ind. Eng. Chem. Res.* **2016**, 55, 1401−1412

Process design & Optimization

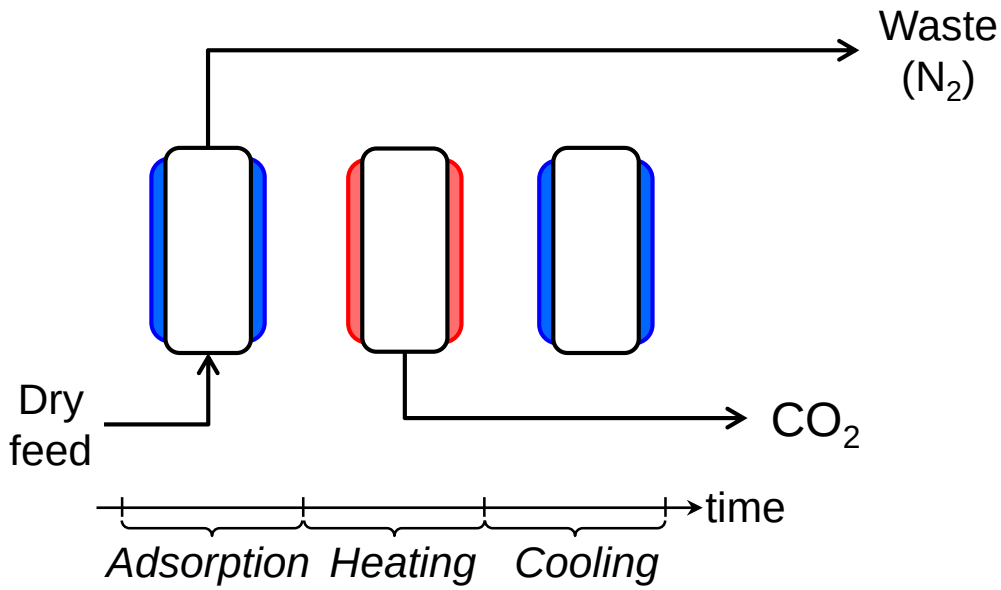
Casas et al, *Sep. Pur. Tech.* **2013**, 104, 183-192
Joss et al., *Ind. Eng. Chem. Res.* **2015**, 54, 3027-3038
Joss et al., *Chem. Eng. Sc.* **2017**, 157, 381-394

TSA processes for CO_2 capture: Cycle A

Zeo 13X



CCS specifications:
Recovery ≥ 90%
Purity ≥ 96%

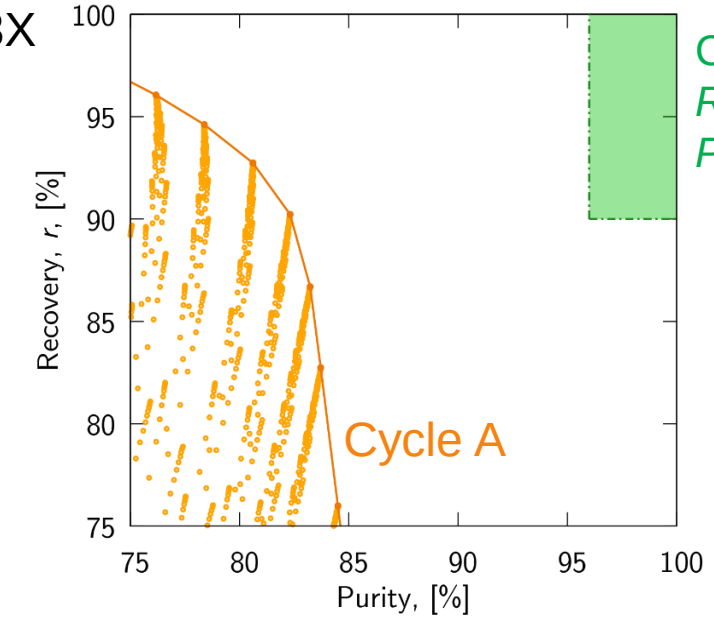


$$\text{Recovery} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 \text{ fed}}$$

$$\text{Purity} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 + N_2 \text{ in product}}$$

TSA processes for CO_2 capture: process design

Zeo 13X



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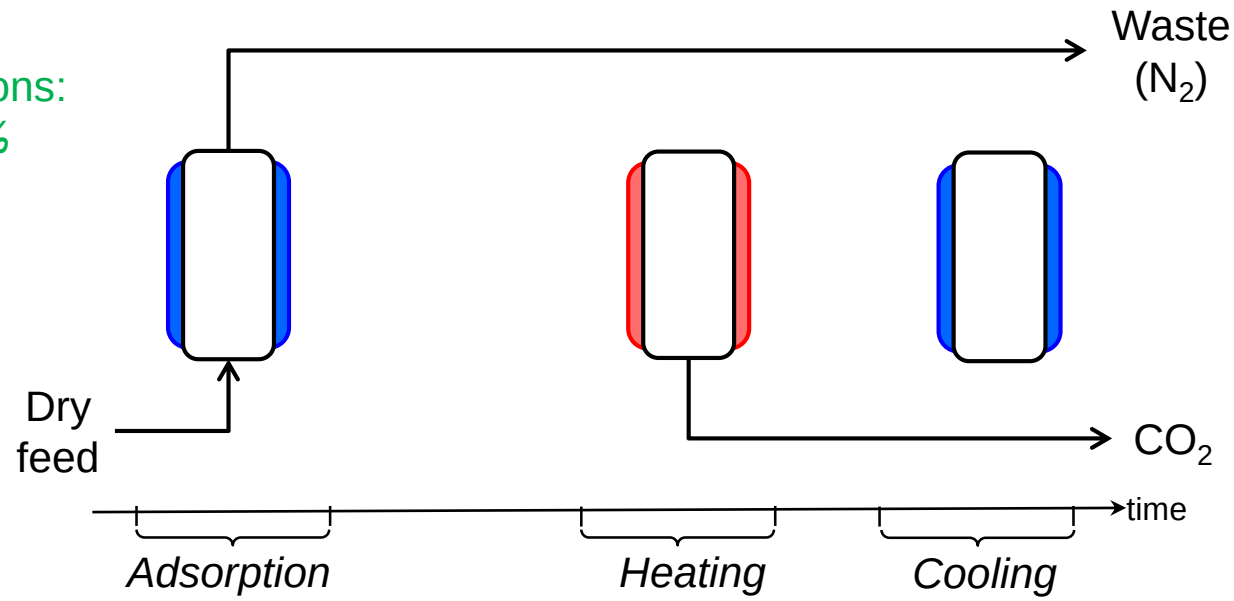

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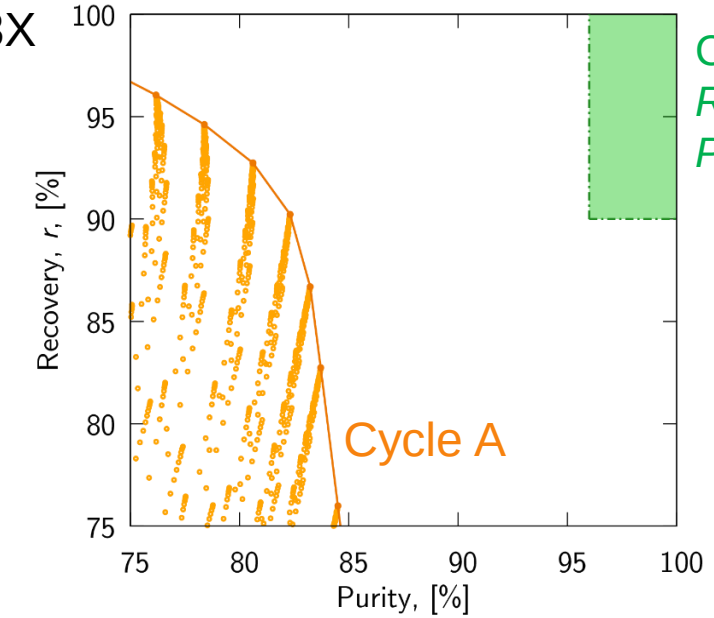
→ Increase recovery

TSA processes for CO_2 capture: process design

Zeo 13X



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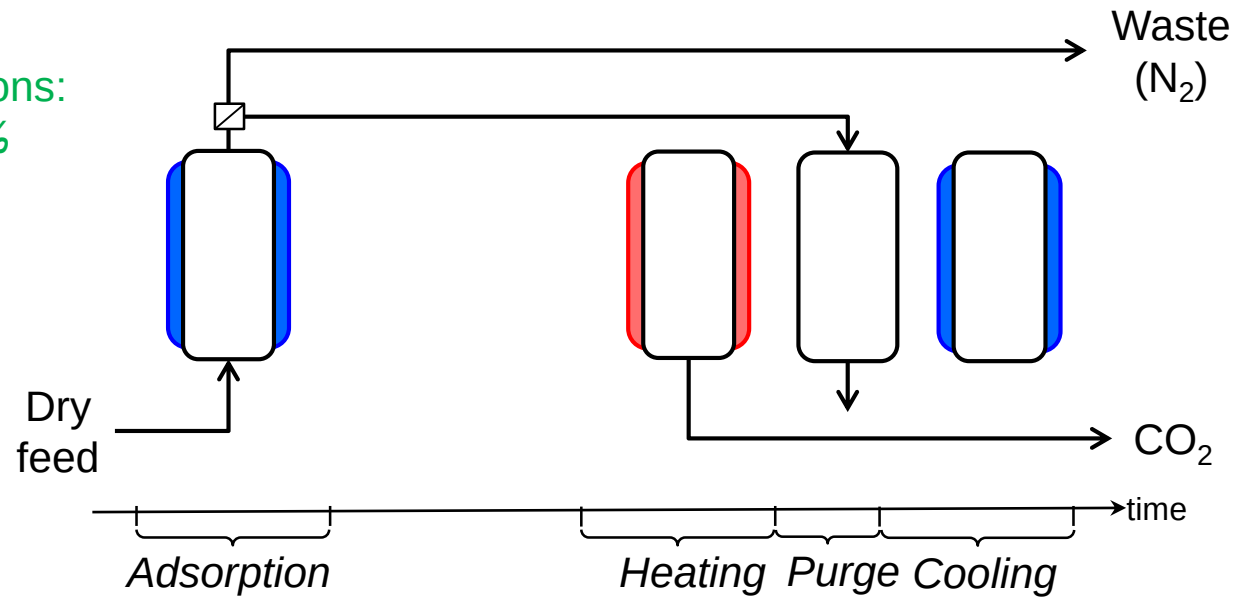

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$$\text{Purity} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 + N_2 \text{ in product}}$$

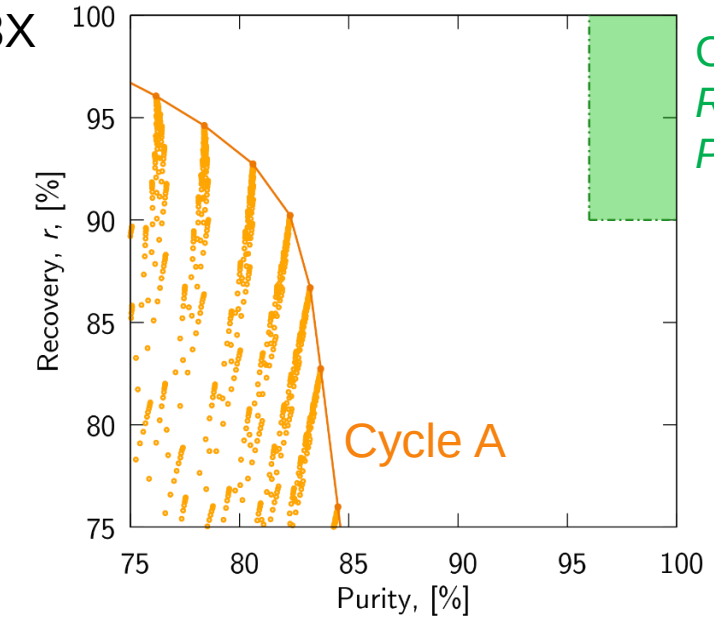
→ Increase recovery

Targeted modifications:

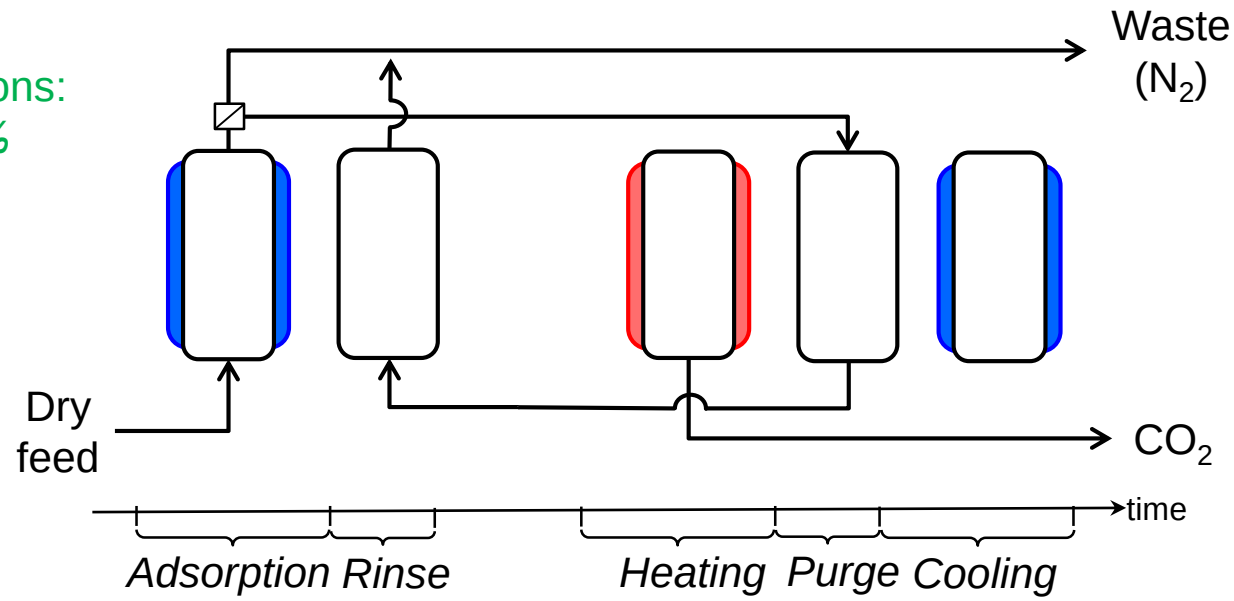
1. Nitrogen purge before cooling/adsorption

TSA processes for CO_2 capture: process design

Zeo 13X



CCS specifications:
Recovery ≥ 90%
Purity ≥ 96%



$$\text{Recovery} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 \text{ fed}}$$

→ Increase recovery

$$\text{Purity} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 + N_2 \text{ in product}}$$

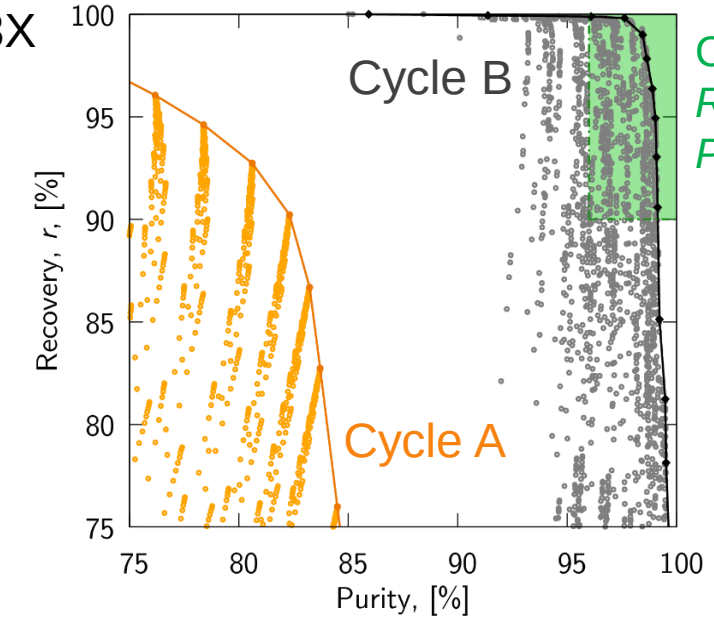
→ Increase purity

Targeted modifications:

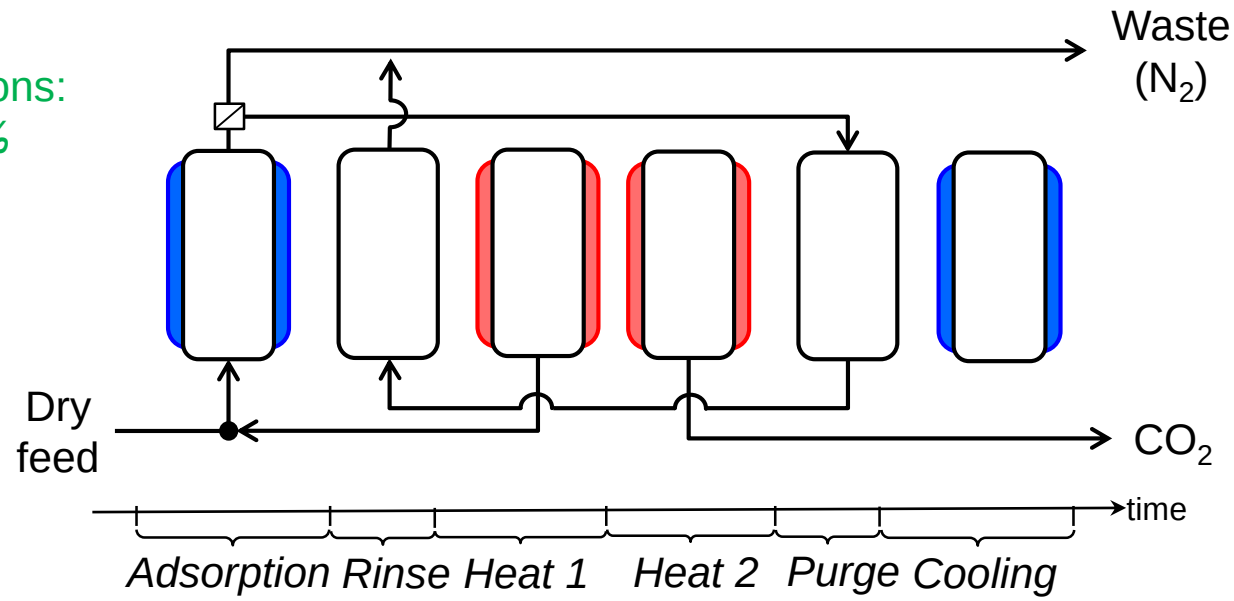
1. Nitrogen purge before cooling/adsorption
2. CO_2-rich recycle before heating

TSA processes for CO_2 capture: Cycle B

Zeo 13X



CCS specifications:
Recovery ≥ 90%
Purity ≥ 96%



$$\text{Recovery} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 \text{ fed}}$$

$$\text{Purity} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 + N_2 \text{ in product}}$$

→ Increase recovery

→ Increase purity

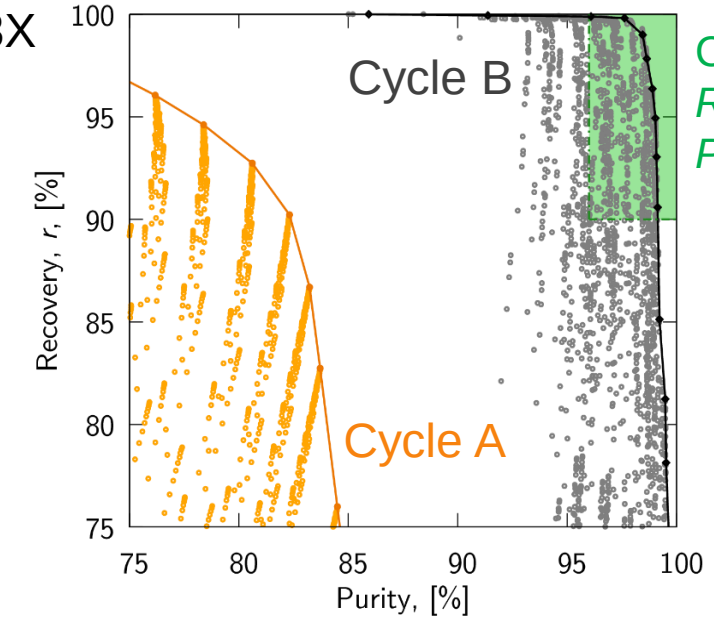
Targeted modifications:

1. Nitrogen purge before cooling/adsorption
2. CO_2-rich recycle before heating
3. Preliminary heating to remove N_2 from product

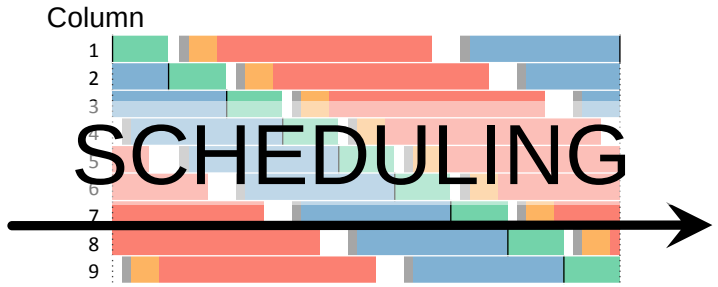
Reference: Joss et al., *Chem. Eng. Sc.* **2017**, 157, 381-394

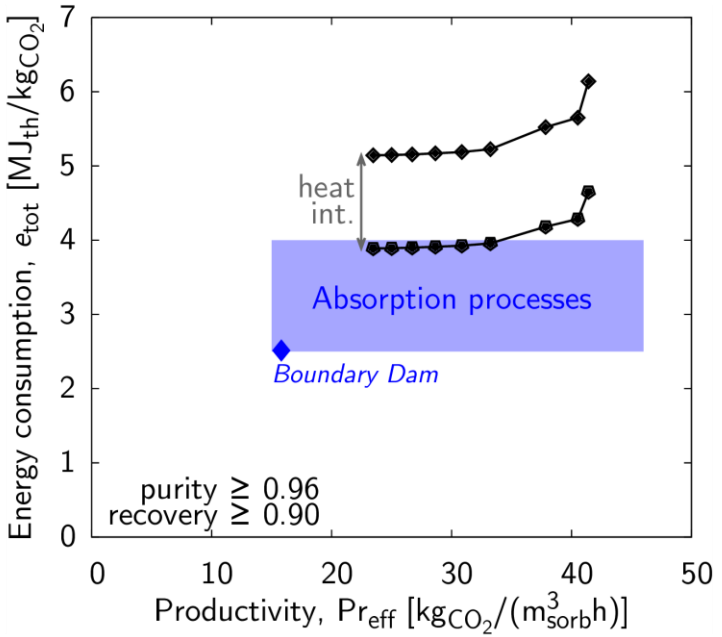
TSA processes for CO_2 capture: Cycle B

Zeo 13X



CCS specifications:
Recovery ≥ 90%
Purity ≥ 96%





Productivity:

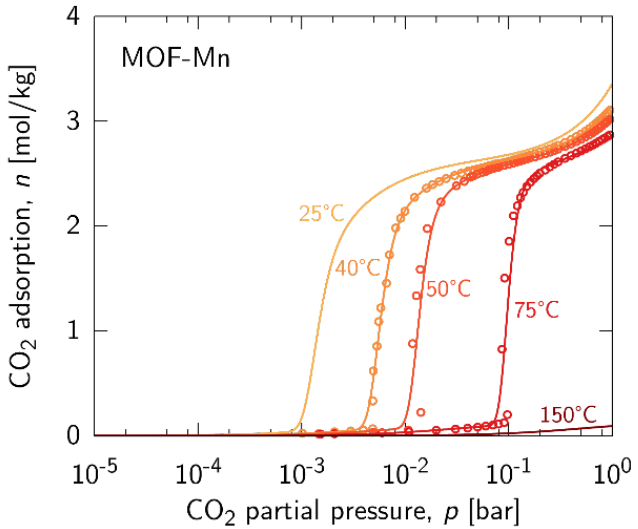
$$\mathrm{Pr} = \frac{CO_2 \text{ produced}}{\text{mass adsorbent} \times \text{time}}$$

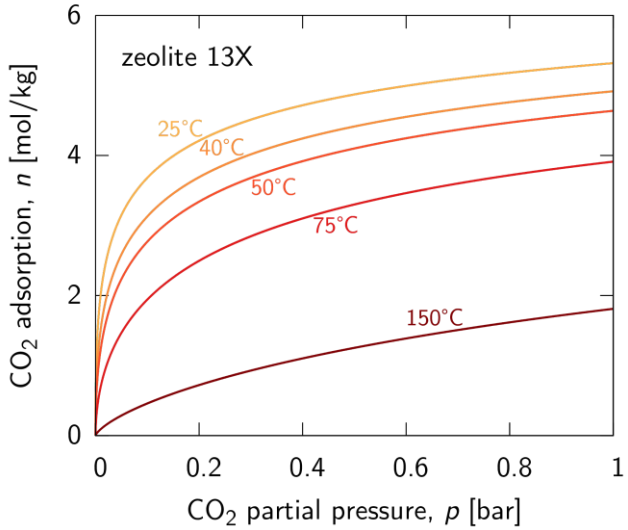
Specific energy consumption (including pre-drying):

$$e_{TSA} = \frac{\text{heating duty}}{CO_2 \text{ produced}}$$

Reference: Joss et al., *Chem. Eng. Sc.* **2017**, 157, 381-394

Non commercial adsorbents: MOFs



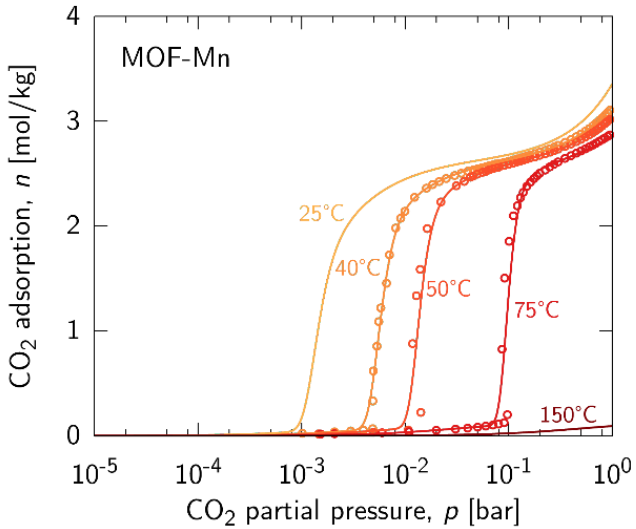


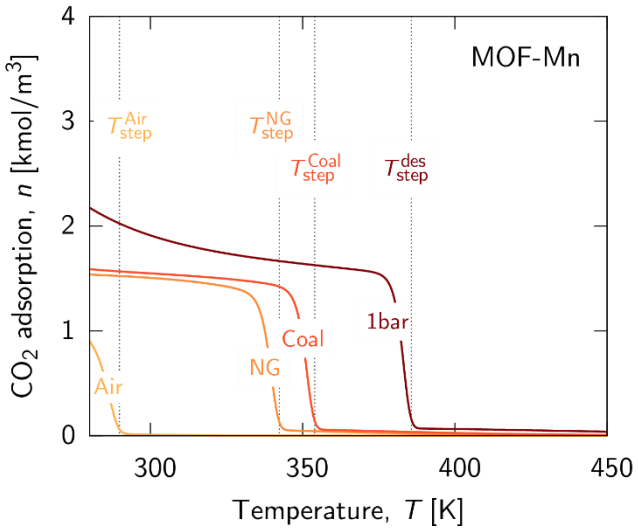
McDonald et al., *Nature* **2015**, 519, 303-308

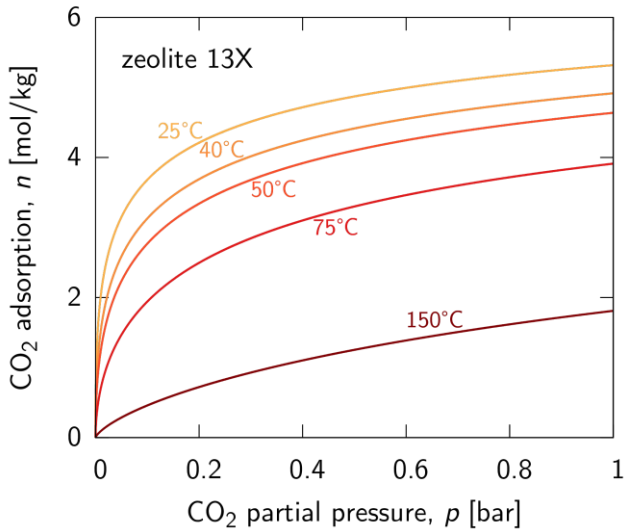
Phase-change adsorbents:

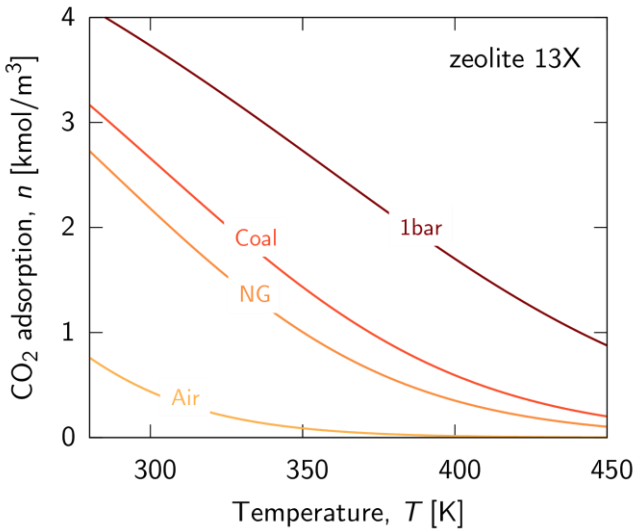
- step-shaped isotherms allow for high working capacity upon small temperature swing

Non commercial adsorbents: MOFs



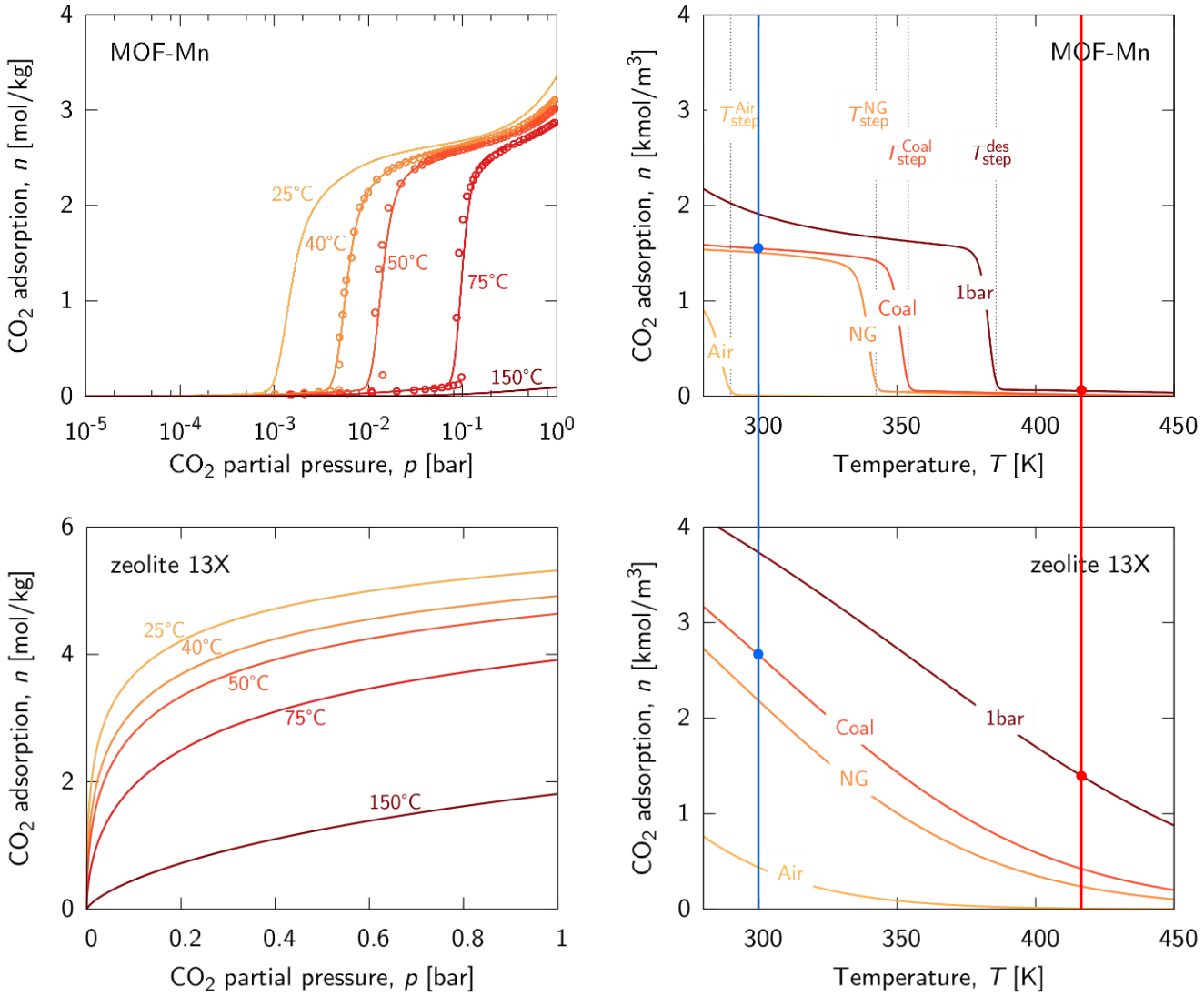






Coal flue gas: 0.12 vol. CO_2

Non commercial adsorbents: MOFs

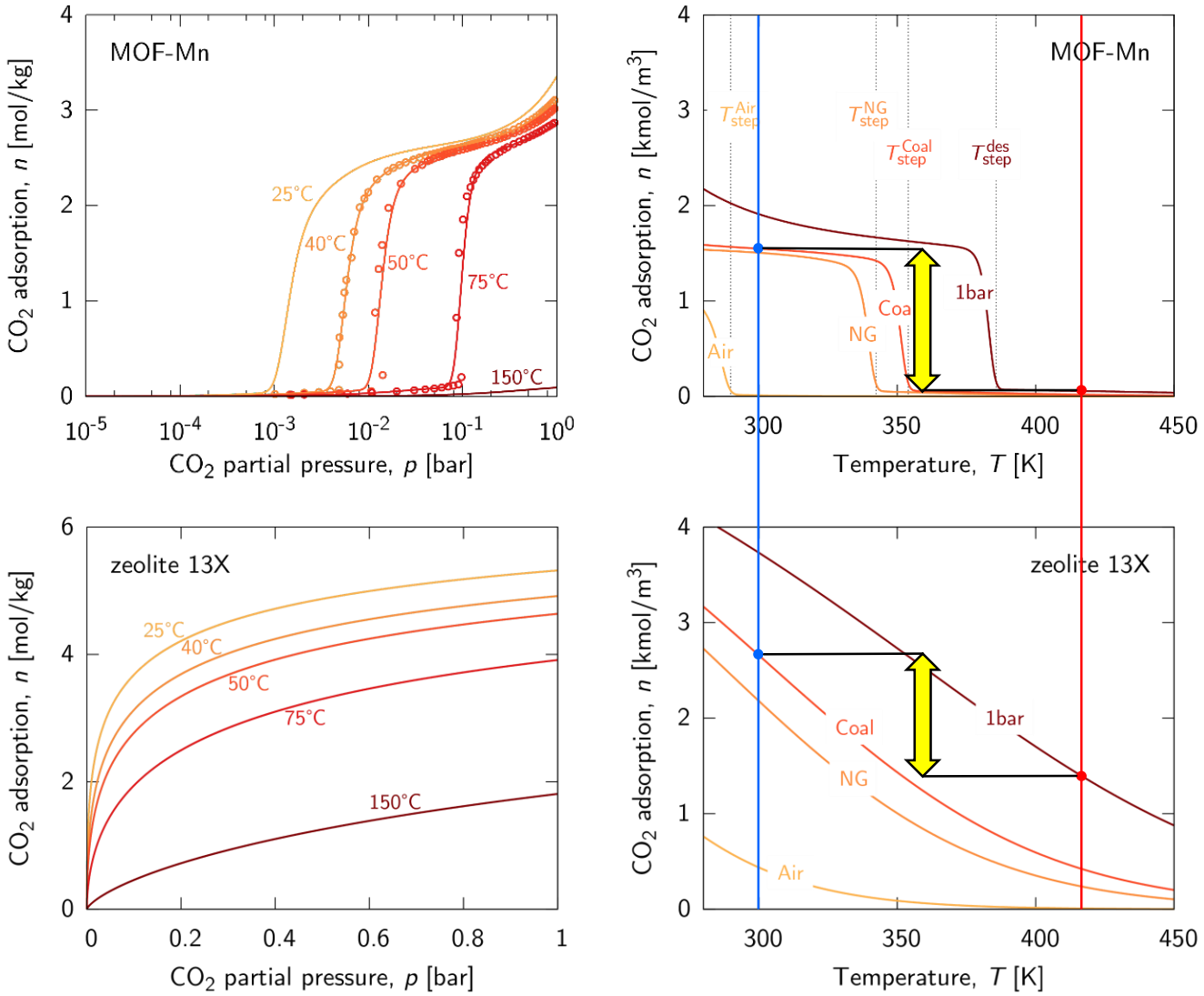


Coal flue gas: 0.12 vol. CO_2

Heat sink: $T = 300$ K

Heat source: $T = 420$ K

Non commercial adsorbents: MOFs



Coal flue gas: 0.12 vol. CO_2

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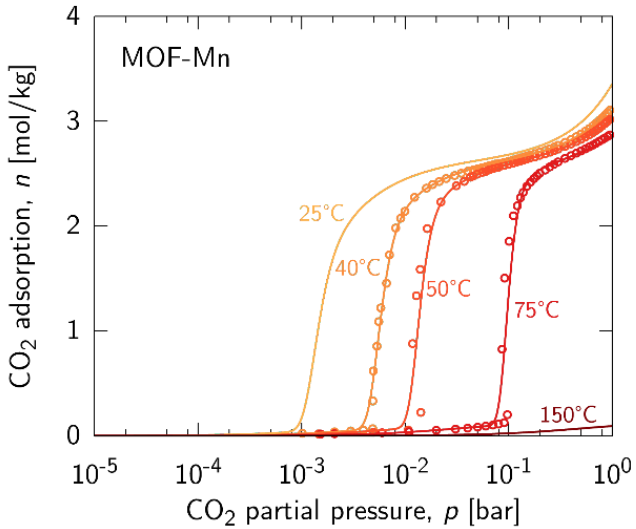
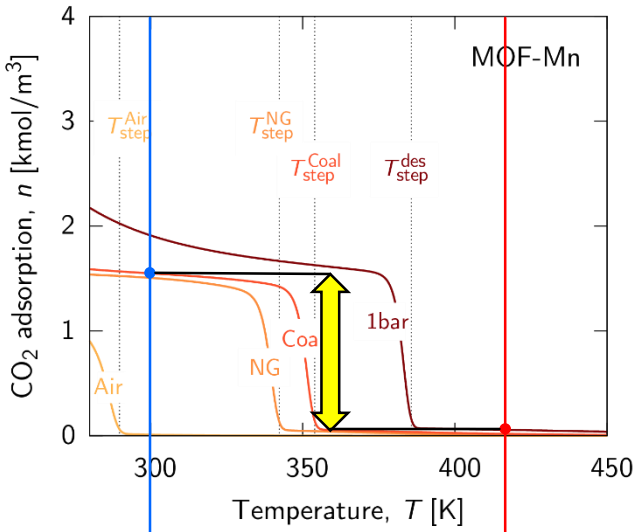
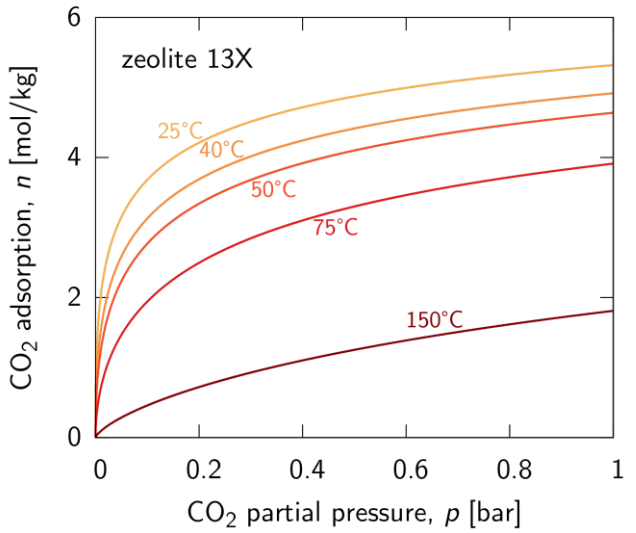
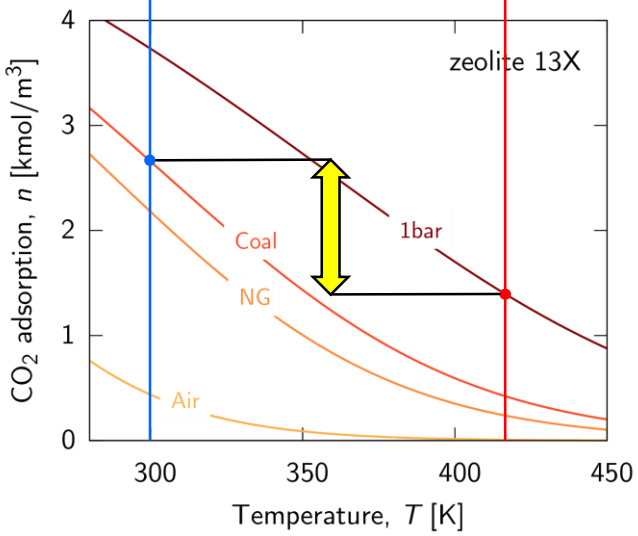
Non commercial adsorbents: MOFs









Coal flue gas: 0.12 vol. CO_2

Heat sink: T = 300 K

Heat source: T = 420 K

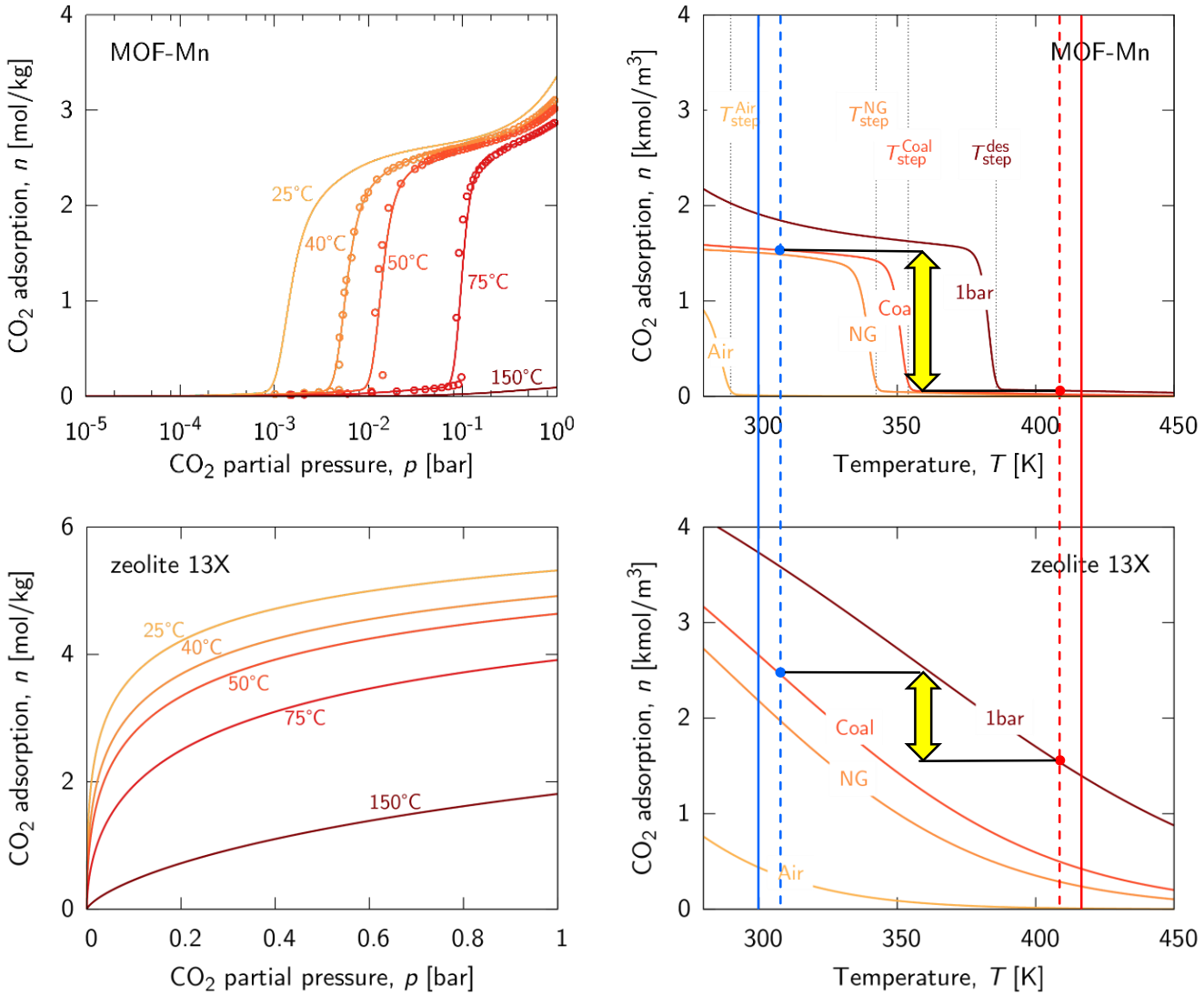
Heat transfer limitations

↓

Reduced heating/cooling step duration means reduced ΔT of the swing:

- reduced heat duty
- lower cycle duration

Non commercial adsorbents: MOFs



Coal flue gas: 0.12 vol. CO_2

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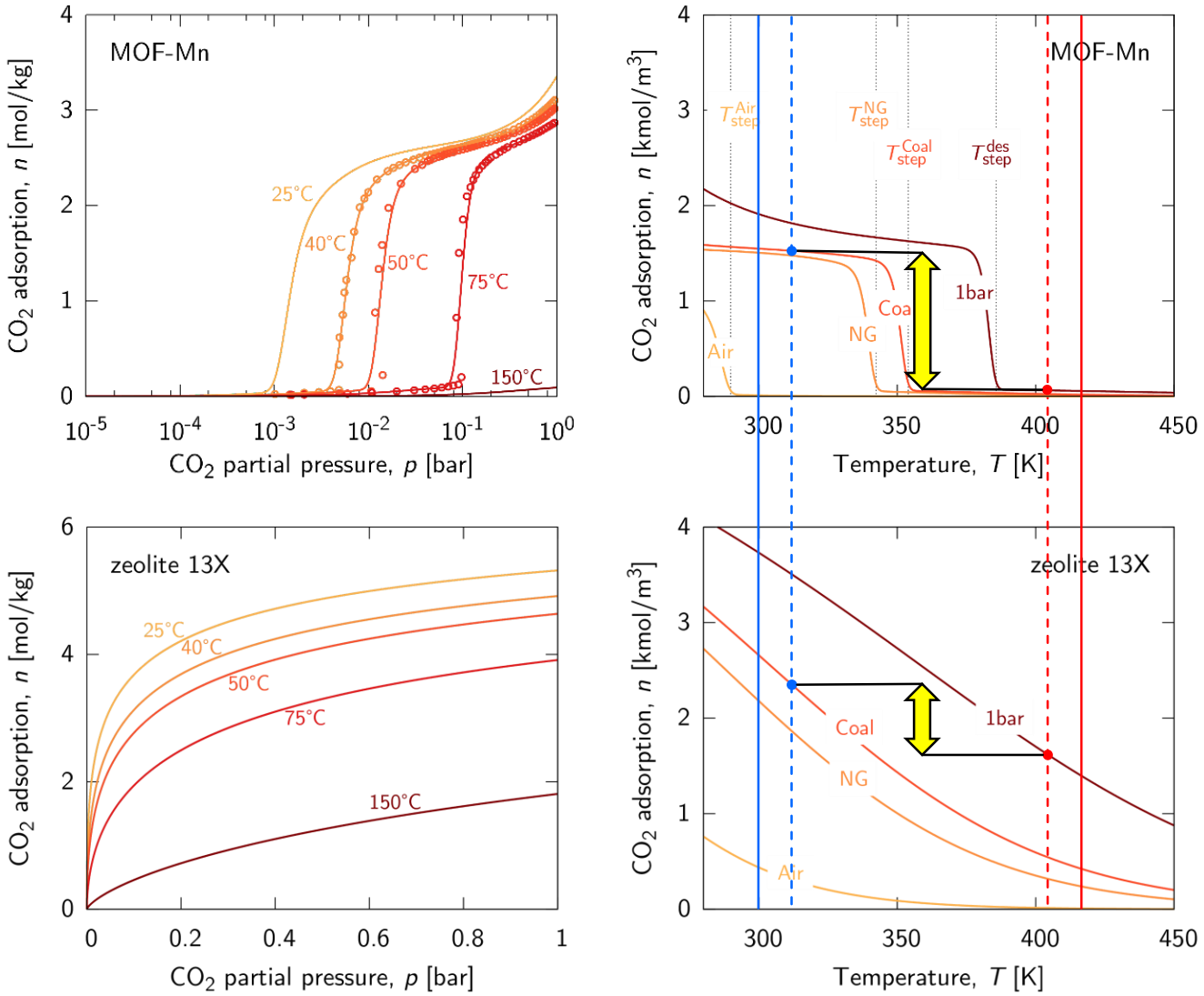
Non commercial adsorbents: MOFs



Coal flue gas: 0.12 vol. CO_2

Heat sink: T = 300 K

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Heat transfer limitations

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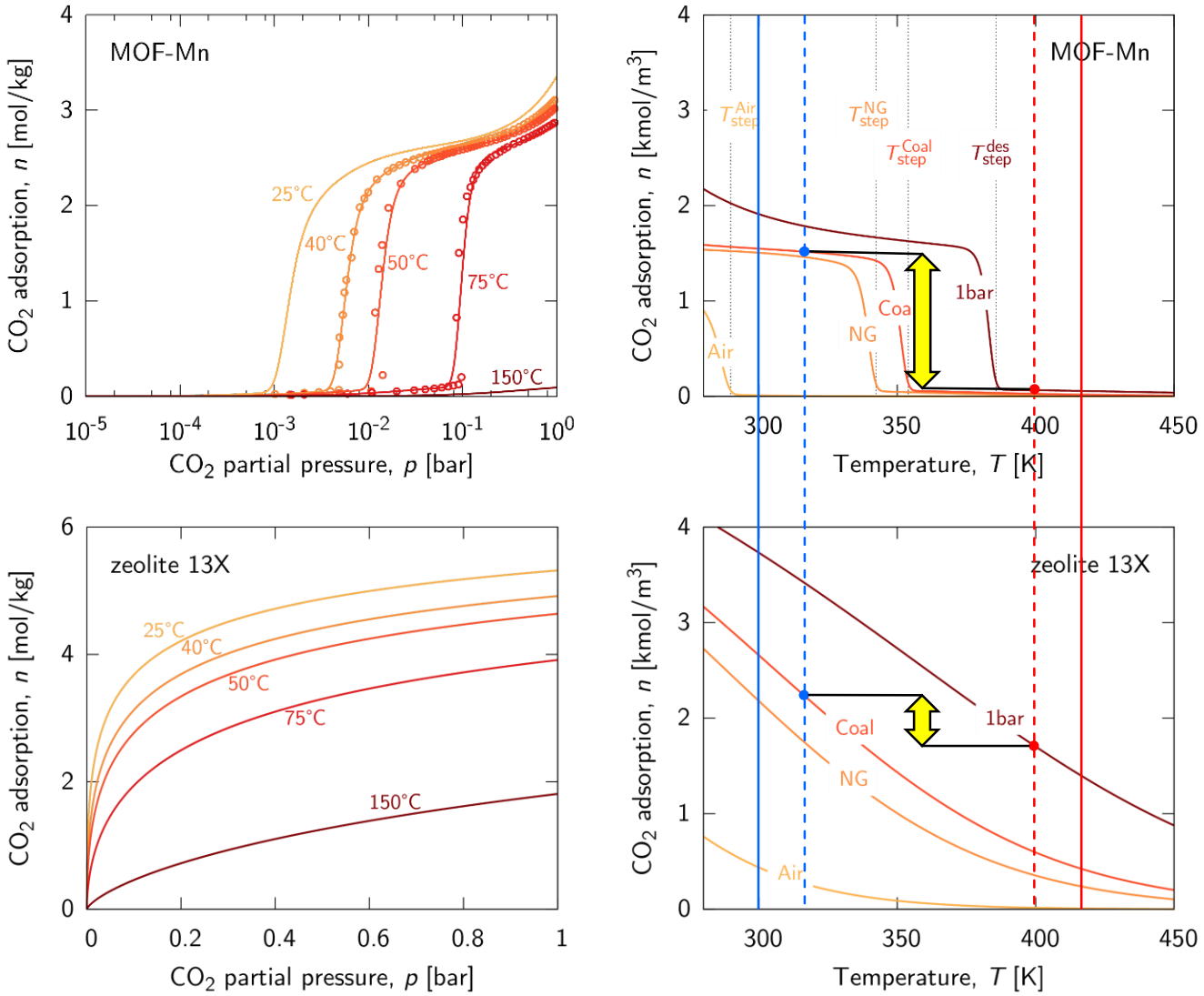
Non commercial adsorbents: MOFs



Coal flue gas: 0.12 vol. CO_2

Heat sink: T = 300 K

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Heat transfer limitations

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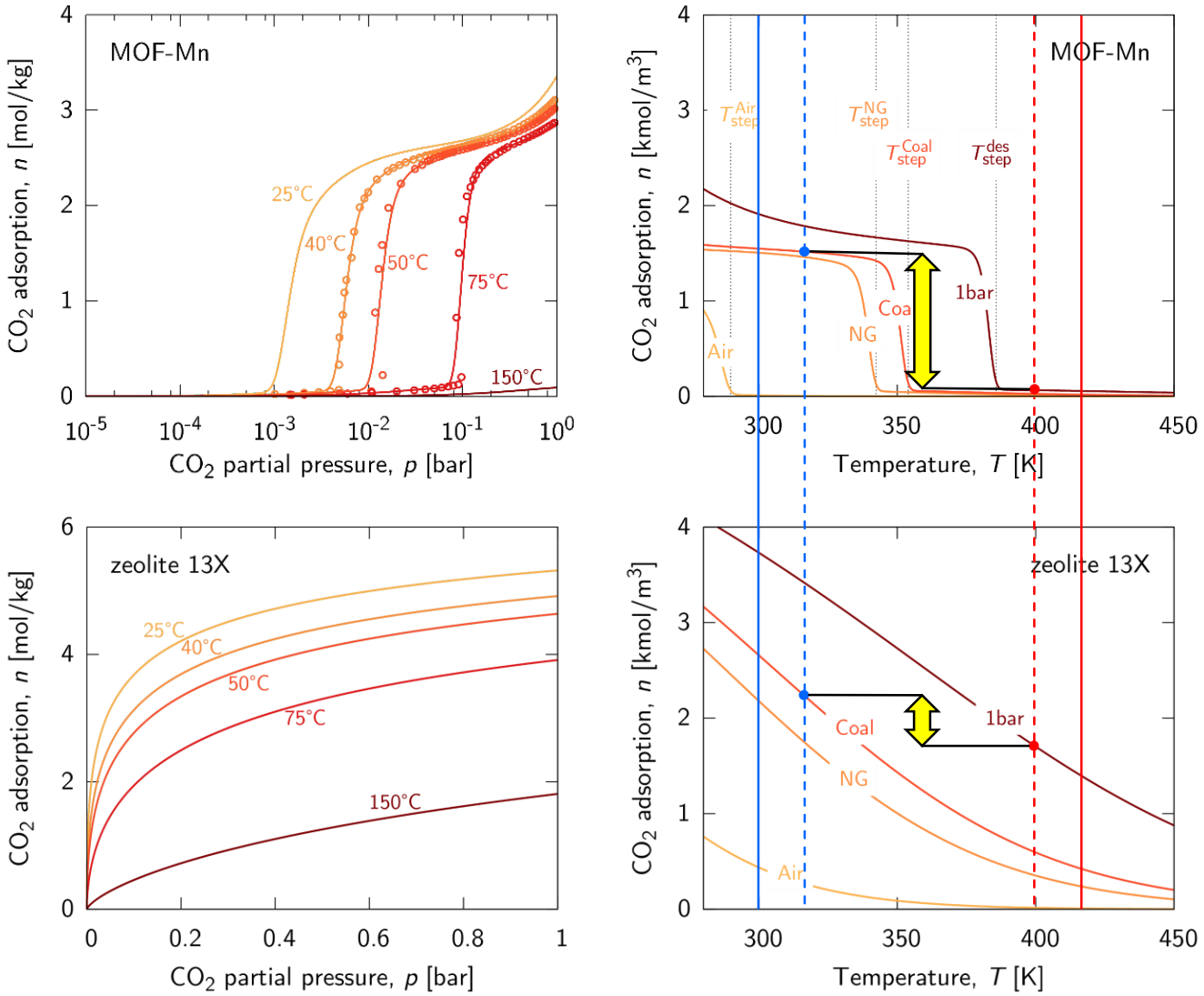
- lower cycle duration

Non commercial adsorbents: MOFs



Coal flue gas: 0.12 vol. CO_2

Heat sink: T = 300 K

Heat source: T = 420 K

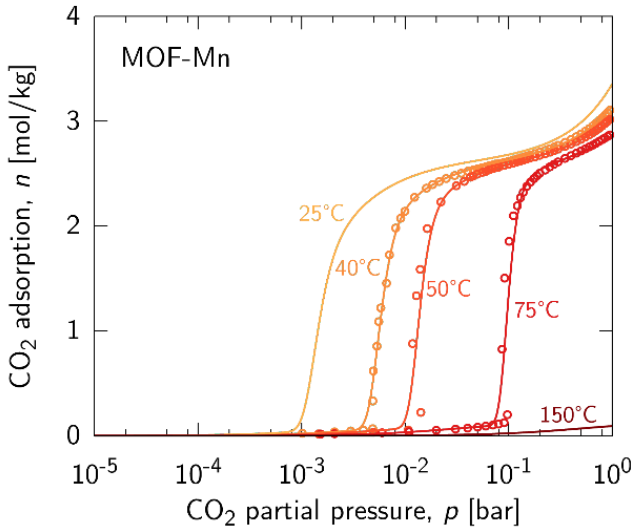
Heat transfer limitations

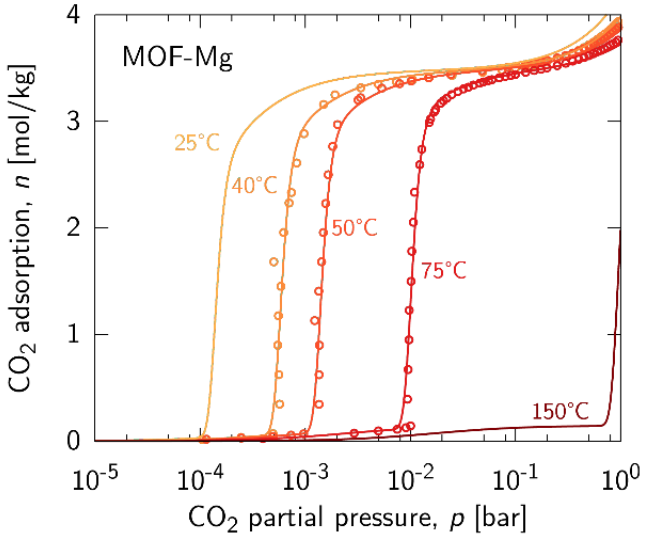
↓

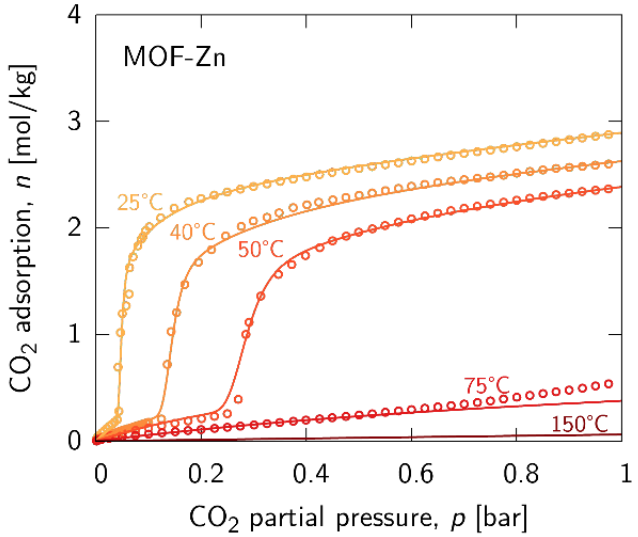
Reduced heating/cooling step duration means reduced ΔT of the swing:

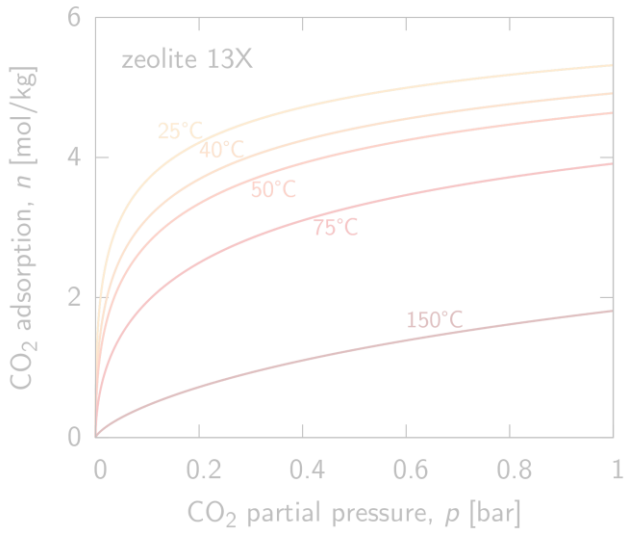
- reduced heat duty
- lower cycle duration
- ⊙ almost constant cyclic capacity for MOFs

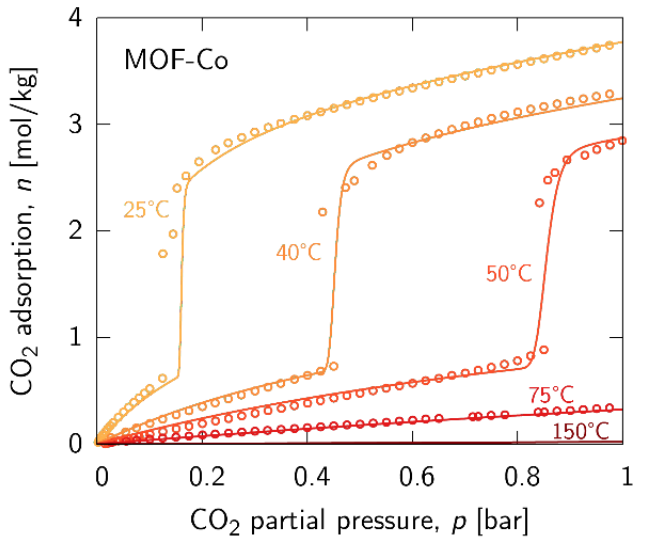
Non commercial adsorbents: MOFs

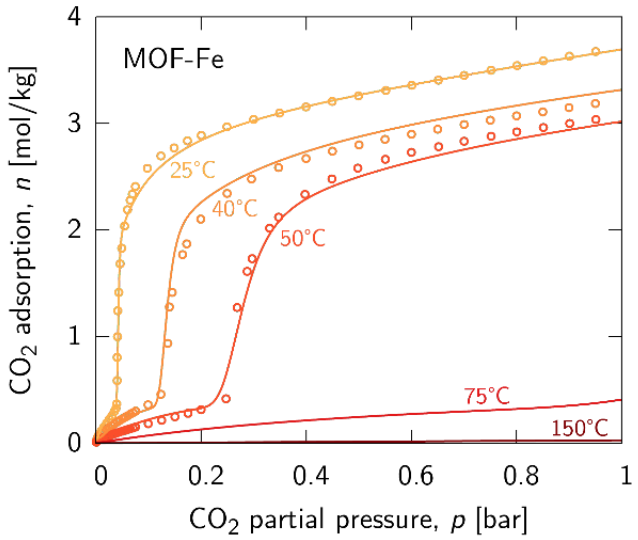




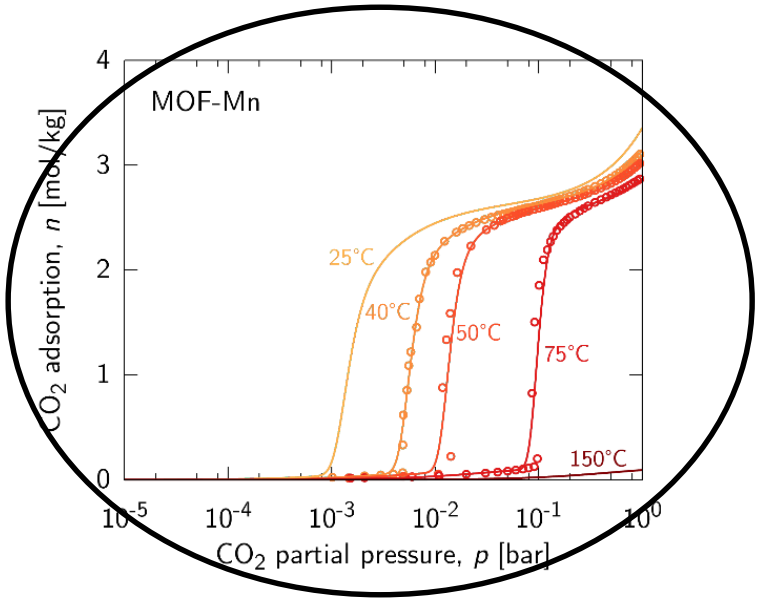




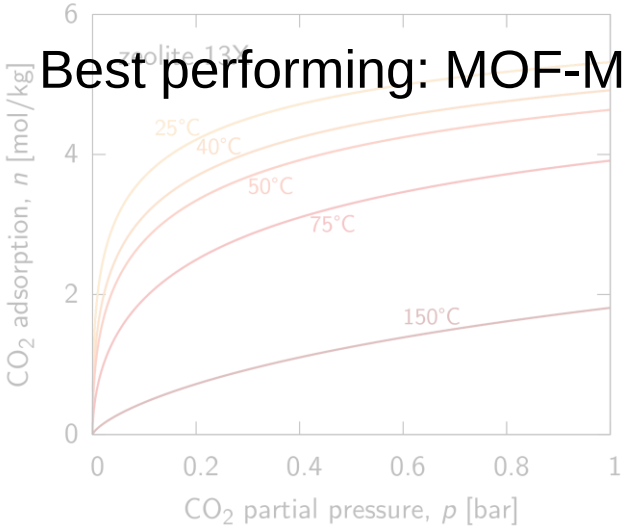


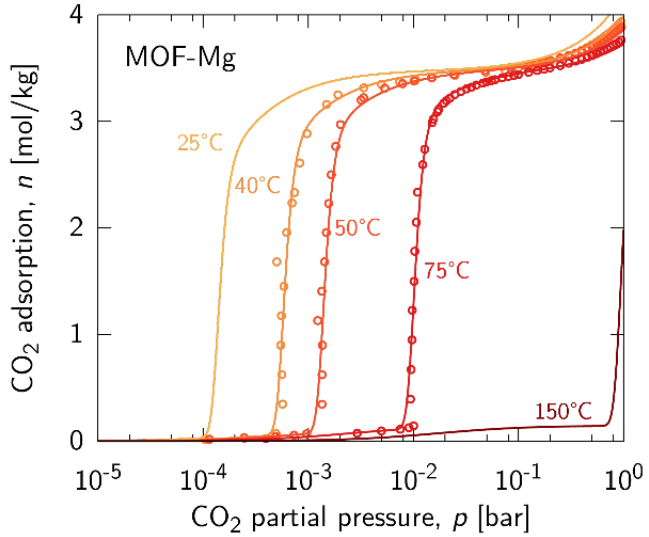


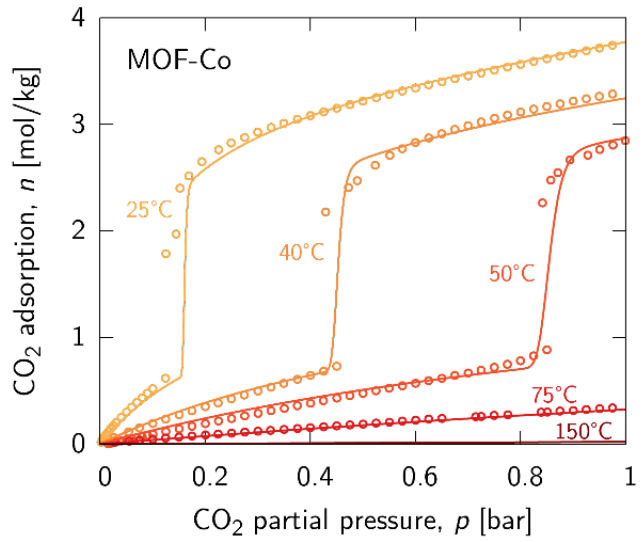
Non commercial adsorbents: MOFs

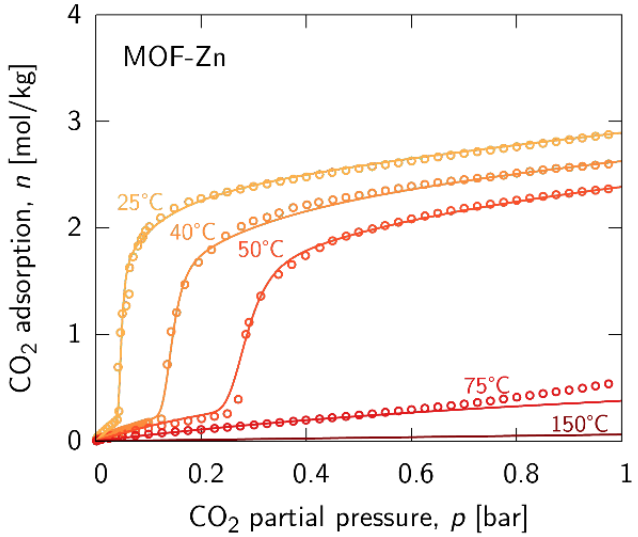


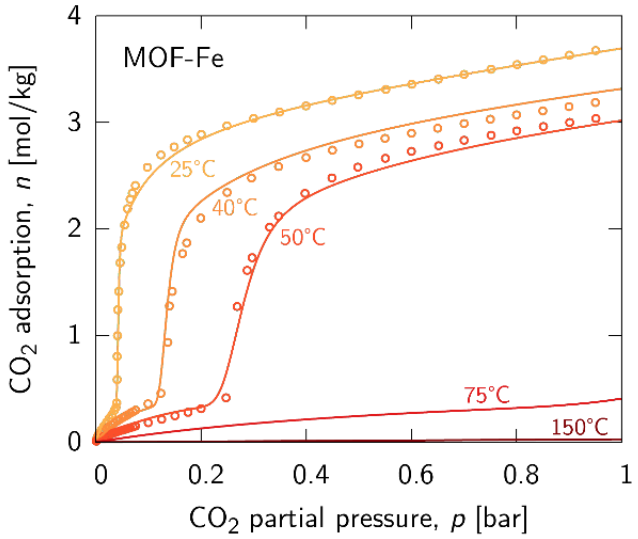
Best performing: MOF-Mn





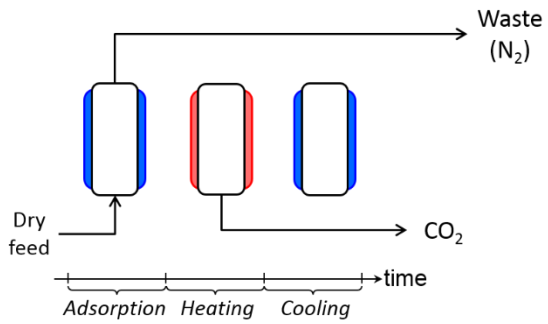




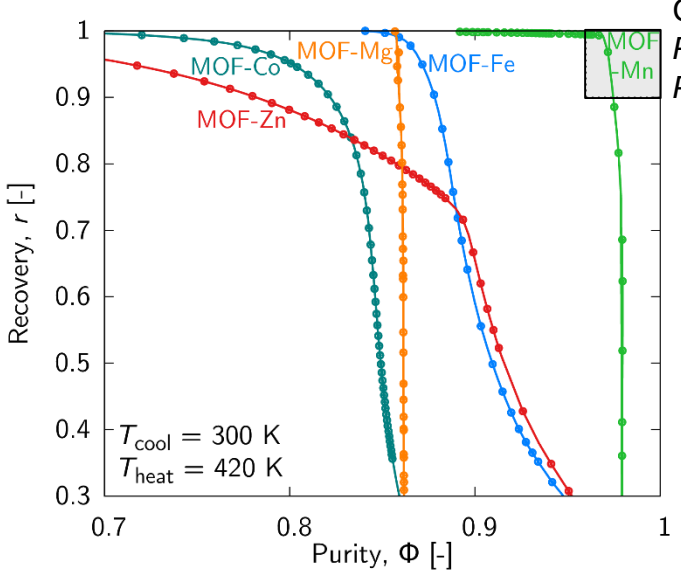


Non commercial adsorbents: MOFs

- Cycle A



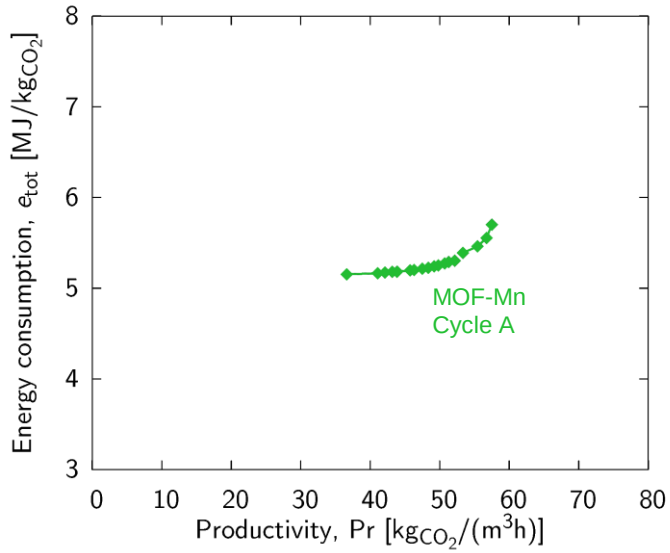
- Negligible N_2 adsorption



CCS specifications:
Recovery ≥ 90%
Purity ≥ 96%

$$\text{Recovery} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 \text{ fed}}$$

$$\text{Purity} = \frac{\text{moles of } CO_2 \text{ in product}}{\text{moles of } CO_2 + N_2 \text{ in product}}$$



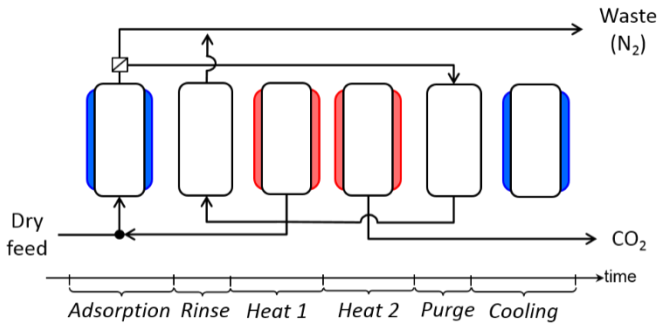
$$Pr = \frac{CO_2 \text{ produced}}{\text{mass adsorbent} \times \text{time}}$$

$$e_{TSA} = \frac{\text{heating duty}}{CO_2 \text{ produced}}$$

Reference: Hefti et al., *Faraday Discuss.*, **2016**,192, 153-179

Non commercial adsorbents: MOFs

- Cycle B



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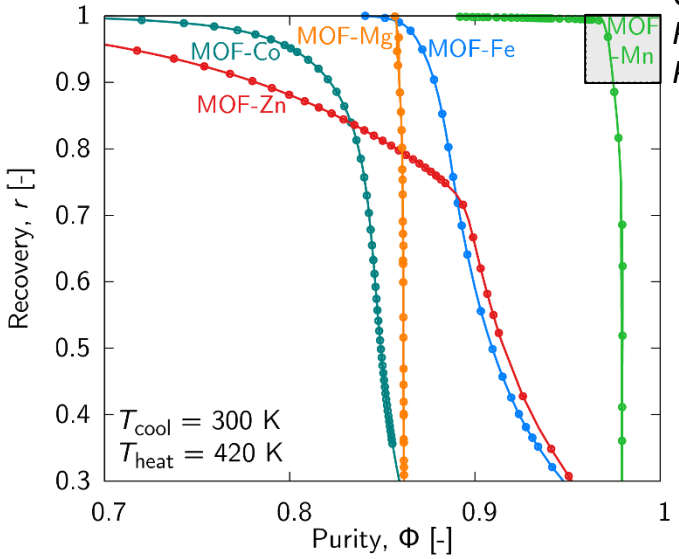

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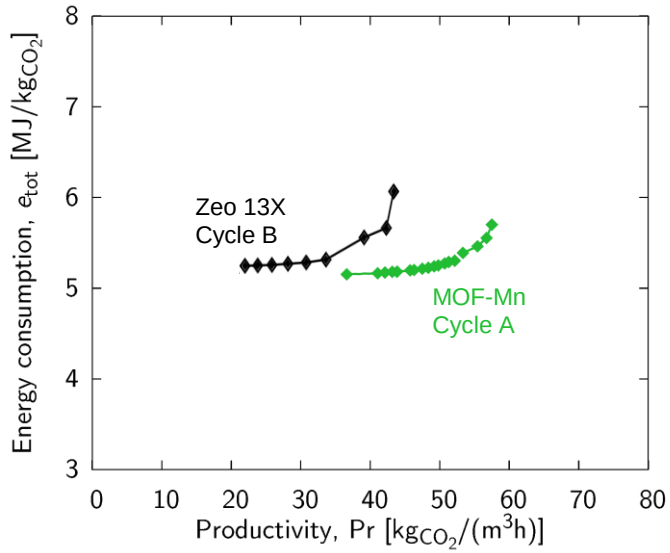

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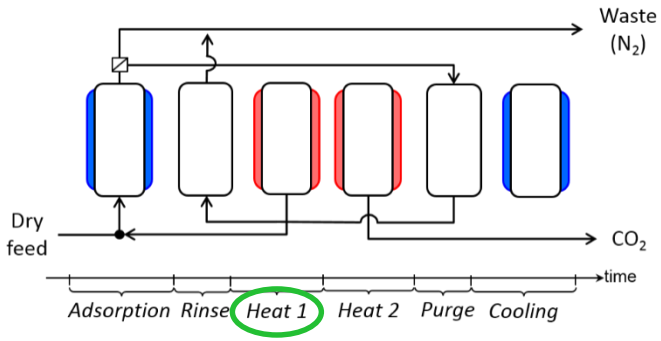

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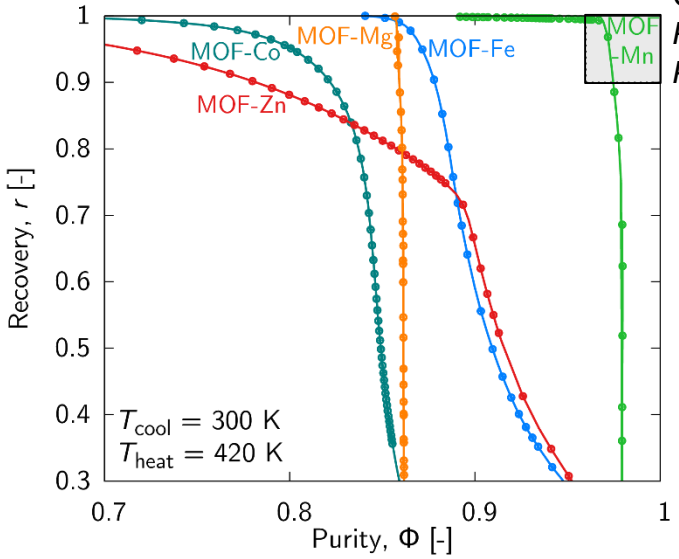

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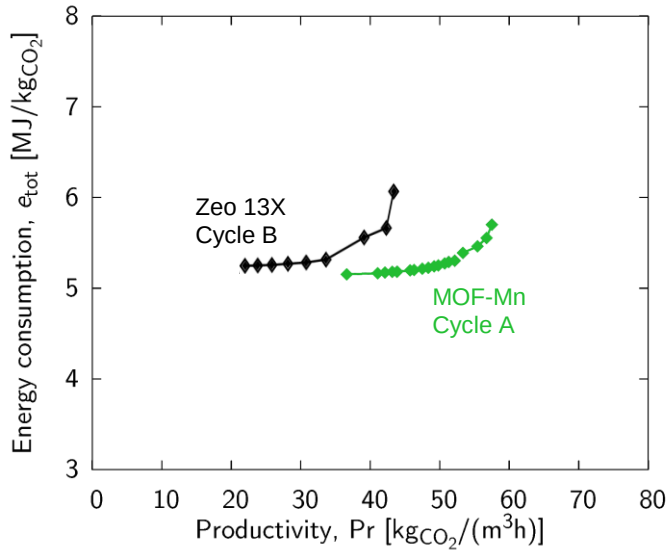

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Reference: Hefti et al., *Faraday Discuss.*, **2016**,192, 153-179

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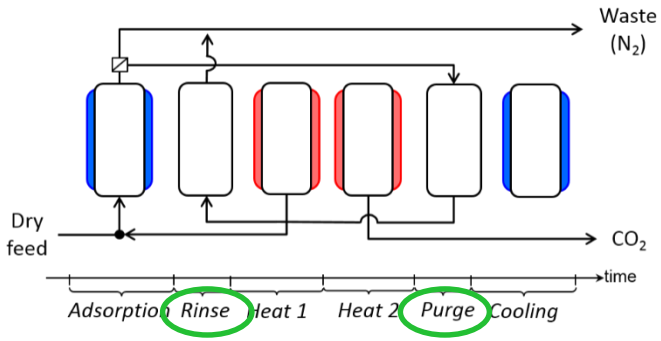

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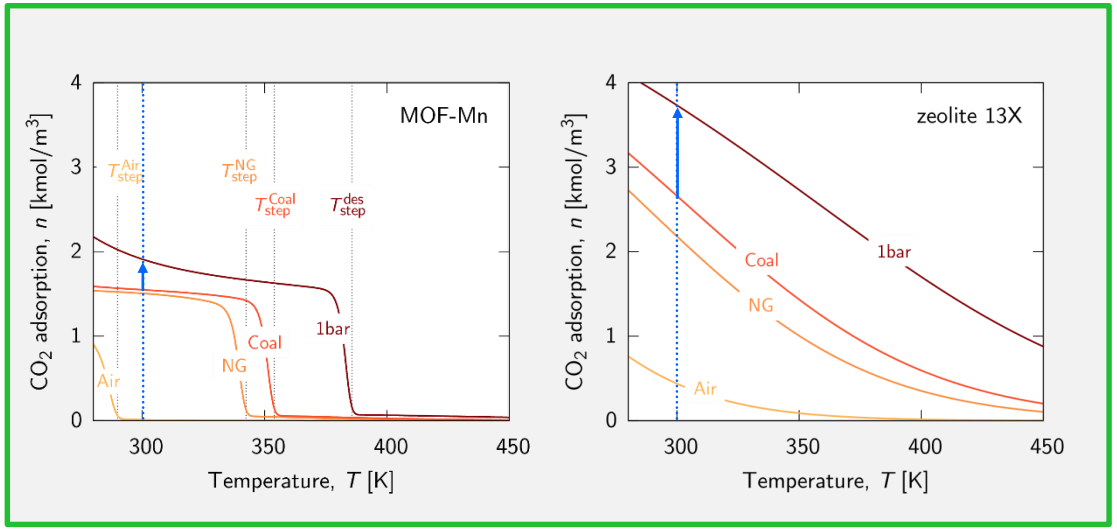

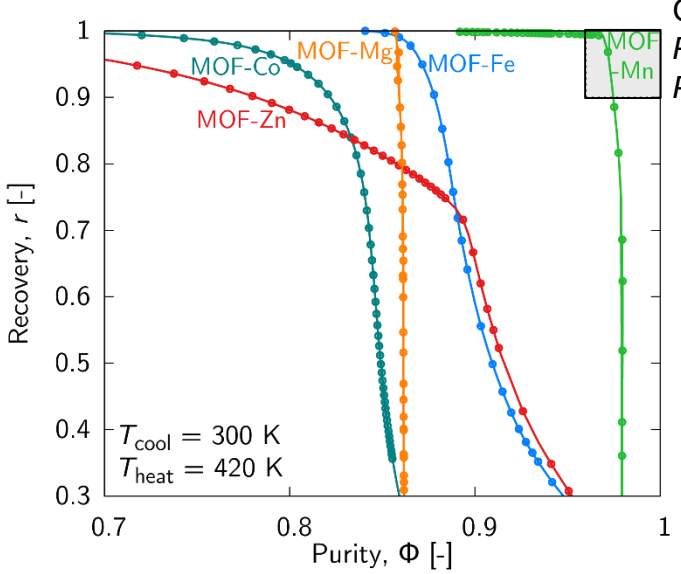

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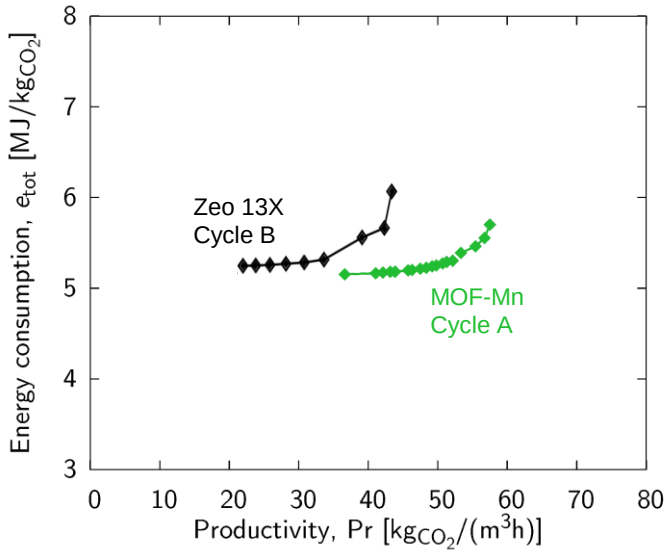

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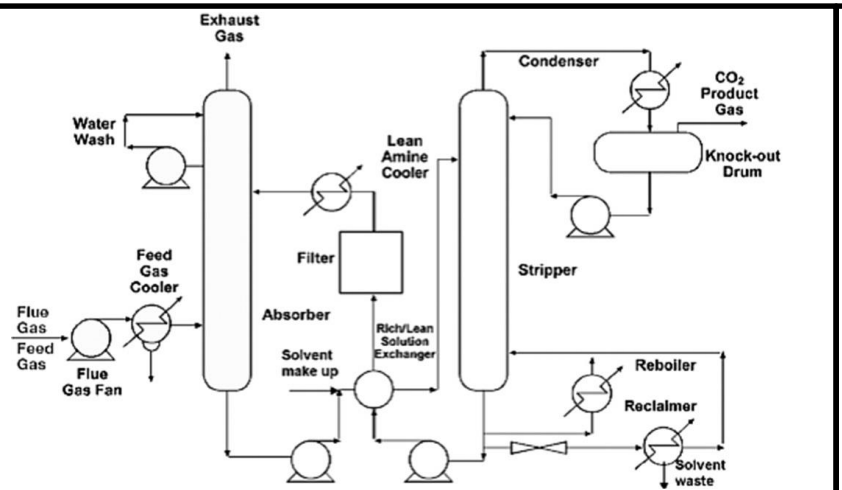
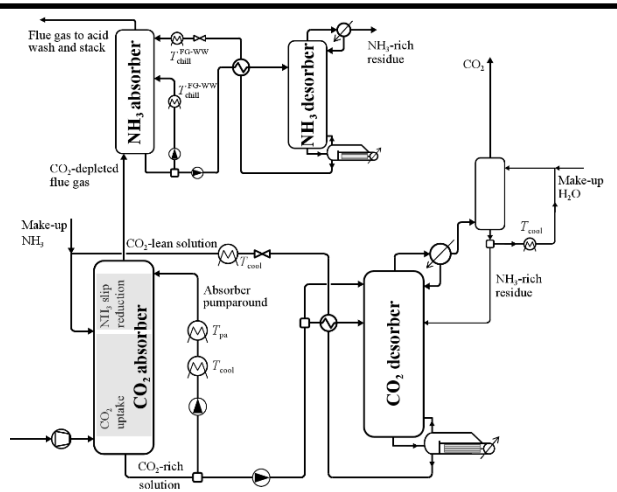
Reference: Hefti et al., *Faraday Discuss.*, **2016**,192, 153-179

Process design

ABS



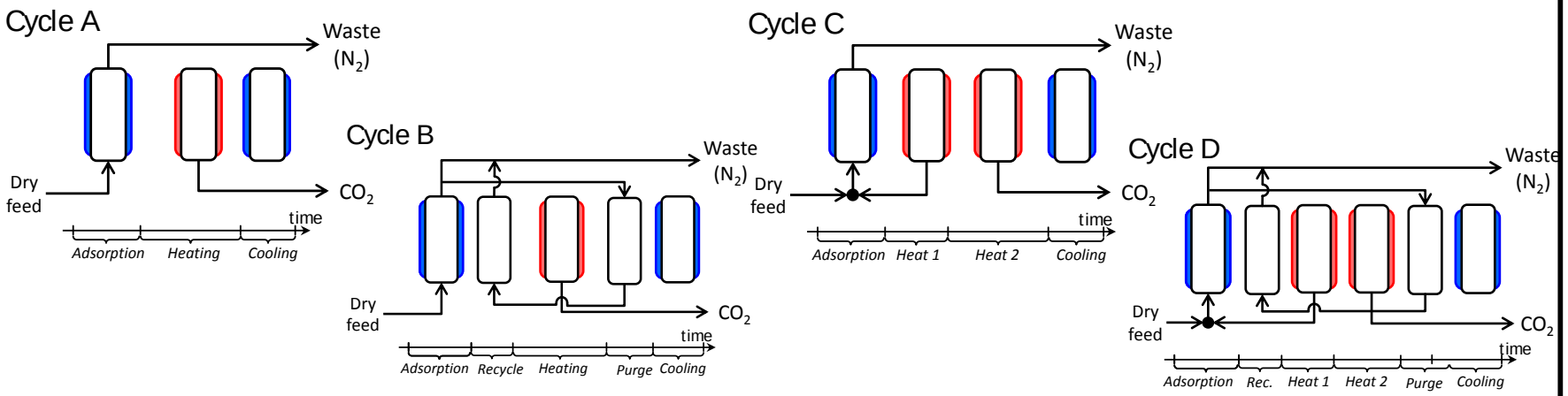
Amines (1)



Ammonia (2)

- solvent degradation
- solvent slip
- solvent loss
- high desorption enthalpy

ADS

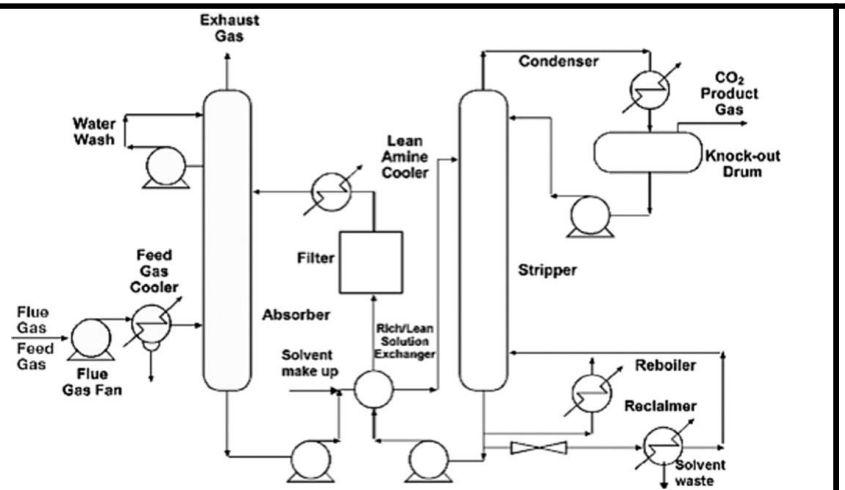


Zeolites

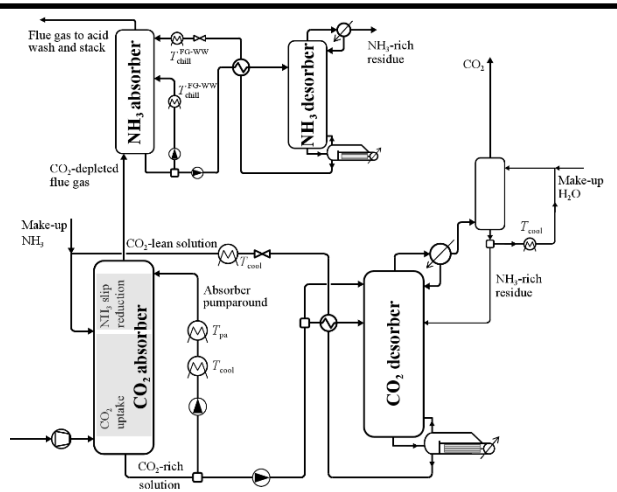
References: (1) IPCC, *Intergovernamental Panel on Climate Change Special Report on Carbon Dioxide Capture and Storage.* Cambridge University press, Cambridge, UK, **2005**
(2) Gazzani et al., Energy Procedia **2014**, 63, 1084-1090

Adsorbent selection

ABS



Amines (1)



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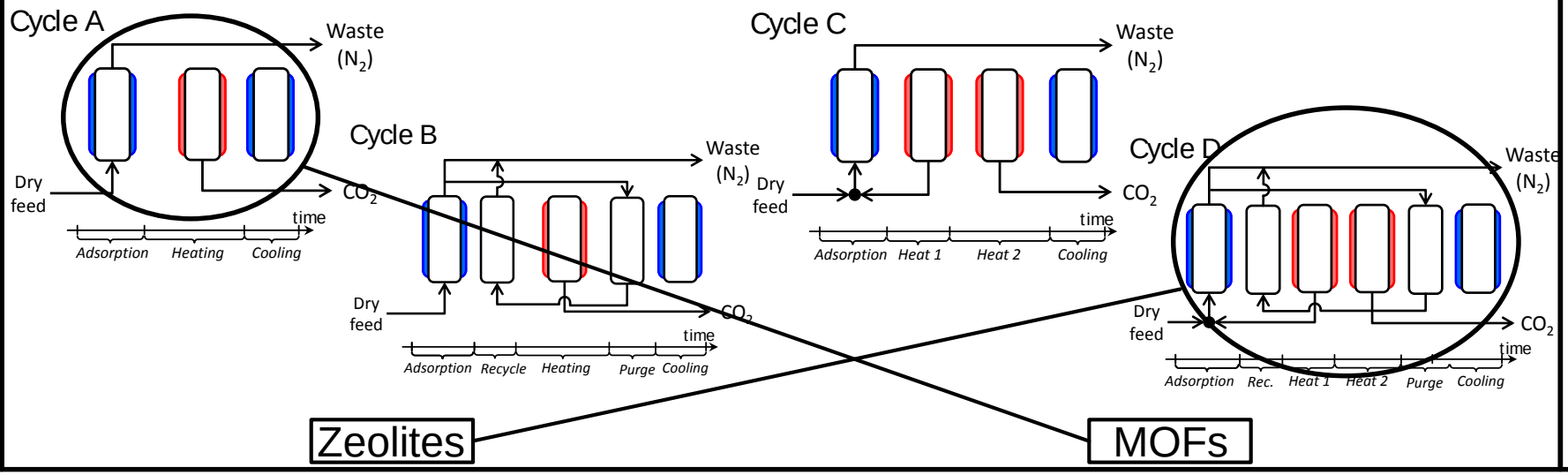
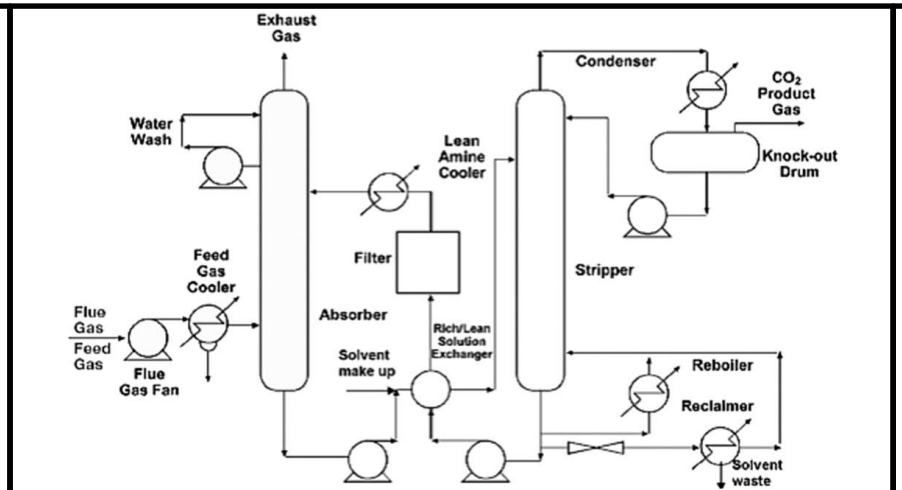


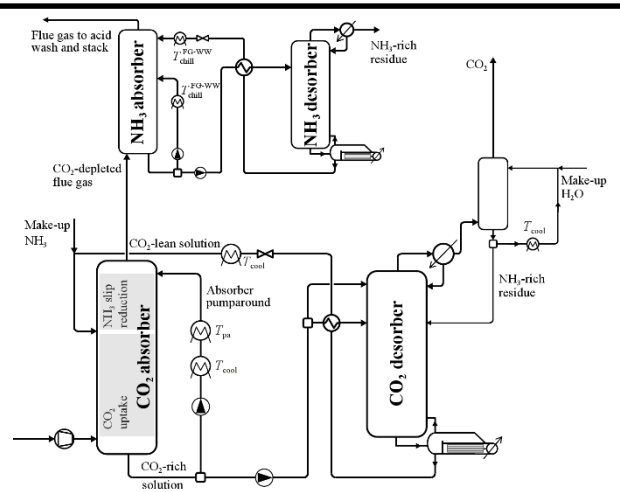
References: (1) IPCC, *Intergovernamental Panel on Climate Change Special Report on Carbon Dioxide Capture and Storage.* Cambridge University press, Cambridge, UK, **2005**
(2) Gazzani et al., Energy Procedia **2014**, 63, 1084-1090

Adsorbent degradation with water

ABS



Amines (1)



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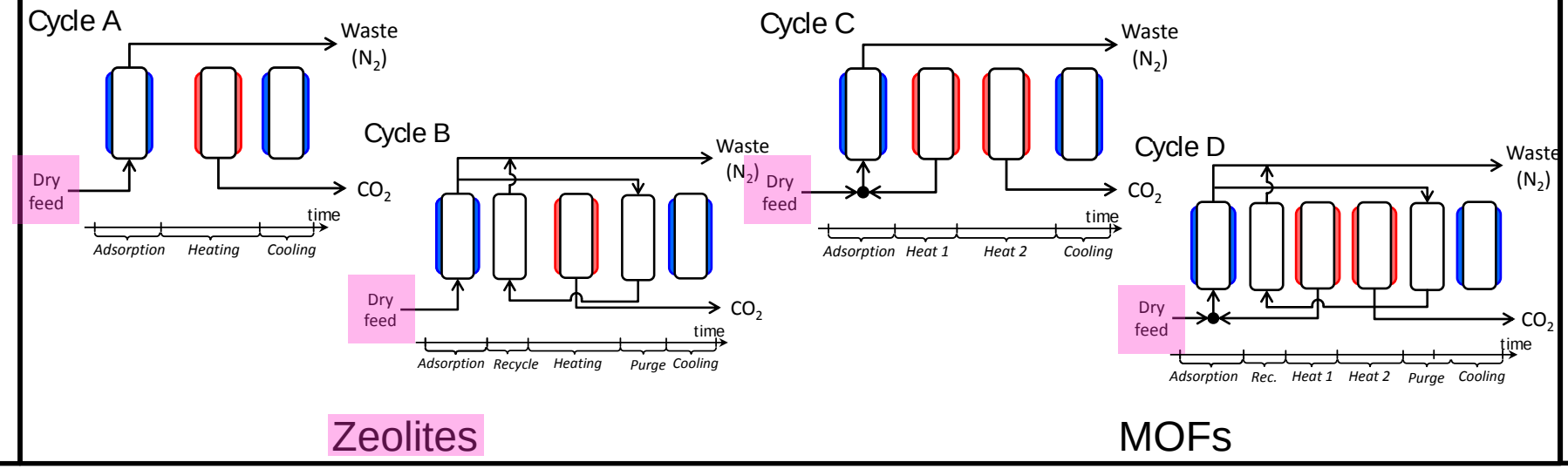
- high desorption enthalpy

ADS



Zeolites

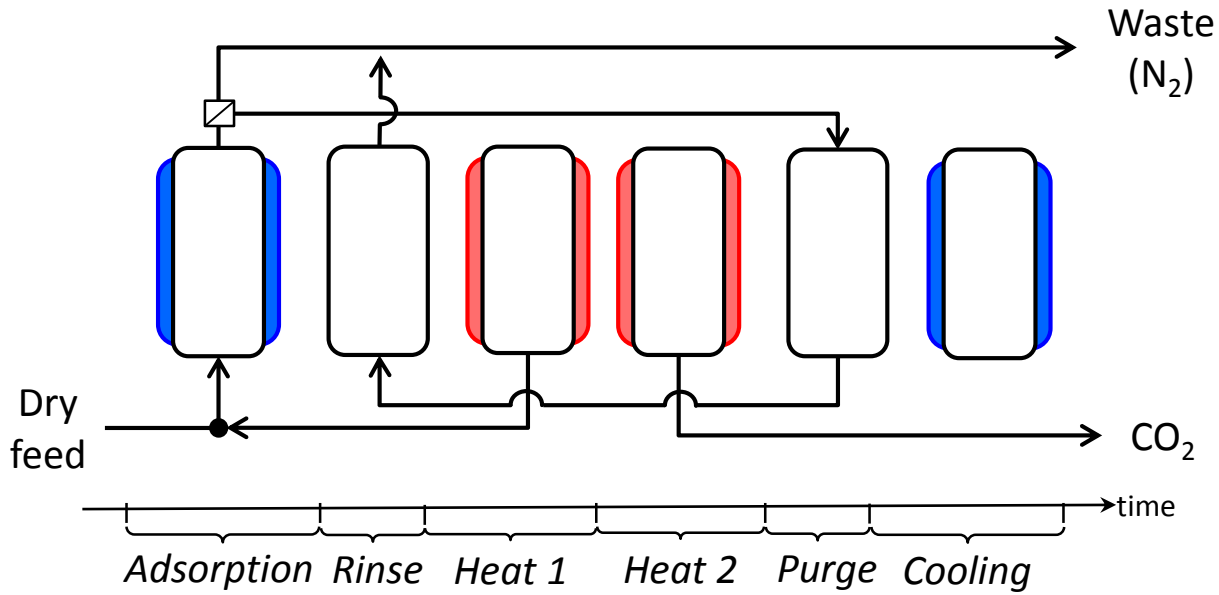
MOFs

- adsorbent performance degradation with water

References: (1) IPCC, *Intergovernamental Panel on Climate Change Special Report on Carbon Dioxide Capture and Storage.* Cambridge University press, Cambridge, UK, **2005**
(2) Gazzani et al., Energy Procedia **2014**, 63, 1084-1090

TSA CO_2 capture from moist flue gas

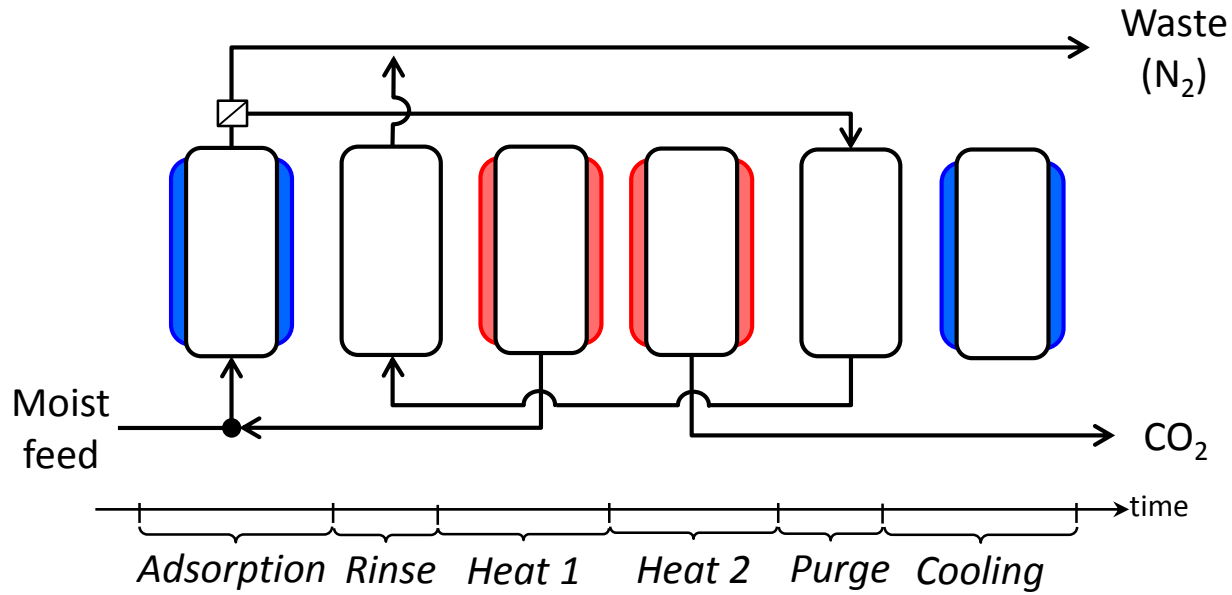
Starting from Cycle B:



TSA CO_2 capture from moist flue gas

Starting from Cycle B:

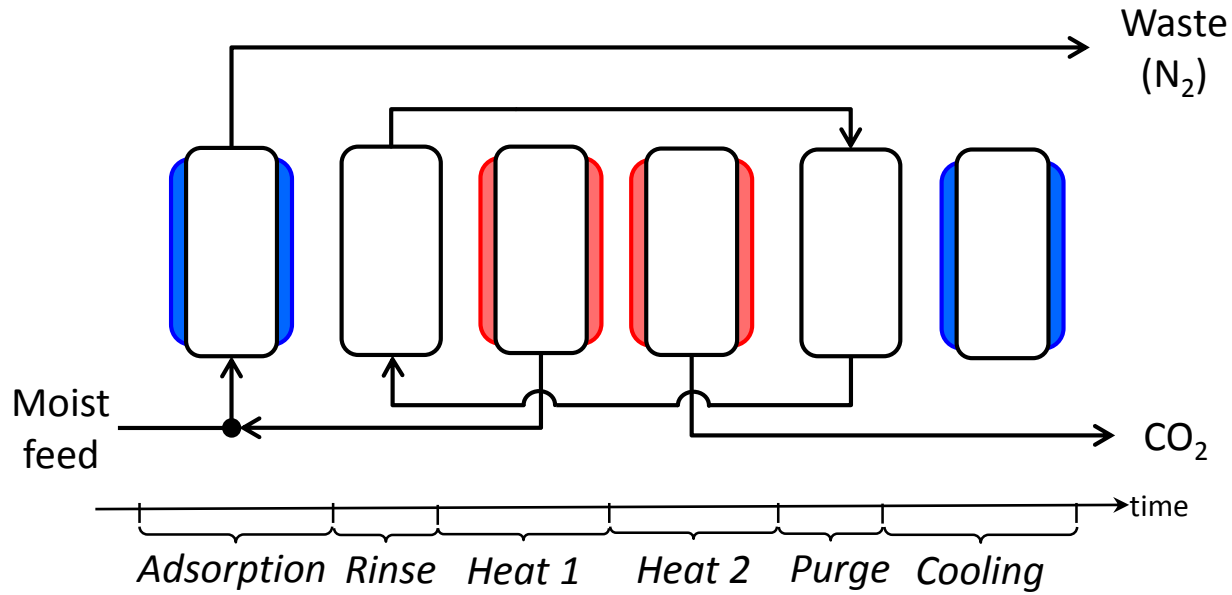
- moist flue gas:
  - 0.12/0.88 v. CO_2/N_2 (dry basis)
  - 0.04 v. water (close to saturation)



TSA CO_2 capture from moist flue gas

Starting from Cycle B:

- moist flue gas:
  - 0.12/0.88 v. CO_2/N_2 (dry basis)
  - 0.04 v. water (close to saturation)
- dual-recycle loop

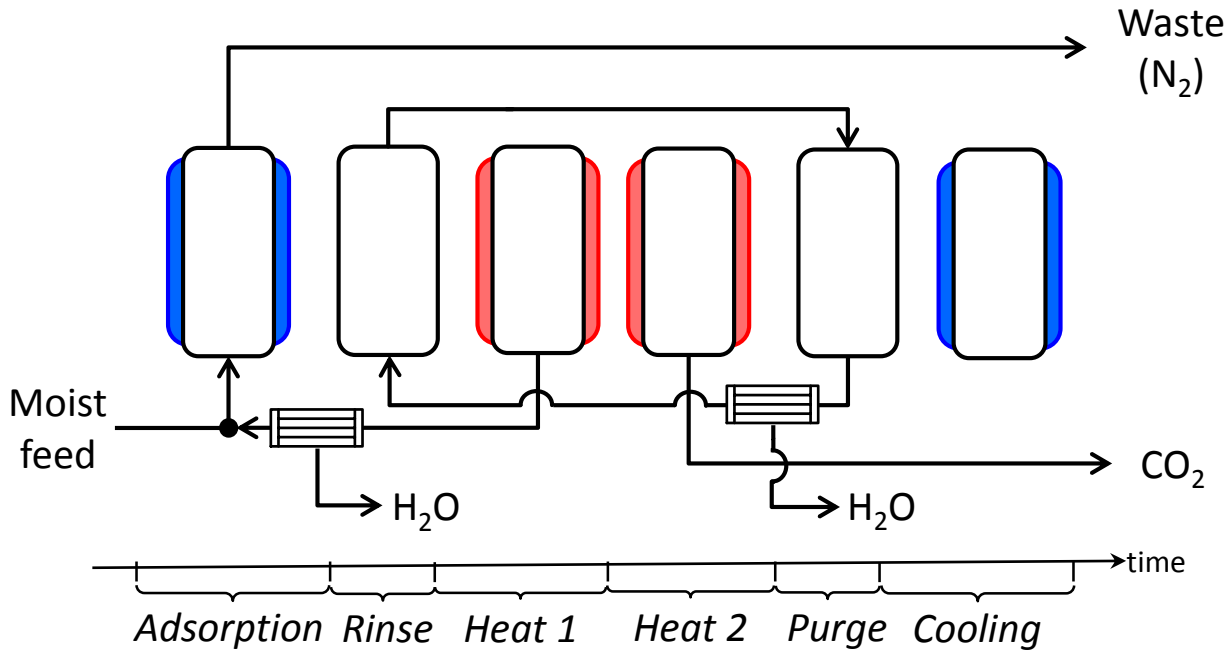


TSA CO_2 capture from moist flue gas: Cycle B*

Starting from Cycle B:

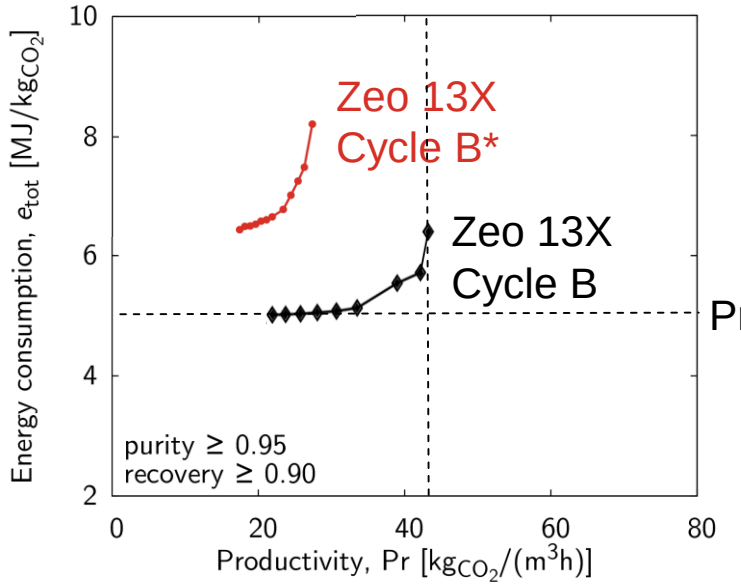
- moist flue gas:
  - 0.12/0.88 v. CO_2/N_2 (dry basis)
  - 0.04 v. water (close to saturation)
- dual-recycle loop
- condensers

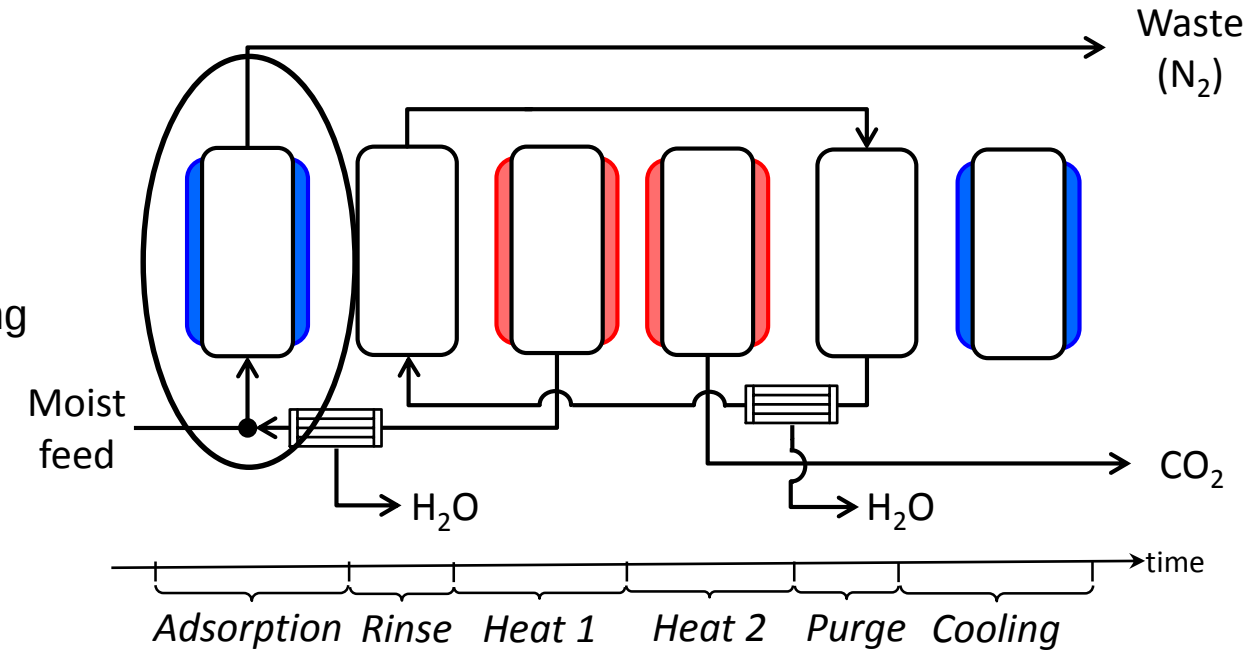
Cycle B*

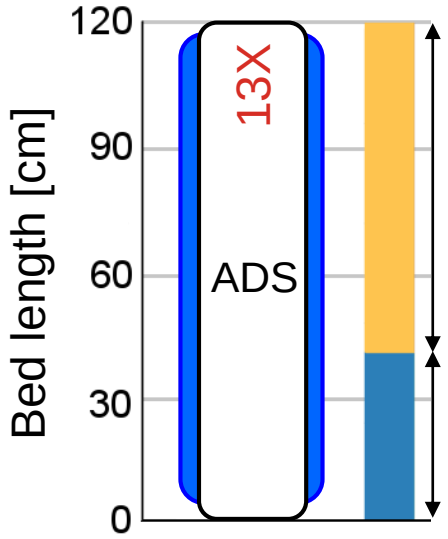


Reference: Hefti et al., **2017** *submitted*
CASALE SA, *patent filed*

TSA CO_2 capture from moist flue gas: Cycle B*







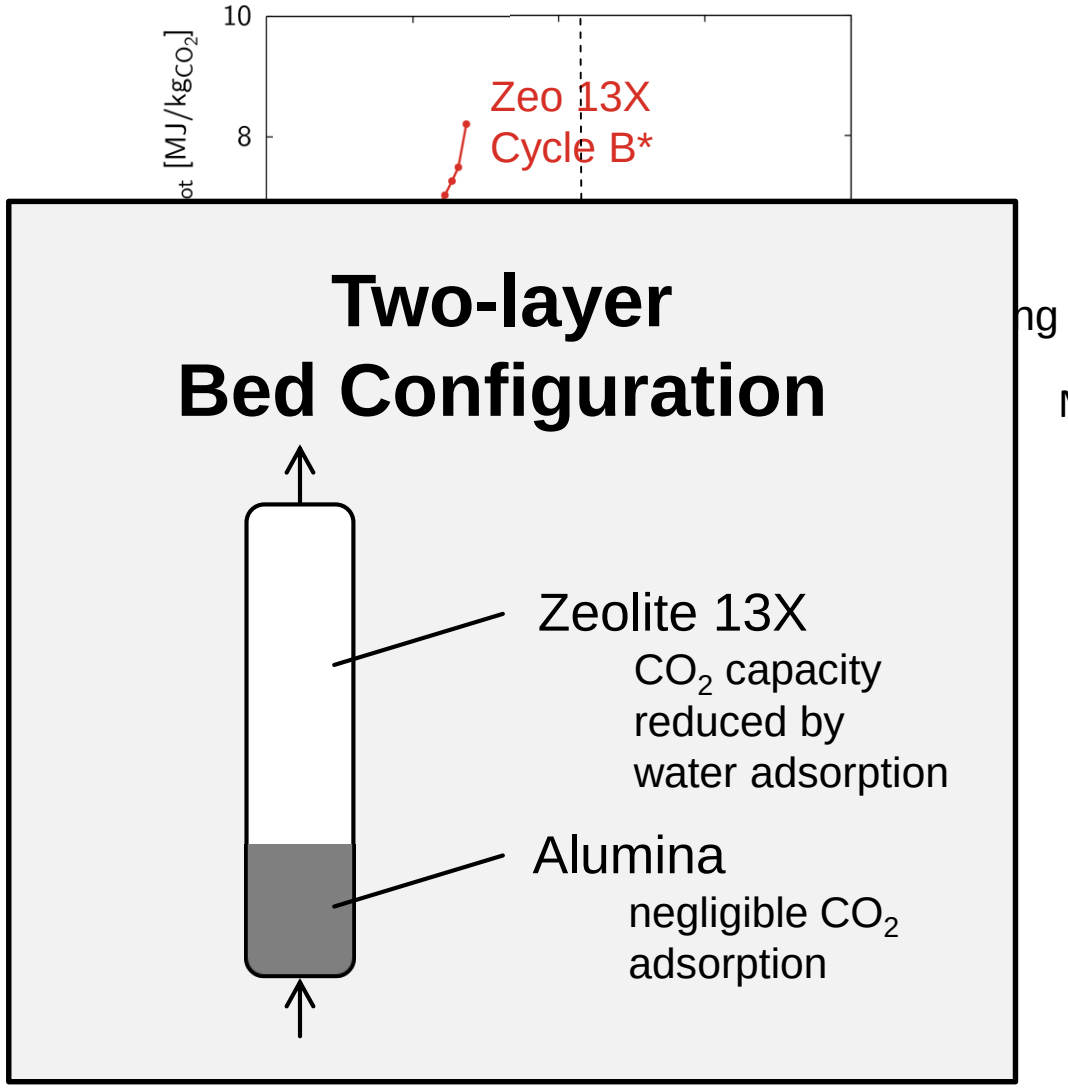
effective separation of CO_2

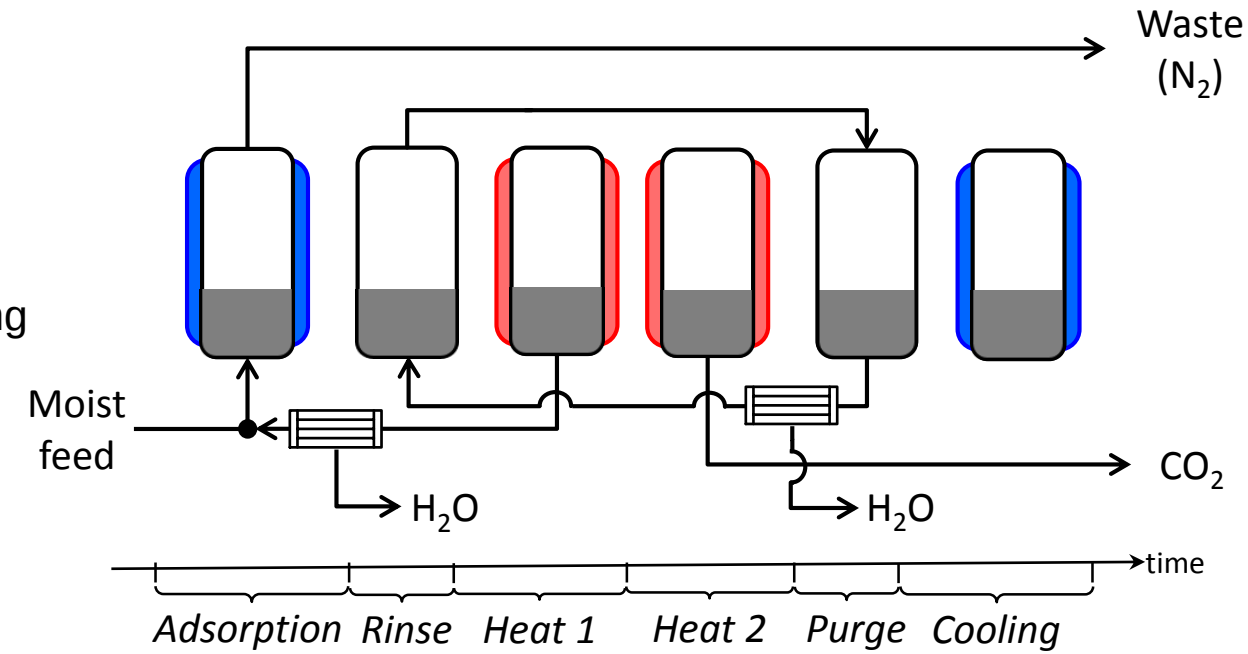
penetration depth of adsorbed water front at the end of the adsorption step

unavailable for CO_2 adsorption

Reference: Hefti et al., **2017** *submitted*
CASALE SA, *patent filed*

TSA CO_2 capture from moist flue gas: two-layer bed





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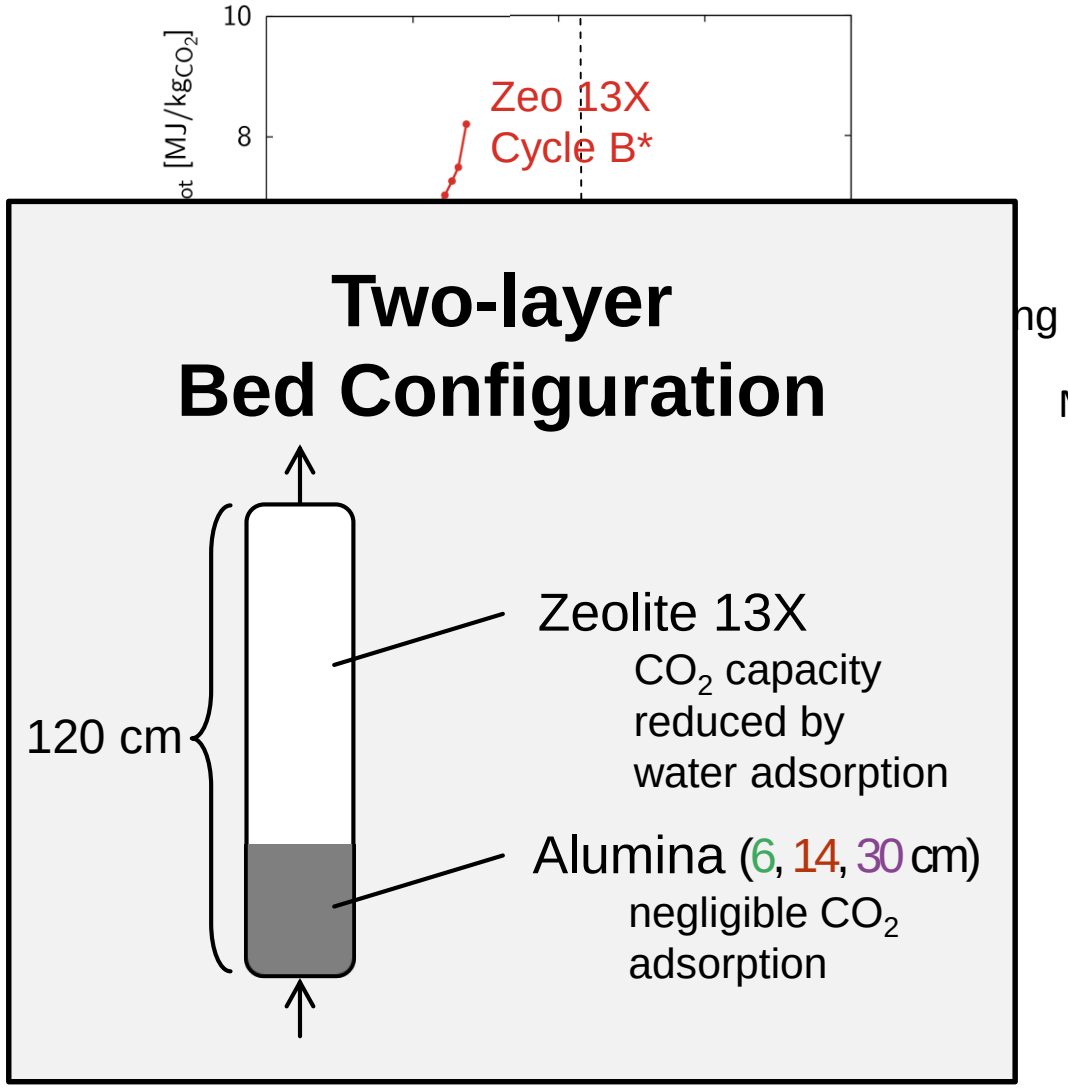

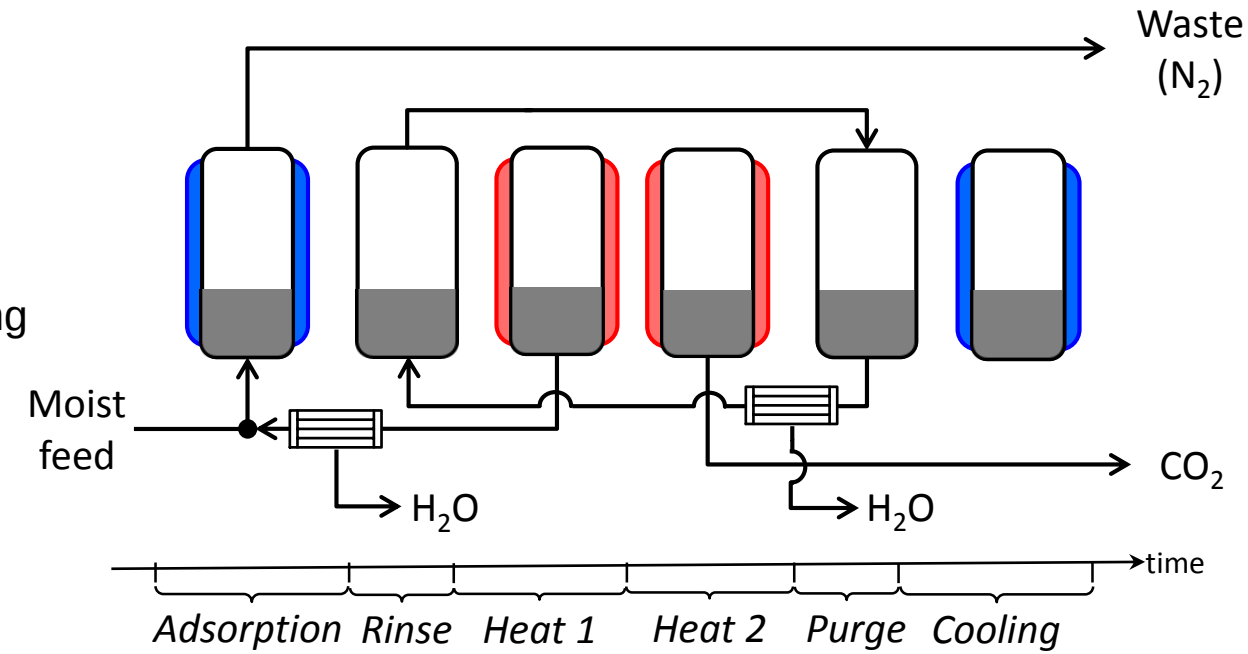

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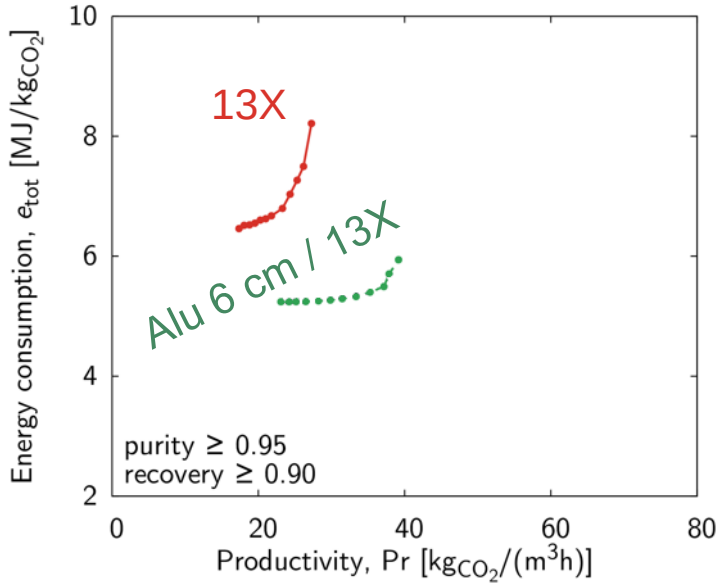

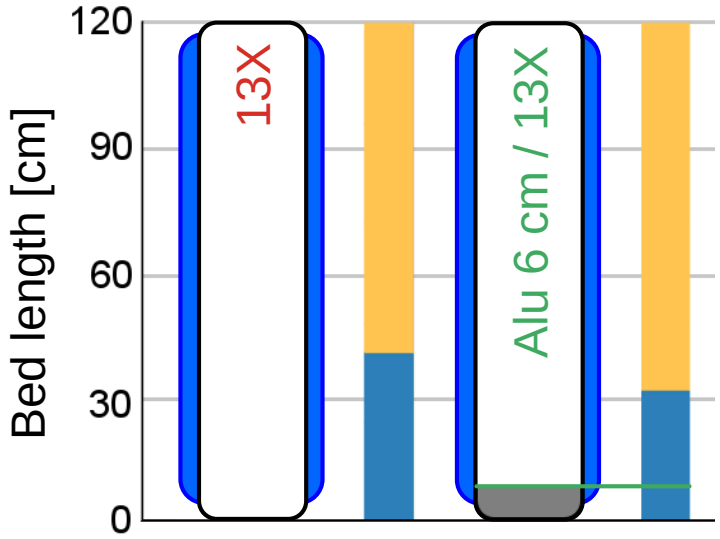

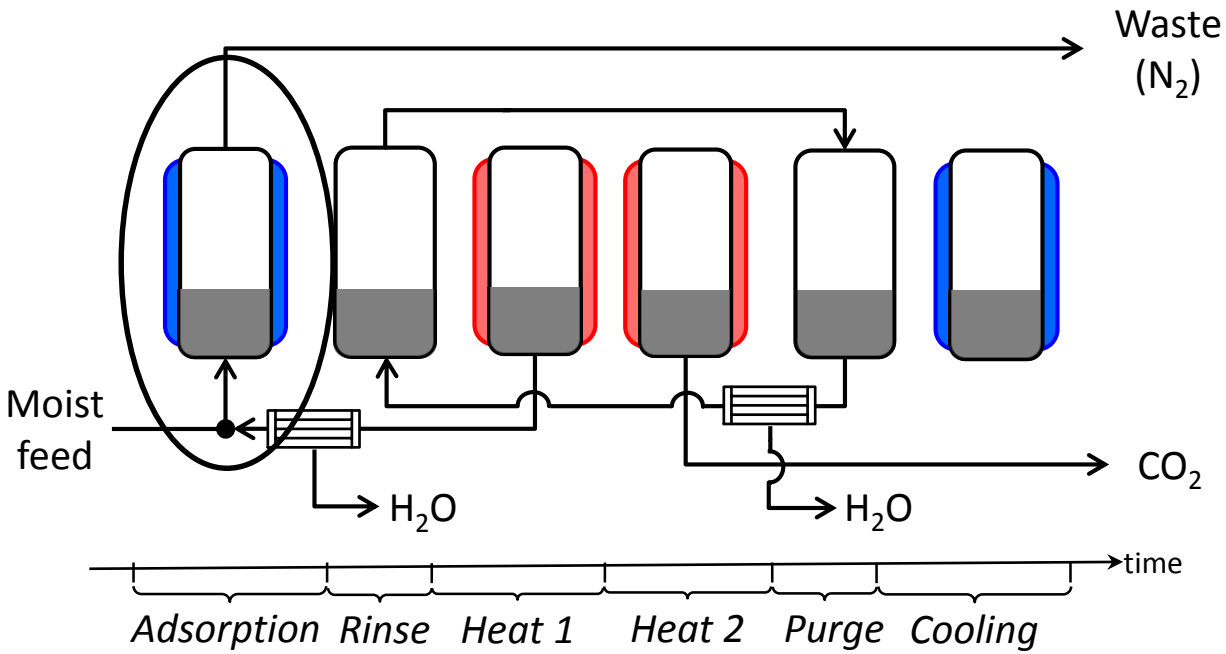

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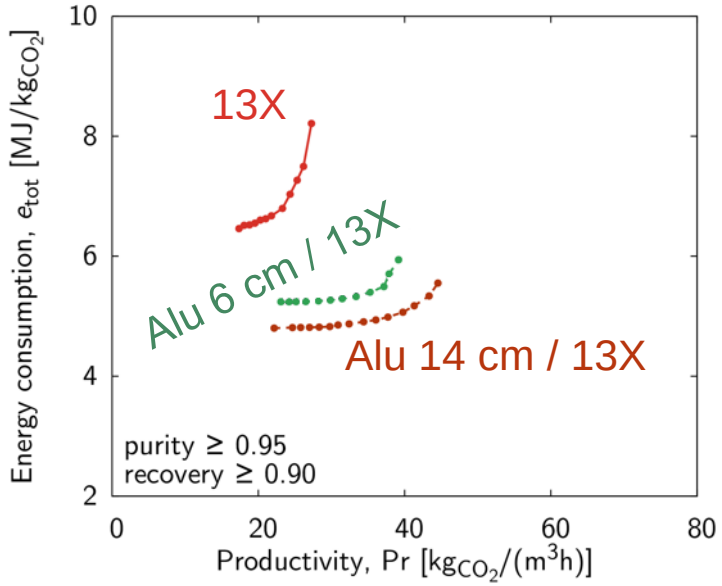

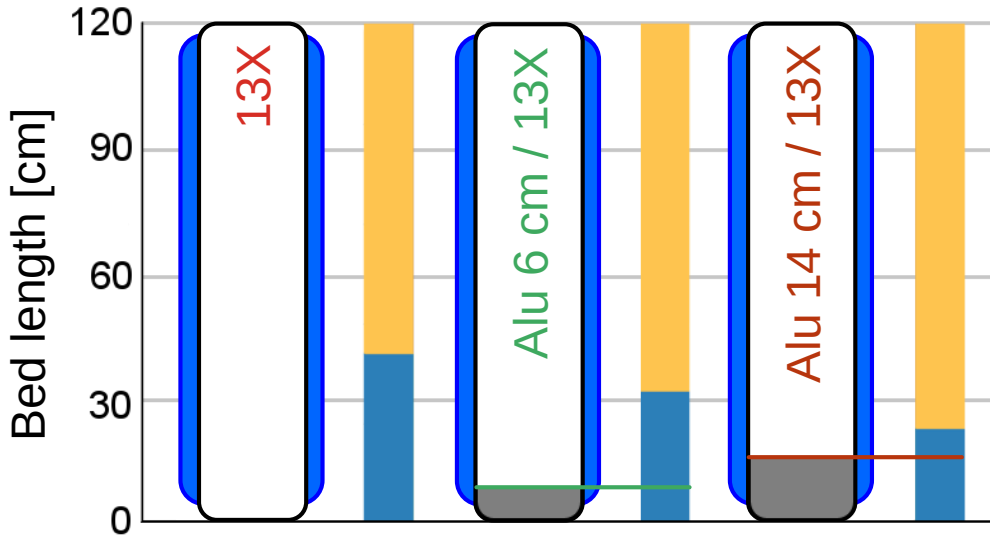

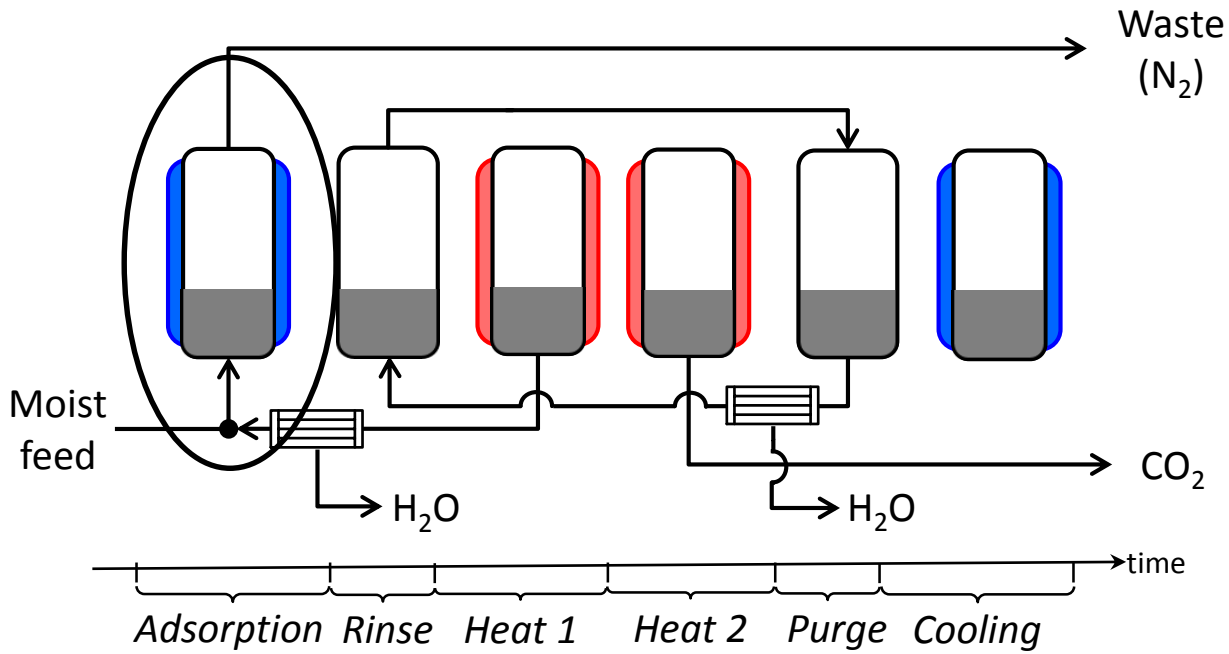

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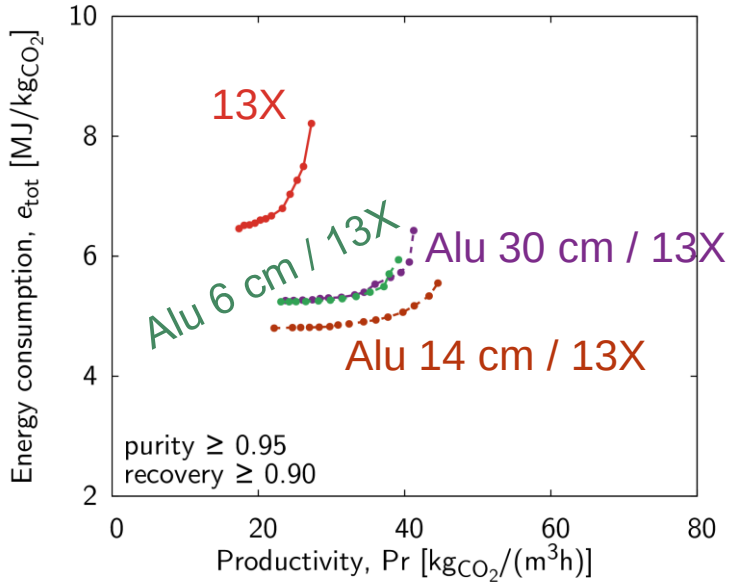

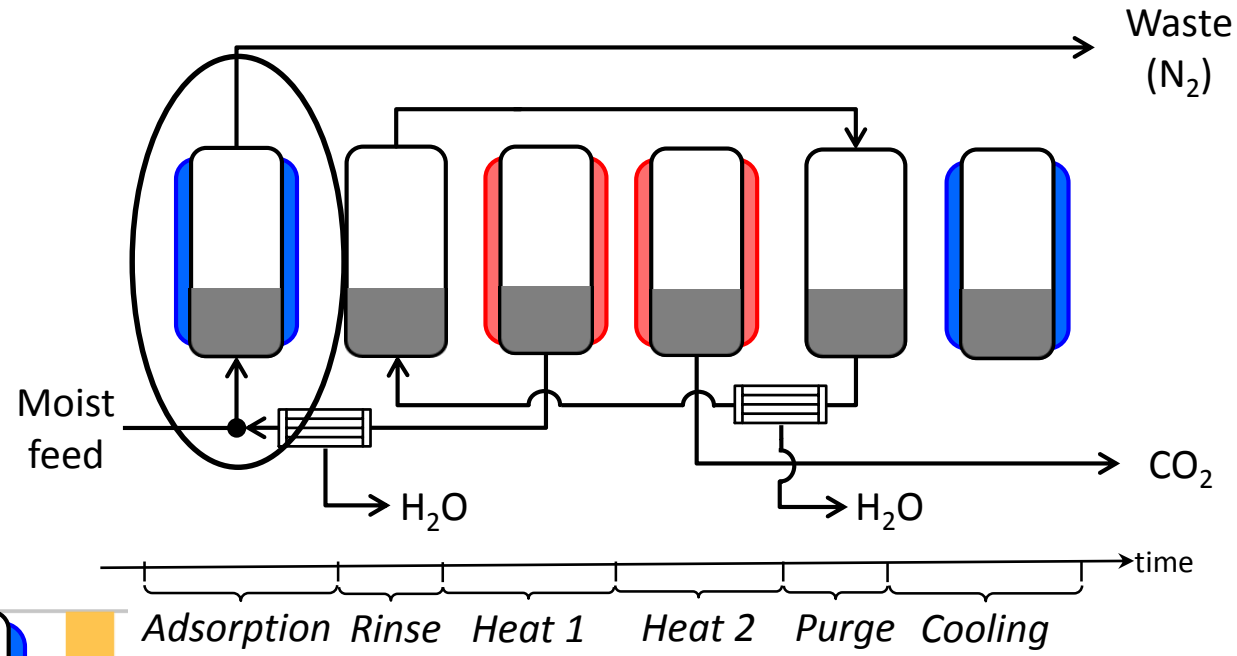

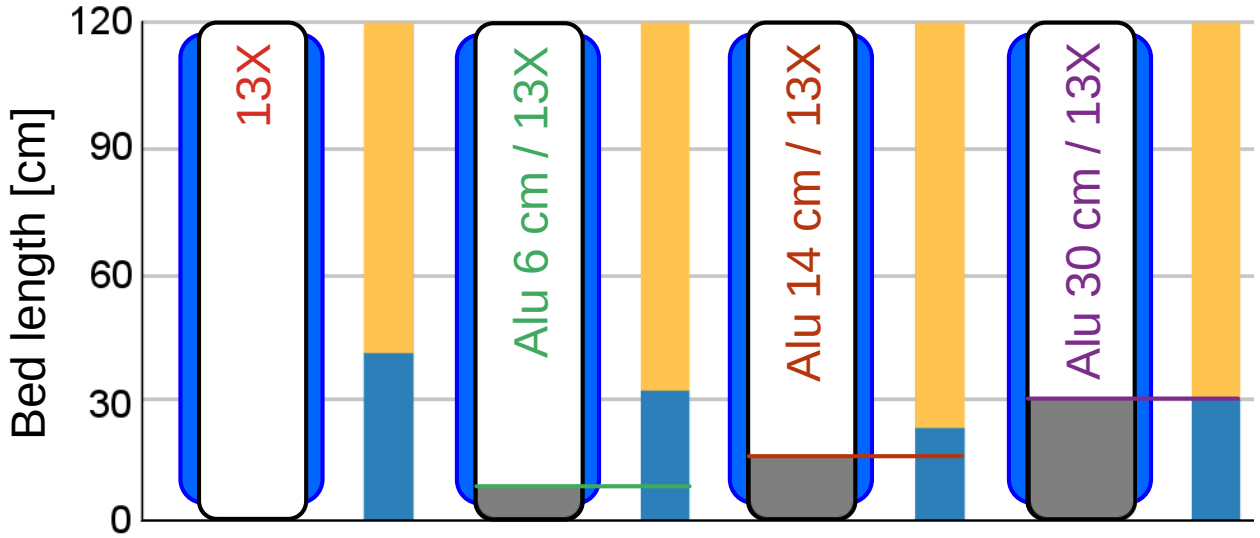

Reference: Hefti et al., **2017** *submitted*
CASALE SA, *patent filed*

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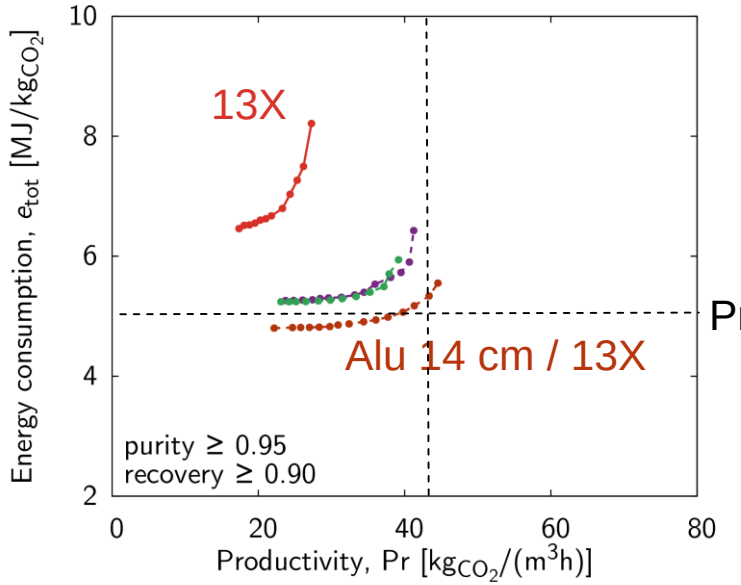
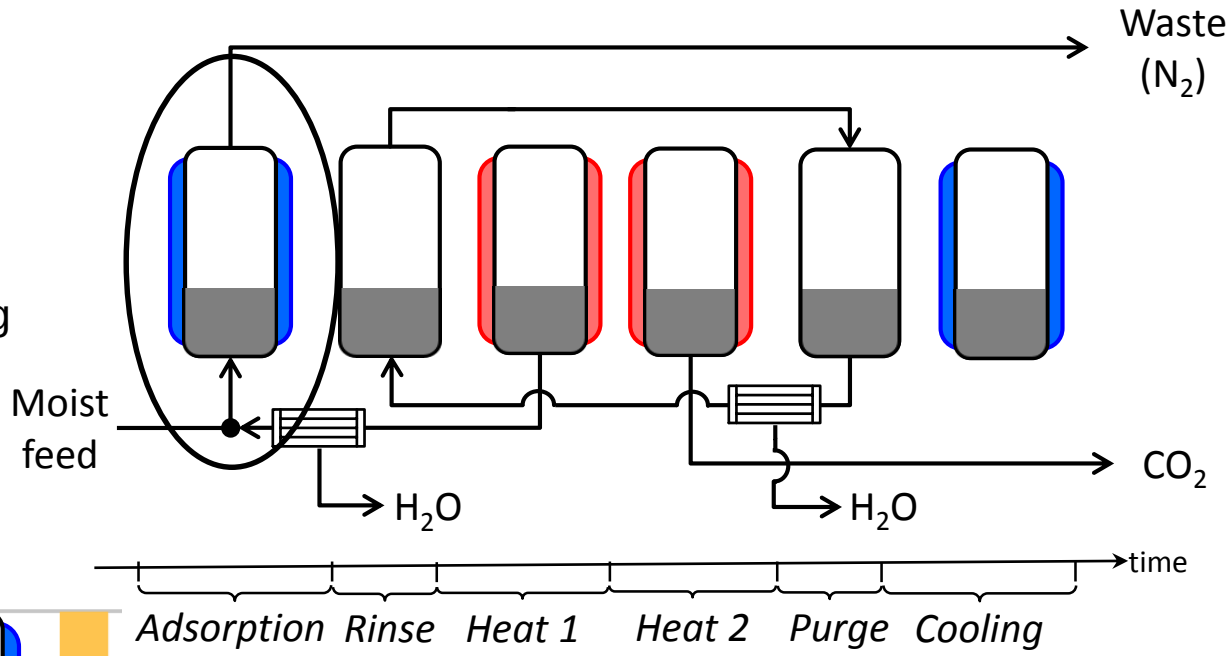
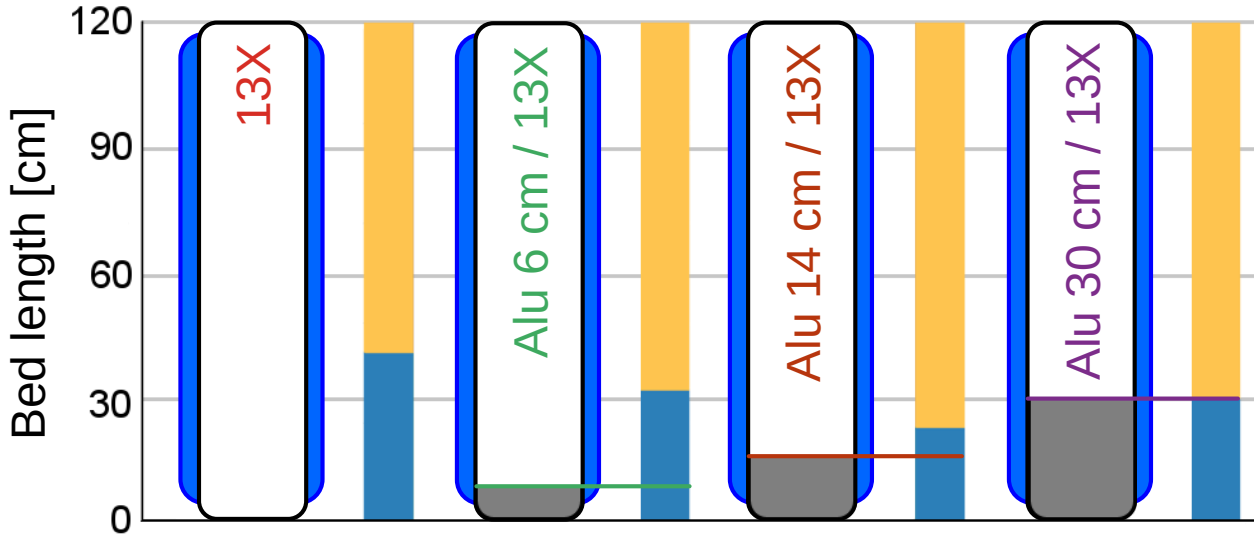


Pre-drying





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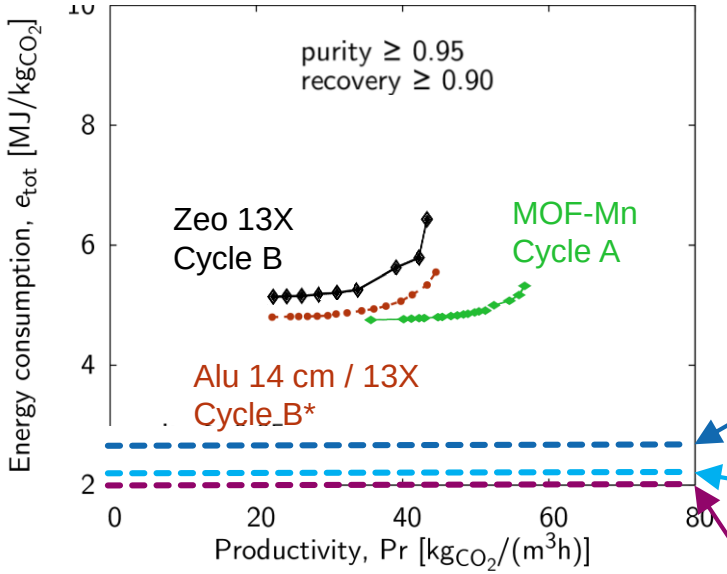


~3.0 MJ/kg$_{CO2capt}$

40wt.% MEA sol.
@ 15v% CO_2 feed – 90% Recovery

Abu Zahra et al., *Int. J. Greenhouse Gas Control* **2007**, 1, 37-46

~2.5 MJ/kg$_{CO2capt}$

Shell ASAP bench-scale pilot (new amine solvent)
@ 10v.% CO_2 feed – 89% Recovery

Singh et al., *Energy Procedia* **2013**, 37, 2021-2046

~2.3 MJ/kg$_{CO2capt}$

DMX process (two-phase solvent)
@ 10v.% CO_2 feed – 90% Recovery

Raynal et al., *Energy Procedia* **2011**, 4, 779-786

Conclusions

- Adsorption processes for CO_2 capture are a potential alternative to absorption-based technologies. They allow to exploit the advantages of employing solid, non-toxic sorbents.

- Temperature-driven regeneration (TSA) is the most convenient way to operate a post-combustion CO_2 capture process via adsorption.

- The evolution and further development of these processes addresses different issues and aspects:
  - cycle design (from simple cycles to more complex ones);
  - adsorbent selection (development of new adsorbents);
  - bed configuration (from single to multi-layer configurations).

- Although the performance of TSA processes does not measure up to that of the most-established absorption-based technologies yet, significant enhancement has been already accomplished and further margin is available for improvement (heat integration, column design…)

Acknowledgements

(Lugano-based Swiss Company, active in the production of ammonia, fertilizers, urea, melamine, methanol and syngas)

Collaboration projects between our group and CASALE (co-funded by the Swiss Commission for Technology and Innovation, CTI):

2012-2015	CTI 12903.1 PFIW-IW	*"Capture of CO2 by adsorption from the flue gas of power- and industrial- plants"*
2017-2019	CTI 25299.1 PFIW-IW	*"Innovative temperature swing adsorption processes for post-combustion CO_2 separation in chemical plants"*

In the context of these projects significant results in the investigation of TSA cycles for CO_2 capture have been produced, and a few patents have been filed.

Conclusions

- Adsorption processes for CO_2 capture are a potential alternative to absorption-based technologies. They allow to exploit the advantages of employing solid, non-toxic sorbents.

- Temperature-driven regeneration (TSA) is the most convenient way to operate a post-combustion CO_2 capture process via adsorption.

- The evolution and further development of these processes addresses different issues and aspects:
  - cycle design (from simple cycles to more complex ones);
  - adsorbent selection (development of new adsorbents);
  - bed configuration (from single to multi-layer configurations).

- Although the performance of TSA processes does not measure up to that of the most-established absorption-based technologies yet, significant enhancement has been already accomplished and further margin is available for improvement (heat integration, column design…)

Back-up

Back-up

1. Mass balances

$$\epsilon\frac{\partial c_i}{\partial t}+(1-\epsilon)\frac{\partial n_i}{\partial t}+\frac{\partial(uc_i)}{\partial z}=\epsilon_b\frac{\partial}{\partial z}\left(D_L c\frac{\partial y}{\partial z}\right)$$

$$\frac{\partial n_i}{\partial t}=k_i(n_i^*-n_i)$$

2. Energy balances

for the fixed bed (solid+gas)

$$\overline{C}_{p,\text{bed}}\frac{\partial T_w}{\partial t}-\epsilon\frac{\partial p}{\partial t}-(1-\epsilon)\sum_j(-\Delta H_j)\frac{\partial n_j}{\partial t}+$$

$$uC_{p,g}\frac{\partial T}{\partial z}+\frac{2h_b}{r_i}(T-T_w)=\epsilon_b\frac{\partial}{\partial z}\left(K_L\frac{\partial T}{\partial z}\right)$$

for the column wall

$$\frac{\partial T_w}{\partial t}=\frac{2\pi}{C_w a_w}(h_b r_i(T-T_w)-h_w r_o(T_w-T_f))$$

3. Constitutive equations

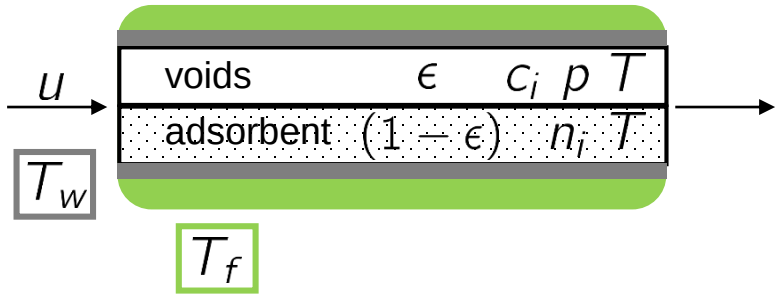
- Non linear adsorption isotherm

$$n_i^*=n_i^*(p,T,\boldsymbol{y})$$

- Pressure drop correlation (Ergun)

4. Boundary conditions

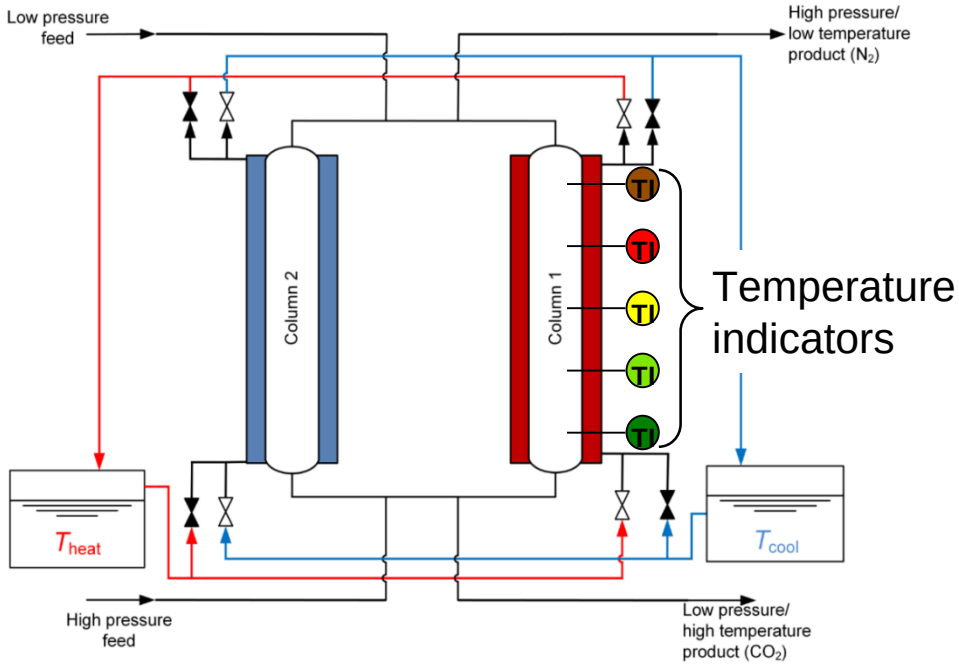
- Initial/feed conditions
- Cyclic boundary conditions that are representativ of a sequence of steps



Back-up

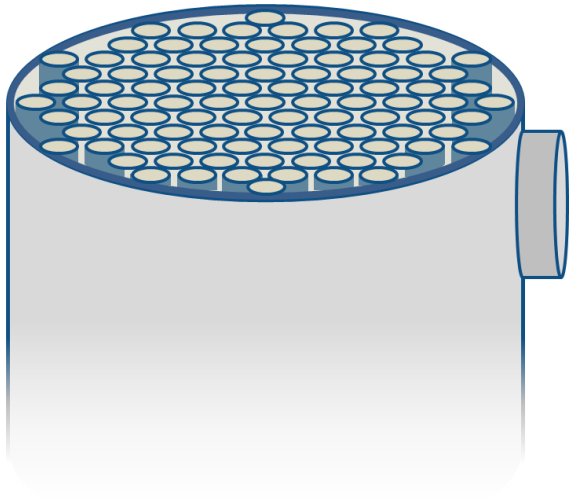
- Thermofluid in column jacket for temperature control
- Two fluid circuits with separate thermostats:
  - Low temperature
  - High temperature

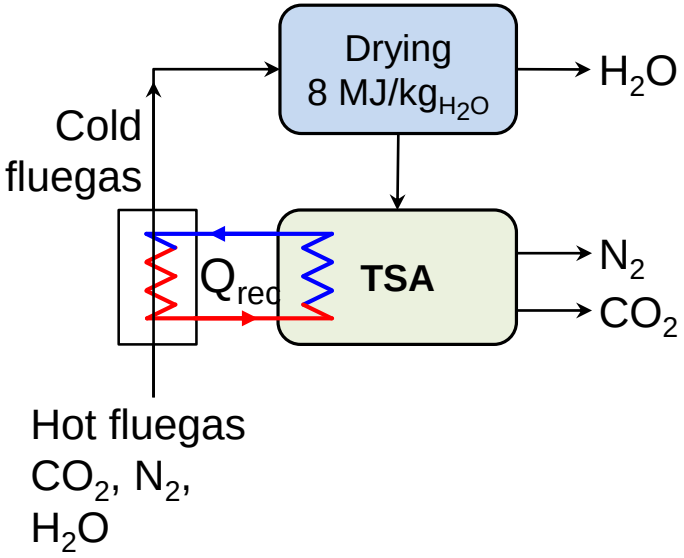
Column dimensions		
column length	L	120 cm
column diameter	D	2.5 cm
bed porosity	ε_b	0.40
total porosity	ε_t	0.72



Back-up

- CO_2/N_2 12:88 v/v (dry)
- 4 vol% H_2O
- Commercial adsorbent: Zeolite 13X
- Shell and tube type adsorber
- Heating at 420 K
- Cooling at 300 K





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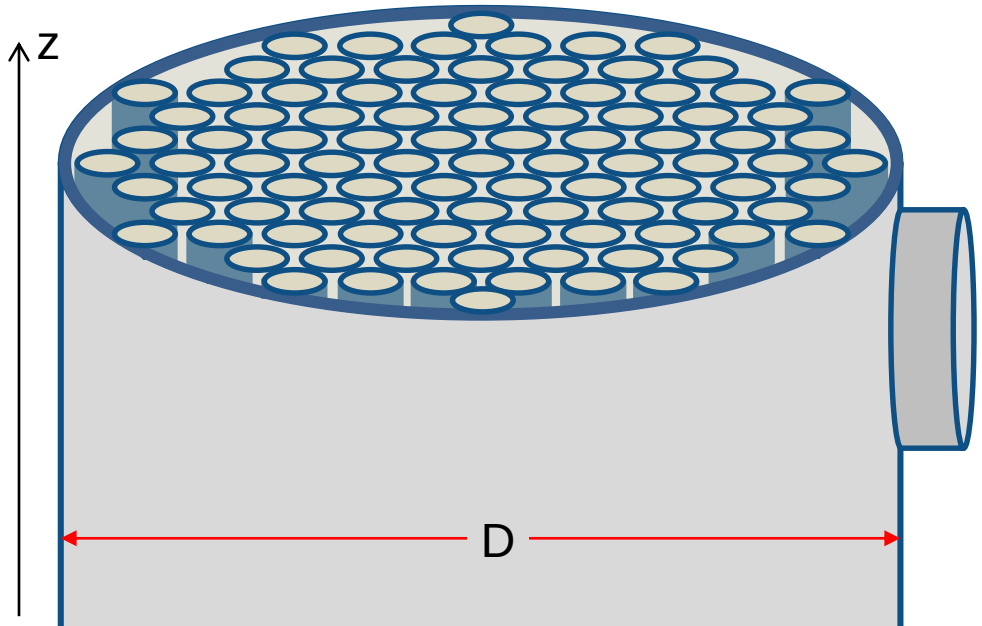
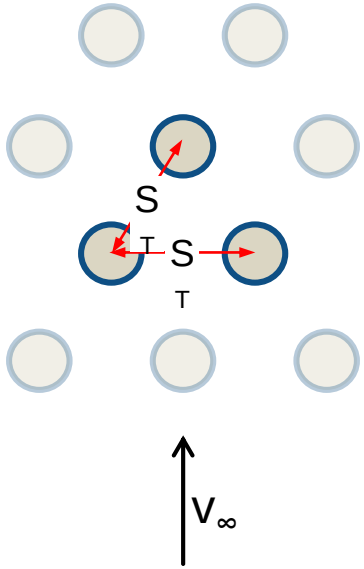


Dimensions:
D = 3.05 m

Number of tubes
N_p = 5164

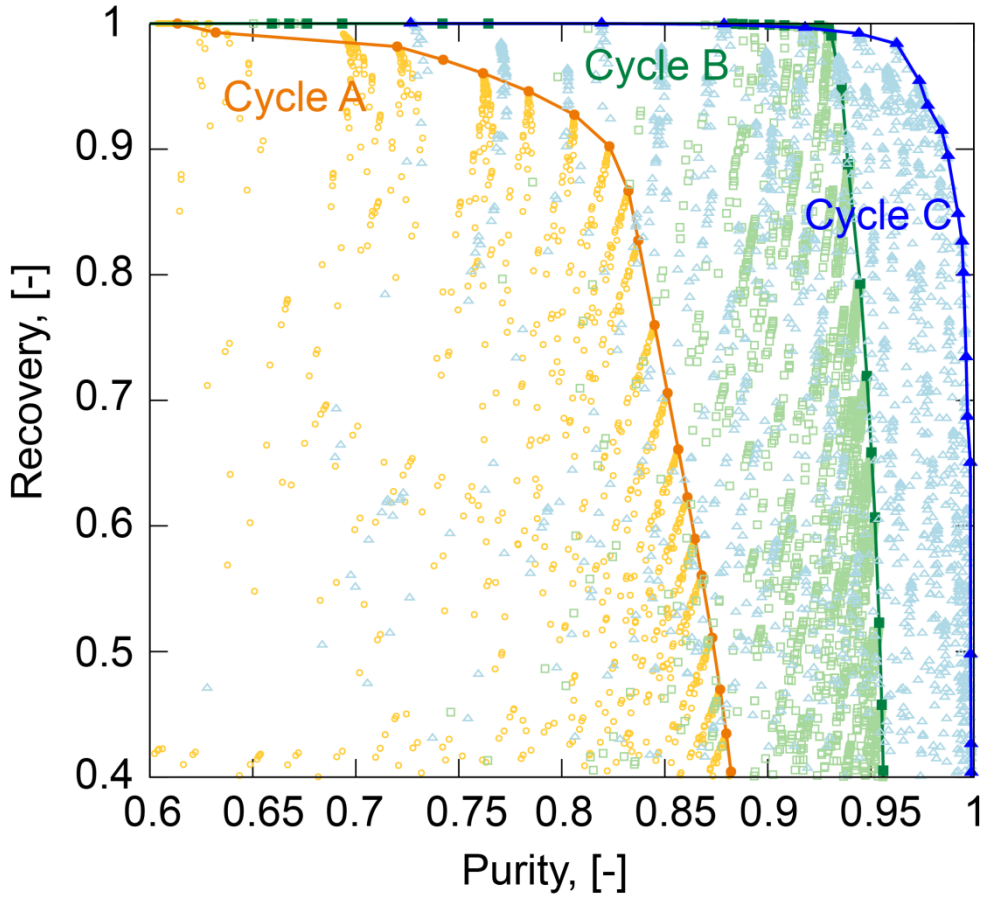
d_o = 0.032 m (1¼ in)
d_i = 0.030 m (BWG 15)
S_T = 0.040 m (1⁹⁄₁₆ in)



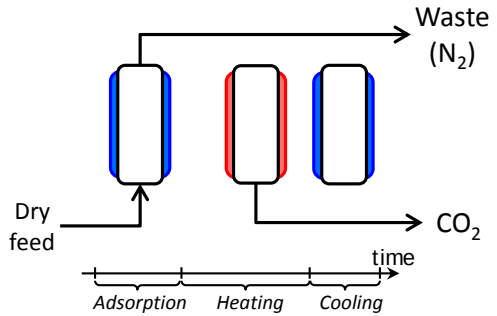
Fixed quantities in scale-up:

- Specific exchange area $S_{ex,s}$ = 130 m^2-surface/m^3-bed
- Specific metal content $V_{m,s}$ = 0.12 m^3-metal/m^3-bed

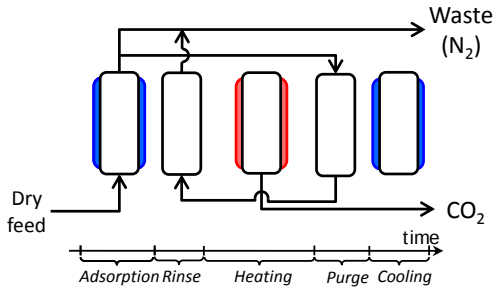
Back-up



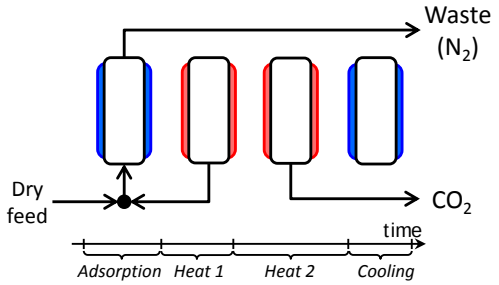
Cycle A



Cycle B



Cycle C

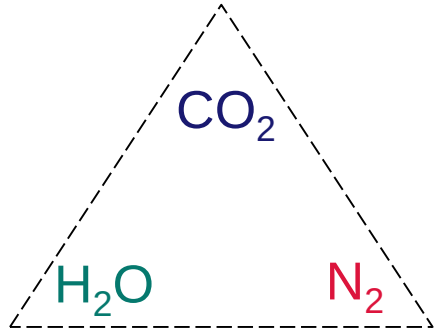


Back-up

Commercial material:

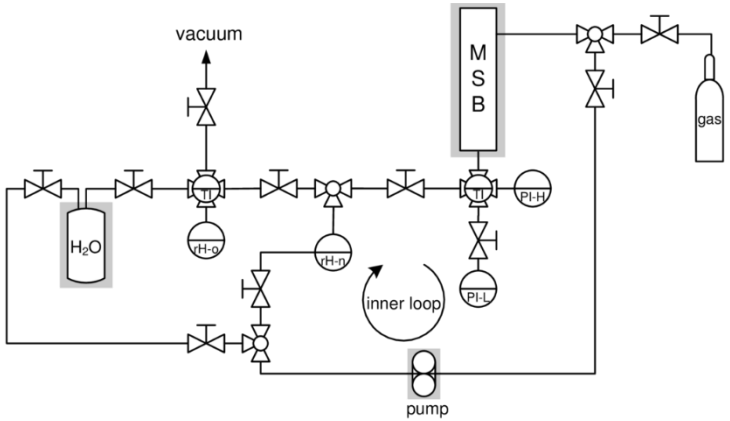
- Zeolite 13X
- Highly porous
- Surface area 400m^2/g

https://www.alibaba.com/zeolite-molecular-sieve-beads-promotion.html

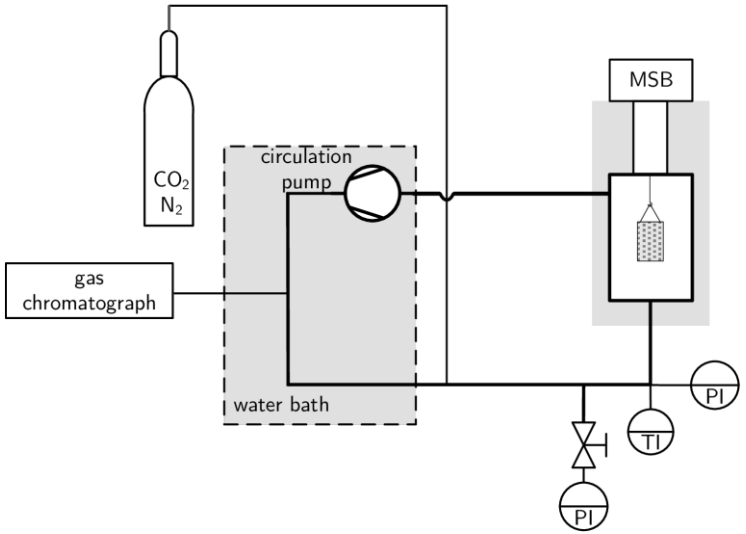


Experimental setups:

H_2O

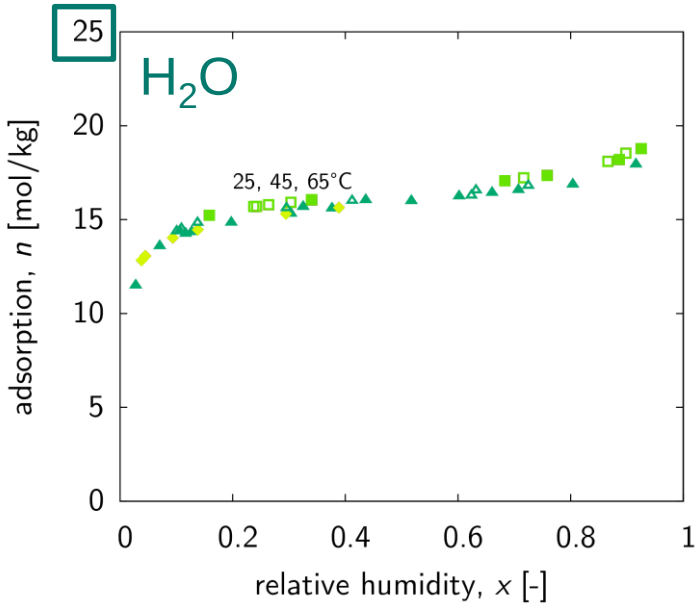


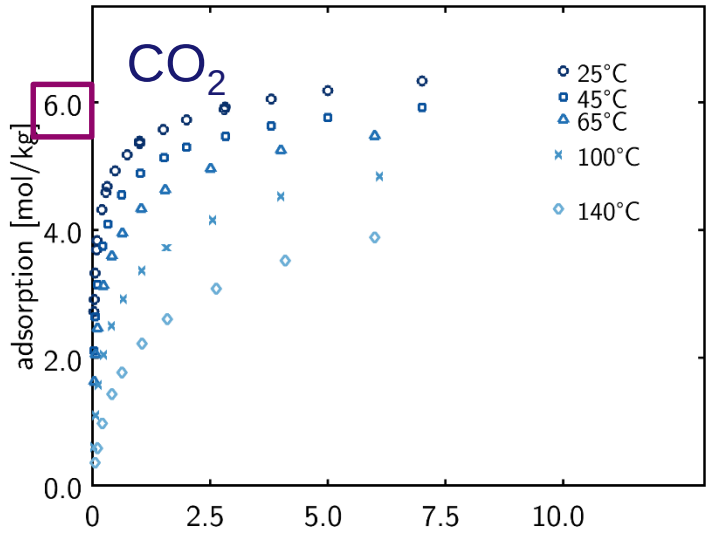
CO_2 N_2

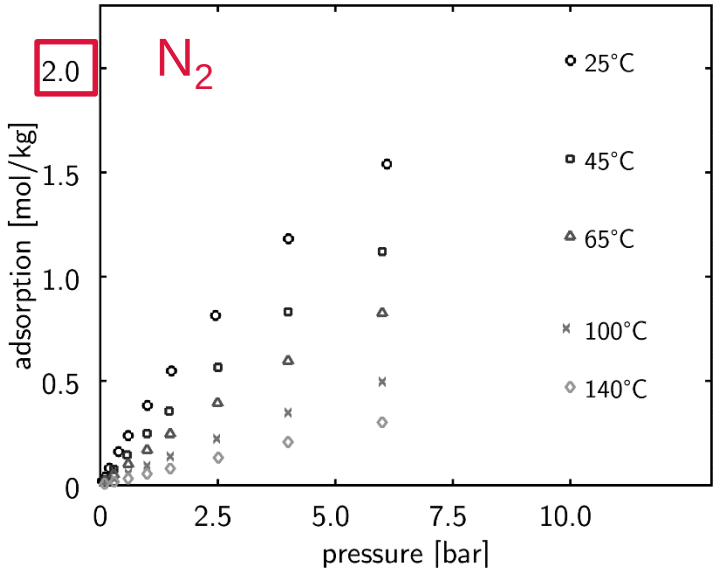


Back-up

- Important characteristics:
  - Adsorption capacity
  - Affinity







Back-up

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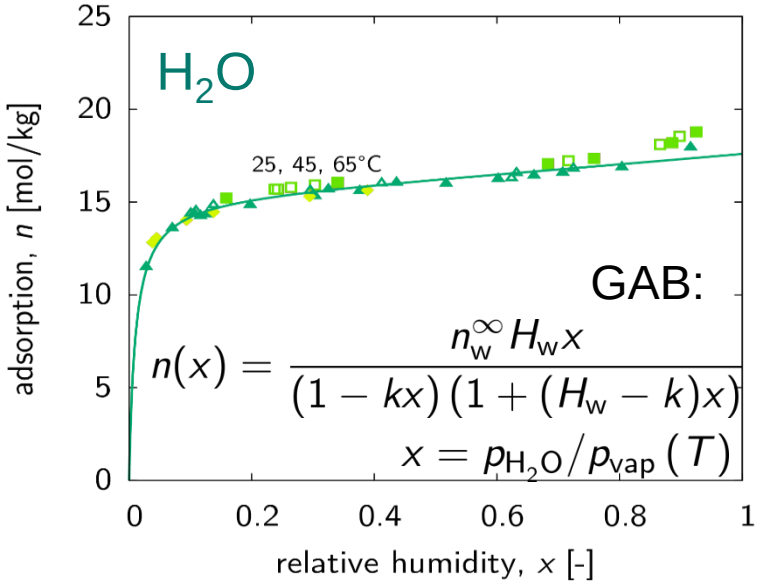
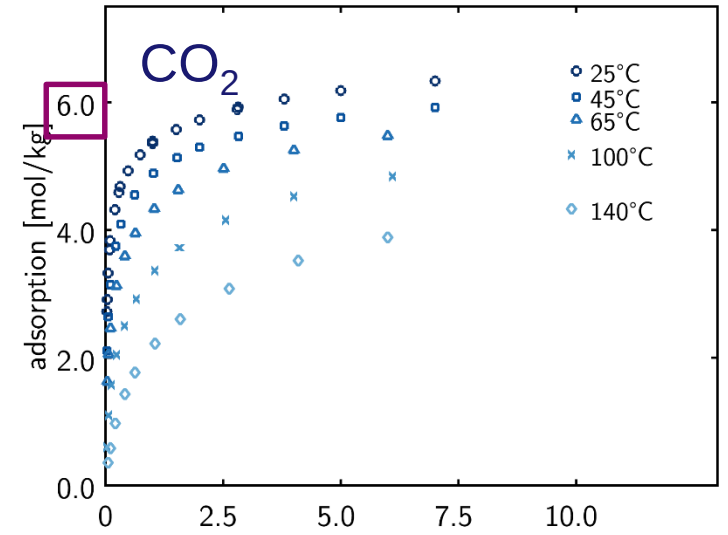
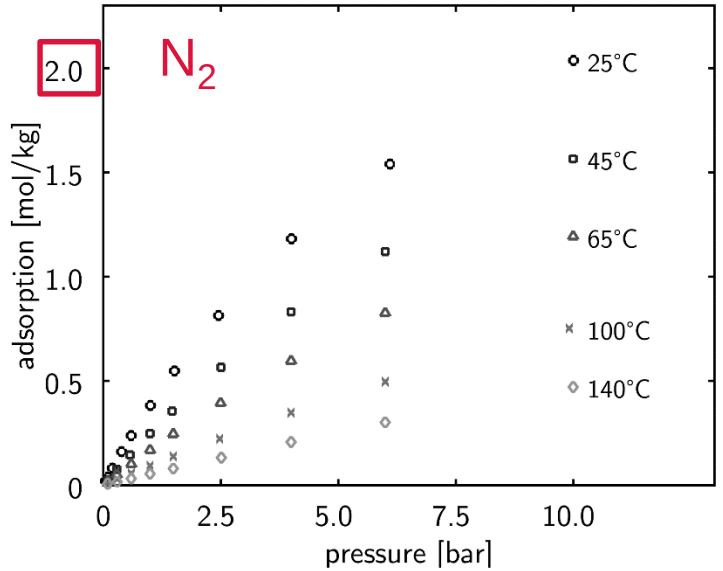
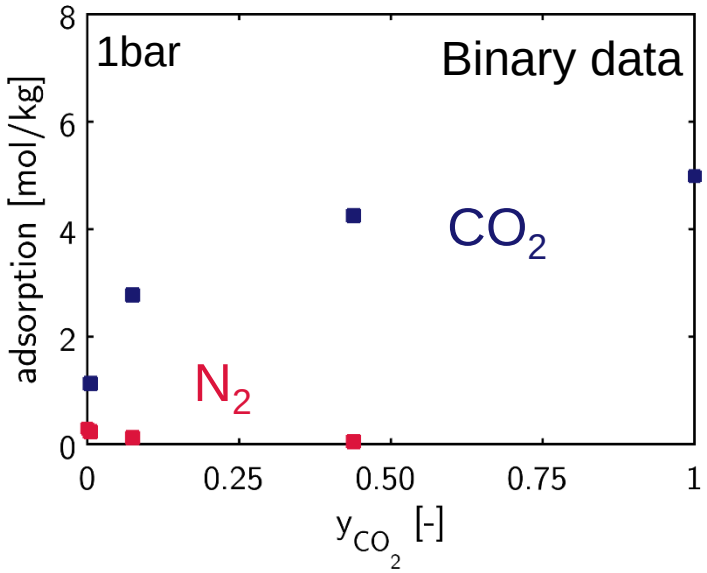


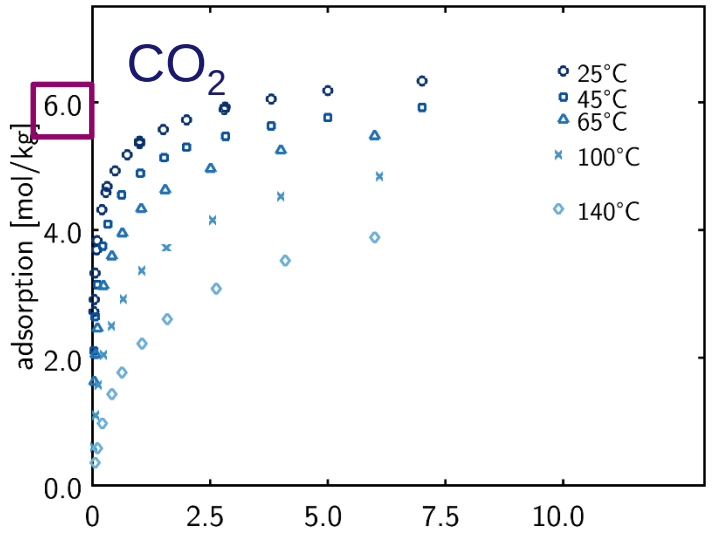


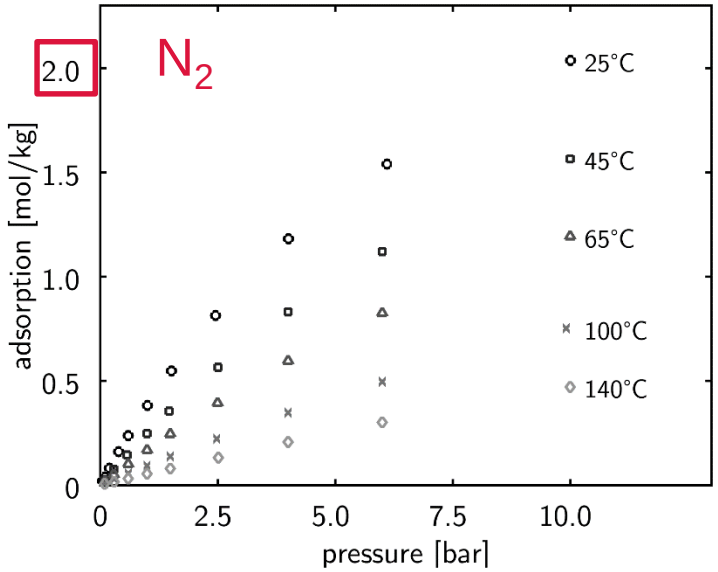


Back-up

- Largest uptake capacity: H_2O
- Largest affinity: H_2O
- Isotherm models:



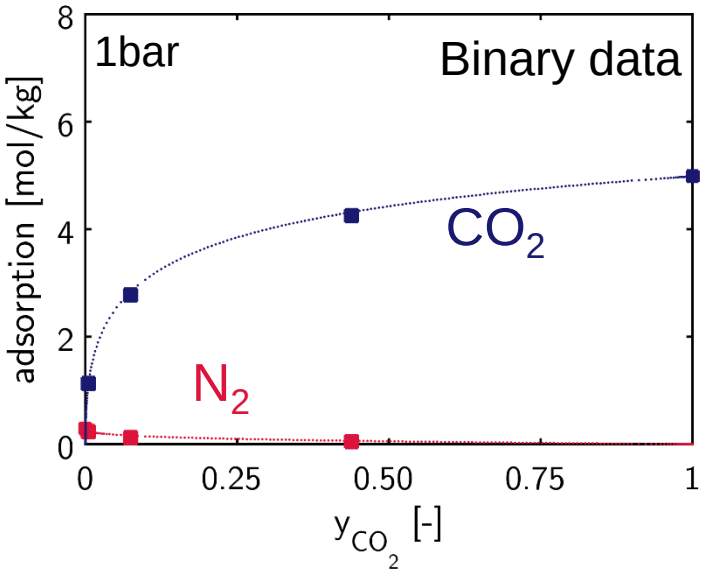


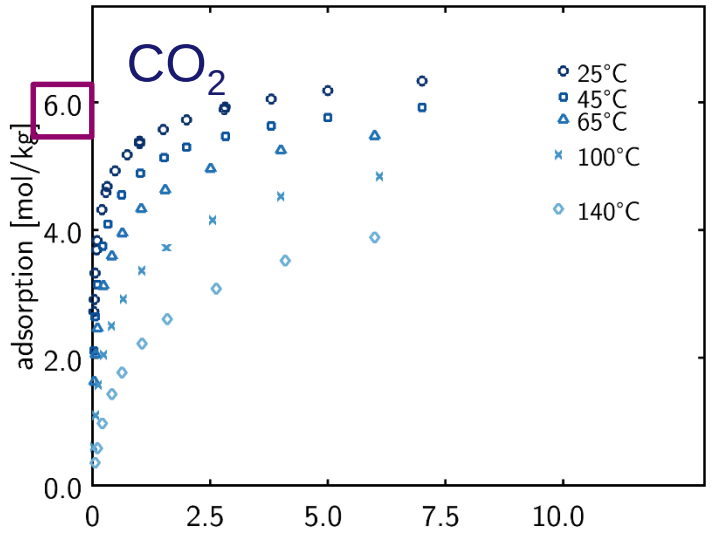


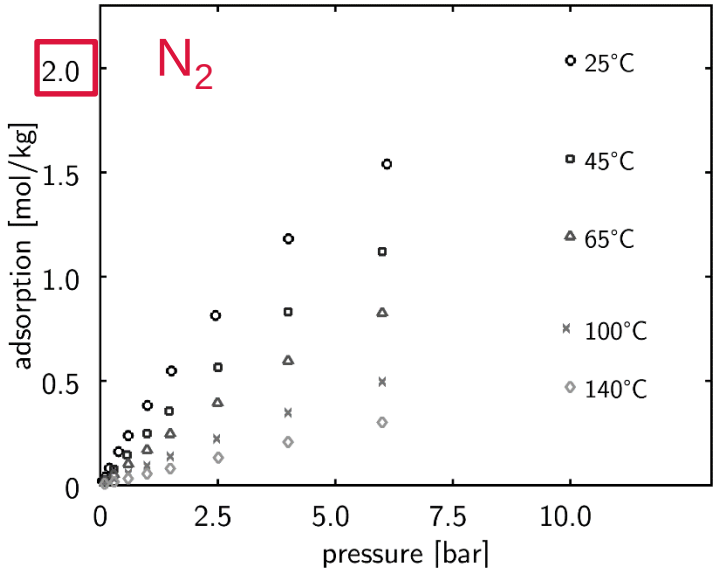
Back-up

- For our process we will use **extended Sips** for it's good description and cheap computation

$$n_i = \frac{n_i^{\infty} (b_i P_i)^{c_i}}{1 + \sum_j (b_j P_j)^{c_j}}$$







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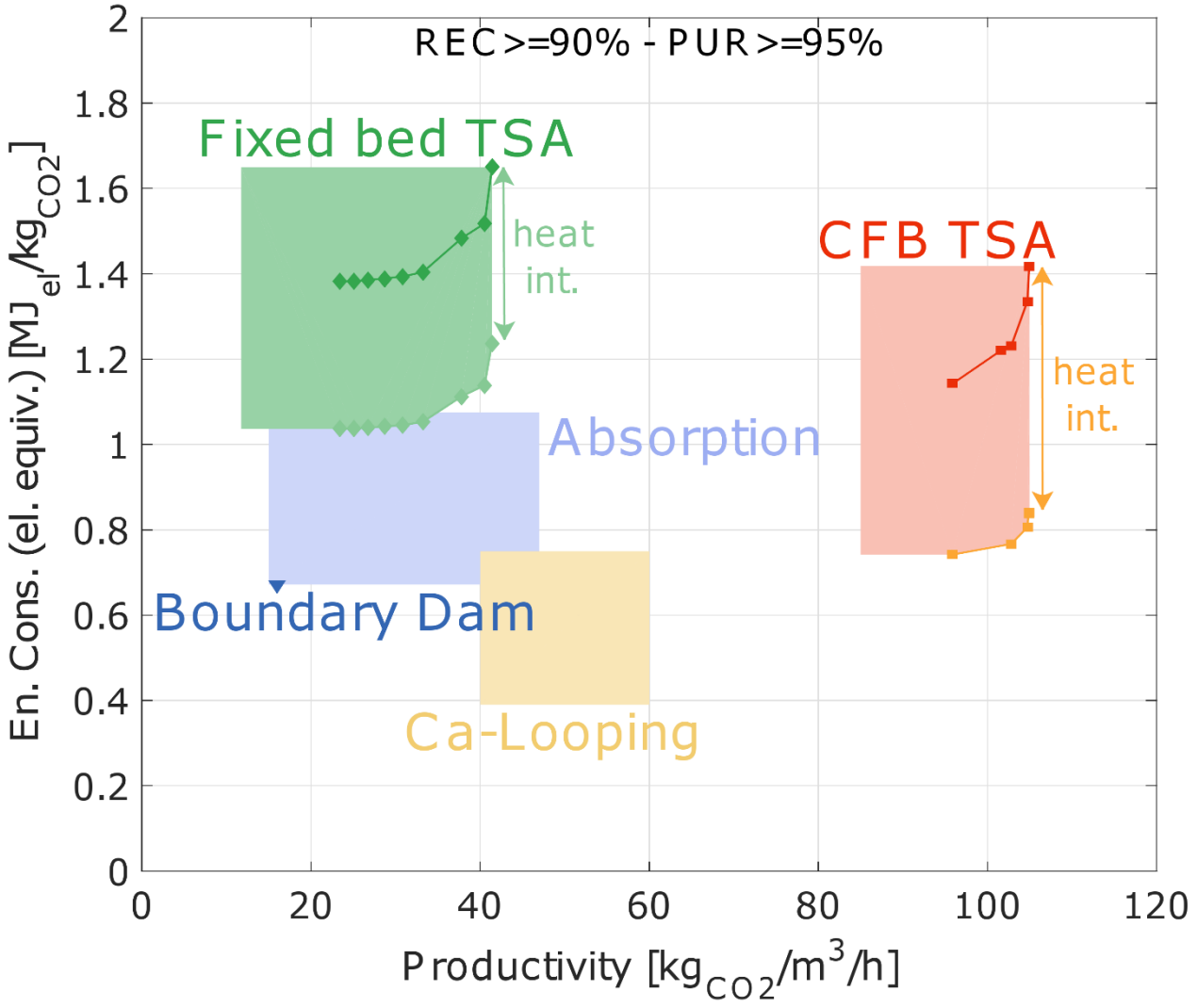

Reference: Zanco et al., **2017** *submitted*