ETH zürich

Energy Science Center

José-Francisco Pérez-Calvo (PhD student)

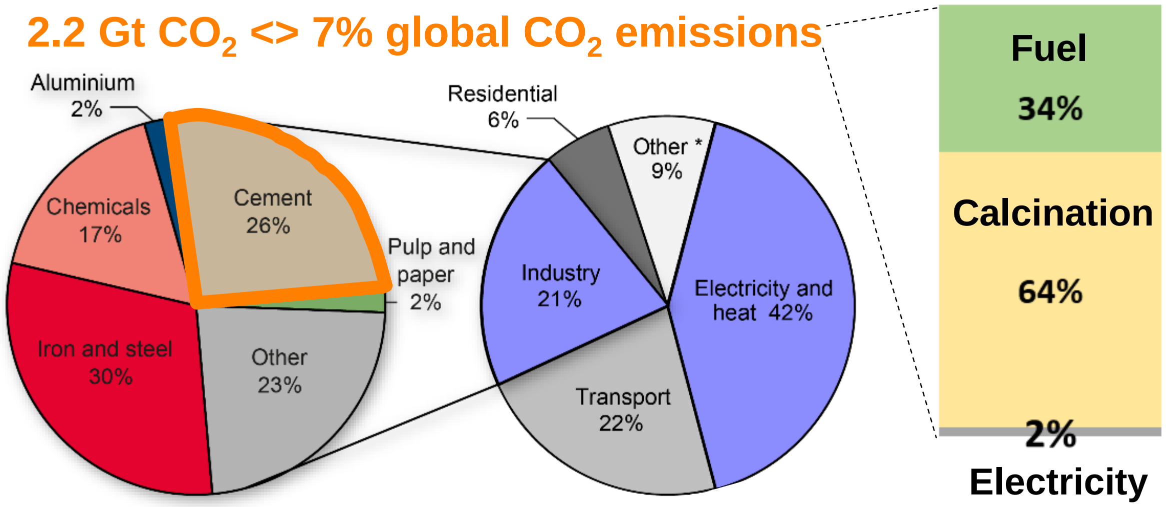
Supervisor: Marco Mazzotti (Separation Processes Laboratory – D-MAVT)

On the application of absorption-based CO_2 capture processes to industrial point sources

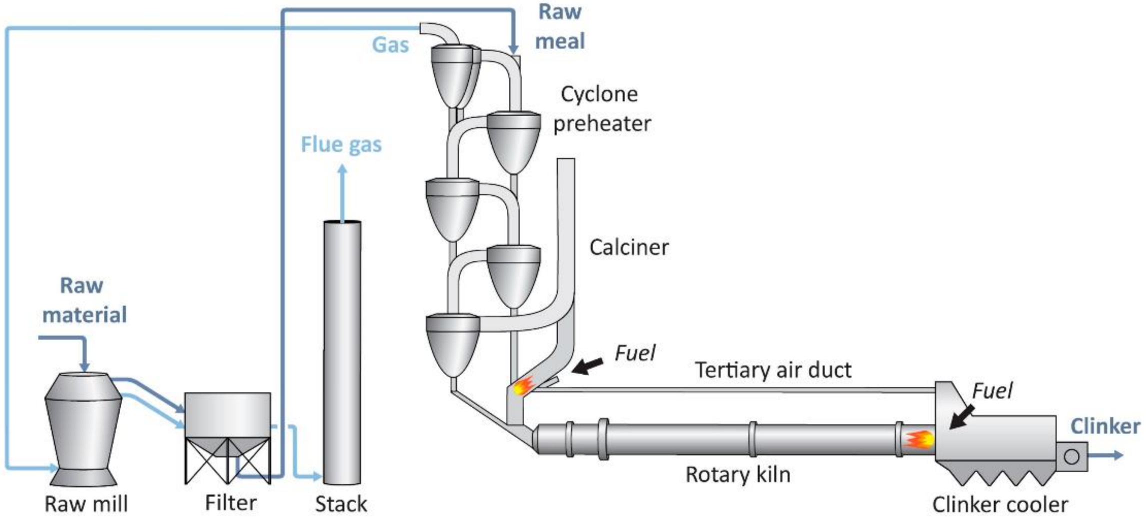
Frontiers in Energy Research
24.03.2020

CO_2 emissions from industrial processes – Cement production

2.2 Gt CO_2 <> 7% global CO_2 emissions



Source: GCCSI, The Global Status of CCS (2017).



- CO_2 emissions intrinsic to the cement manufacturing process
- Higher CO_2 concentration in the flue gas with respect to only combustion

Fuel combustion with air: $C\ (g,l,s) + O_2\ (g) \rightarrow CO_2\ (g)$

Raw material calcination: $CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$

Post-combustion CO_2 capture

Source

Cement manufacturing:	14 – 33 vol% CO_2
Iron and steel production:	5 – 30 vol% CO_2
Power plant:	3 – 14 vol% CO_2

Flue gas →

Separation

High throughput

Sufficient recovery

Low parasitic energy

CO_2-lean →

Exhaust

Gaseous

Low in CO_2

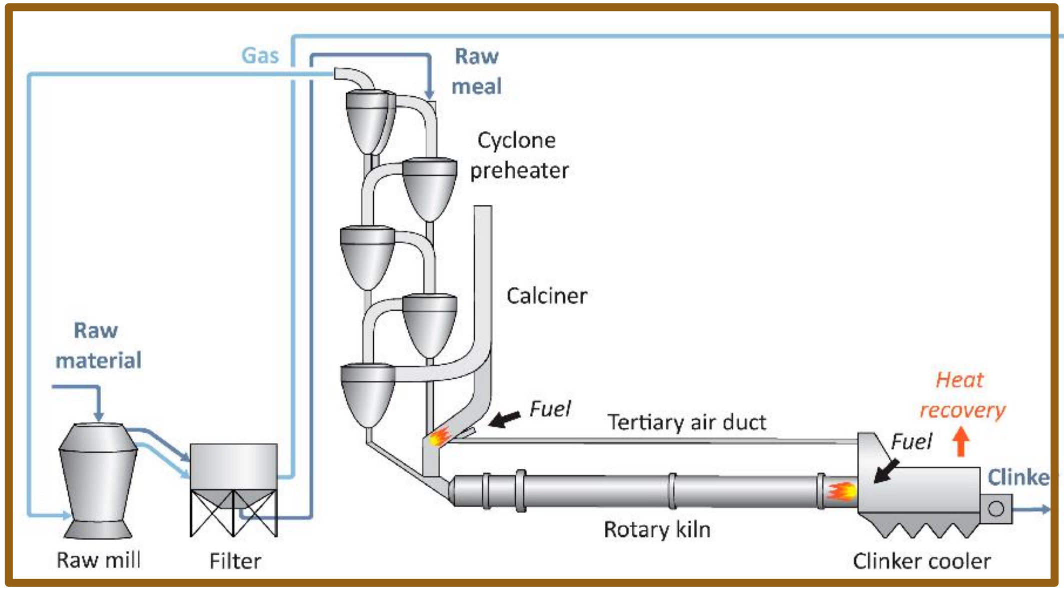
Fed to stack

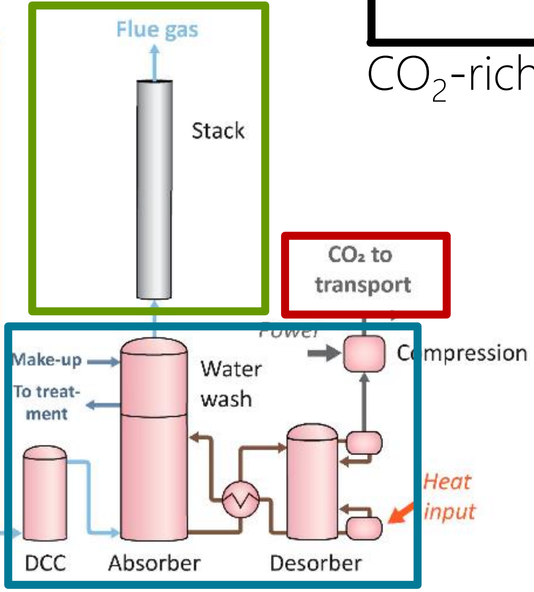
CO_2-rich →

CO_2 product

High purity

Ready to transport

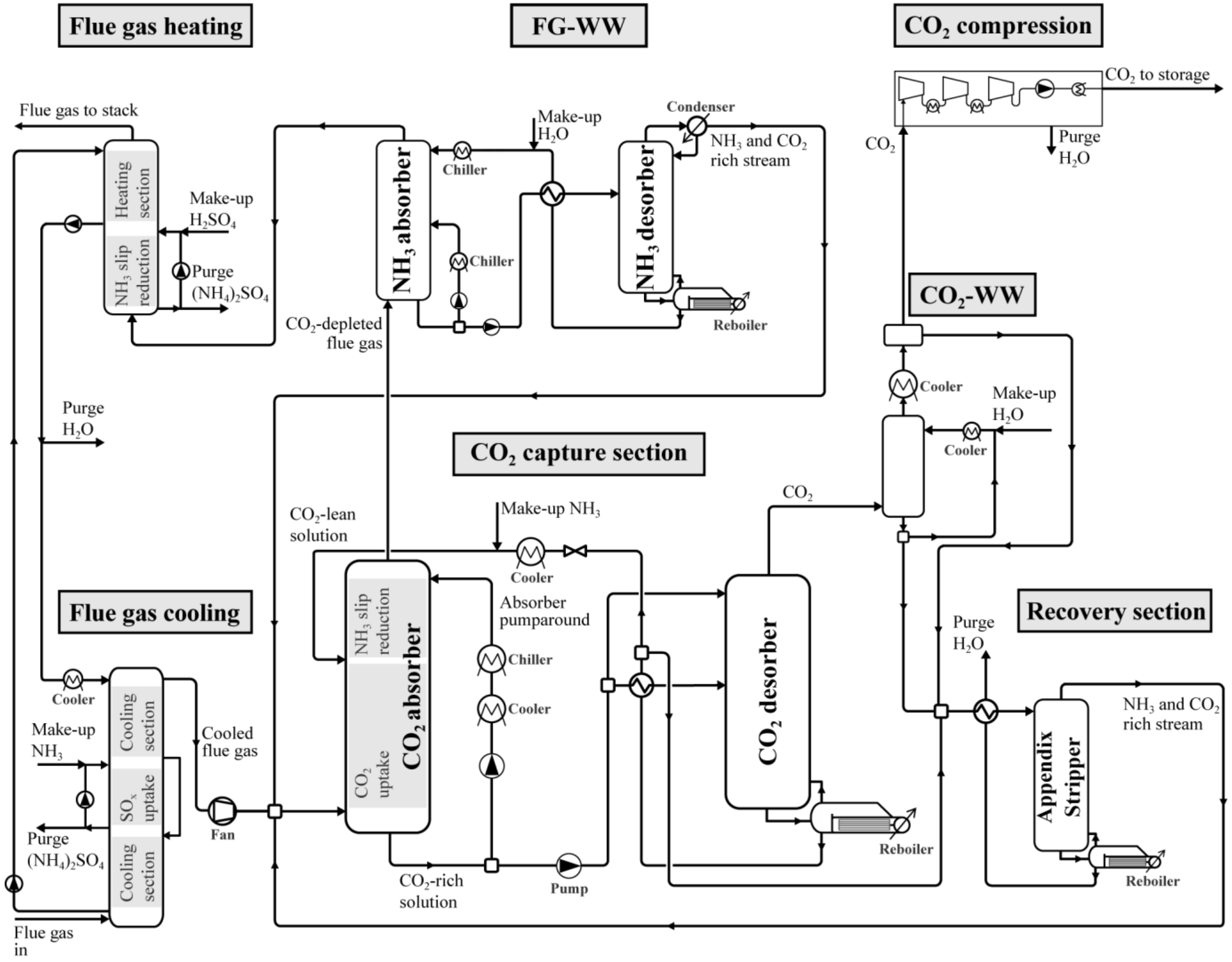




Solvent-based capture processes:

- The industrial process does not change
- Allows for timely de-carbonization
- Commercial technology for CO_2 capture from power plants

The Chilled Ammonia Process (CAP)



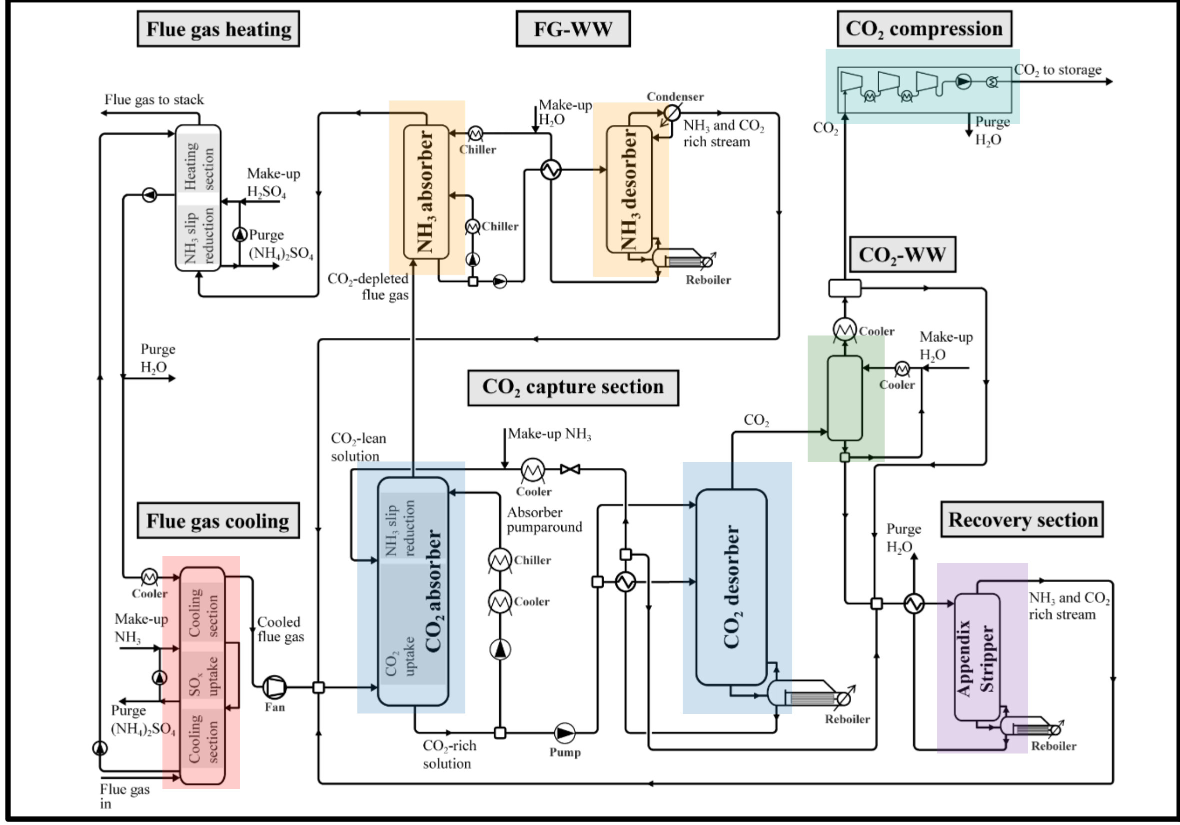
- ✓ NH_3 **does not degrade** in the presence of impurities
- ✓ NH_3 is **globally available**
- ✓ NH_3 has **low environmental footprint and cost**
- ✓ The CAP requires a very **competitive thermal energy** for regeneration
- ✓ **Apply** the **knowledge** acquired in its application to **power plants**

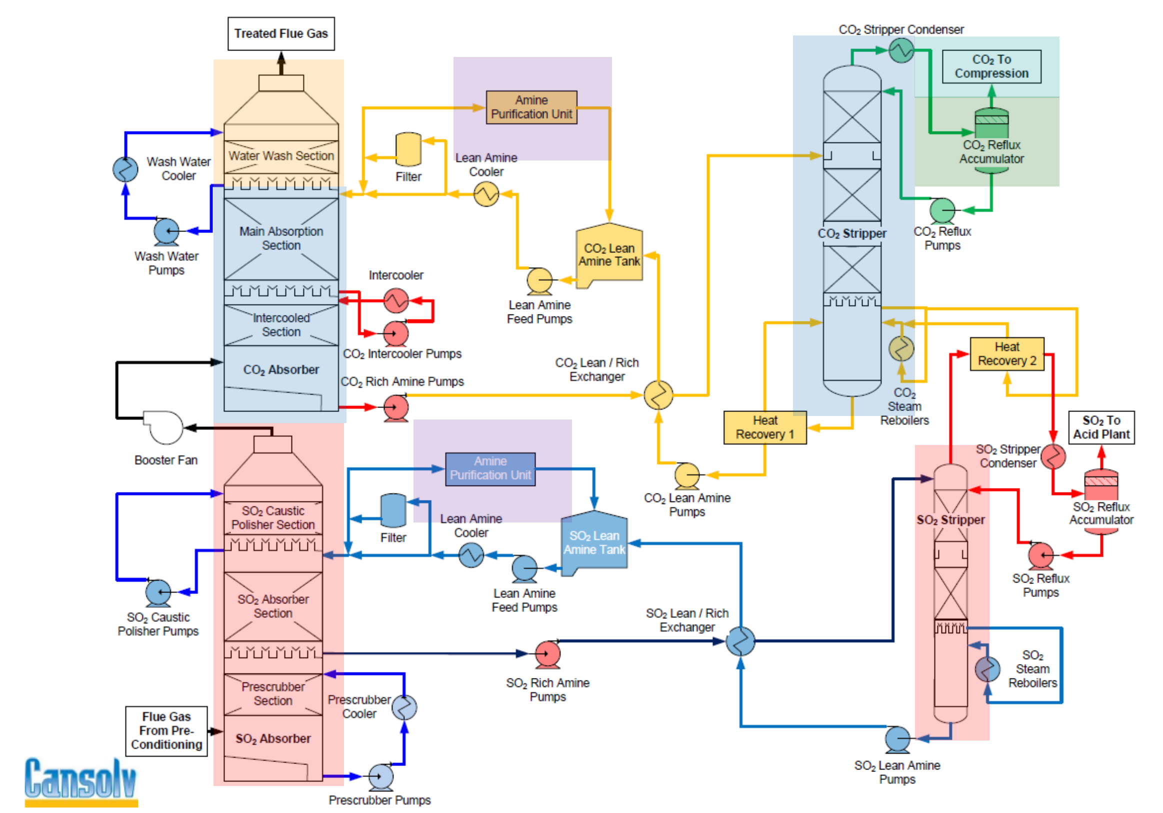
- ✗ **Steam requirements**, common to all absorption-based post-combustion CO_2 capture processes
- ✗ **System complexity** that may lead to solid formation
- ✗ **Process complexity** derived from NH_3 volatility

[1] Sutter et al. *Faraday Discuss* 192 (2016) 59-83
[2] Li et al. *Environ Sci Technol* 16 (2015) 10243-10252
[3] Jiang et al. *Appl Energy* 202 (2017) 496-506

The CAP vs Amine-based capture processes: Process Flow Diagram

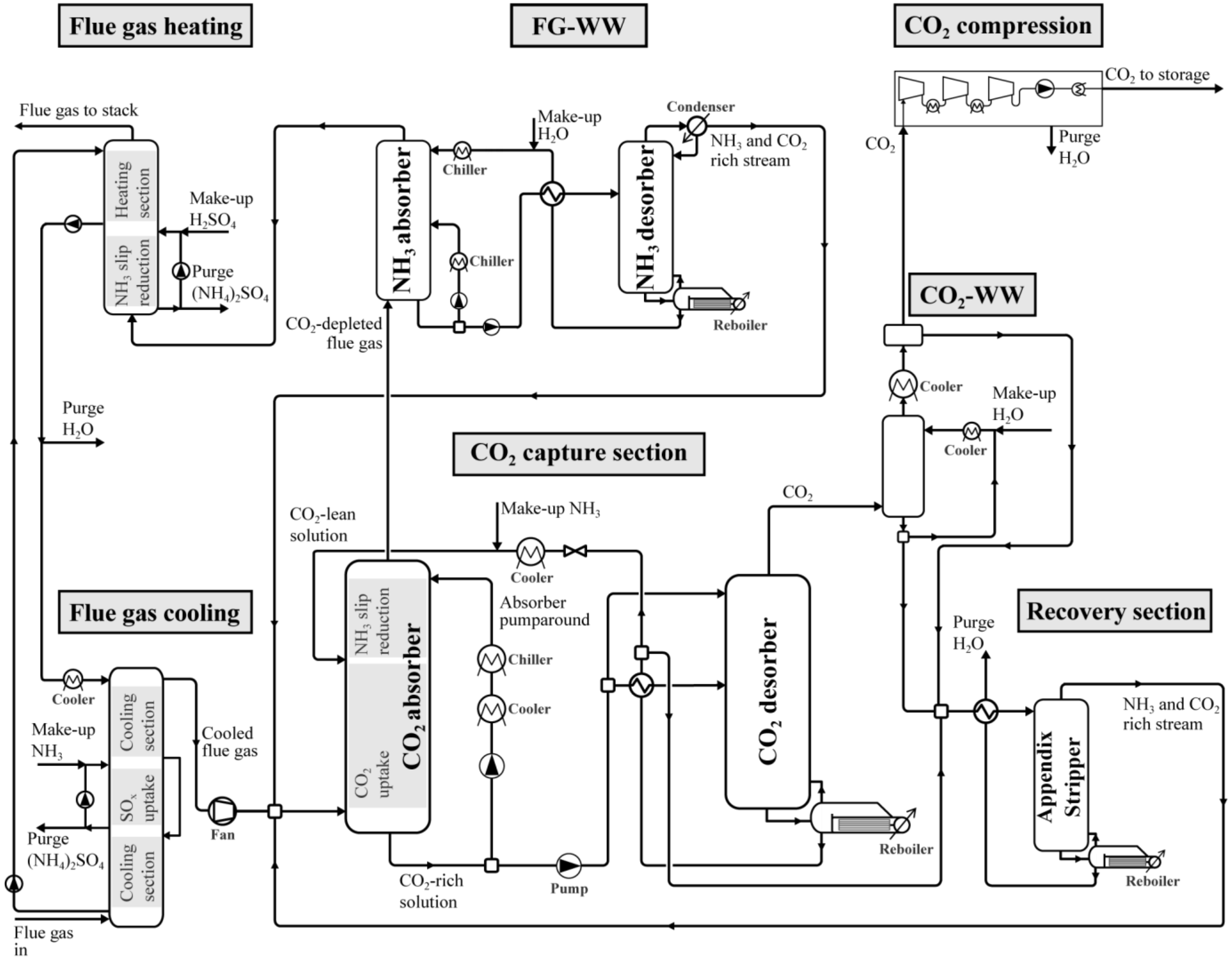
Chilled Ammonia Process	Boundary Dam – Amines





CO_2 absorption – desorption	FG post-conditioning	CO_2 purification
FG pre-conditioning (SO_x removal)	Solvent recuperation/reclaiming	CO_2 compression

From power plants to industrial point sources



Inlet flue gas specifications

Power plants:	~ **3-14 vol% CO_2**
▪ NG power plants	~ **4 vol% CO_2**
▪ Coal-fired power plants	~ **14 vol% CO_2**
Industrial point sources:	~ **7 – 44 vol% CO_2**
▪ Cement plants	~ **18-22 vol% CO_2**

CO_2 capture efficiency

Power plants:	~ **90%**
Industrial point sources:	~ **50 – 99%**

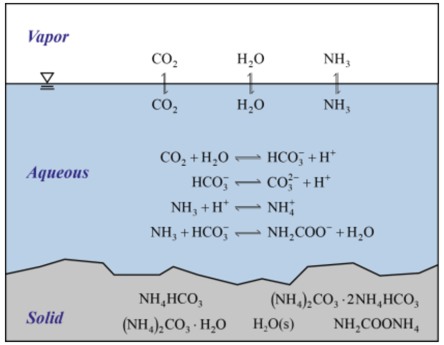
GOAL

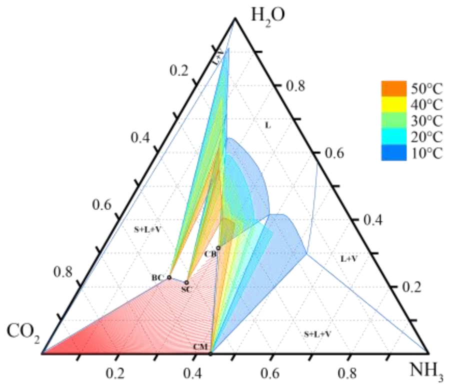
Find new optimal:

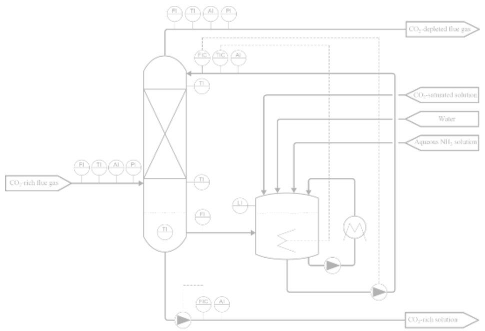
- Process configurations
- Set of operating conditions

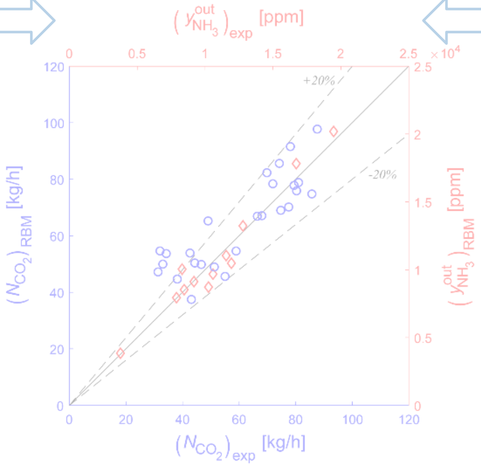
Holistic process development

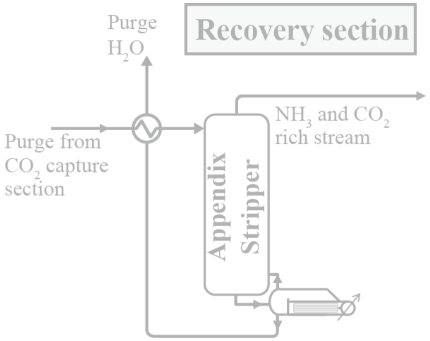
Rate-based model development		Model-based process development		
Thermodynamics	Trans Phenom & Kin	Synthesis	Optimization	Integration

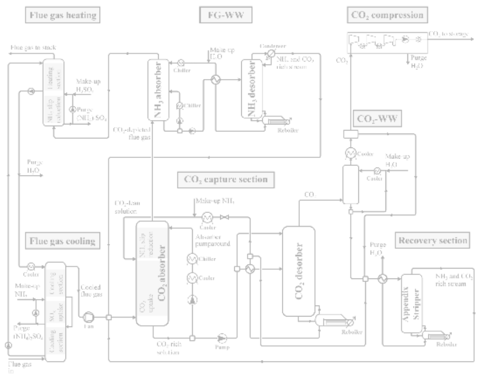


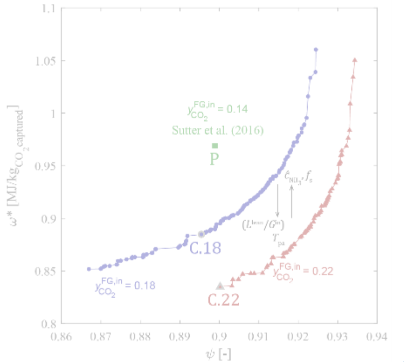


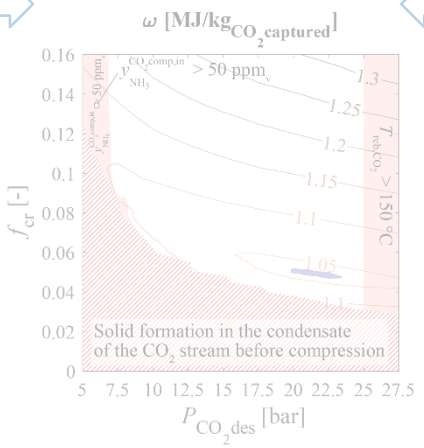


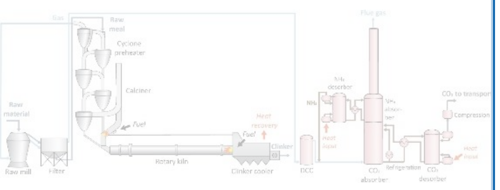


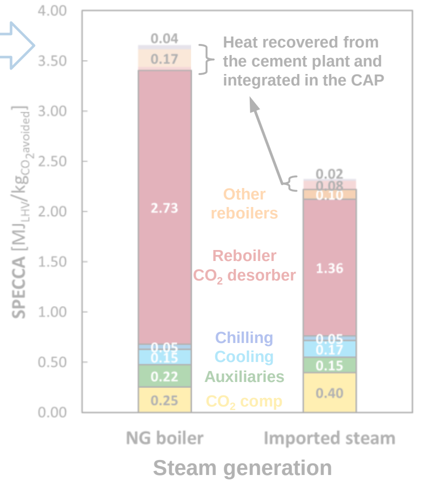






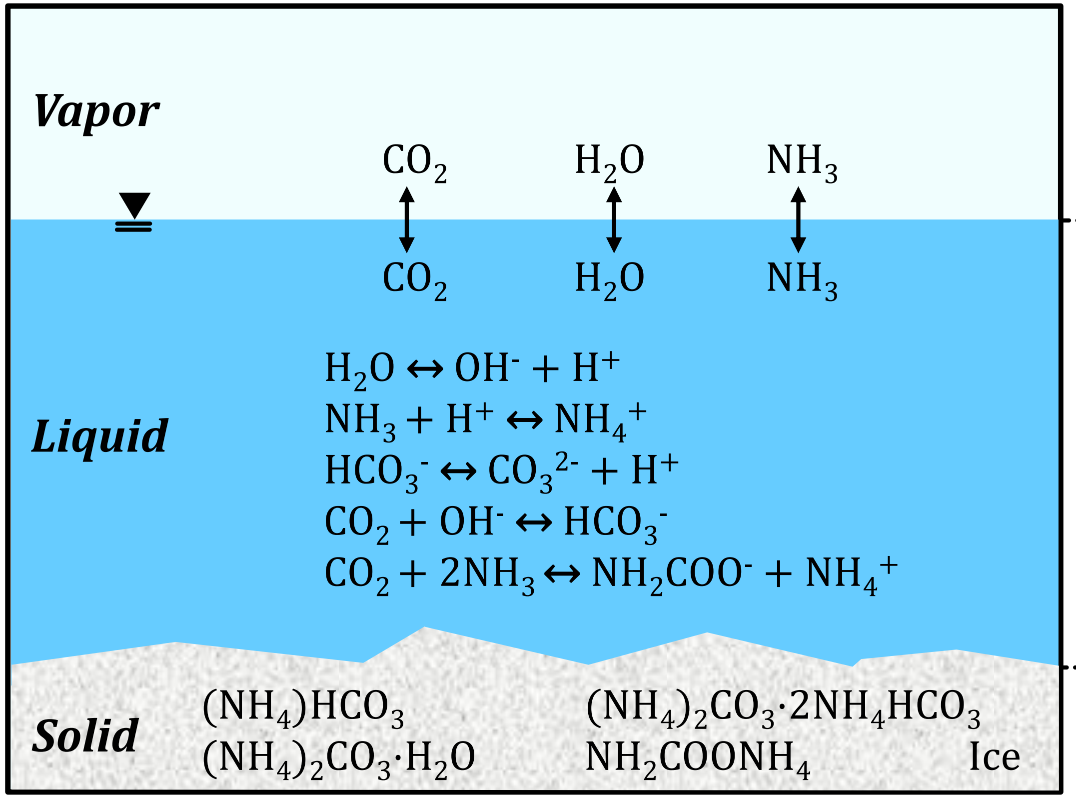






Thermodynamic model: CO_2-NH_3-H_2O system

Thomsen model to predict the system thermodynamics



SRK for gas fugacities

VLE

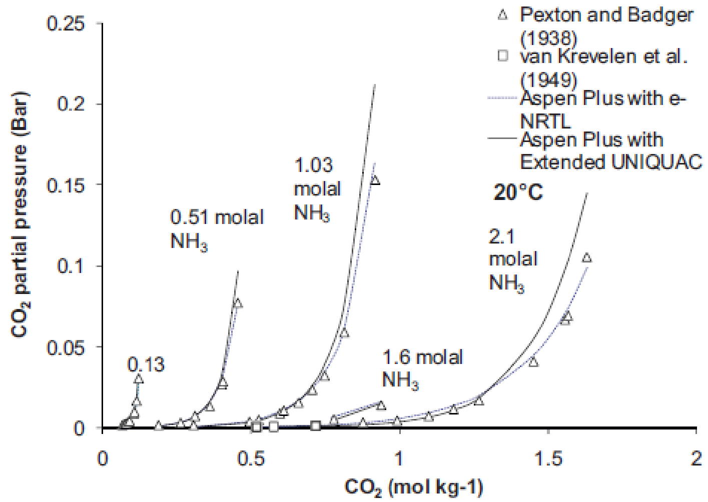
Extended UNIQUAC (Thomsen-Darde[1])

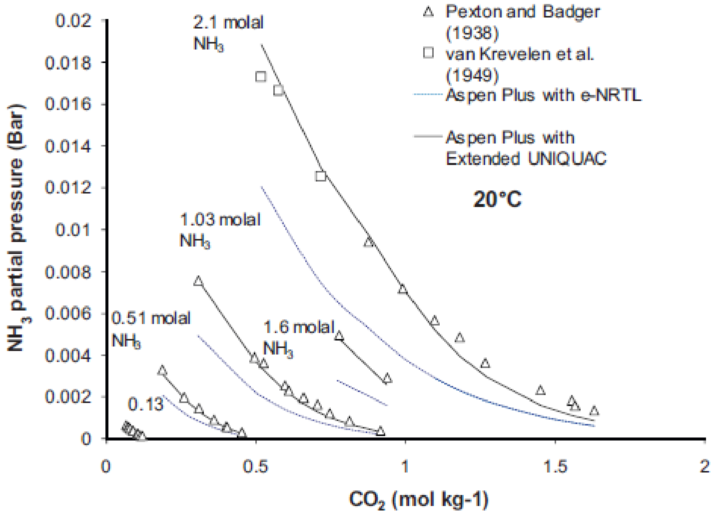
Solubility data for solids fitted on Jänecke[2]

SLE

Pure solids, activity = 1

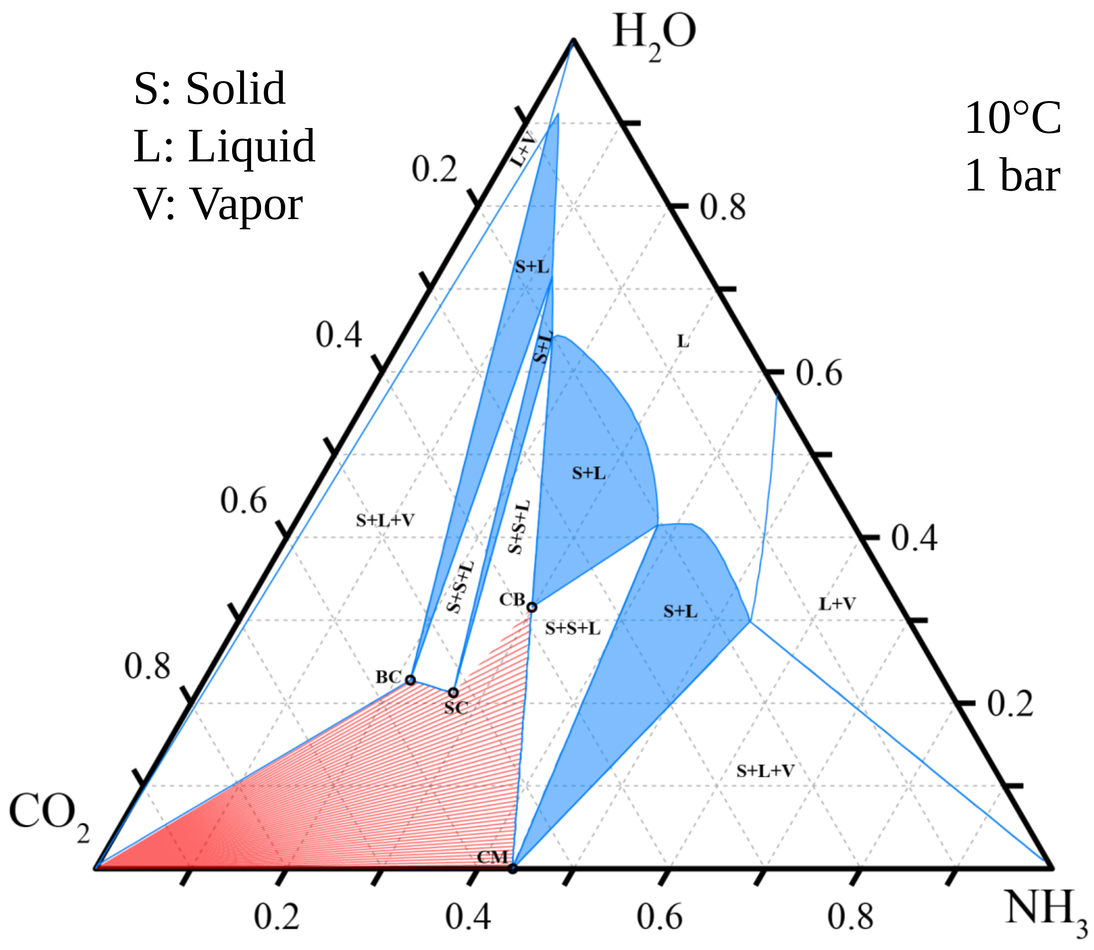
External routine in Aspen from Thomsen group





[1] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[2] Jänecke *Z Elektrochem* 35 (1929) 9:716-28
[3] Darde et al. *Int J Greenh Gas Con* 8 (2012) 61-72

Phase diagram: CO_2-NH_3-H_2O system



Pure solids

BC: ammonium bicarbonate
$(NH_4)HCO_3$

SC: ammonium sesqui-carbonate
$(NH_4)_2CO_3{\cdot}2NH_4HCO_3$

CB: ammonium carbonate
$(NH_4)_2CO_3{\cdot}H_2O$

CM: ammonium carbamate
NH_2COONH_4

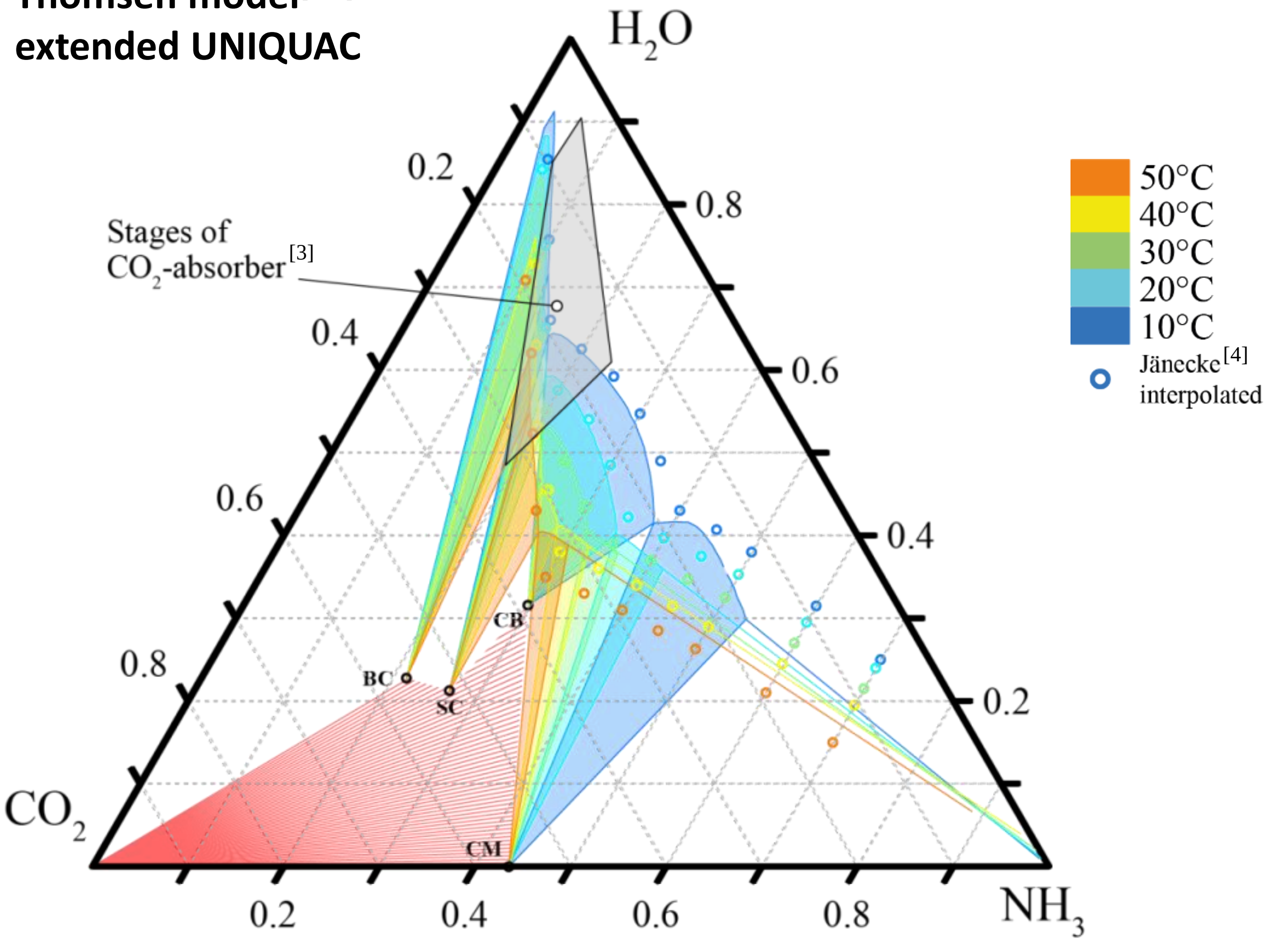
Light blue area:
Two-phase region where the solid exists in its mother liquor

Red area:
The algorithm does not converge

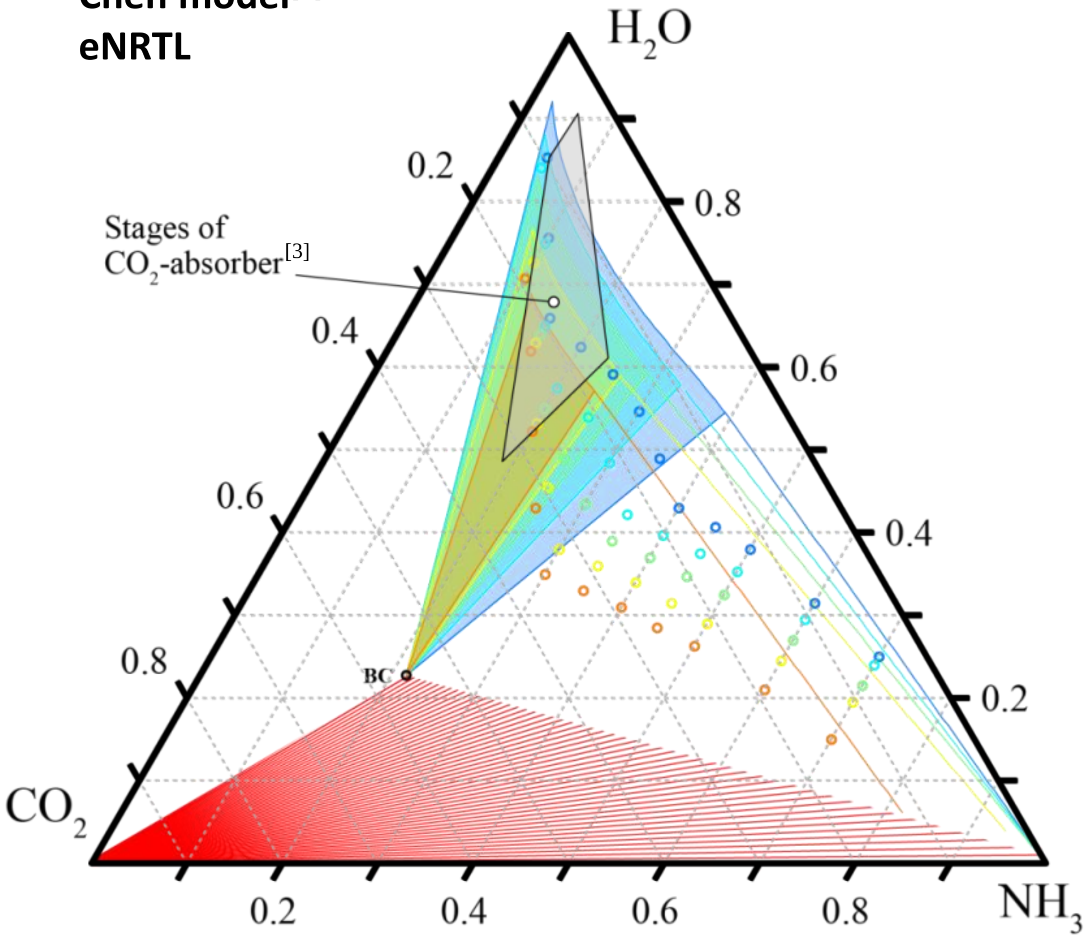
José-Francisco Pérez-Calvo, francisco.perezcalvo@ipe.mavt.ethz.ch

Thermodynamic model: Comparison

Thomsen model[1,2]
extended UNIQUAC



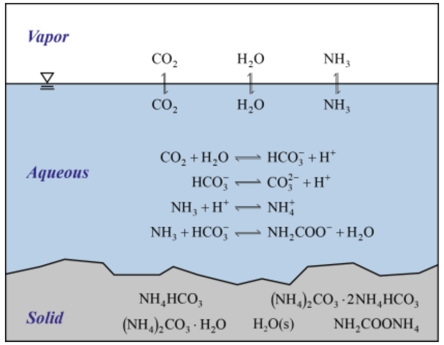
Chen model[5]
eNRTL

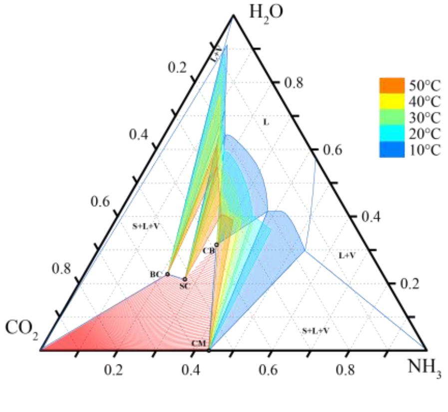


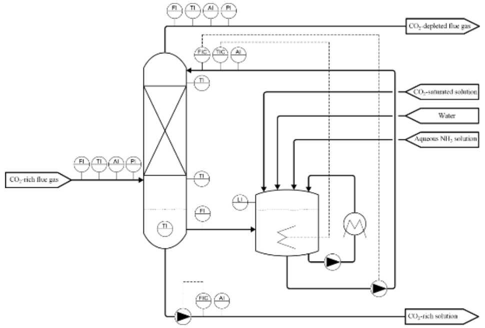
[1] Thomsen and Rasmussen *Chem Eng Sci* 54 (1999) 1787-1802
[2] Darde et al. *Ind Eng Chem Res* 49 (2010) 12663-74
[3] Sutter et al. *Chem Eng Sci* 133 (2015) 170-180
[4] Jänecke *Z Elektrochem* 35 (1929) 9:716-728
[5] Que and Chen *Ind Eng Chem Res* 50 (2011) 11406-11421

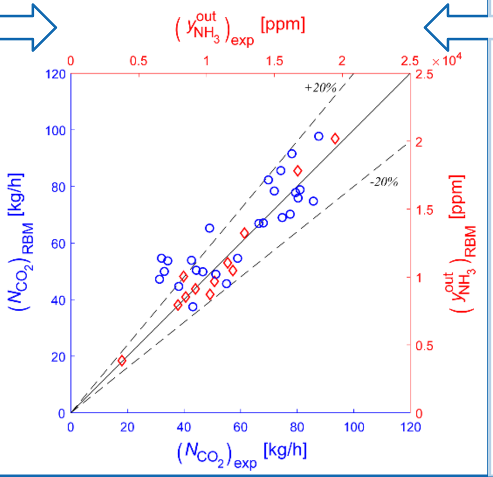
Holistic process development

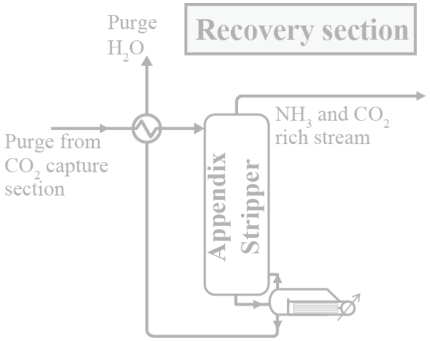
Rate-based model development		Model-based process development		
Thermodynamics	Trans Phenom & Kin	Synthesis	Optimization	Integration

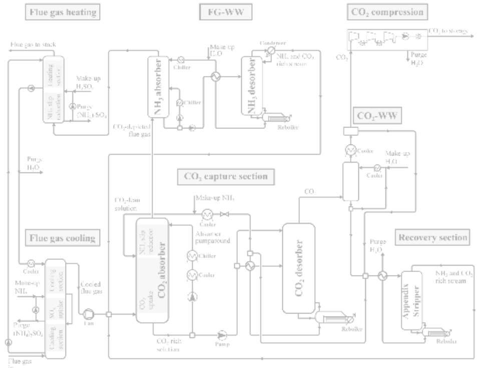


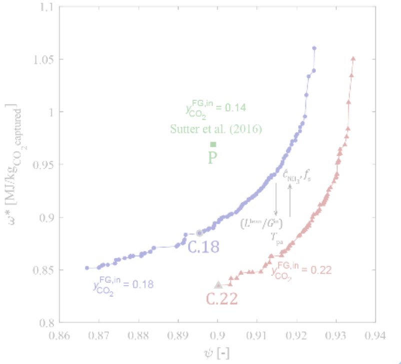


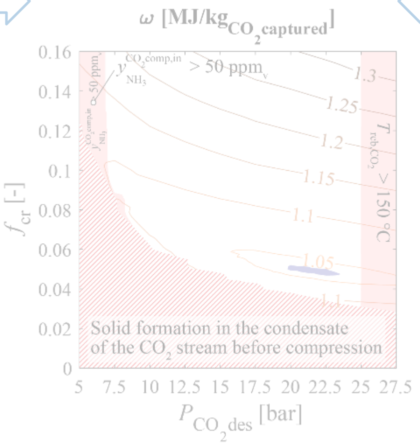


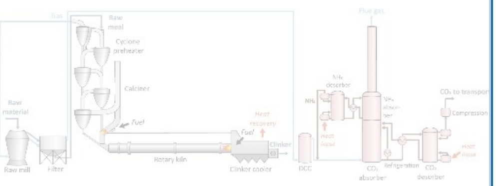


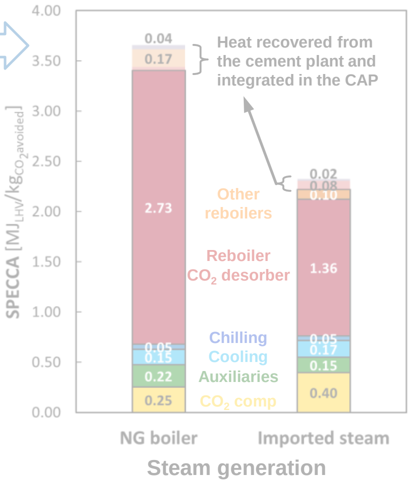












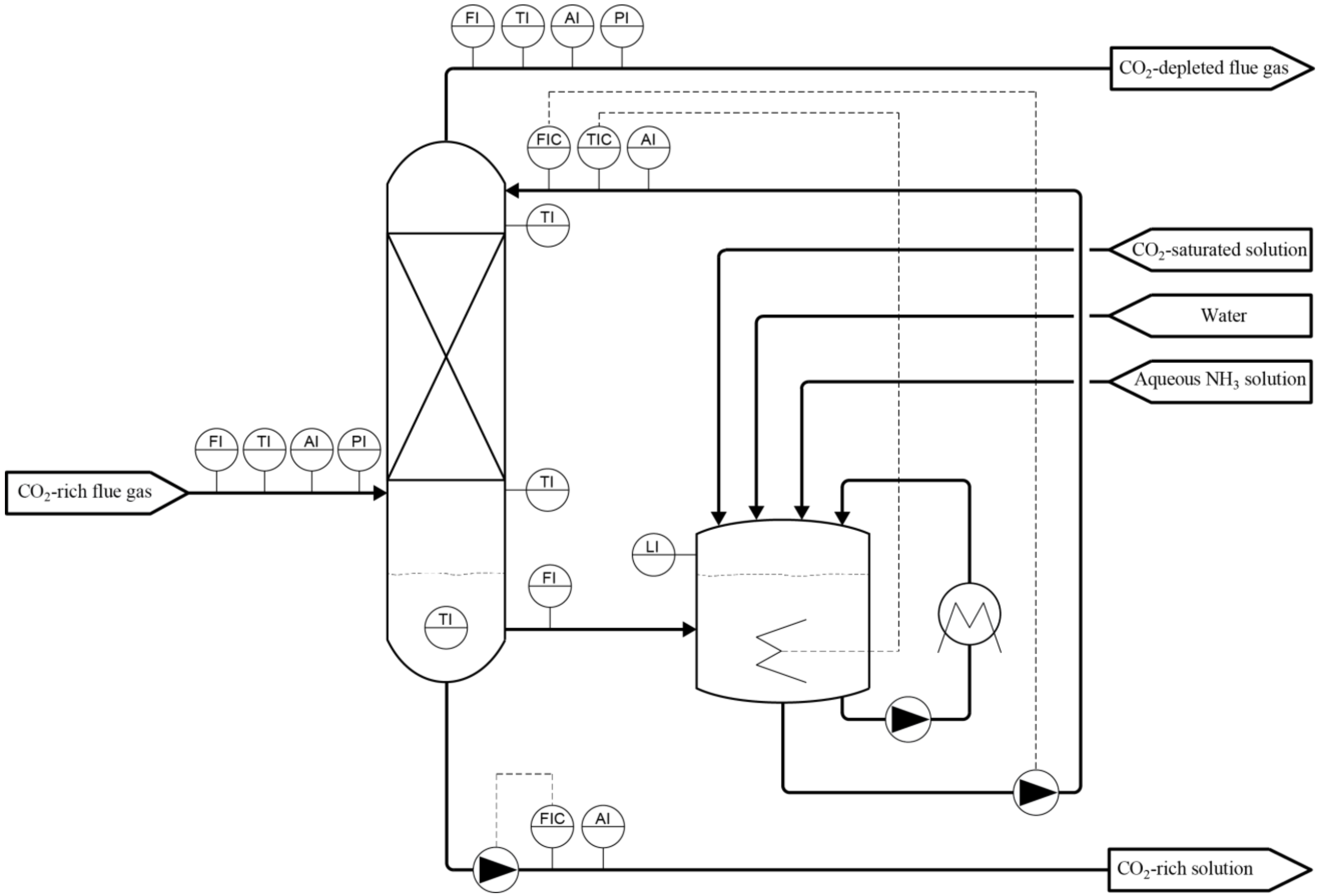
Rate-based model

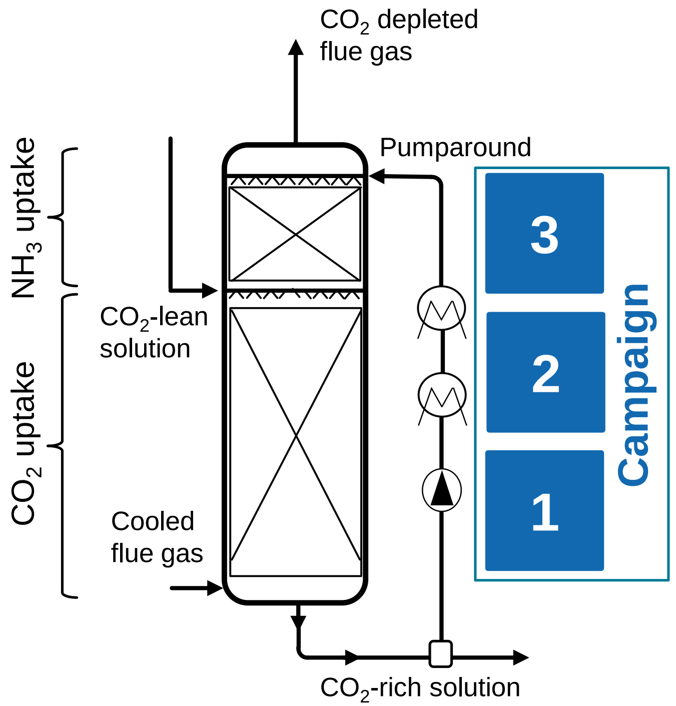
Aspen Plus RadFrac distillation model (RateSep)

Simplifying: $N_{CO_2} = A_{eff} K_{G,CO_2} \left(p_{CO_2,G} - p^*_{CO_2,L} \right)$, with $\frac{1}{K_{G,CO_2}} = \frac{RT}{k_{g,CO_2}} + \frac{H_{CO_2}}{E k^0_{l,CO_2}}$

Phase equilibria	**Thomsen model**	✓ *Predicts SLE in addition to VLE*
Transport phenomena	**Rochelle model** [1] Wang et al. *Ind Eng Chem Res* 55 (2016) 5357-84	✓ *Range of structured packings: X, Y, Z, 150-350* ✓ *Aqueous solutions for CO_2 capture*
Reaction kinetics	**This work** [2] Pérez-Calvo et al. *Chem Eng Trans* 69 (2018) 145-150	✓ *CO_2 absorption pilot plant tests* ✓ *Commercial structured packing* ✓ *Synthetic flue gases containing up to 35 vol% CO_2* ✓ *Aqueous ammonia solutions containing up to 17 wt% NH_3*

Test rig and experimental matrix





Pérez-Calvo et al. *Chem Eng Trans* 69 (2018) 145-150

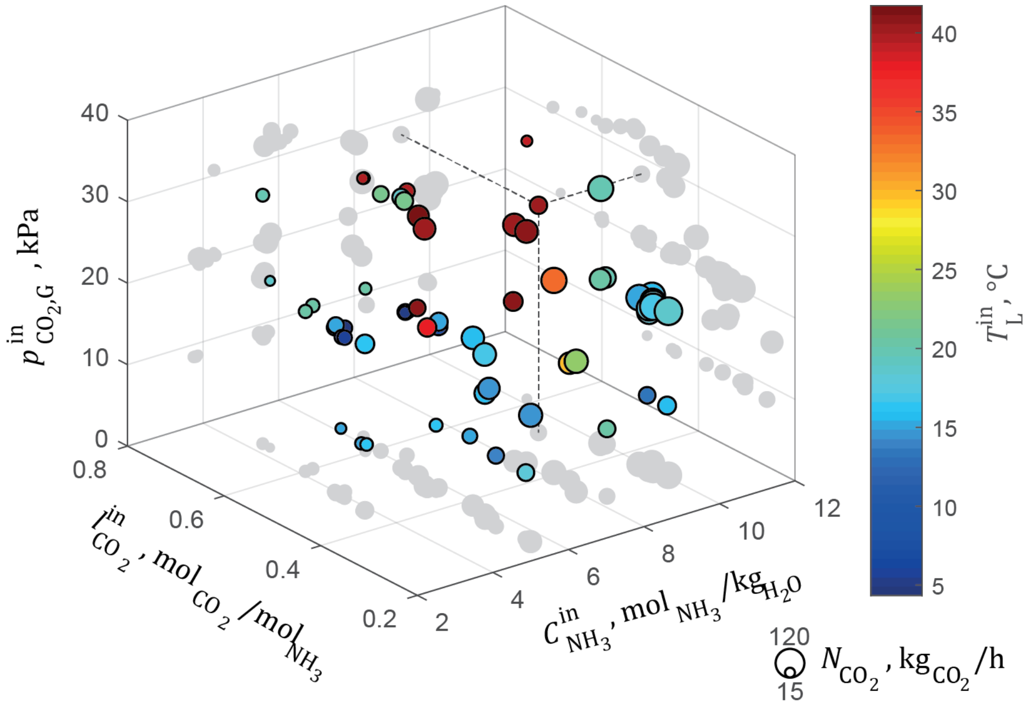
Reaction kinetics – Test results and model fitting

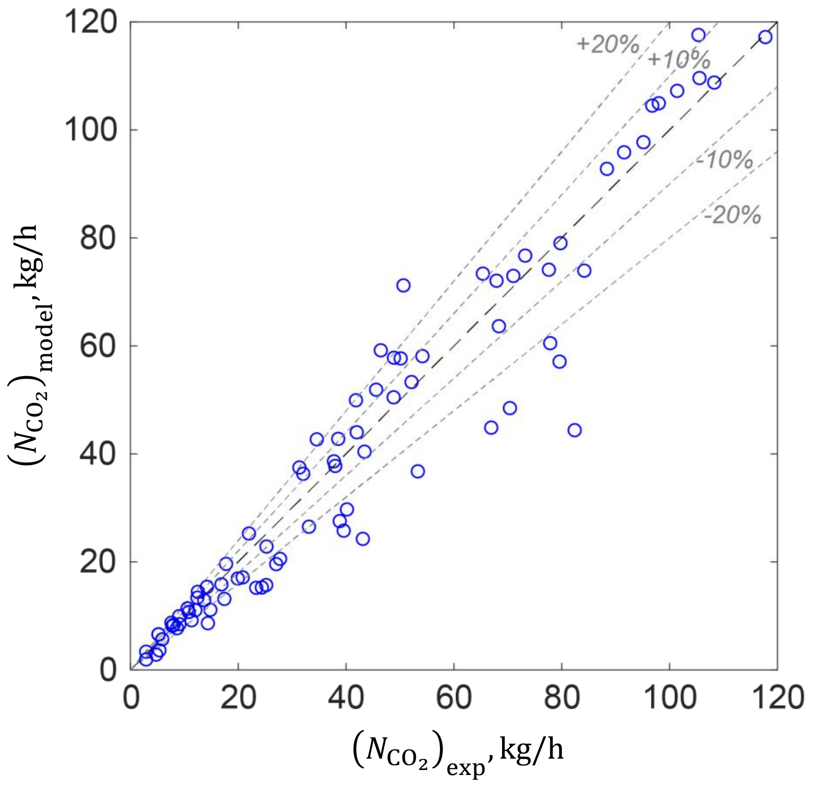
$$CO_2 + 2NH_3 \xrightarrow{k_{cm}} NH_2COO^- + NH_4^+$$

$$r_{cm} = k_{cm} C_{NH_3}^{\boldsymbol{n}} C_{CO_2}$$

$$k_{cm} = \boldsymbol{k_{0cm,T_{ref}}} \exp\left(-\frac{\boldsymbol{E_{a,cm}}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

82 experimental points





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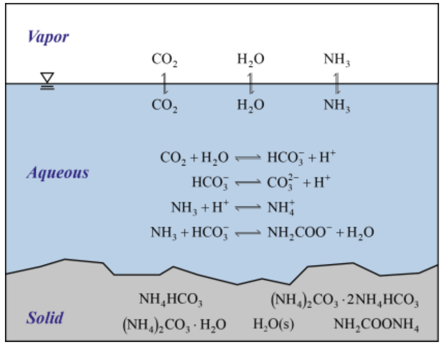
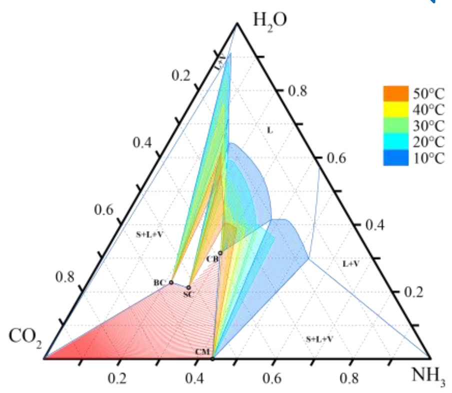
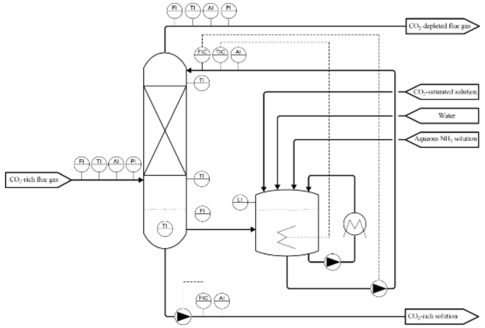
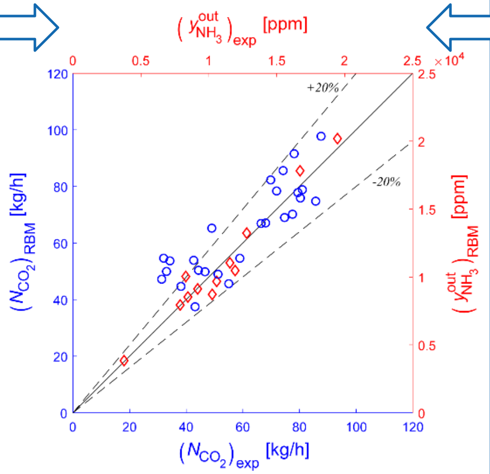
Thermodynamics



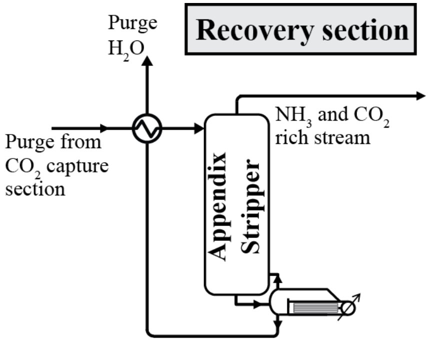


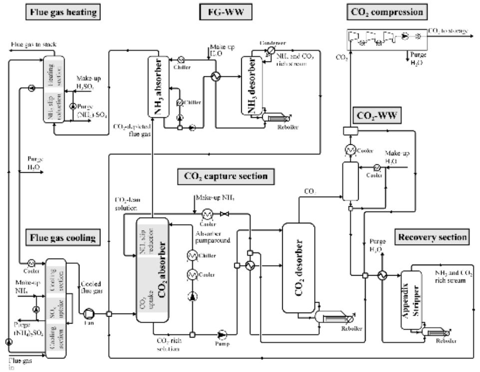
Trans Phenom & Kin



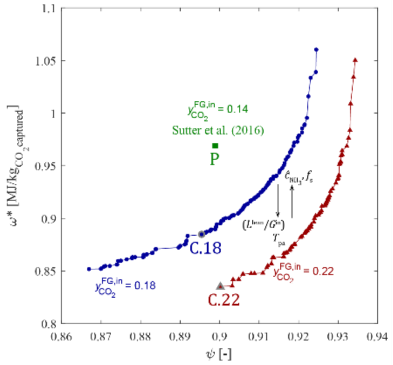


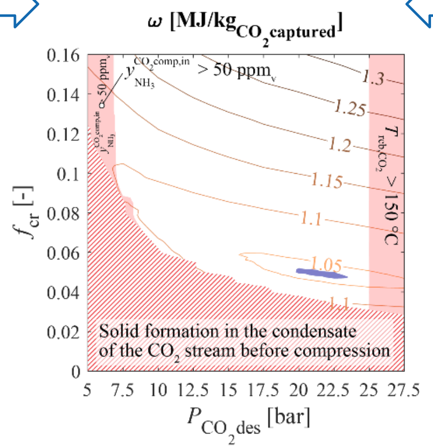
Synthesis



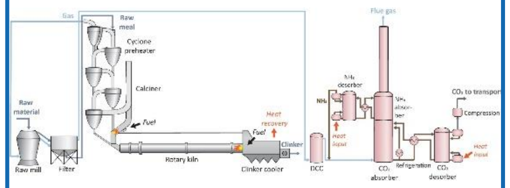


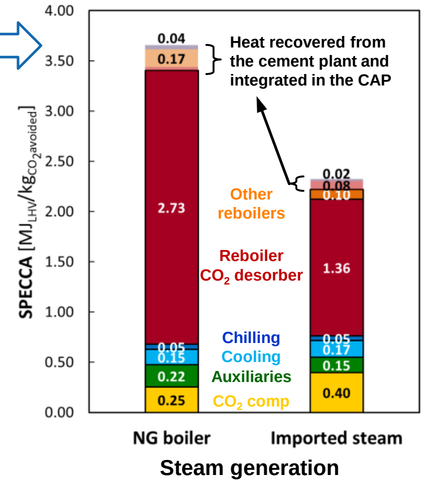
Optimization



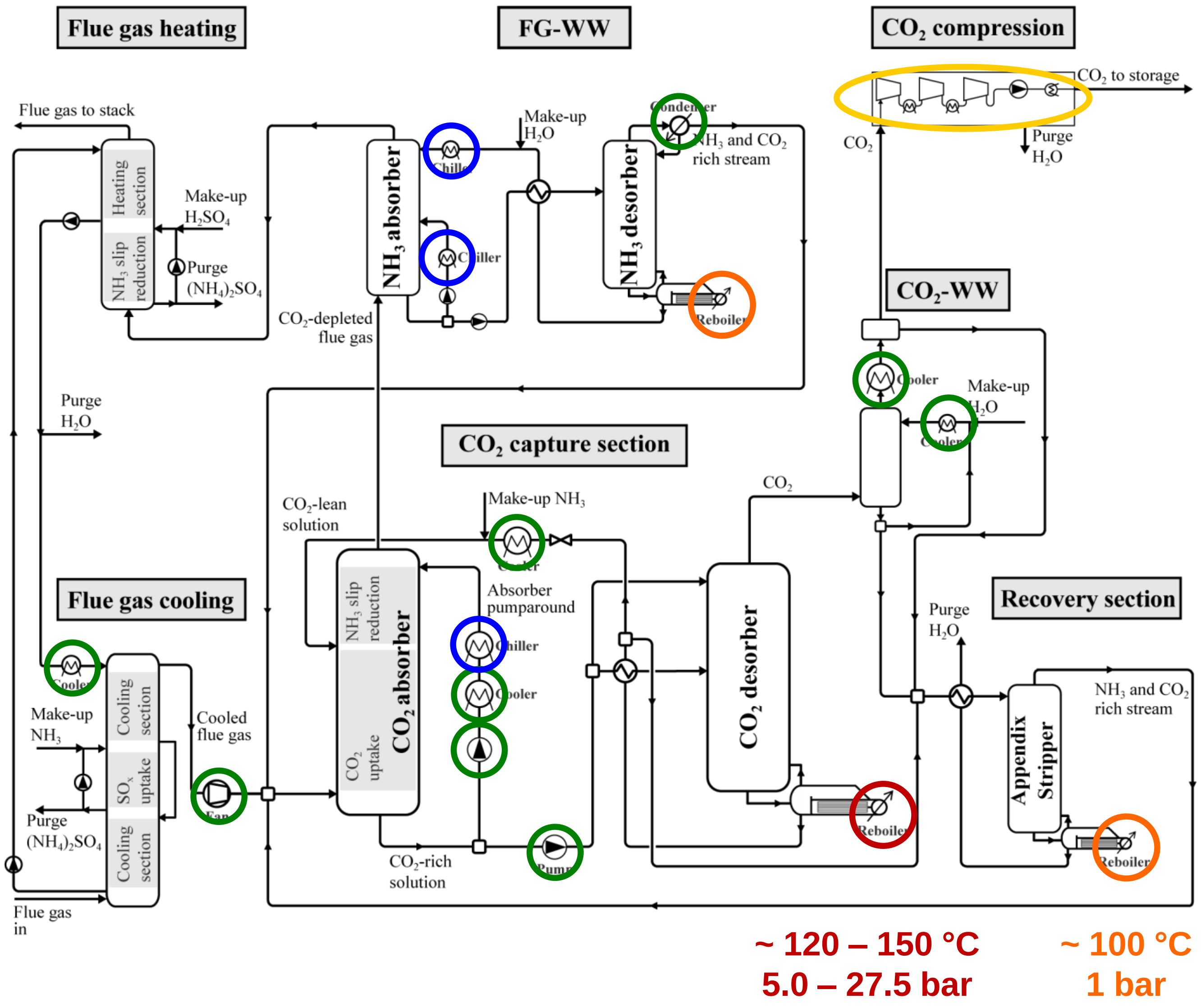


Integration





Model-based process development



Performance indicators

- CO_2 capture efficiency, ψ [-]

$$\psi = \frac{\dot{m}_{CO_2}^{FG,in} - \dot{m}_{CO_2}^{FG,out}}{\dot{m}_{CO_2}^{FG,in}}$$

- Productivity, Pr [kg_{CO_2}captured m^{-3} h^{-1}]

$$\mathrm{Pr} = \frac{1}{\frac{1}{\mathrm{Pr}_{CO_2 abs}} + \frac{1}{\mathrm{Pr}_{NH_3 abs}}} = \frac{\dot{m}_{CO_2}^{storage}}{V_{CO_2 abs} + V_{NH_3 abs}}$$

- Specific equivalent work, ω [MJ/$kg_{CO_2 captured}$]
  - Steam – Reboilers
  - Electricity
    - Chillers
    - Auxiliaries – Pumps, fans and coolers
    - CO_2 compressor

Specific equivalent work

Reboilers:

$$\omega_{\mathrm{reb},i} = \frac{\dot{Q}_{\mathrm{reb},i}}{\dot{m}_{\mathrm{CO_2}}^{\mathrm{FG,in}} - \dot{m}_{\mathrm{CO_2}}^{\mathrm{FG,out}}} \left(1 - \frac{T_{\mathrm{amb}}}{T_{\mathrm{reb},i} + \Delta T_{\mathrm{steam}}}\right)$$

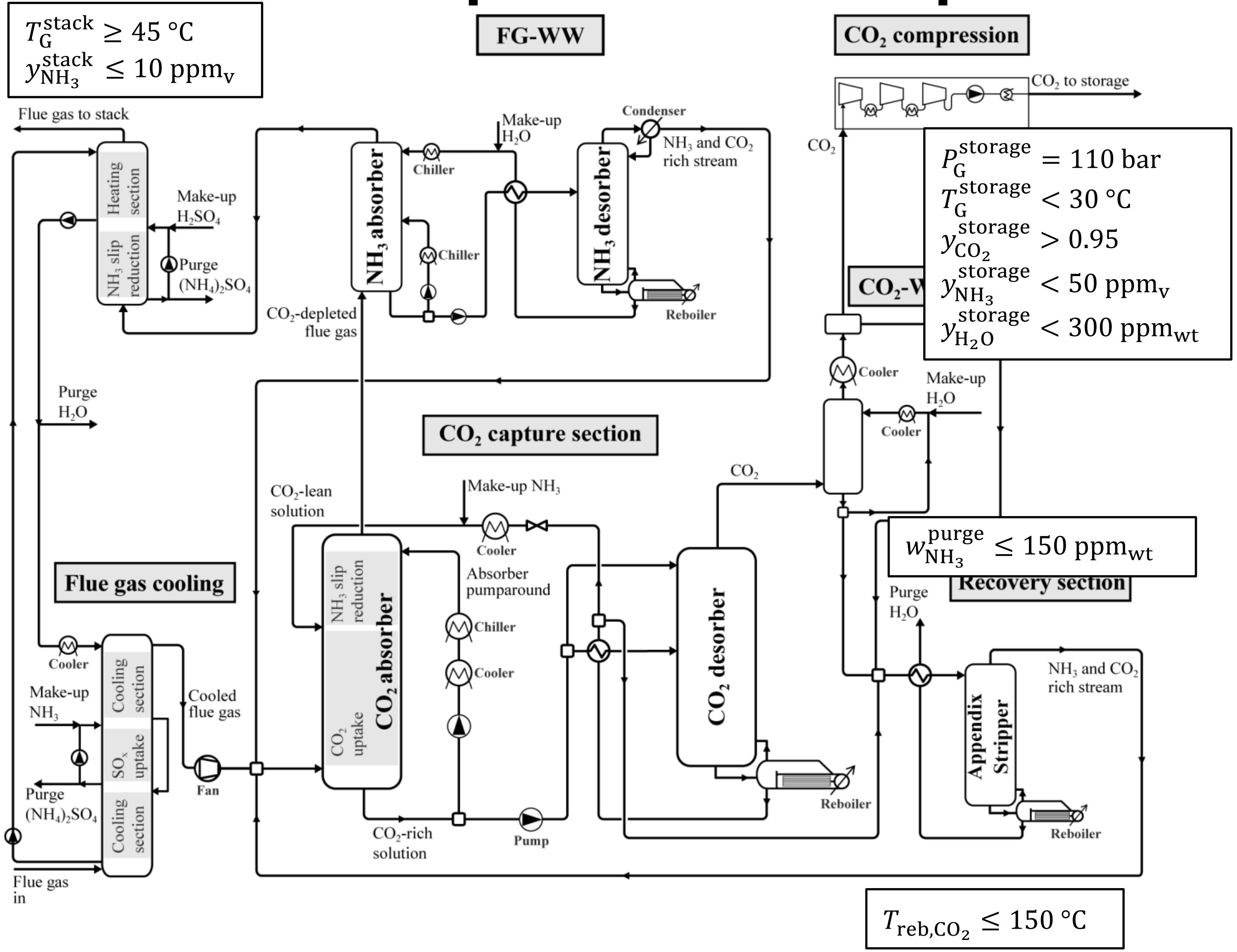
Chilling:

$$\omega_{\mathrm{chill},i} = \frac{\dot{Q}_{\mathrm{chill},i} / \mathrm{COP}_i}{\dot{m}_{\mathrm{CO_2}}^{\mathrm{FG,in}} - \dot{m}_{\mathrm{CO_2}}^{\mathrm{FG,out}}}$$

Auxiliaries:

$$\omega_{\mathrm{aux}} = \frac{\frac{\dot{W}_{\mathrm{fan}}^{\mathrm{ideal}}}{\eta_{\mathrm{comp}}} + \frac{1}{\eta_{\mathrm{pump}}} \sum_i \dot{W}_{\mathrm{pump},i}^{\mathrm{ideal}} + \phi_{\mathrm{cool}} \sum_j \dot{Q}_{\mathrm{cool},j}}{\dot{m}_{\mathrm{CO_2}}^{\mathrm{FG,in}} - \dot{m}_{\mathrm{CO_2}}^{\mathrm{FG,out}}}$$

Model-based process development



Specifications and constraints

- CO_2 capture efficiency
- Flue gas conditions at the stack
- NH_3 concentration in waste-water streams
- CO_2 specifications
- Maximum temperature for liquid streams
- No solid formation

Inlet flue gas specifications

Power plants:	~ **3-14 vol% CO_2**
- NG power plants	~ **4 vol% CO_2**
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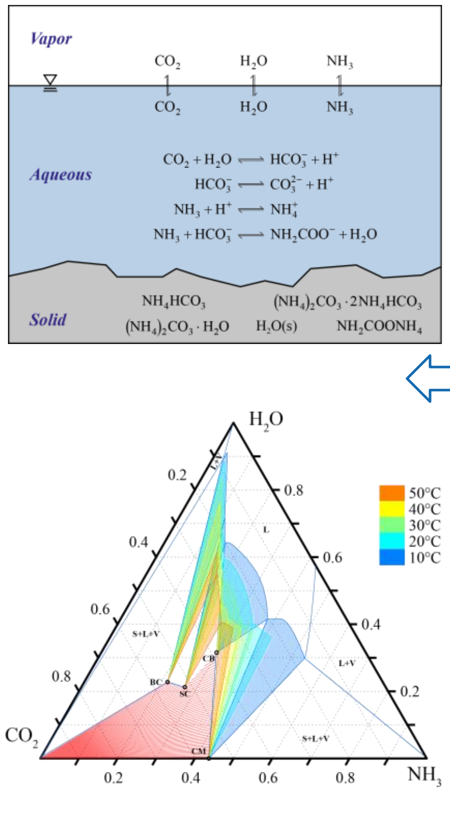
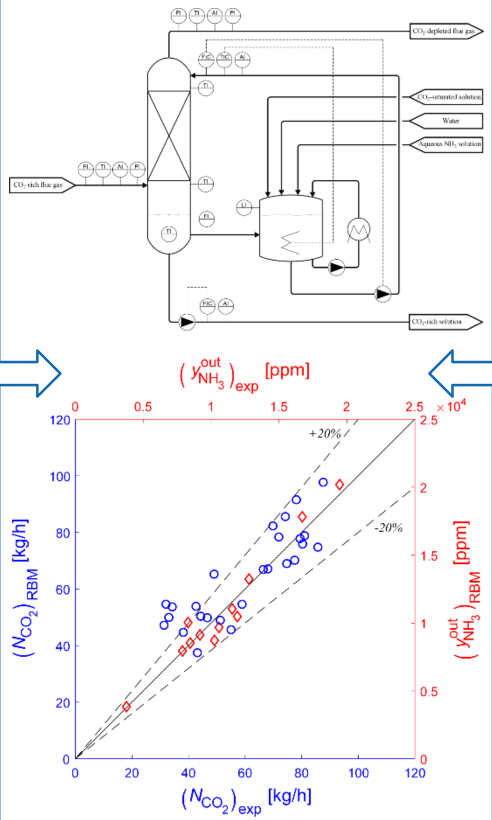
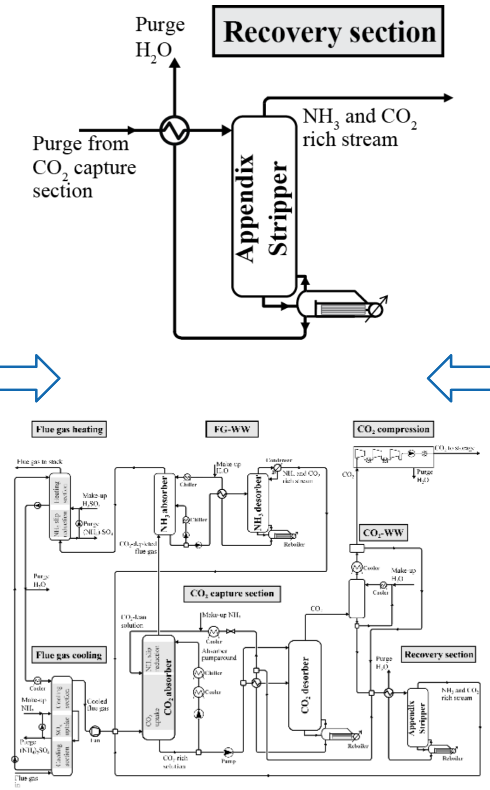
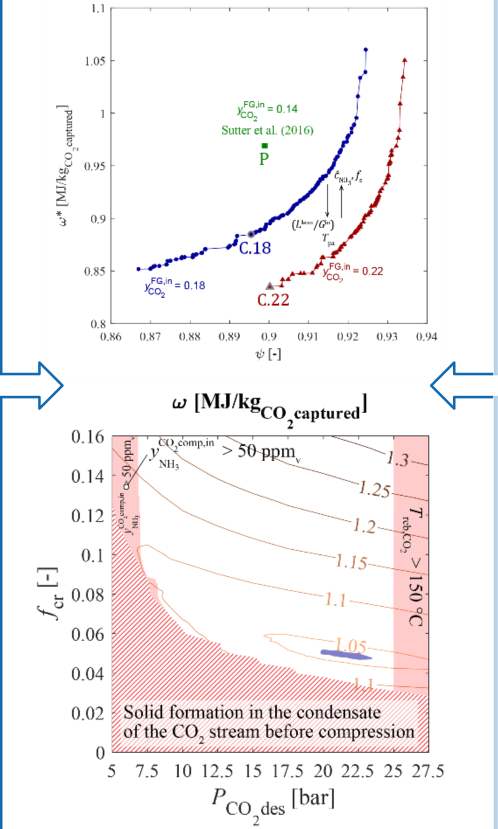
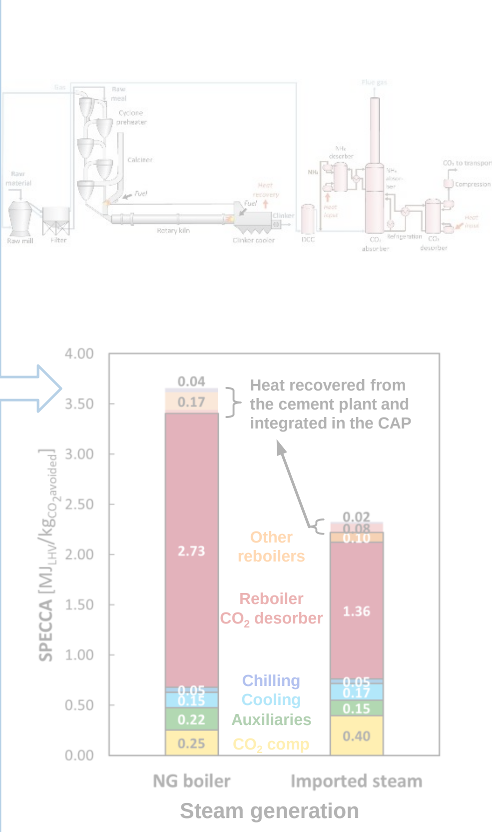




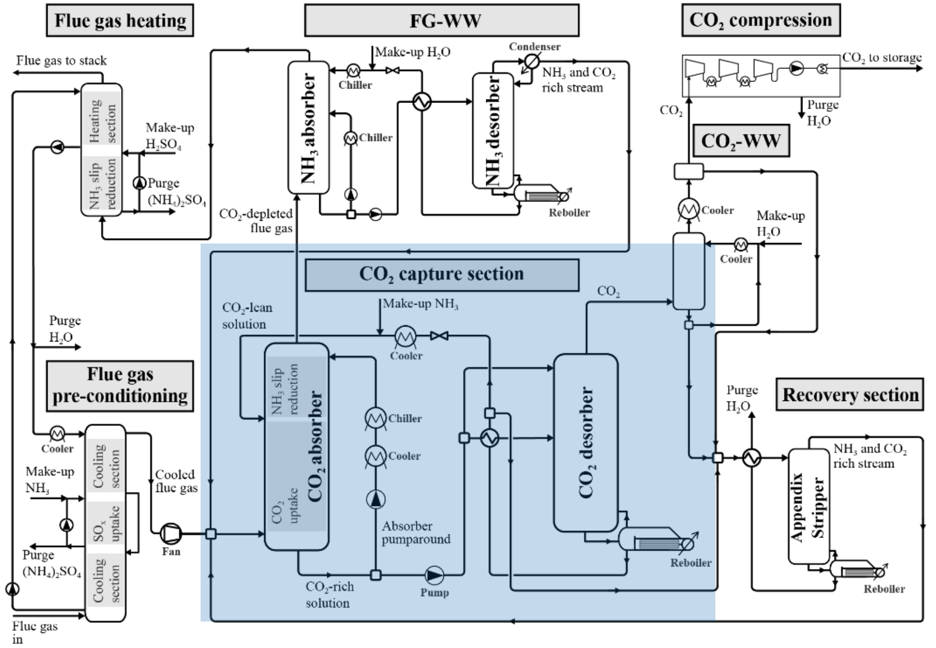


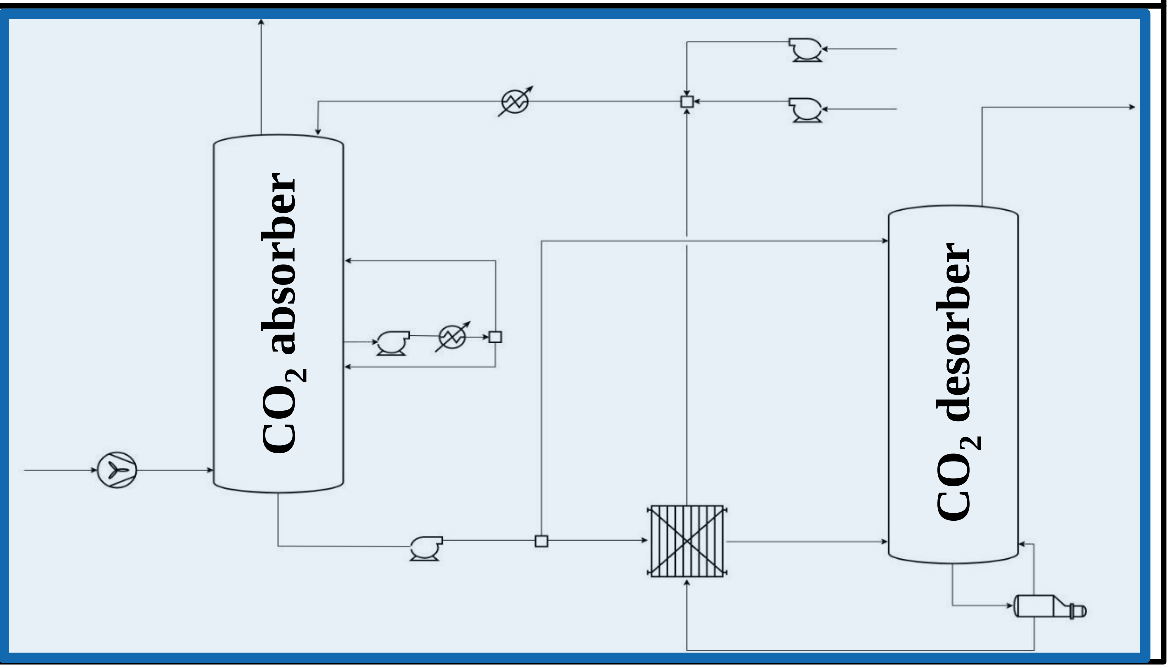




Process optimization

Heuristic optimization	Rigorous optimization
Multivariable sensitivity analysis	Derivative-free algorithms

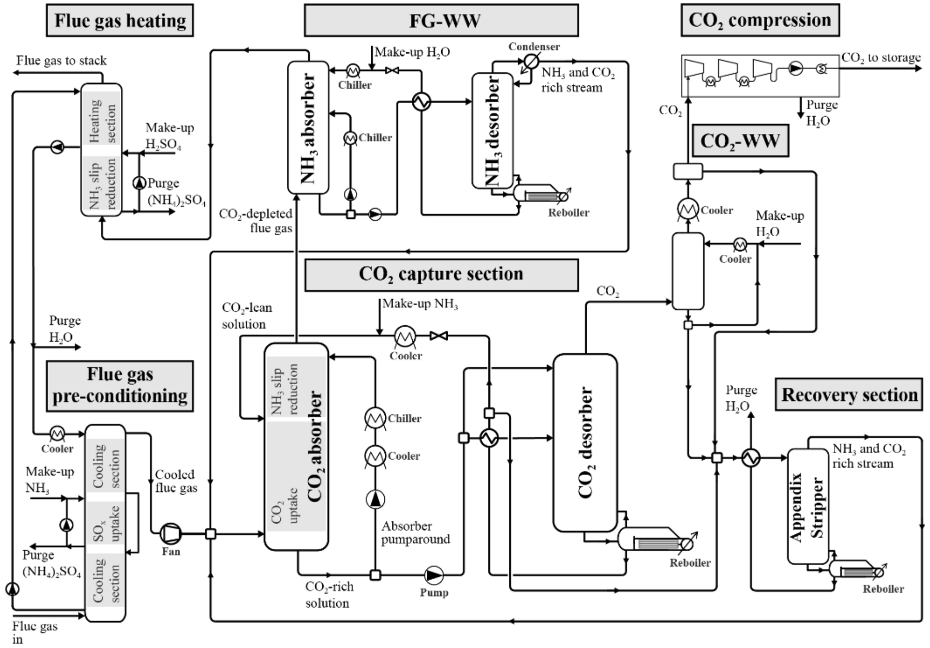


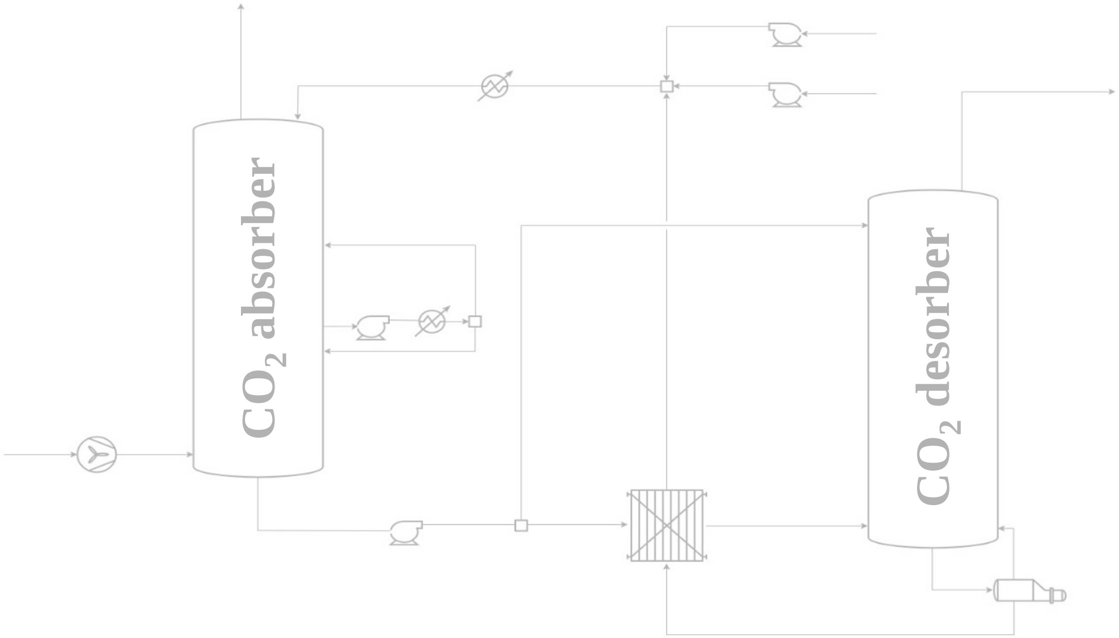


Process optimization

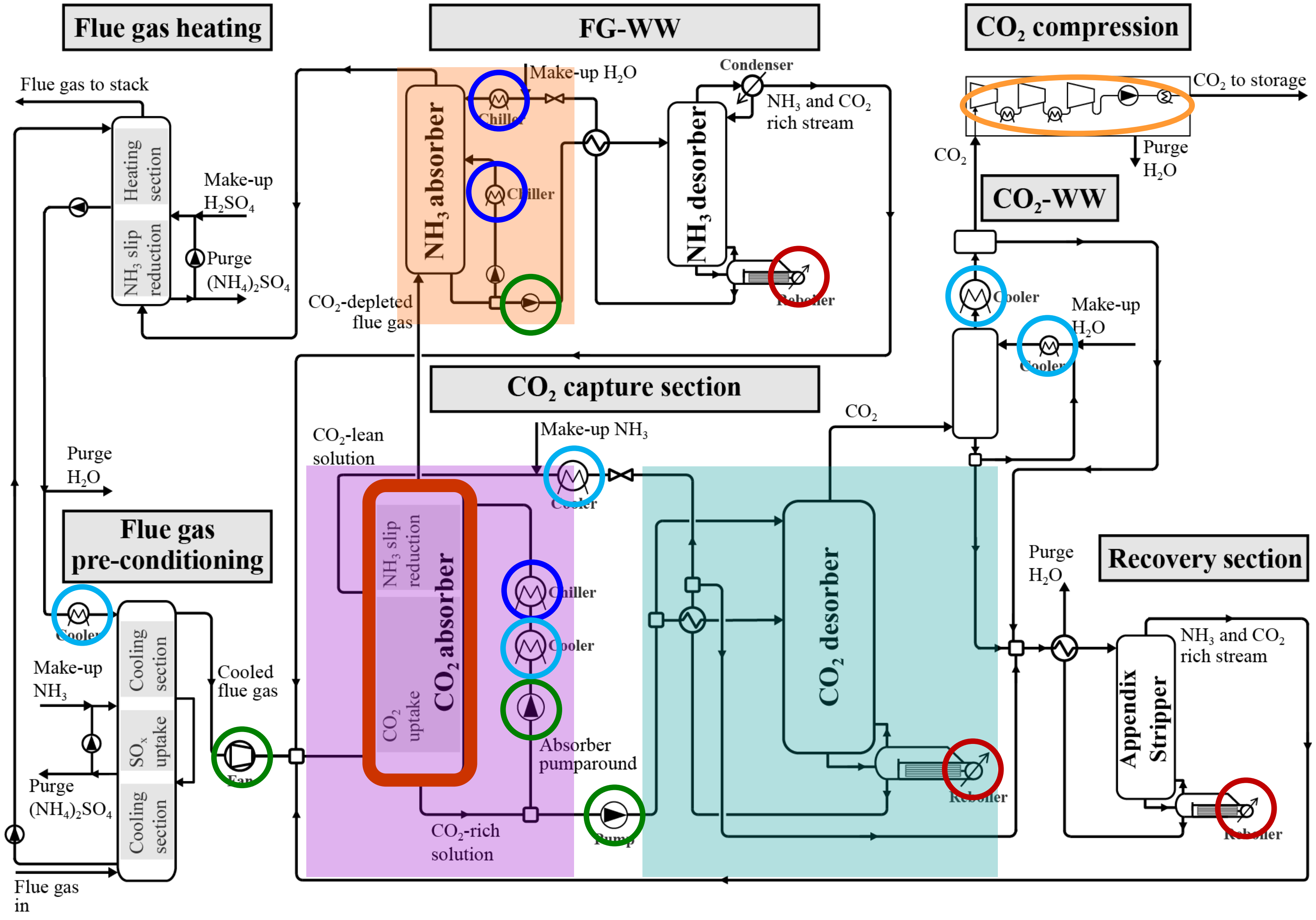
Heuristic optimization	Rigorous optimization

Multivariable sensitivity analysis	Derivative-free optimizer (MOPSO)





Heuristic process optimization



c_{NH_3}	l_{lean}	L/G
T_{pa}	f_s	$c_{NH_3}^{FG-WW}$
$p_{CO_2 des}$	f_{cr}	$(L/G)^{FG-WW}$

ω [MJ/kg$_{CO_2 captured}$]

Pr [kg$_{CO_2}$captured m^{-3} h^{-1}]

Decision variables → **Multi-variable sensitivity analysis[1,2]** → **Objective function**

[1] Sutter et al. *Faraday Discuss* 192 (2016) 59-83
[2] Pérez-Calvo et al. *Energy Procedia* 114 (2017) 6197-205

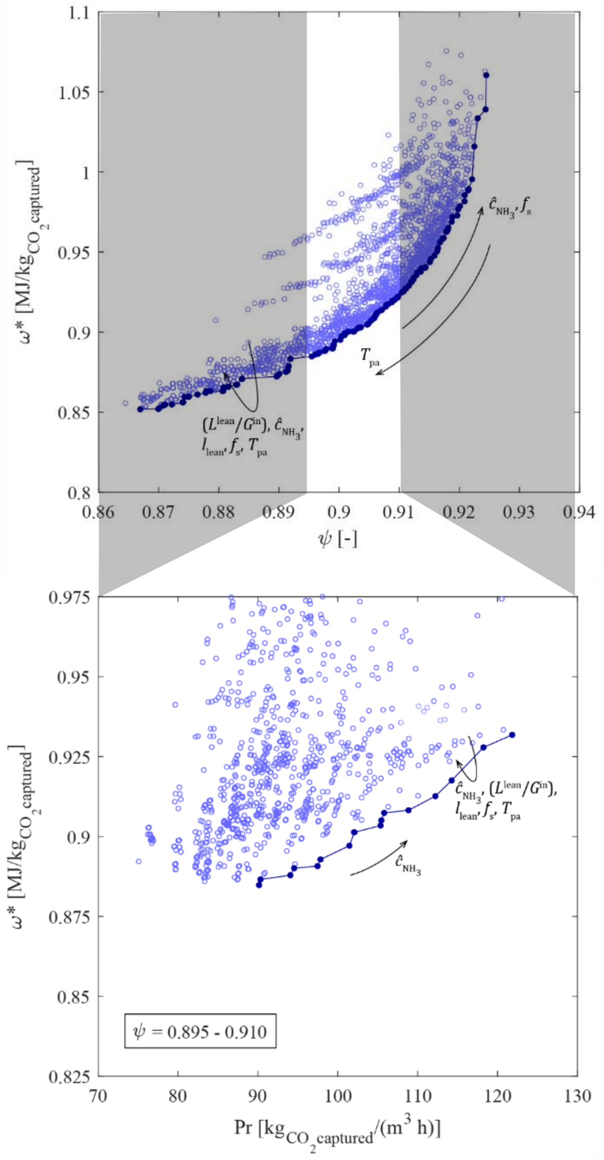
Inlet flue gas characteristics

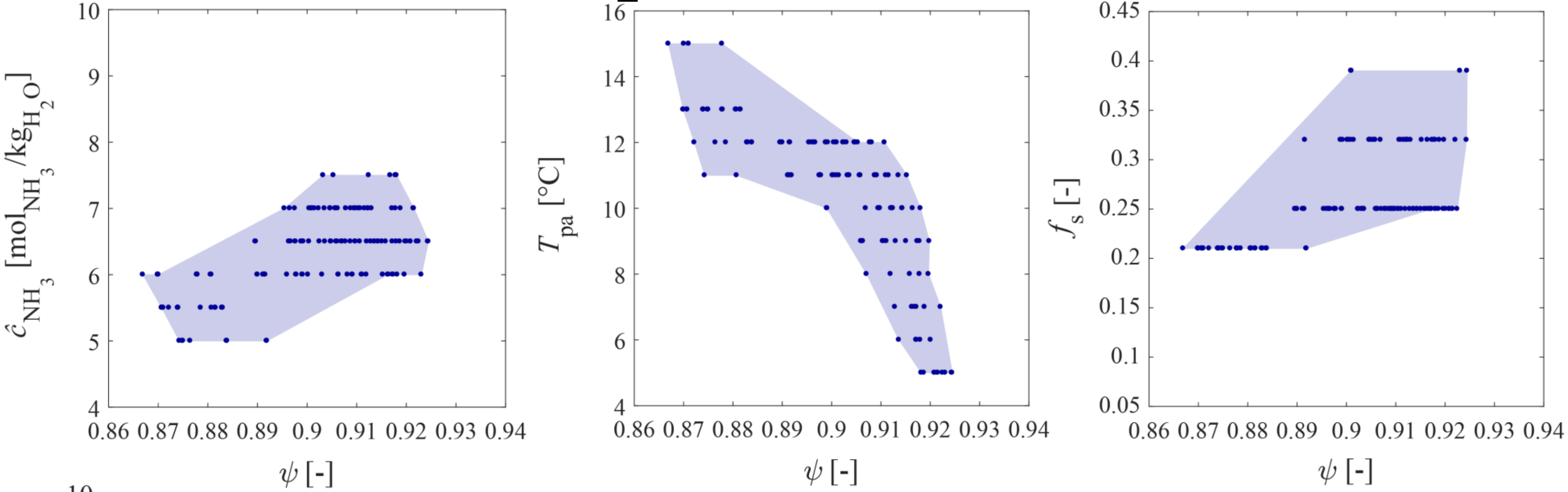
- 14, 18 and 22 vol% CO_2 (~1bar)

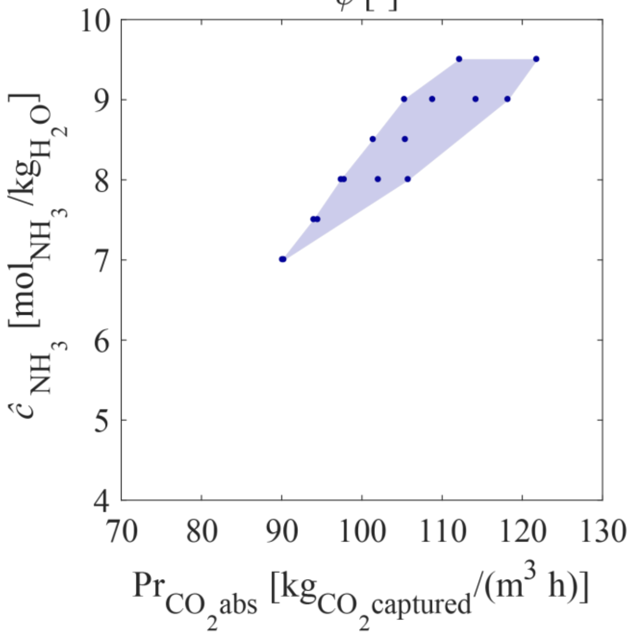
Specifications and constraints

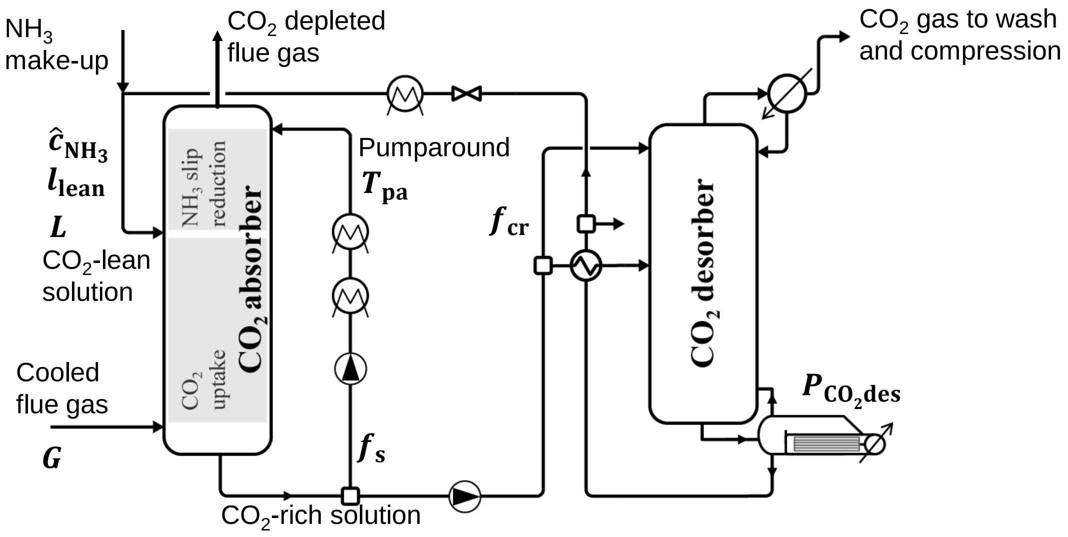
- $\psi > 0.85$
- NH_3 slip < 200 ppm (< 10 ppm at stack)
- CO_2 specifications for transport by pipeline
- No solid formation

Heuristic process optimization – CO_2 absorber results

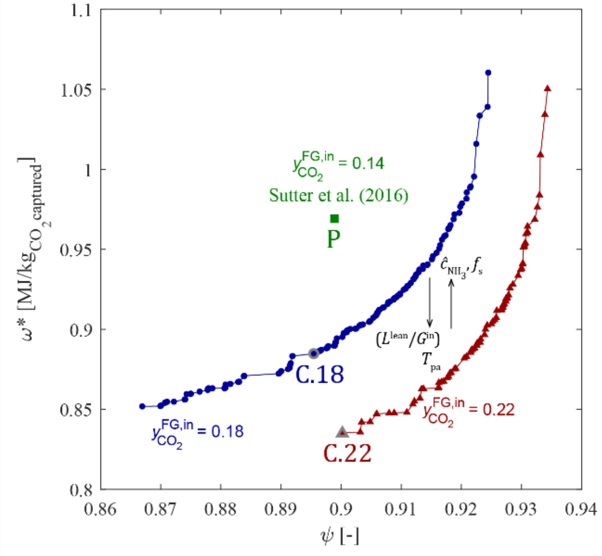


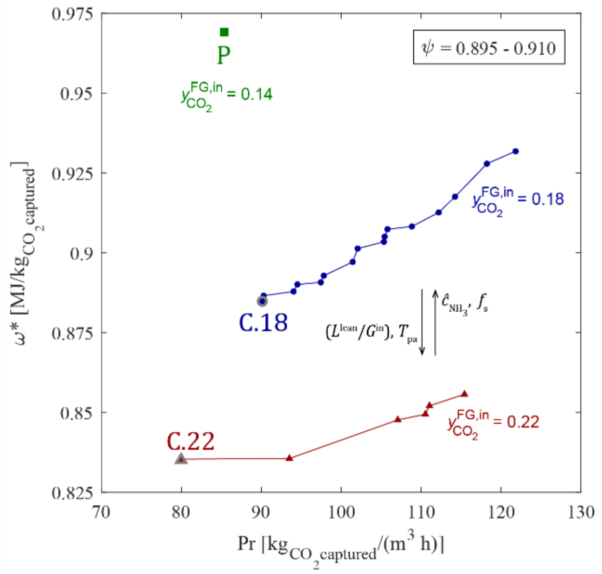


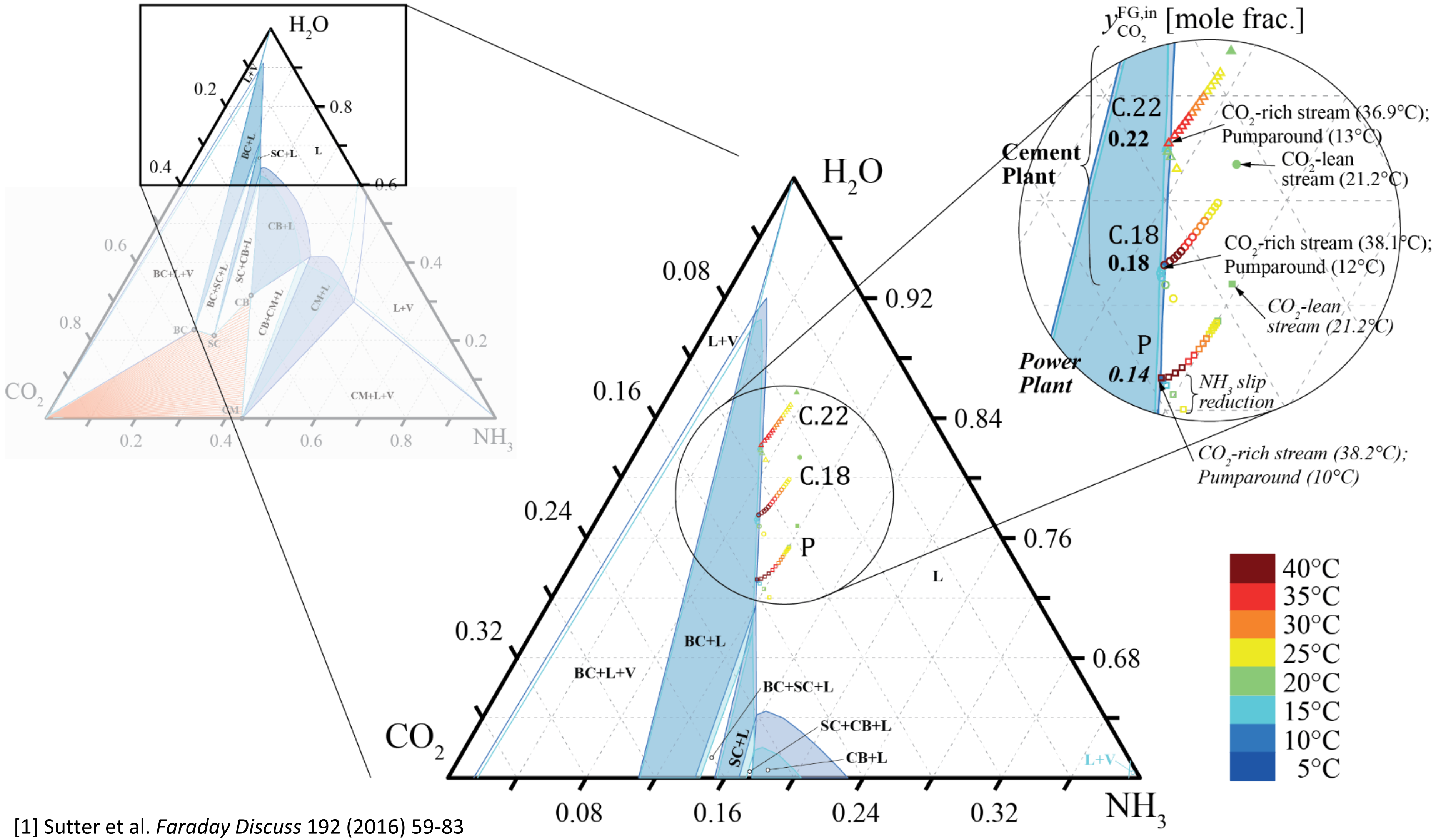




Heuristic process optimization – CO_2 absorber results







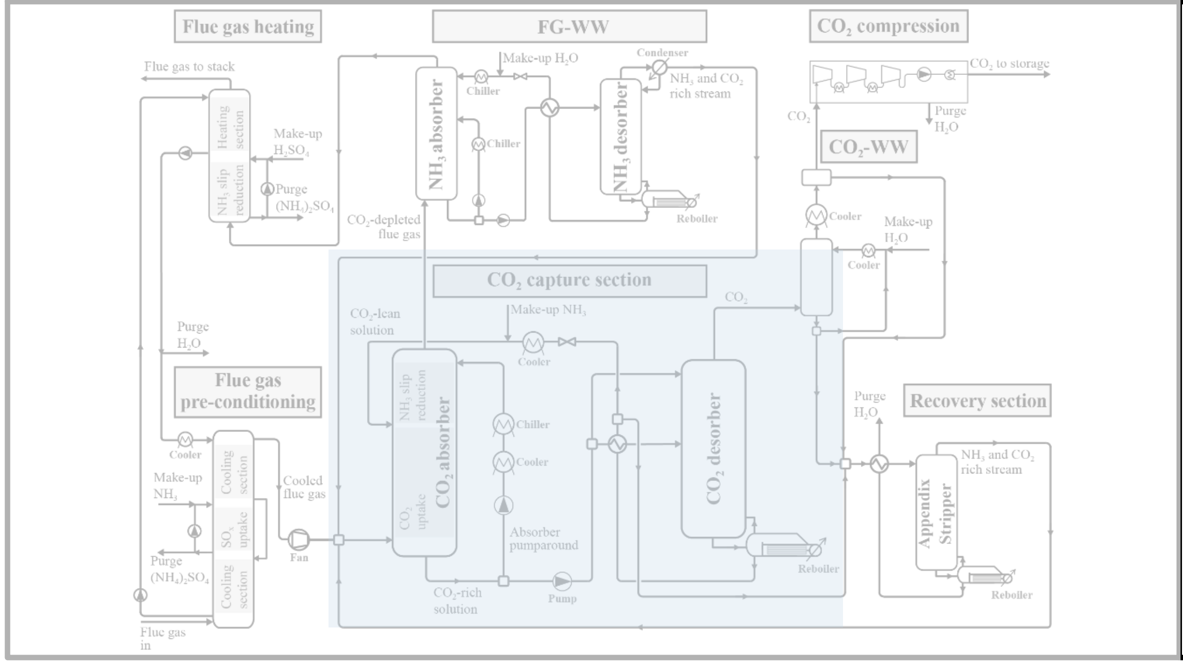
[1] Sutter et al. *Faraday Discuss* 192 (2016) 59-83
[2] Pérez-Calvo et al. In preparation

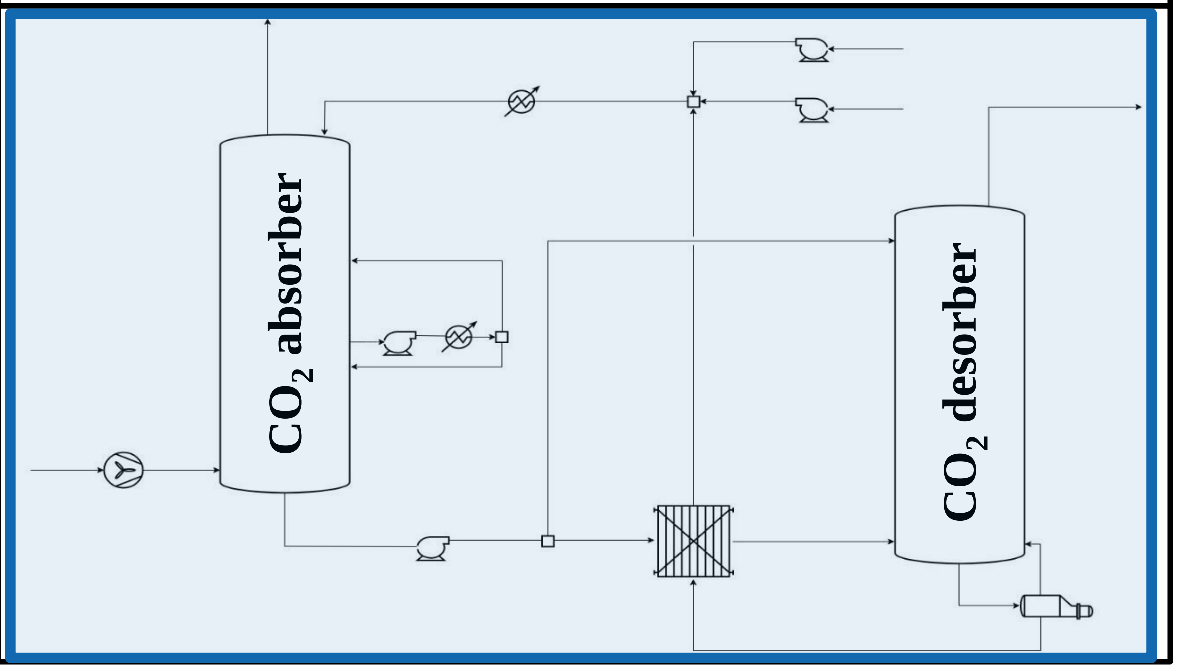
Process optimization

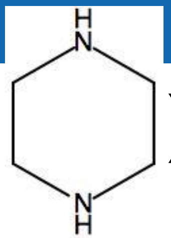
Heuristic optimization	Rigorous optimization

MATLAB

Multivariable sensitivity analysis	Derivative-free optimizer

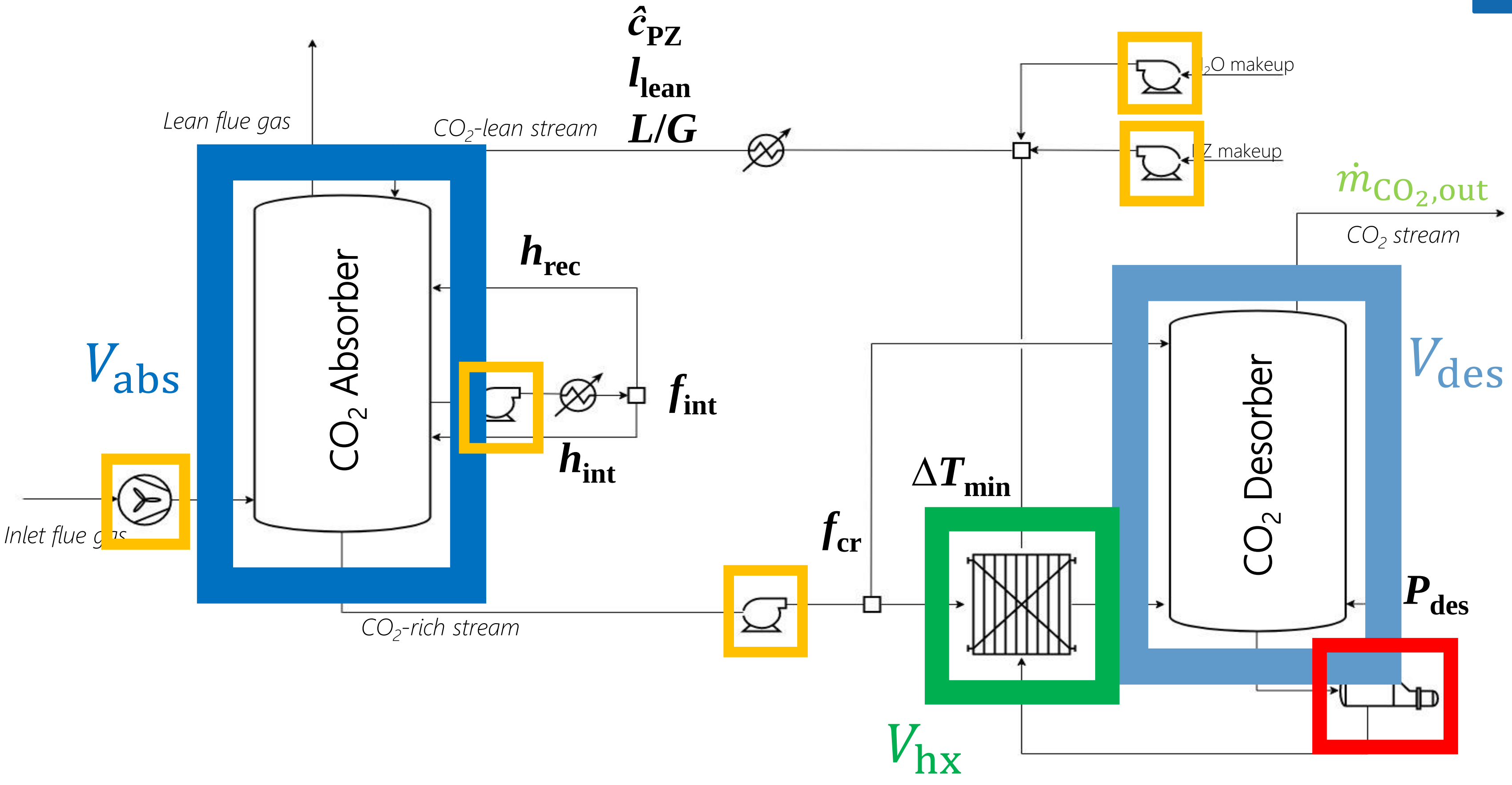




Rigorous process optimization (aqueous PZ )

$$\omega \, [\mathrm{MJ/kgCO_{2captured}}] = \omega_{\mathrm{reb}} + \omega_{\mathrm{aux}} + \omega_{\mathrm{liq}}$$

$$\mathrm{Pr}\, [\mathrm{kgCO_2 captured\ m^{-3}\ h^{-1}}] = \frac{\dot{m}_{\mathrm{CO_2,out}}}{V_{\mathrm{abs}} + V_{\mathrm{des}} + V_{\mathrm{hx}}}$$



Decision variables → **Multi-objective particle swarm optimization (MOPSO)** → **Objective function**

Heris *www.yarpiz.com* (2015)

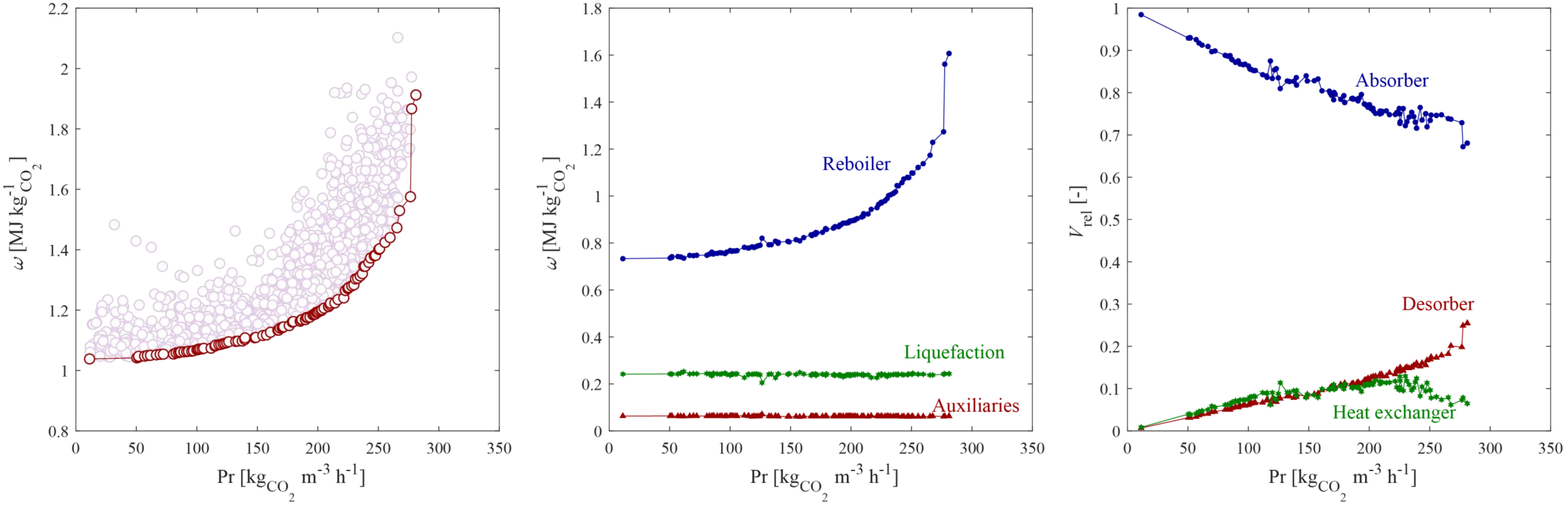
Inlet flue gas characteristics

- 12 vol% CO_2 (~1bar)

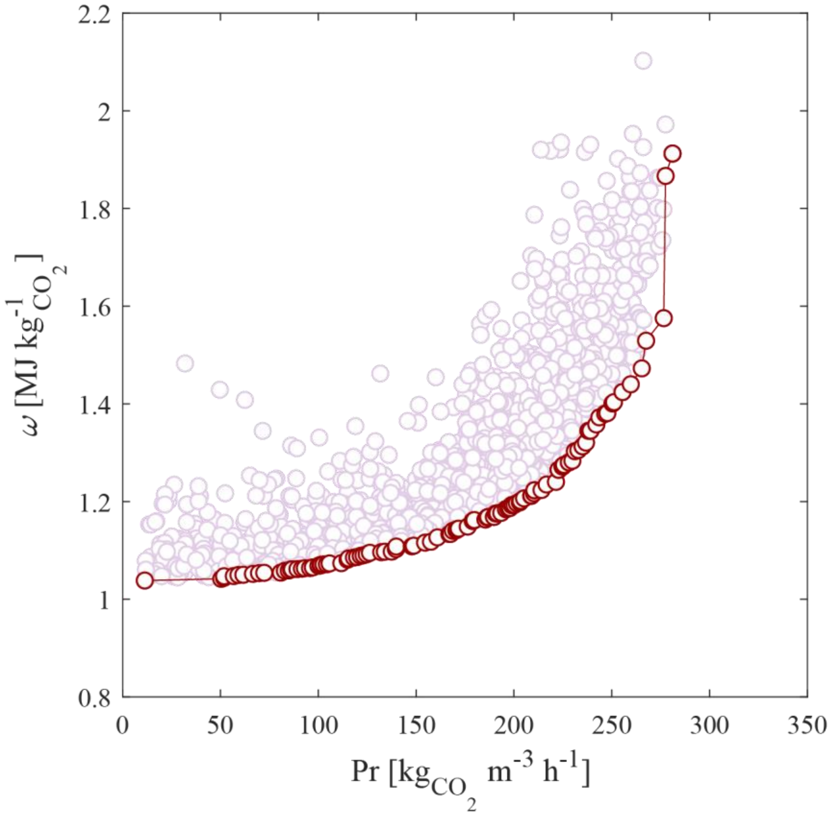
Specifications and constraints

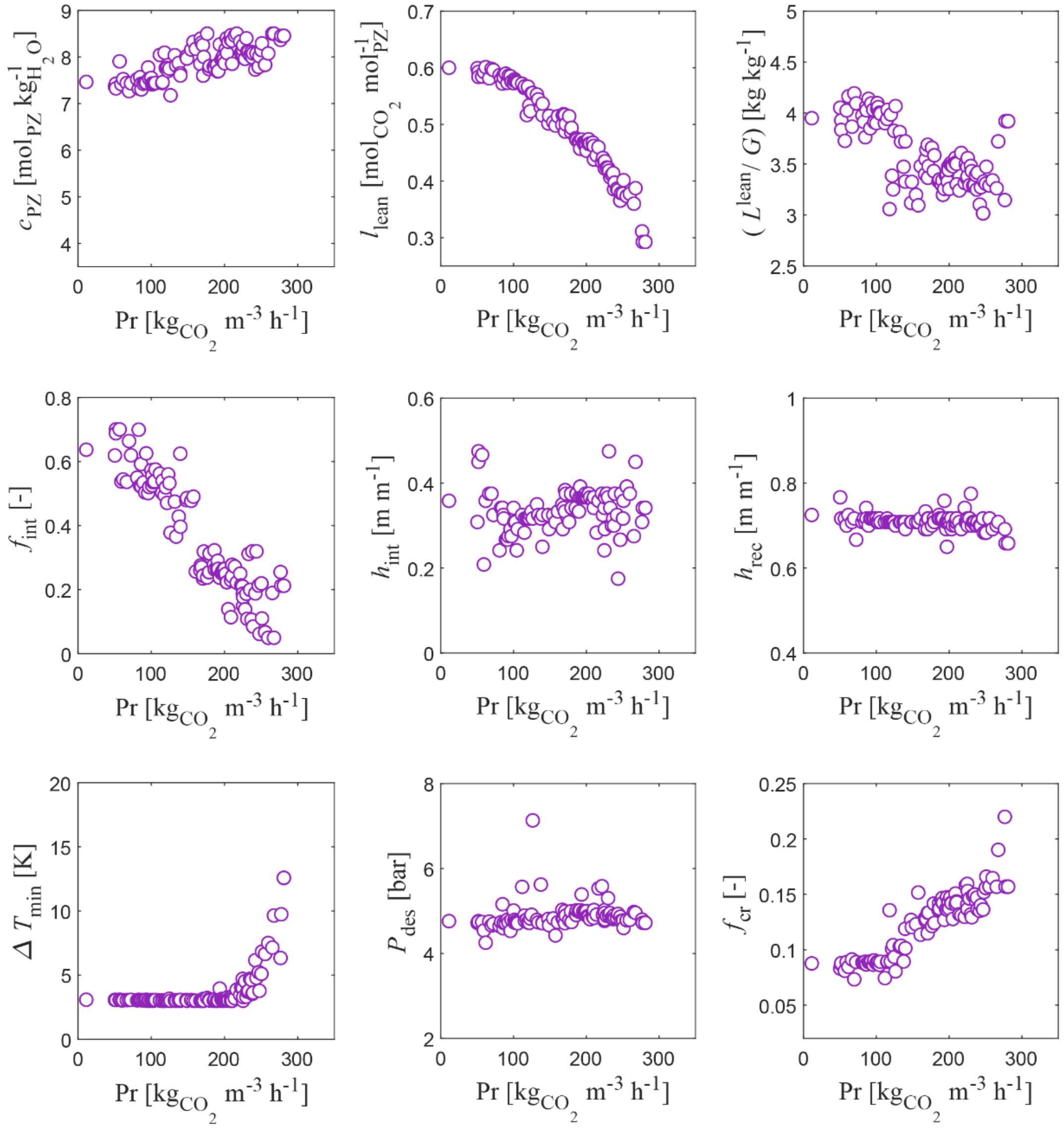
- ψ = 0.50, 0.90, 0.95, 0.99
- CO_2 specifications for transport by train
  - 20 bar
  - -20 °C
  - > 96 vol% CO_2

Rigorous process optimization (aqueous PZ) – Results

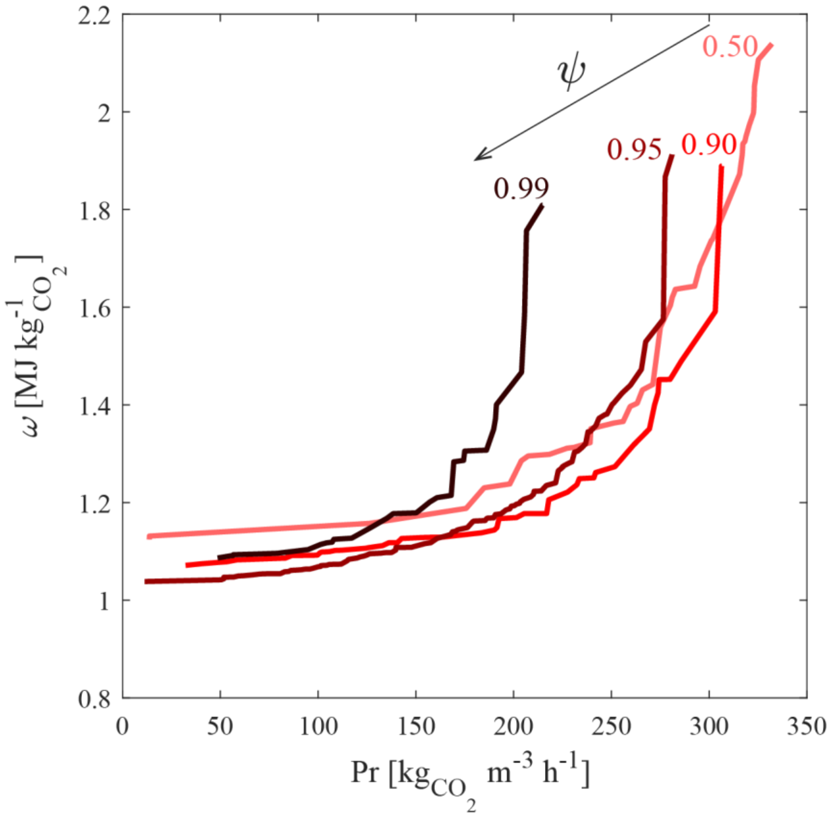


Rigorous process optimization (aqueous PZ) – Results





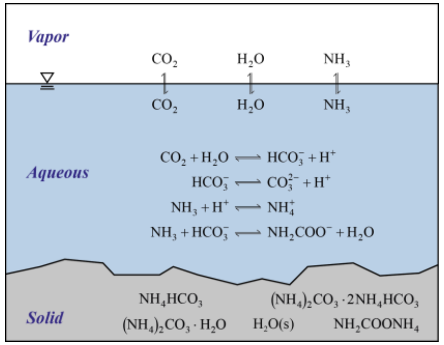
Rigorous process optimization (aqueous PZ) – Results

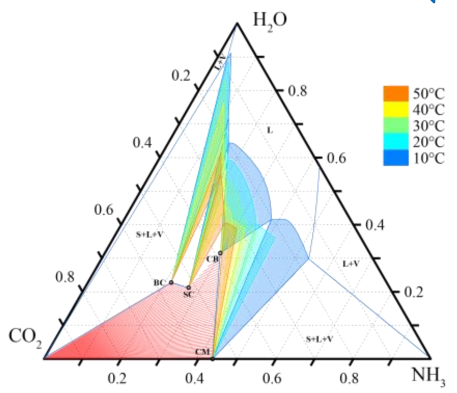


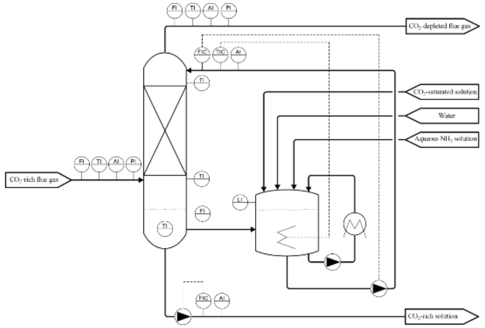
- Higher productivities (Pr) can be reached for lower CO_2 capture efficiencies (ψ)
- Minimum specific equivalent work (ω) depends on productivity (Pr) level
  - Low Pr ➔ $\psi = 0.95$
  - Mid Pr ➔ $\psi = 0.90$
  - High Pr ➔ $\psi = 0.50$
- Optimal CO_2 capture efficiency (ψ) depends on:
  - The solvent system
  - The CO_2 capture process configuration
  - The process specifications and constraints
  - The inlet flue gas properties and flowrate
- The selection of the optimal set of operating conditions requires cost estimations

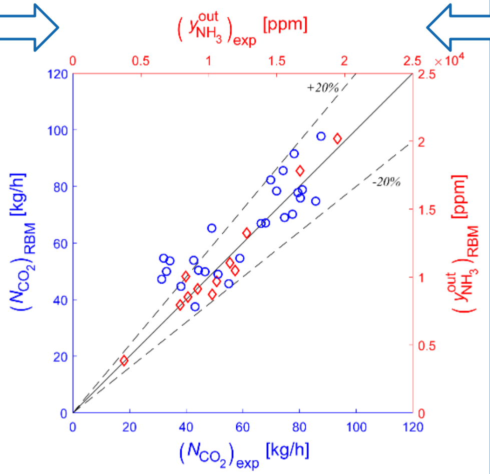
Holistic process development

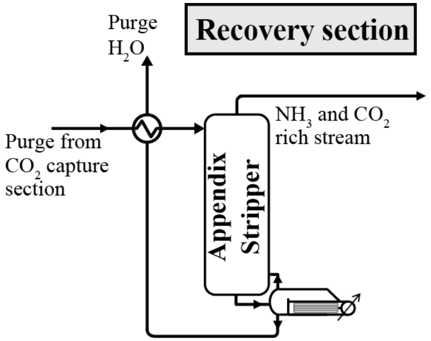
Rate-based model development		Model-based process development		
Thermodynamics	Trans Phenom & Kin	Synthesis	Optimization	Integration

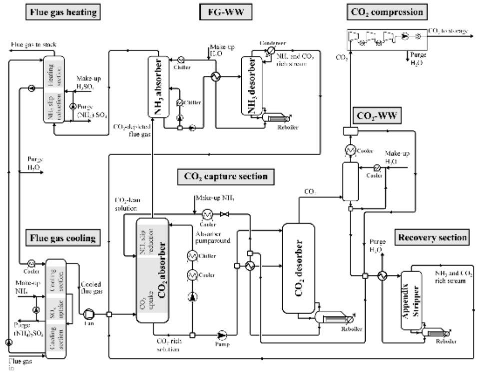


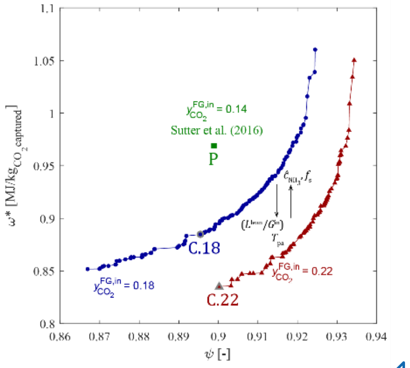


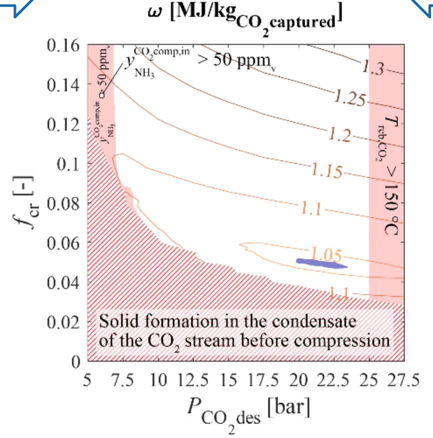


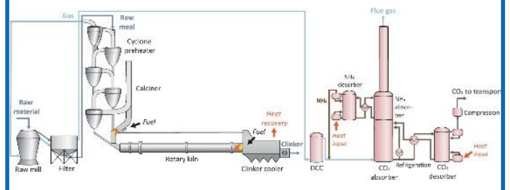


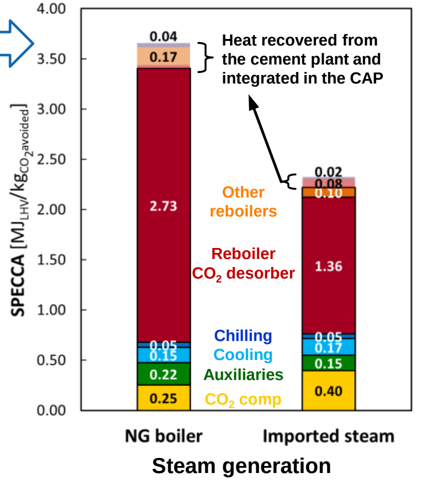




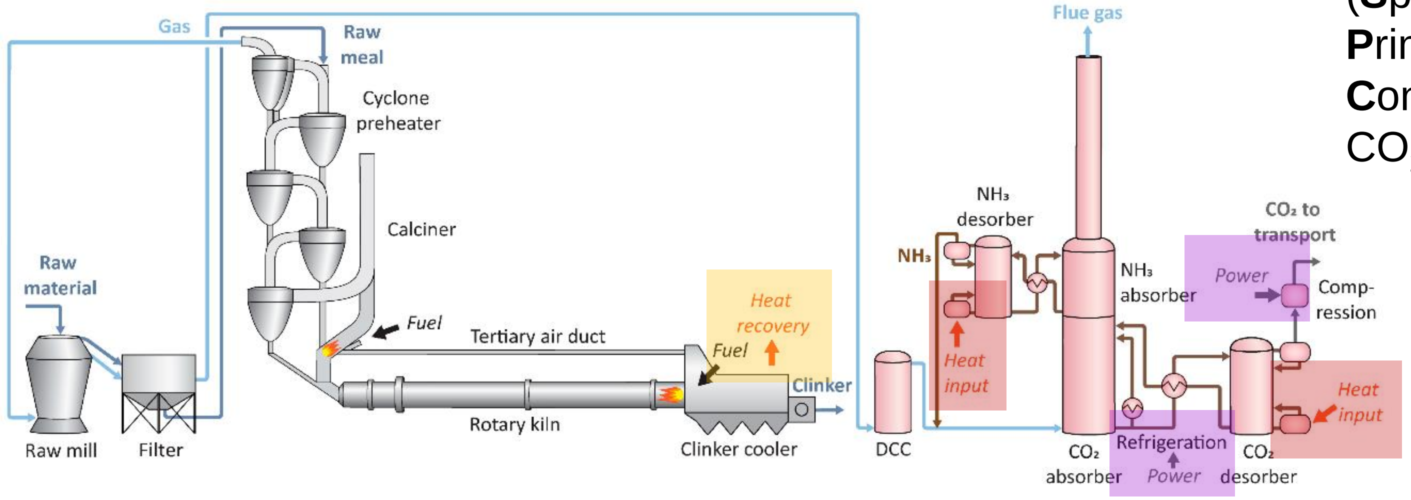






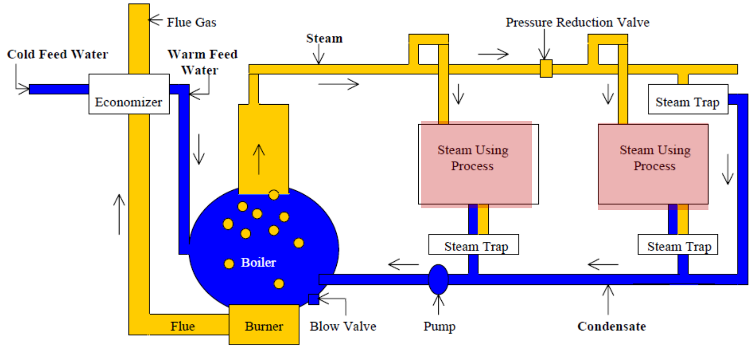


Process integration



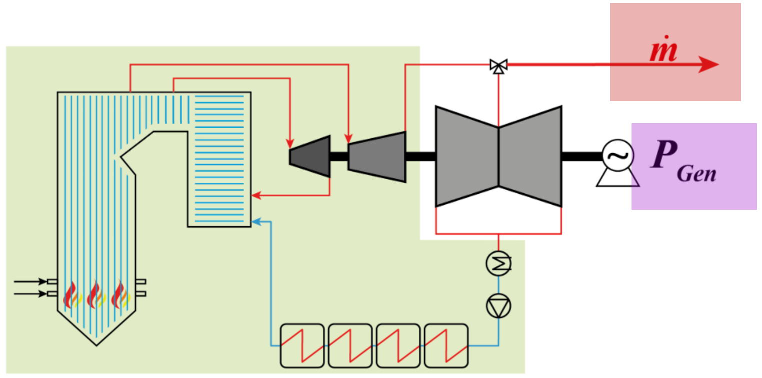
(**S**pecific **P**rimary **E**nergy **C**onsumption for CO_2 **A**voided)

$$\textbf{SPECCA} = \frac{(q_{clk})_{CCS} - (q_{clk})_{ref}}{(e_{clk})_{ref} - (e_{clk})_{CCS}}$$



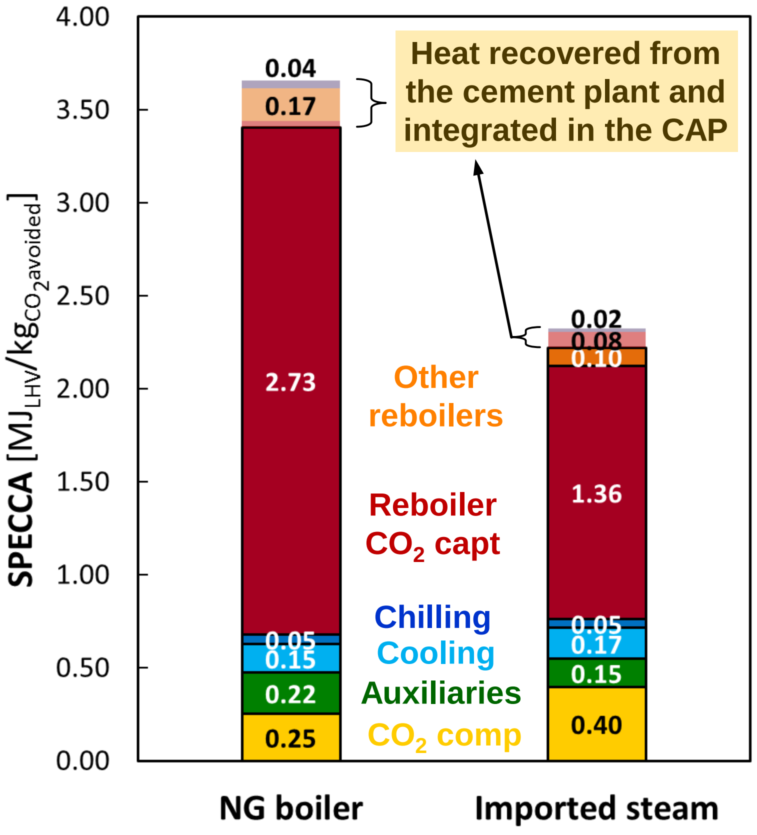
The ENERGY STAR Ammonia and Nitrogenous Fertilizer Guide (2017)

Steam produced on-site in a Natural Gas (**NG**) **boiler**

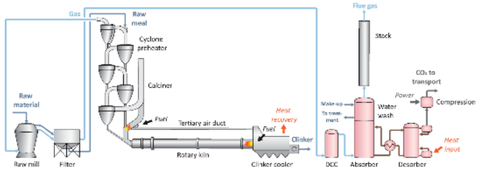


USC from European Benchmarking Task Force (2011)

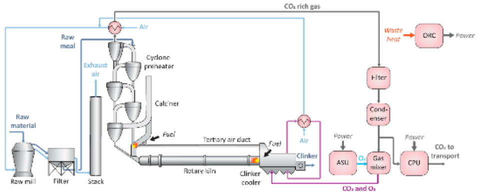
Imported steam from a Combined Heat and Power (CHP) plant



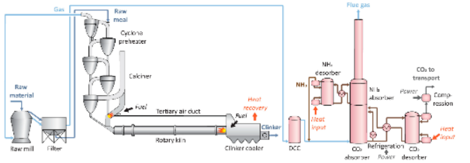
Process integration – Comparison among technologies



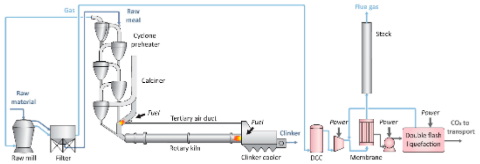
Absorption with aqueous **MEA** solution



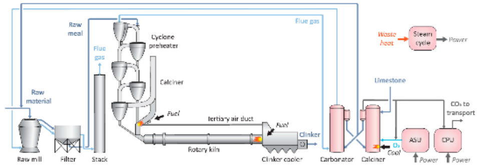
Cement production with oxy-combustion (**oxyfuel**)



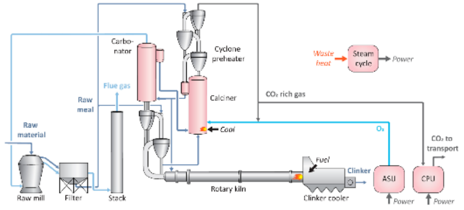
Chilled Ammonia Process (**CAP**) – Absorption with aqueous NH_3 solution



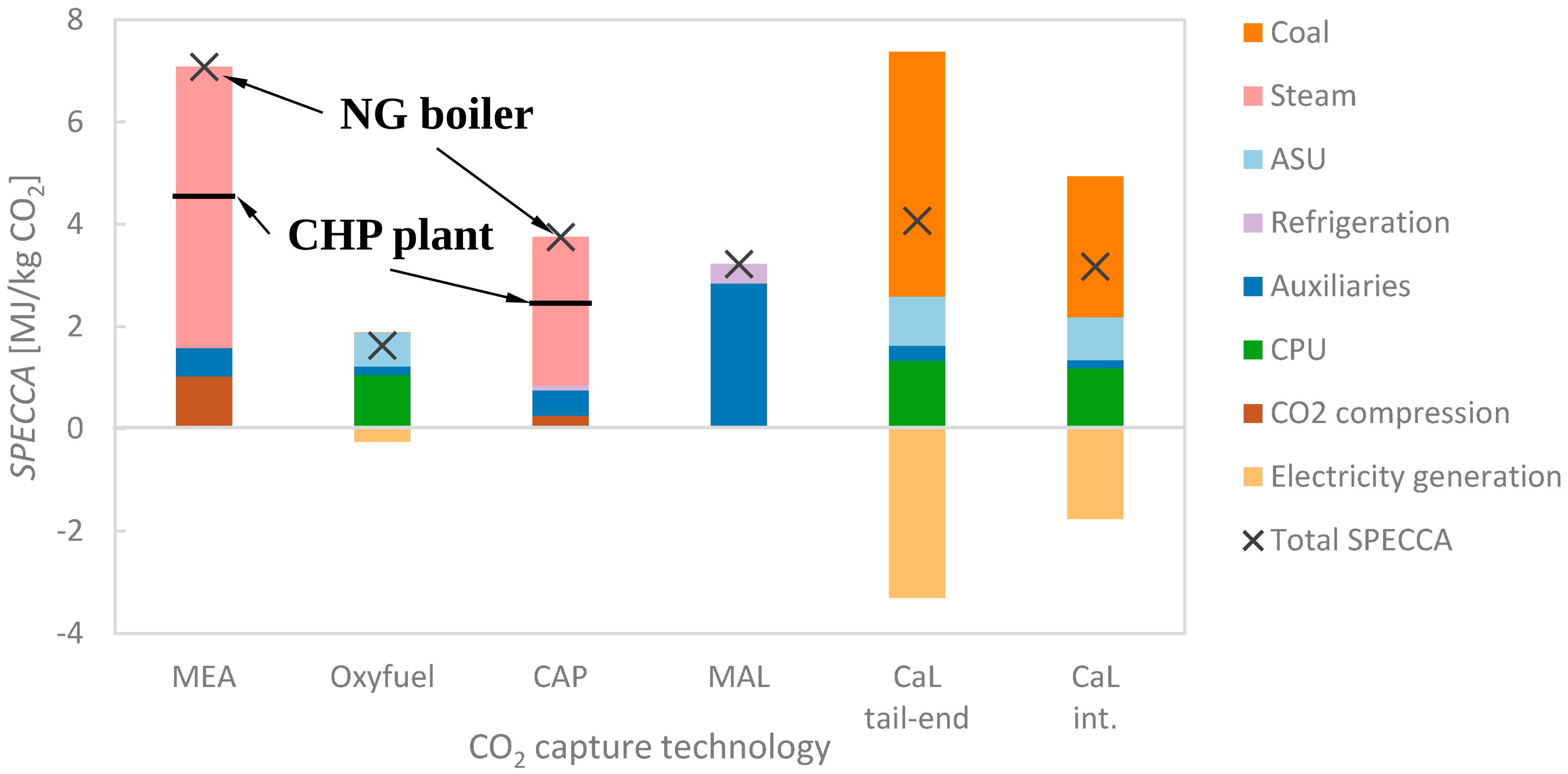
Membranes and liquefaction (**MAL**)



Tail-end calcium looping (**CaL tail-end**)



Integrated calcium looping (**CaL int.**)



[1] Voldsund et al. *Energies* 12 (2019) 559

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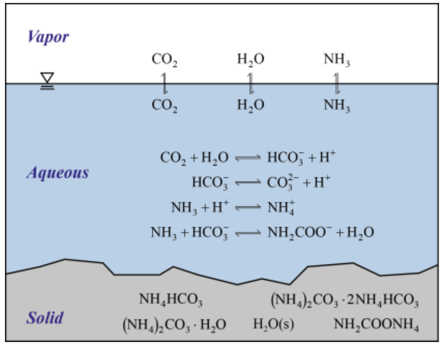

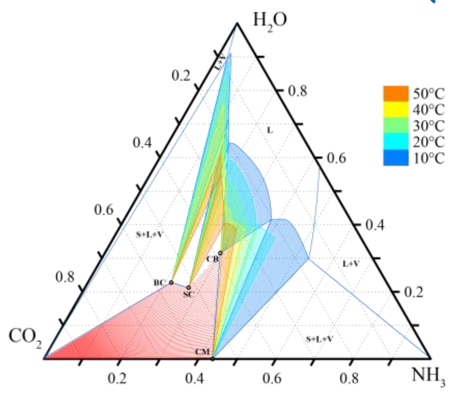

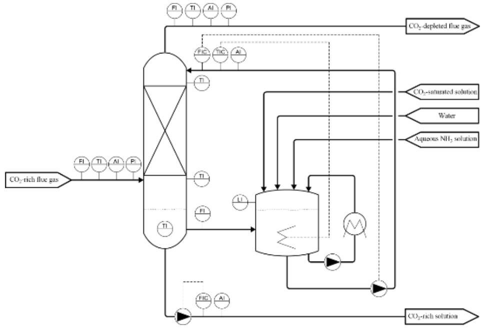

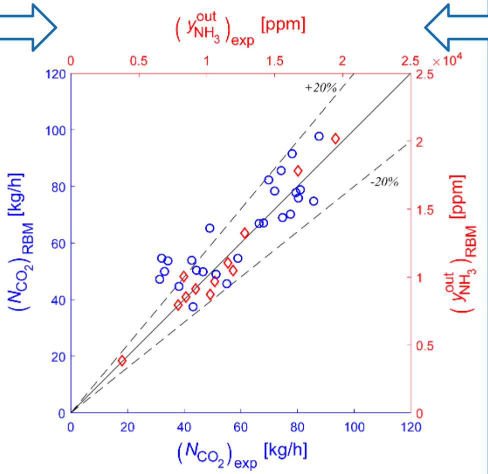

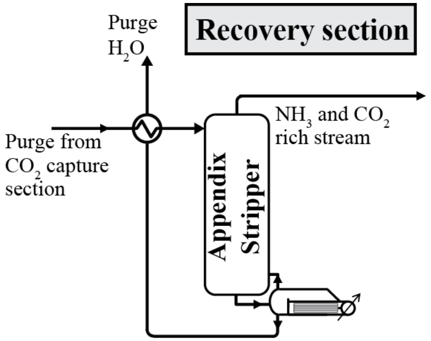

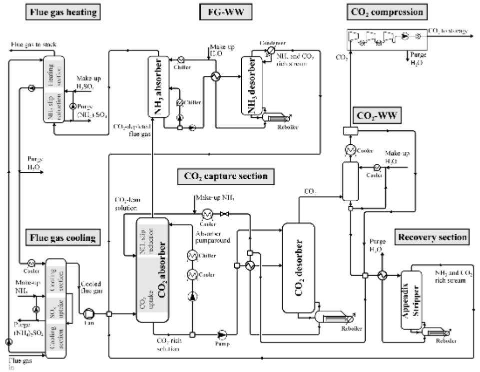

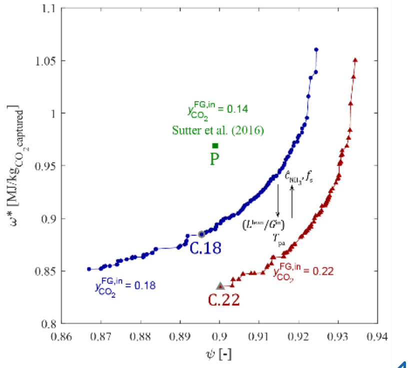

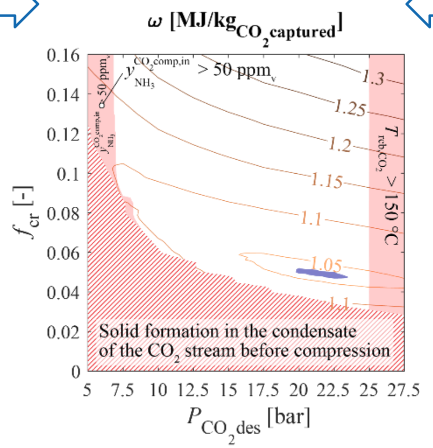

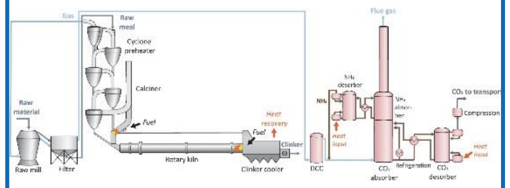

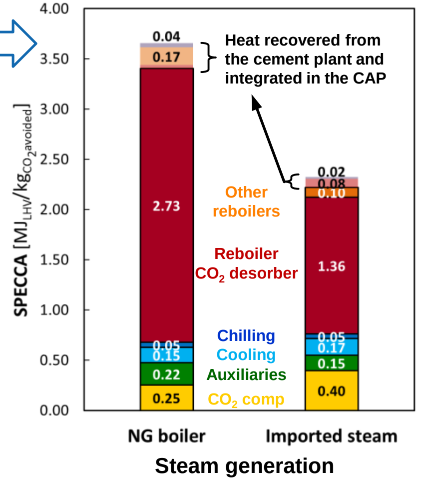

Acknowledgements

This project has been partially funded through the European Union's Horizon 2020 research and innovation programme under grant agreement no 641185

This work was partially supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

The authors would like to thank Kaj Thomsen (Department of Chemical and Biochemical Engineering, Technical University of Denmark) for making the thermodynamic model available and for providing the relevant software

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Energy Science Center

Frontiers in Energy Research
24.03.2020

José-Francisco Pérez-Calvo (PhD student)
Supervisor: Marco Mazzotti (Separation Processes Laboratory – D-MAVT)

On the application of absorption-based CO_2 capture processes to industrial point sources