BioRECO$_2$VER

CO_2 capture by hybrid chemo-enzymatic process

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Horizon 2020
European Union Funding
for Research & Innovation

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 760431.

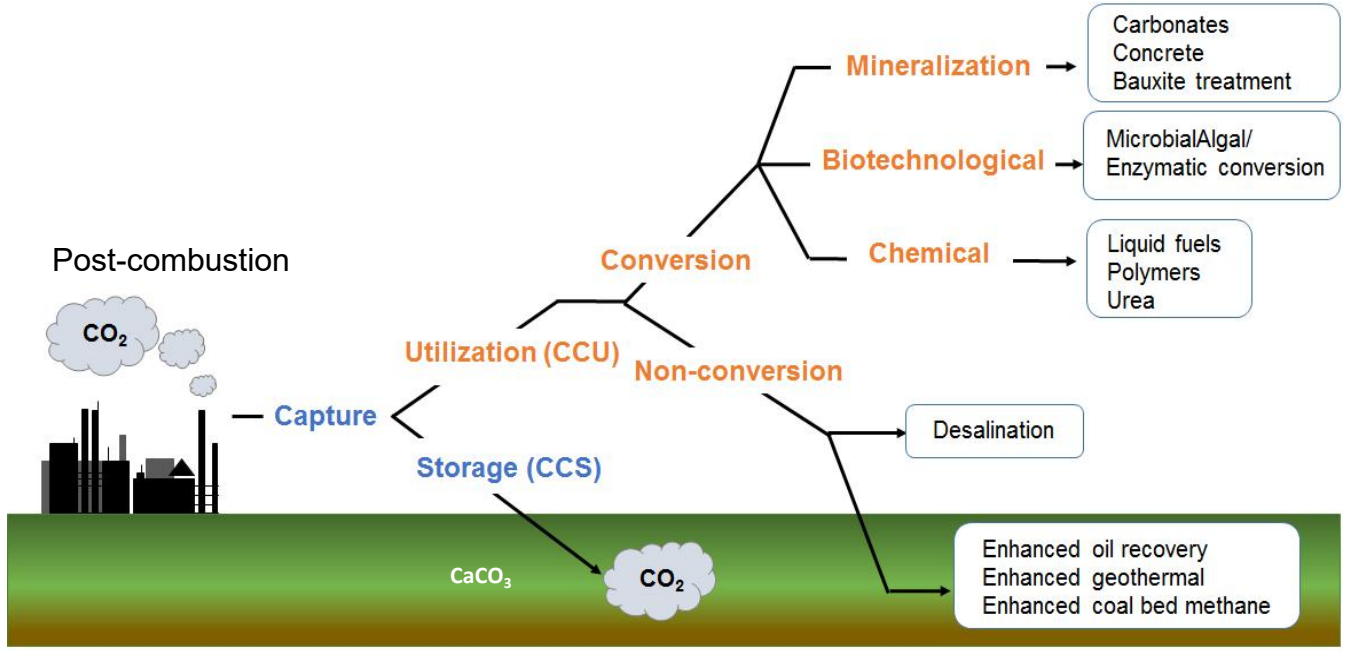
CO_2 capture as a measure against climate change

European Green Deal:
Carbon-neutral by 2050

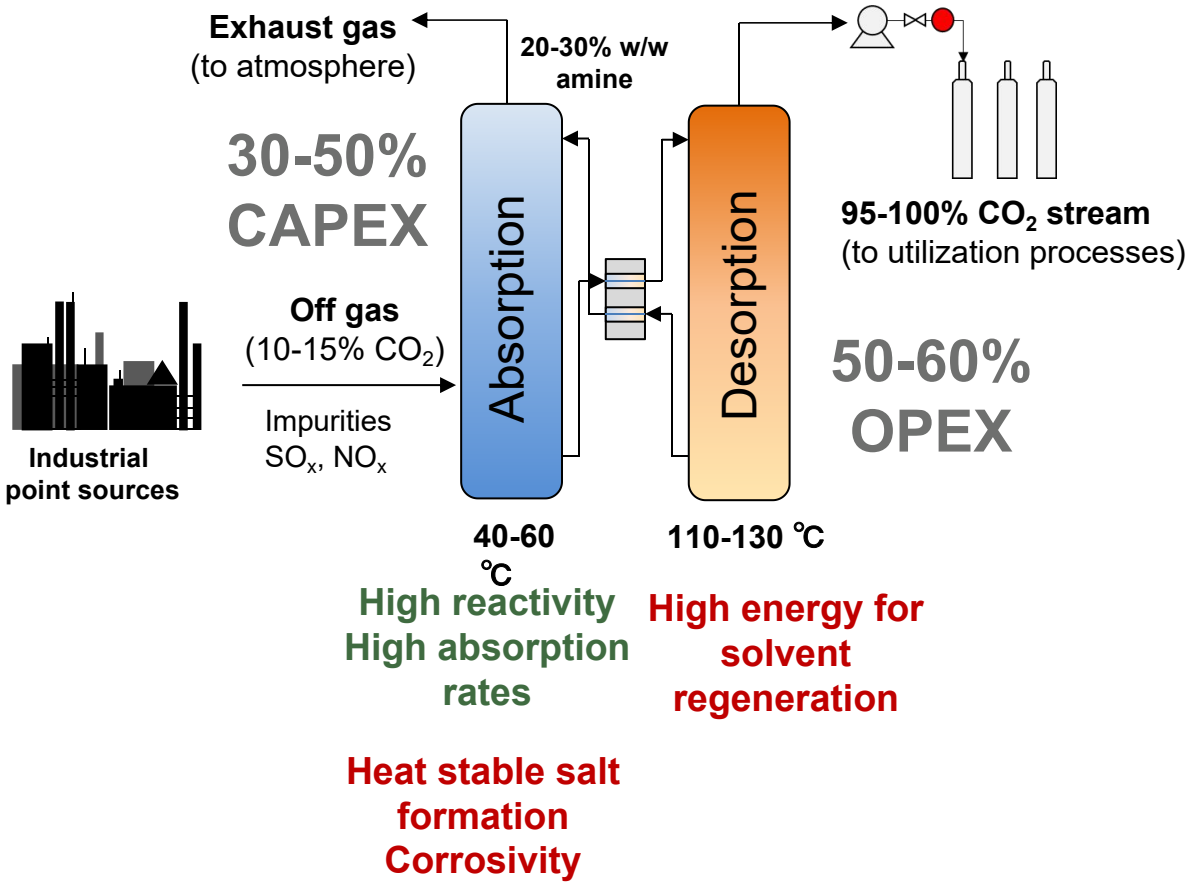
- The role of carbon capture in reaching the EU's long-term emissions reduction goal is acknowledged

Sweden's Climate Act and Climate Policy Framework:
Zero-net emissions by 2045

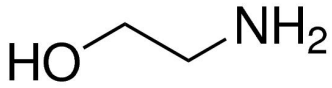
- 85% lower than in 1990
- Rest 15% through supplementary measures, such as CCS



Amine-based CO_2 capture: Current gold standard



Monoethanolamine (MEA)



Reactions:

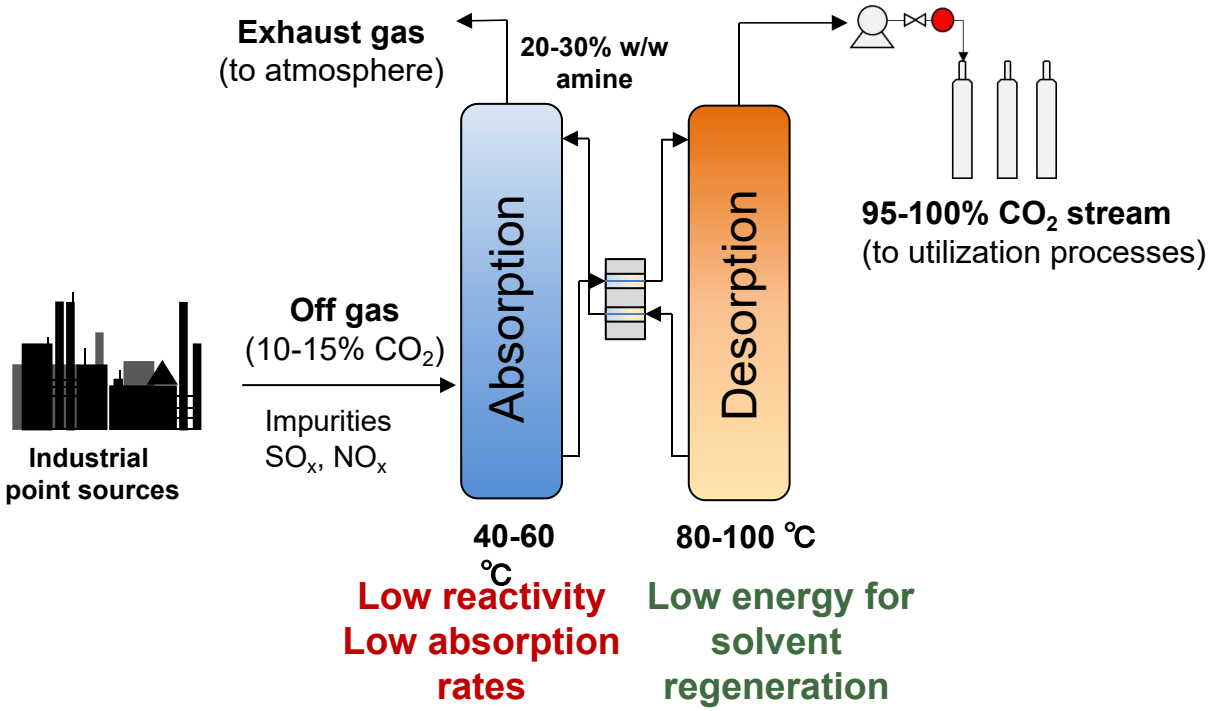
$R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+COO^-$ (zwitterion)

$R_1R_2NH^+COO^- + B \leftrightarrow R_1R_2NCOO^-$ **(carbamate)** + BH^+

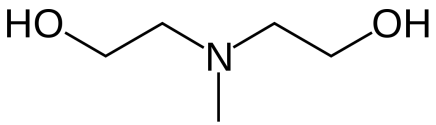
$R_1R_2NCOO^- + H_2O \leftrightarrow R_1R_2NH + HCO_3^-$ **(bicarbonate)**

Where R_2 is a hydrogen for primary amines and B base

Amine-based CO_2 capture: Alternative solvent



Methyl diethanolamine (MDEA)

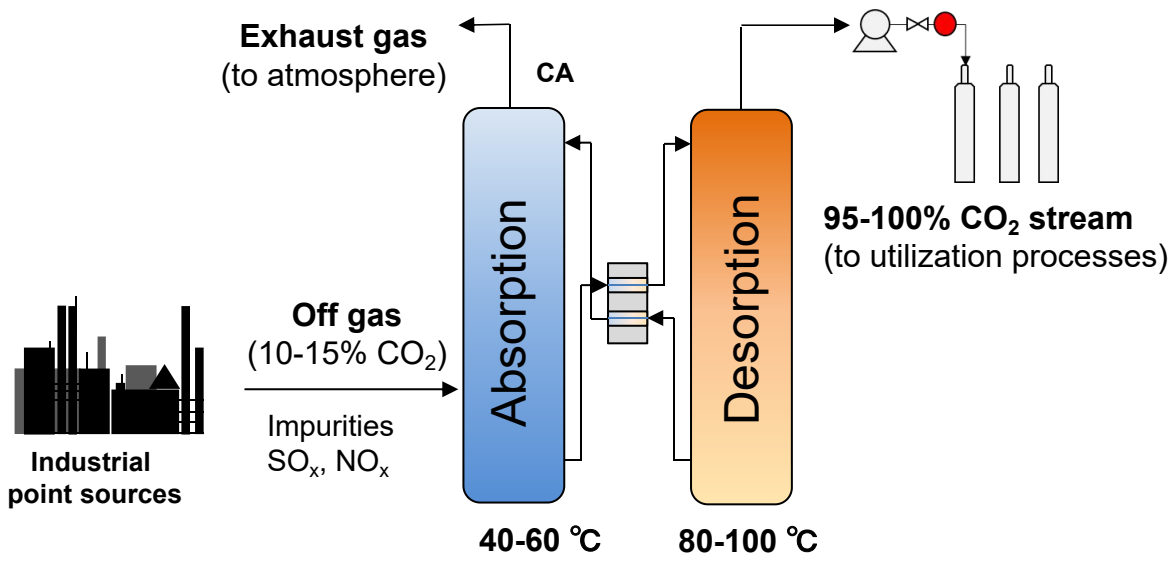


Reactions:

$R_1R_2R_3N + CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3^-$

(bicarbonate)

Enzymatic CO_2 capture



Higher absorption rates than MDEA

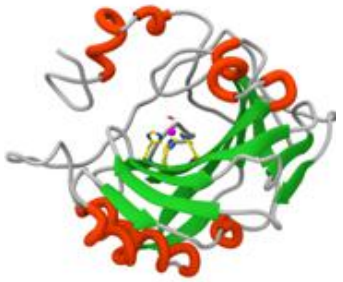
Mild conditions (pH 8.0)

No use of harsh solvents

Lower absorption rates than MEA

Low energy for solvent regeneration

Carbonic anhydrase (CA)

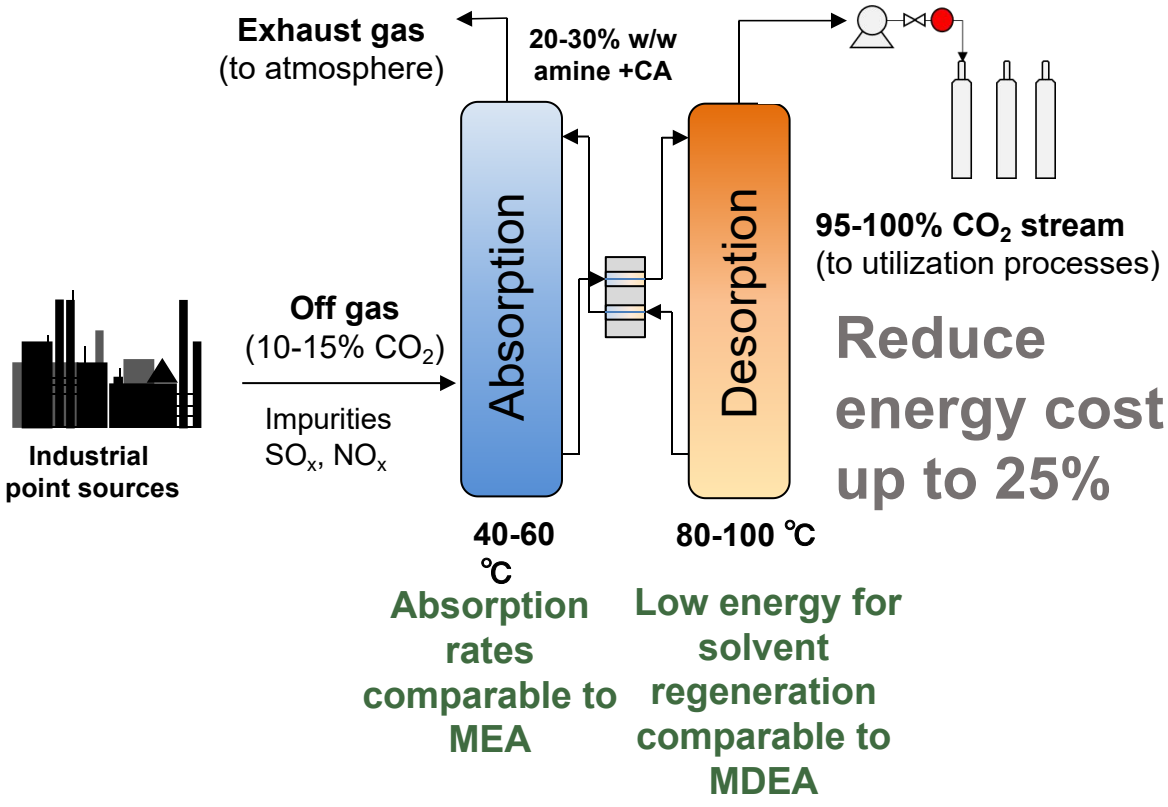


Reaction:

$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$ **(bicarbonate)**

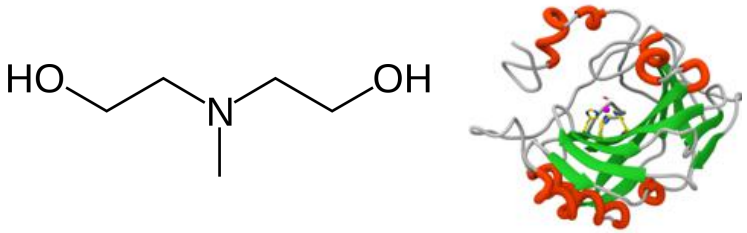
- was first discovered in vertebrate erythrocytes in the 1930s
- can be found in many organisms (humans, animals, bacteria…)
- is one of the fastest enzymes in nature (turnover up to 10^7 s^{-1})

Chemo-enzymatic CO_2 capture



Reduce energy cost up to 25%

Tertiary-amine based solvent + Carbonic anhydrase (CA)



Predominant reactions:

$CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3$ **(bicarbonate)**

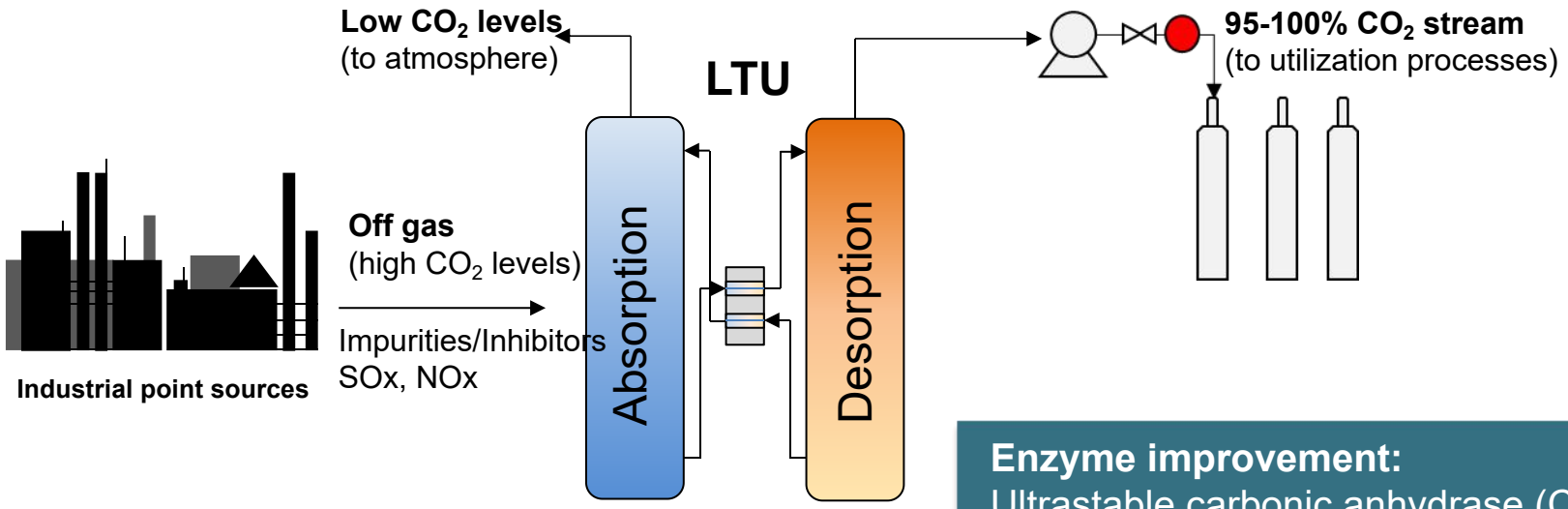
$CO_2 + H_2O \leftrightarrow H^+ + HCO_3$ **(bicarbonate)**

Challenges to overcome

Compatibility of enzymes with operating conditions:

- **Thermal stability:** introduction of free enzymes in the absorption (40-60^{o}C) and if possible stripping column (80-110^{o}C).
  Most known available CAs are mesophilic
- **Solvent stability:** enzymes need to be incubated with amines, novel solvents with good enzyme compatibility is desired
- **Inhibitor stability:** flue gas with impurities (NOx, SOx) is used in reality that can have inhibitory action
- **Cost effectiveness:** enzyme production is expensive, we need to reuse them, thus immobilization is often a requirement

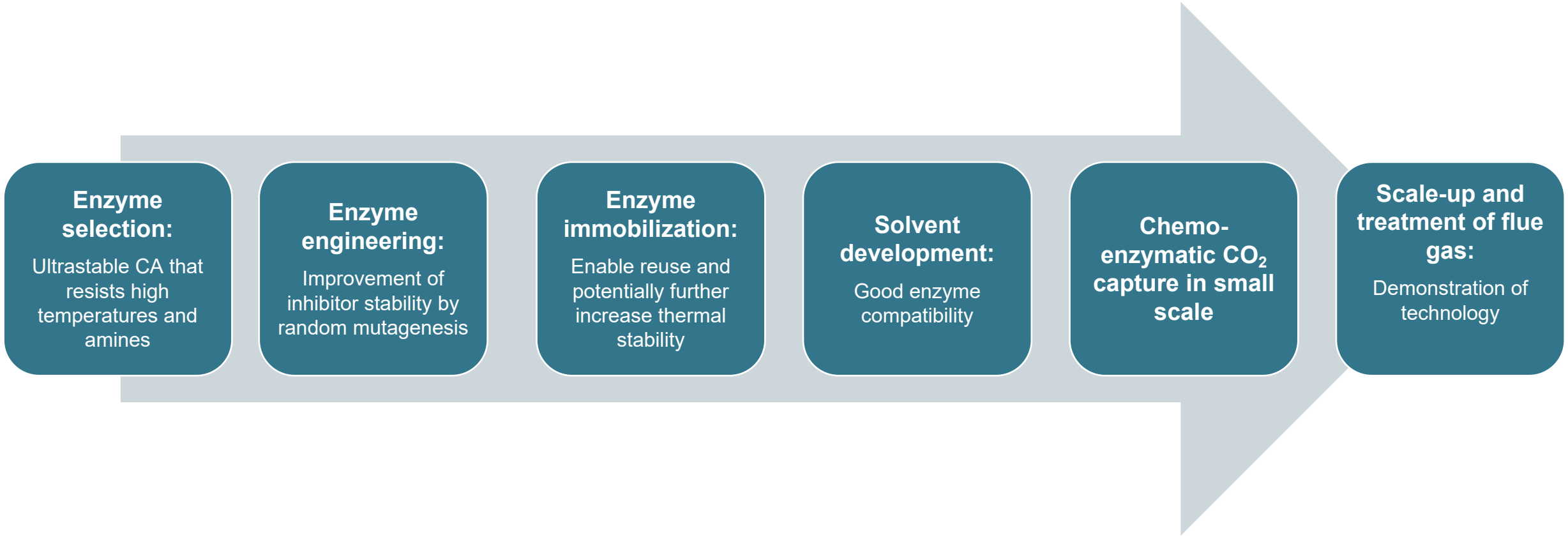
General concept



Enzyme improvement:
Ultrastable carbonic anhydrase (CA) from *Desulfovibrio vulgaris* (DvCA8.0)

Solvent development:
Novel hybrid aminoacid ionic liquid (AAIL): amine blend (5% PEHAp 25%MDEA)

Stages in technology development



Enzyme selection

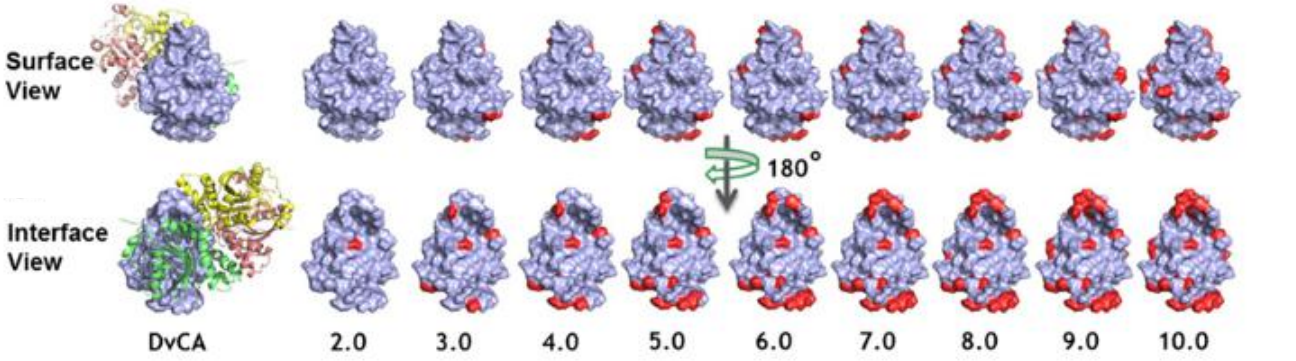
Ultrastable CA variant from *Desulfovibrio vulgaris* (DvCA8.0)

Enzyme engineering method:
saturation mutagenesis/combinatorial

Enzyme properties:

- tolerate temperatures of **up to 107 °C** in the presence of 4.2 M alkaline amine solvent at pH >10.0
- the evolved catalyst enhanced the rate of CO_2 absorption **25-fold compared** with the noncatalyzed reaction

Variant	Position: 56 30 40 84 120 139 37 68 95 119 145 213 219 31 43 70 124 148 157 170 44 129 144 49 126 196 136 174 195 89 96 100 121 181 207 216	pI_{calc}	T_{50} (°C)	Wild-Type Identity
DvCA	A T A A G T K E A Q N N A R Q V H H V M H M S Y S D P P D G D V A A M S	6.72	44.5	100.0%
DvCA2.0	S T A A G T K E A Q N N A R Q V H H V M H M S Y S D P P D G D V A A M S	6.72	49.3	99.6%
DvCA3.0	S R L Q R M K E A Q N N A R Q V H H V M H M S Y S D P P D G D V A A M S	7.84	61.3	97.3%
DvCA4.0	S R L Q R M R A V M W E T R Q V H H V M H M S Y S D P P D G D V A A M S	7.85	68.8	94.2%
DvCA5.0	S R L Q R M R A V M F E T P M I R T A F H M S Y S D P P D G D V A A M S	7.79	79.9	91.0%
DvCA6.0	S R L Q R M R A V M C E T P M I R T A F L F R Y S D P P D G D V A A M S	8.55	85.5	89.7%
DvCA7.0	S R L Q R M R Q V M C E T P M I R T A F L F R F N D P P D G D V A A M S	8.59	87.6	88.8%
DvCA8.0	S R L Q R M R Q V M C E T P M I R T A F L F R F N S P P D G D V A A M S	8.95	88.3	88.3%
DvCA9.0	S R L Q R M R Q V M C E T P M I R T A F L F R F N D R E A G D V A A M S	8.95	88.8	87.0%
DvCA10.0	S R L Q R M R Q V M C E T P M I R I A F L F R F N D R E A A E T Q K A D	8.94	89.0	83.9%



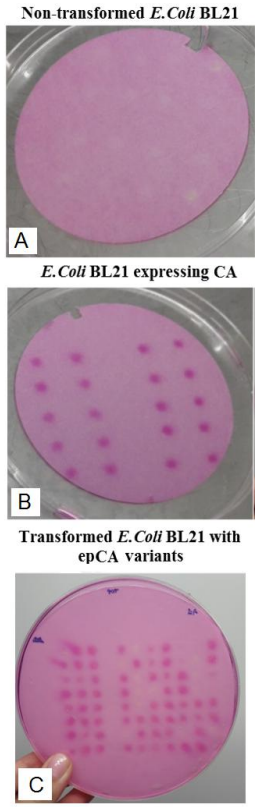
Alvizo et al. (2014) Directed evolution of an ultrastable carbonic anhydrase for highly efficient carbon capture from flue gas. PNAS 111 (46) 16436-16441

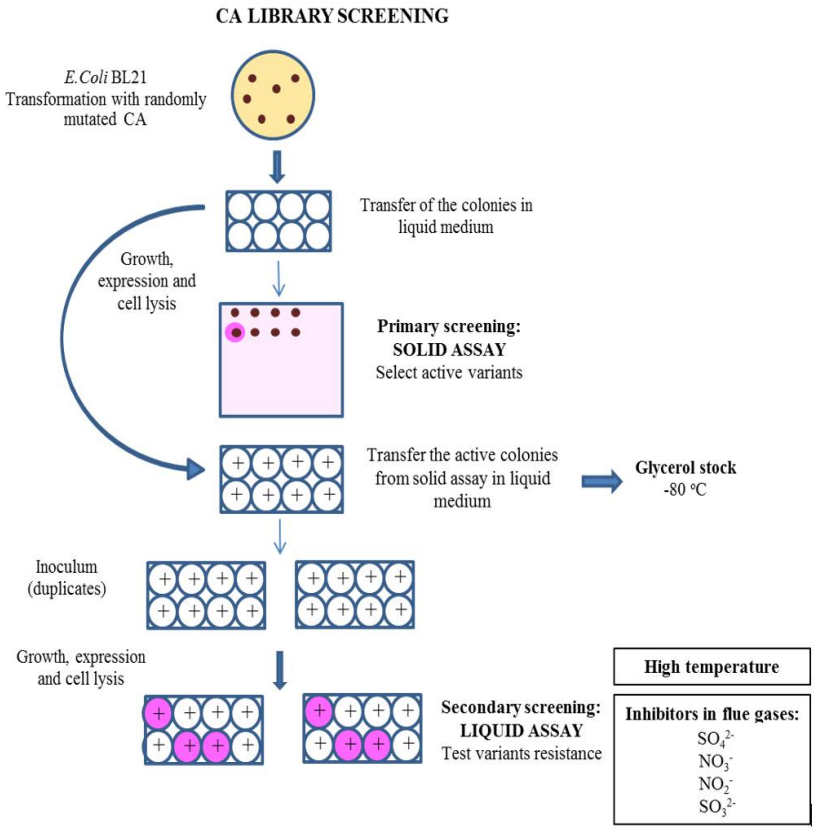
Enzyme engineering

Further CA improvement aiming to increase resistance to major gas inhibitors:

Library construction:
1000 epCA variants generated with error-prone PCR
Library screening:
-Primary screening to select active variants
-Secondary screening to select variants with resistance to inhibitors
Scaled-up production of most promising variants
Sequencing for identification of mutations

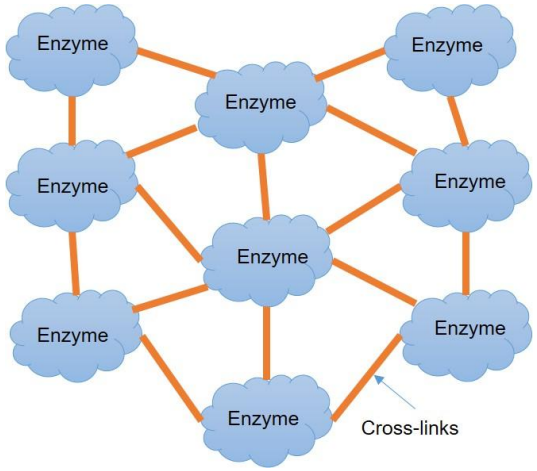
- **3 mutants showed 50% resistance increase to flue gas inhibitors (mix of NO_2^-,NO_3^-,SO_3^{-2},SO_4^{-2})**



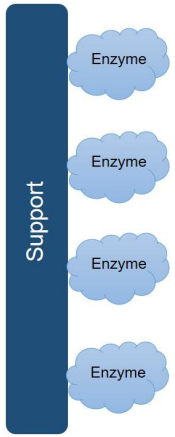


Enzyme immobilization

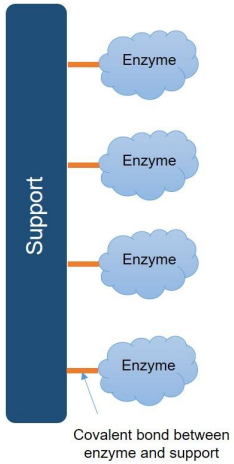
Cross-linked aggregates (CLEAs)



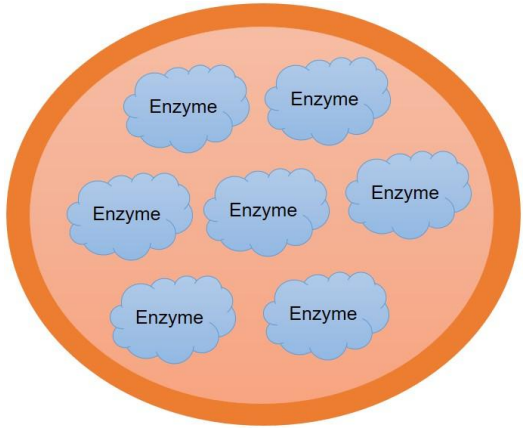
Adsorption



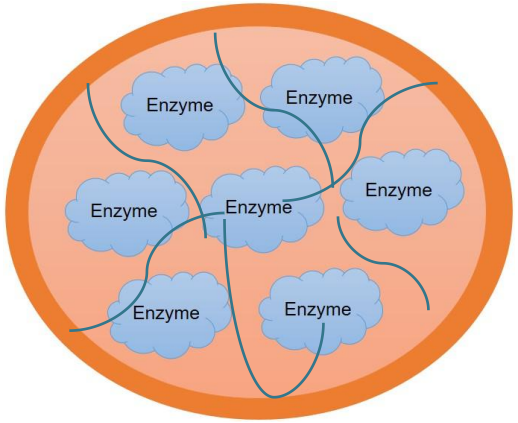
Covalent bonding



Encapsulation



Entrapment



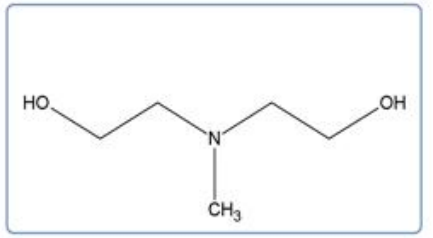
Up to 90% residual enzyme activity after immobilization but…

Few immobilized forms showed good activity in CO_2 capture integrated with amines

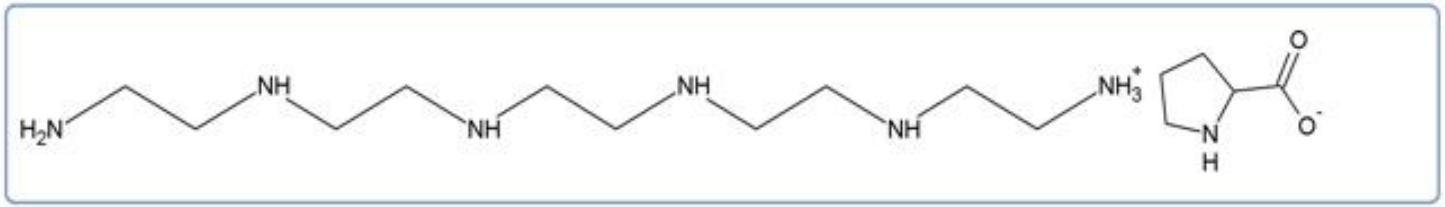
Solvent development

Novel hybrid solvent:
aminoacid ionic liquid (AAIL):
amine blend (PEHAp: MDEA)

MDEA

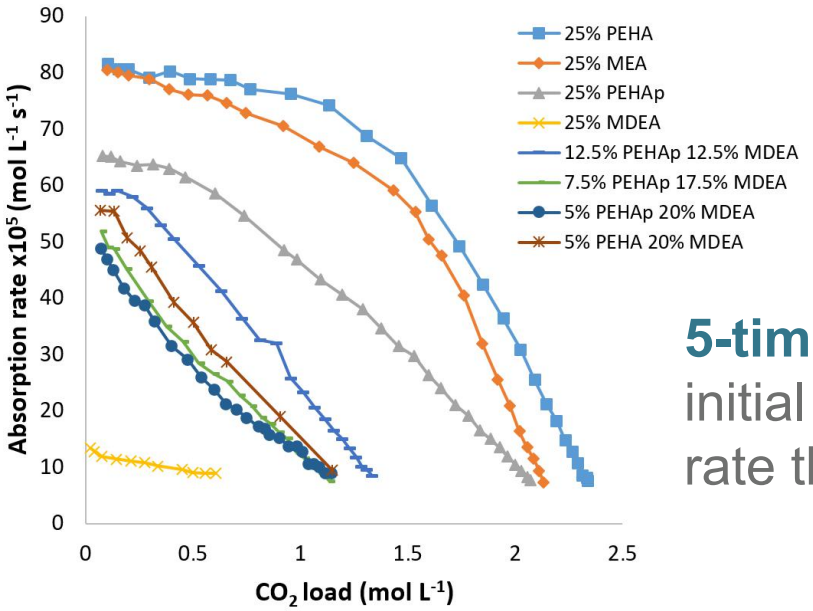


Pentaethylenehexamine prolinate (PEHAp)



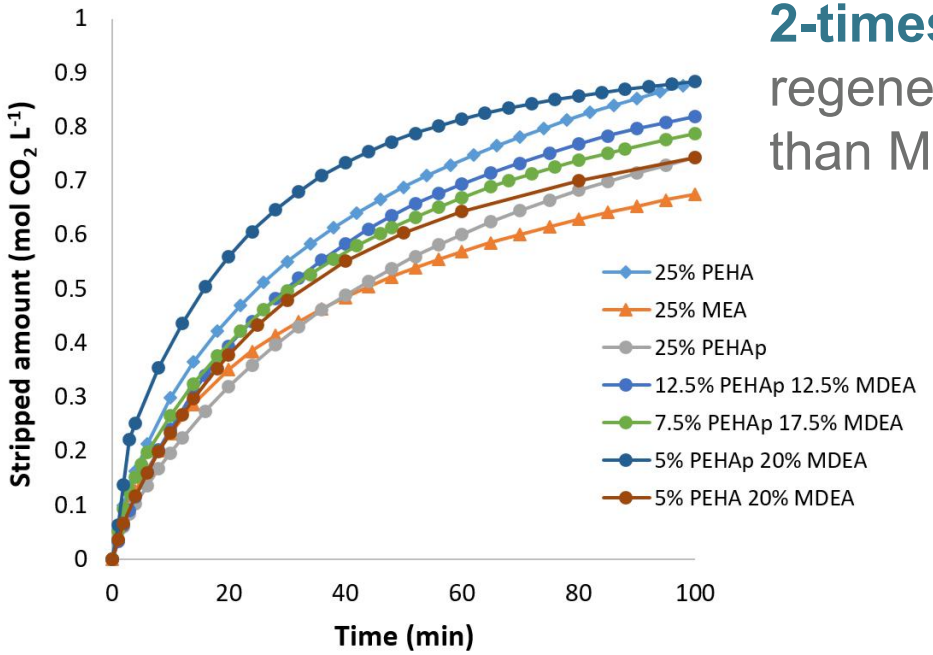
Solvent development

CO_2 absorption (40°C)



5-times higher initial absorption rate than MDEA

CO_2 desorption (80°C)



2-times higher regeneration than MEA

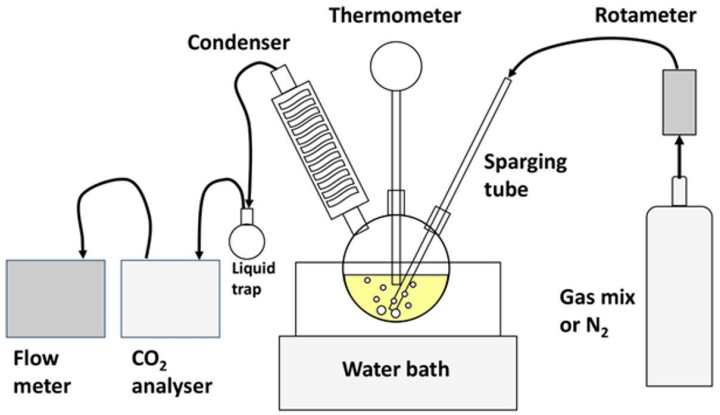
Sjöblom et al. (2020) Enzyme-assisted CO_2 absorption in aqueous amino acid ionic liquid amine blends. ACS Sustainable Chemistry and Engineering, 8(36), 13672-13682

Best hybrid: 5% PEHAp: 20% MDEA

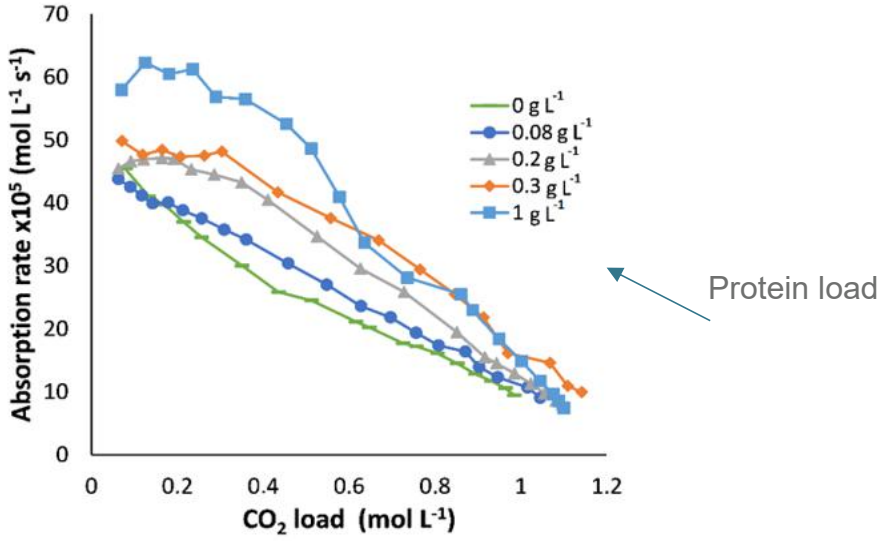
Chemo-enzymatic CO_2 capture in small scale

Integrated approach:
5% PEHAp 20% MDEA+CA

Small-scale reaction: 100 mL



CO_2 absorption (40°C)



31.7% further increase in the mass of absorbed CO_2 compared to the noncatalyzed reaction

Sjöblom et al. (2020) Enzyme-assisted CO_2 absorption in aqueous amino acid ionic liquid amine blends. ACS Sustainable Chemistry and Engineering, 8(36), 13672-13682

Chemo-enzymatic CO_2 capture in small scale

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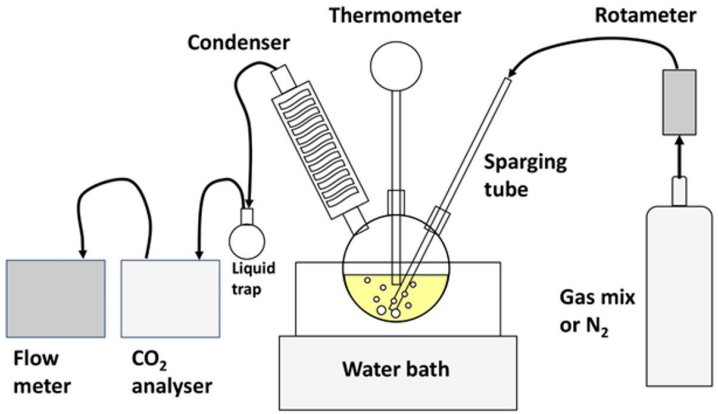


Sjöblom et al. (2020) Enzyme-assisted CO_2 absorption in aqueous amino acid ionic liquid amine blends. ACS Sustainable Chemistry and Engineering, 8(36), 13672-13682

CO_2 desorption (80°C)

Solvent	Solvent regeneration (%)
25% MEA	35.4
5% PEHAp 20% MDEA	81.1
5% PEHAp 20% MDEA+ CA	83.0

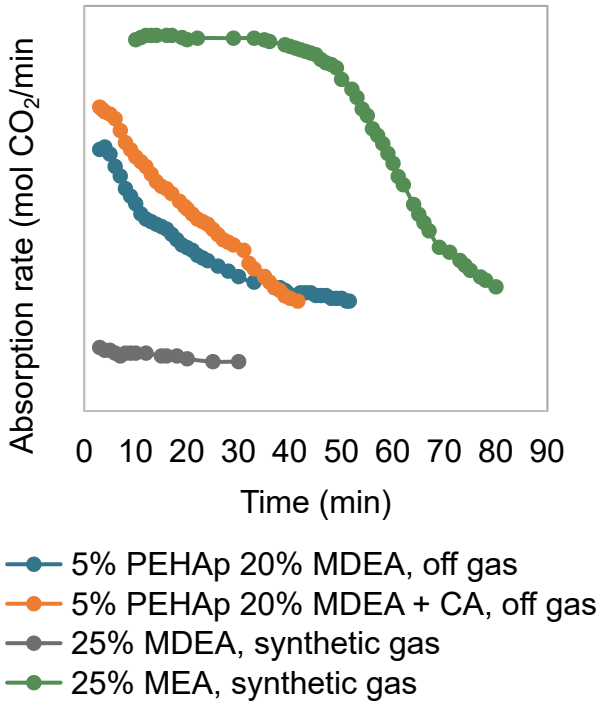
No difference in desorbed mass of CO_2 after CA addition in the novel hybrid solvent

Scale-up and treatment of industrial flue gas

CO_2 capture using a packed column (1 m)
Up to 100 L solvent capacity

A) CHE626 Automated Absorption and Stripping Pilot Plant and B) CH906 Hot Water Generator (HFT Global Ltd, Derbyshire, UK) at LTU.

CO_2 absorption (40°C)



Initial absorption rate:

- **5 times higher** than **MDEA**
- **82%** of that of **MEA**

Achievements and future goals

We aimed to:

- Combine **enzymatic absorption** with **ionic liquid-amine blends**
- **Reduce energy and cost** of CO_2 capture **up to 25%**
- Increase process impurity resistance
- Provide **a 95% yield** concentrated CO_2 gas stream

Future goals:

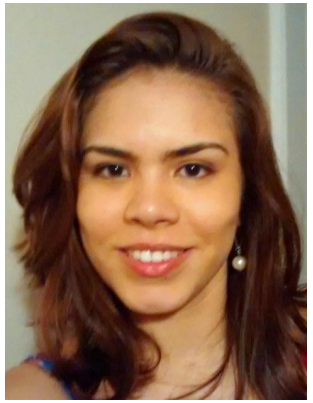
- Expand our enzyme portfolio and further investigate integration between conventional and sustainable technologies for a carbon neutral future

Acknowledgments

The LTU team:

Prof. Paul Christakopoulos

Prof. Ulrika Rova



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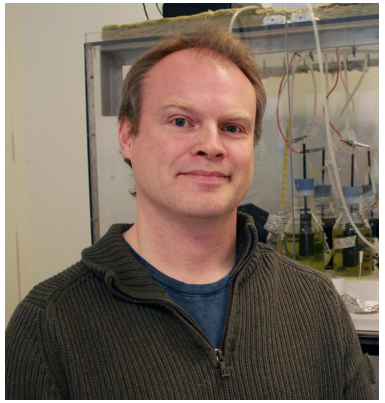

Dr. Magnus Sjöblom

Dr. Simona Varriale

Thank you for your attention!

Horizon 2020
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