BioRECO2VER

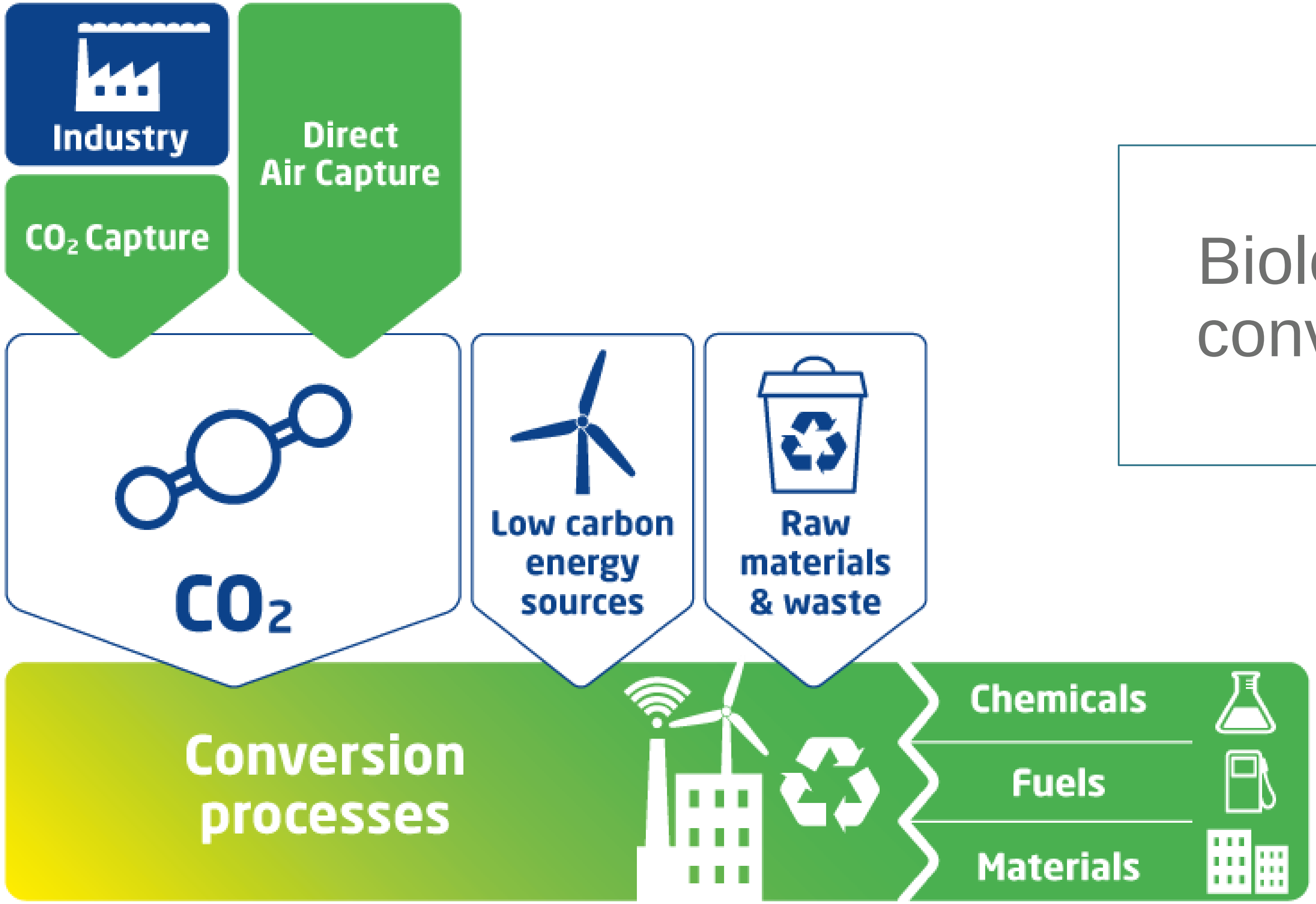
$eCO_2nference$, PKN Orlen

Heleen De Wever and project partners, 7 October 2021

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.

Carbon Capture and Utilization



BioRECO$_2$VER:
Biological routes for CO_2 conversion into chemical building blocks

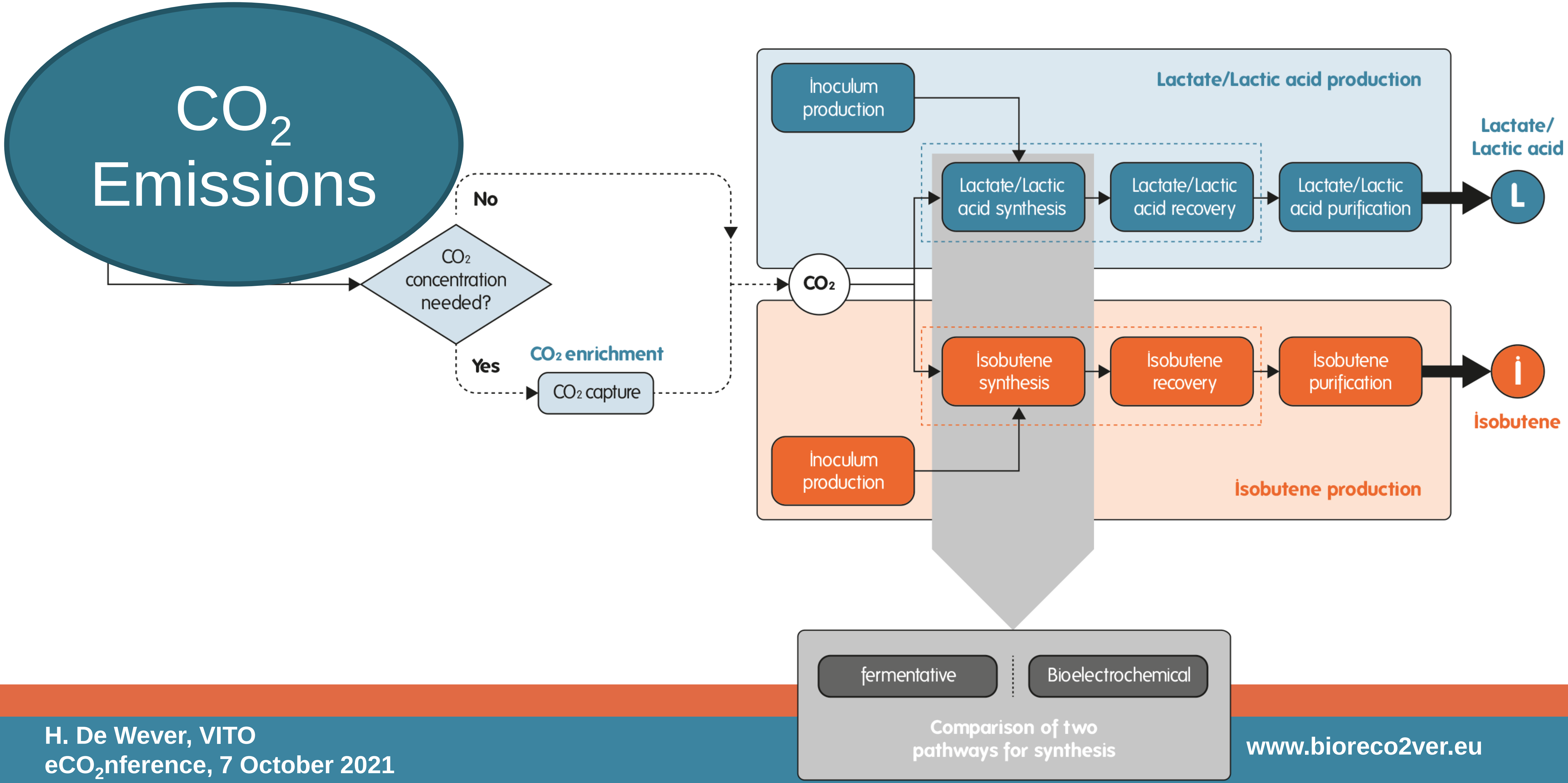
Source: https://www.co2value.eu/ccu/

Why biotechnology?

Chemocatalysis	Biotechnology
(Precious) Metal catalysts – Replacement/recycling	Whole cell catalysts - Self reproducing
Reactions at high temperatures and pressures	Reaction at milder/ambient conditions (safety, sustainability)
Broader range of optimal conditions	
Low specificity/selectivity of the catalysts	High specificity/selectivity
Usually C1 chemicals	Also more complex molecules
Gas phase reaction	Aqueous media
High conversion rates	Low productivity / turnover rates
Product concentration high	Products in dilute (aqueous) stream (and sensitive to product toxicity)
Low tolerance to contaminants or variations gas composition → gas pre-treatment/conditioning	High tolerance for gas impurities and variations in gas composition

Sources: Lee et al. (2019), Köpke and Simpson (2020), Refai (2021)

Overall project concept



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ORLEN

Emission data and sectoral information
Refinery & Petrochemistry

1 million tonne of crude oil

CO_2	0,1 – 0,4 million t

VOC	50 – 1000 t
SO_2	30 - 1500 t
NO_x	60 - 500 t
CO	20 - 400 t
PM	4 – 75 t
BTX	1 - 70 t

Benzene	5 – 8000 kg
Lead	1 – 1000 kg
Nickel	3 – 1300 kg
Vanadium	1 – 1000 kg

Amount of main air pollutants from 1 million tonne of treated crude oil

- Multiple sources CO_2
- Emissions mainly connected with **energy production** for refining processes (**heaters, furnaces, gas turbines** etc. **≈60%** of emissions)

Main sources of CO_2 emissions in refineries:
(depend on complexity of production plant)

- **crude distillation unit (CDU)**
- **hydrogen production unit**
- **fluid catalytic cracking (FCC)**

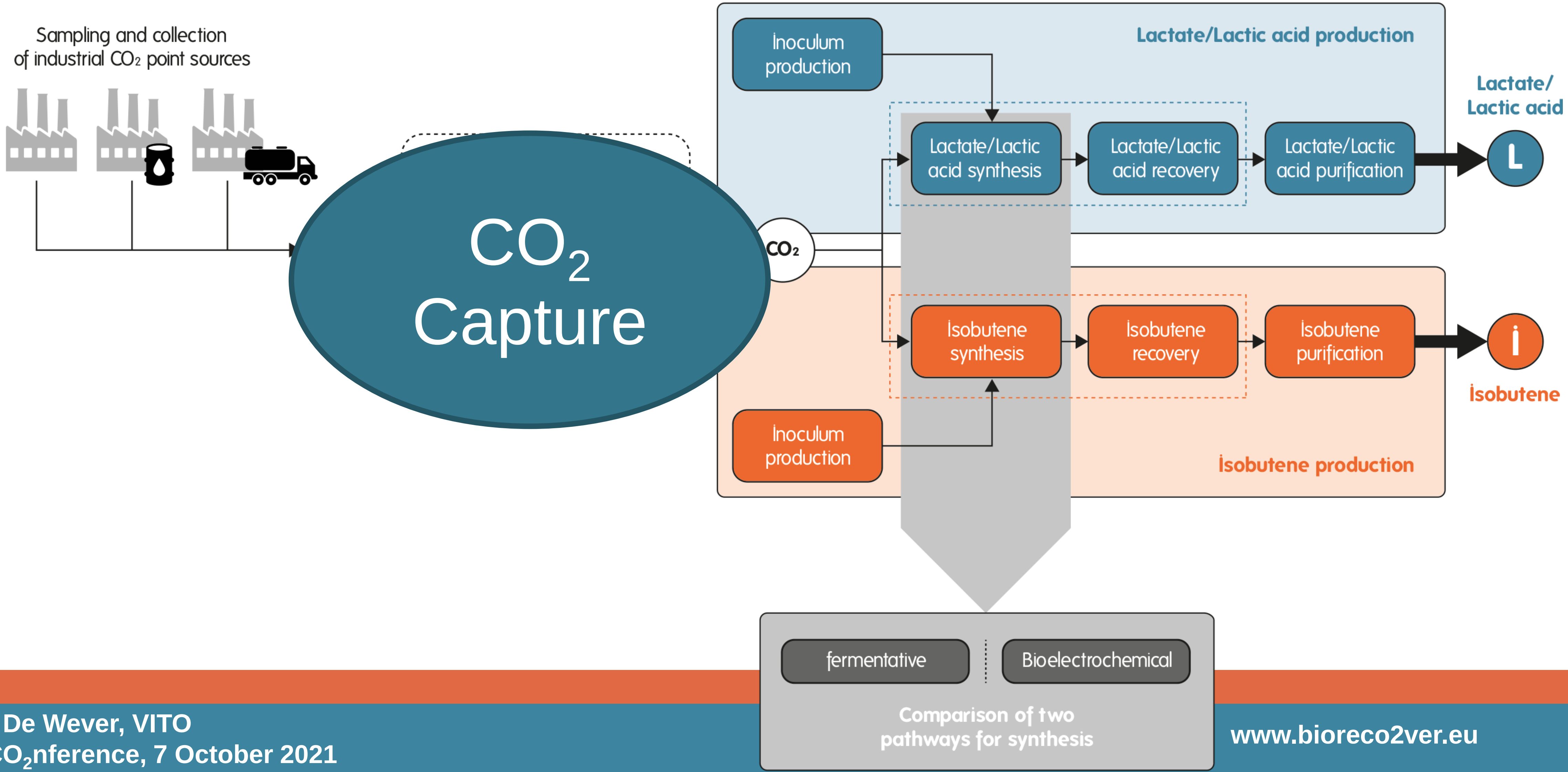
Sources:
The potential for application of CO_2 capture and storage in EU oil refineries, CONCAWE report no. 7/11
Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas.

Issues with emission sampling

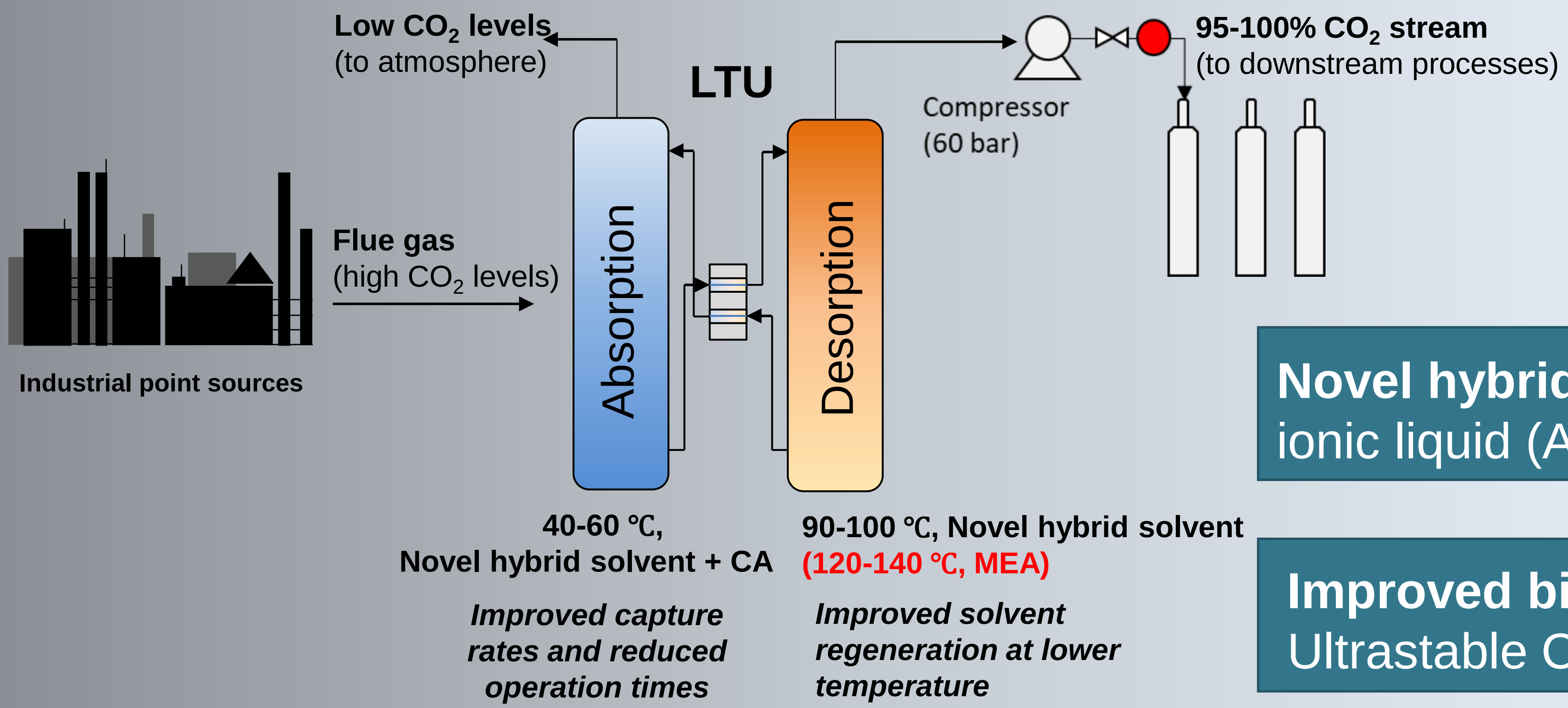
Sampling of gas stream from Refinery&Petrochemistry complex (Poland)

- CO_2 content
- O_2 vs. anaerobic microbial platforms
- Potentially explosive zone
- Uncertainty of composition (long-term storage in bottles and stream fluctuation)

Overall project concept



CO_2 capture: novel hybrid 3-component mixture



Novel hybrid solvent: Aminoacid ionic liquid (AAIL): amine blend

Improved biocatalyst: Ultrastable Carbonic Anhydrase (CA)

$$(R_1R_2R_3)N + AAIL + CO_2 \underset{}{\overset{CA}{\rightleftarrows}} (R_1R_2R_3)NH^+ + AAIL\text{-}carbamate + HCO_3^-$$

MEA: Monoethanolamine

Enzyme improvement by directed evolution

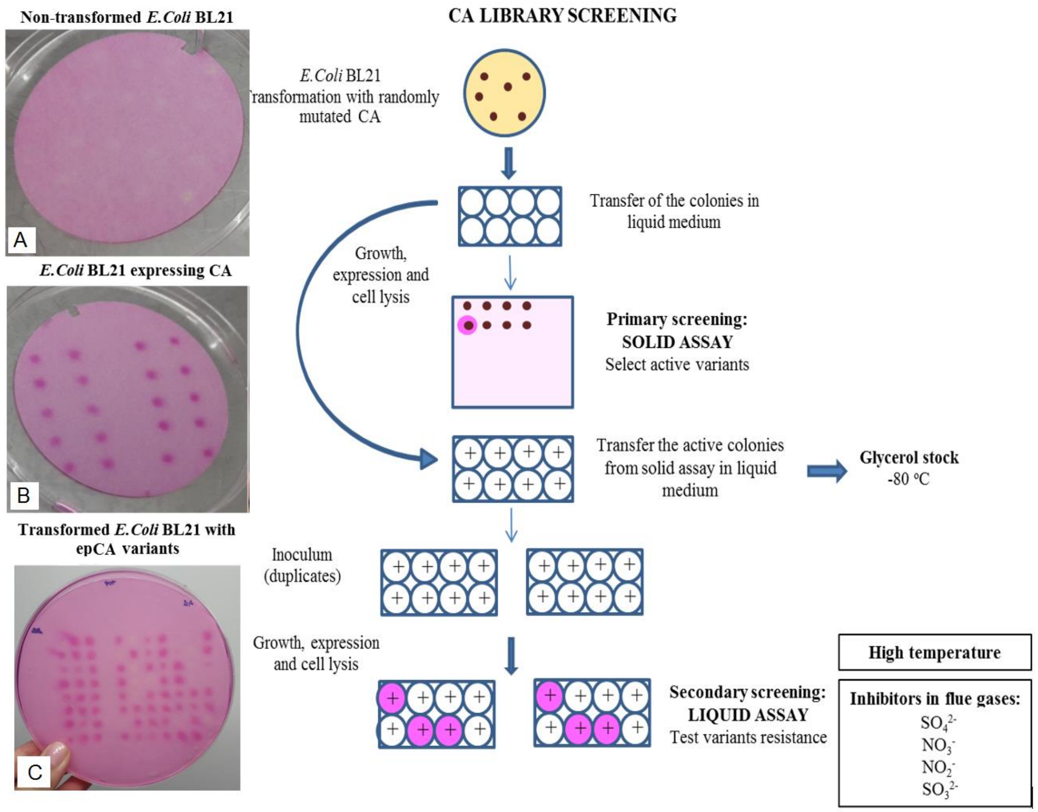
Library construction

Library screening

Scaled-up production of most promising variants

Sequencing for identification of mutations

- **3 mutants showed 50% increased resistance to flue gas inhibitors**

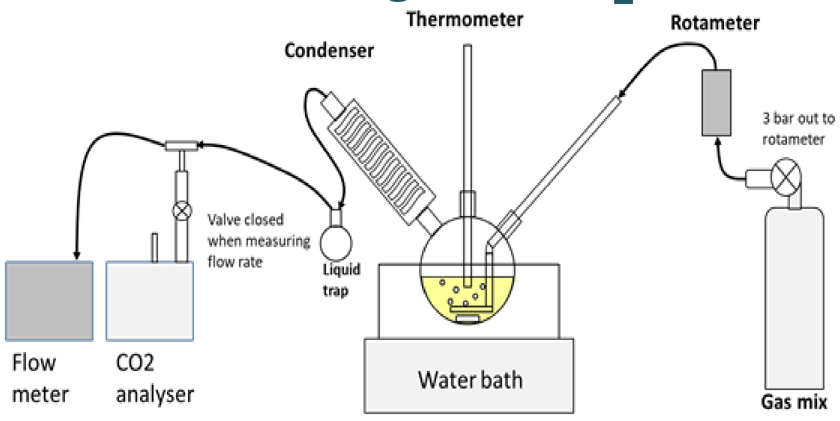


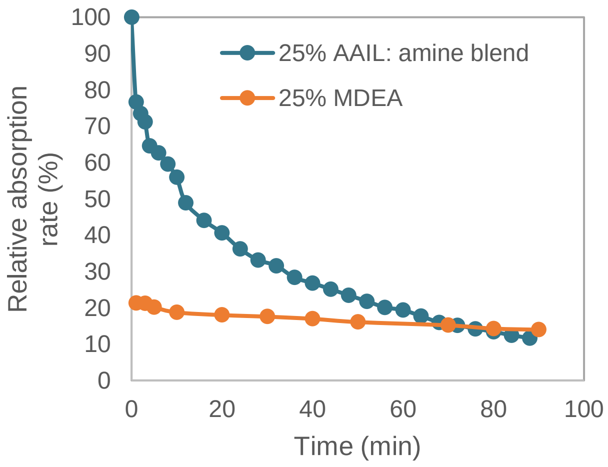
Novel hybrid solvent with competitive absorption and desorption properties

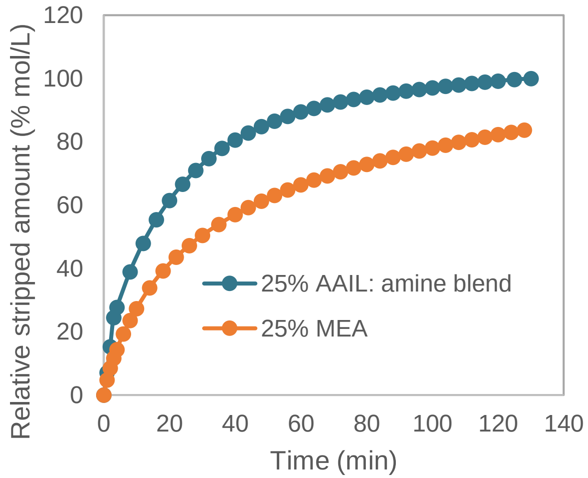
Screening of different AAIL:tertiary amine blends resulted in selection of solvent with

- **5-fold higher initial absorption rate**
- **2-fold higher CO_2 load compared to MDEA**

- **2-fold higher regeneration at 80ºC**
- **>15% reduction in desorption T compared to MEA**







MDEA: Methyl diethanolamine; MEA: Monoethanolamine

CO_2 capture in large-scale packed bed absorption equipment

Scaled-up trials revealed even higher benefit with use of developed solvent blend

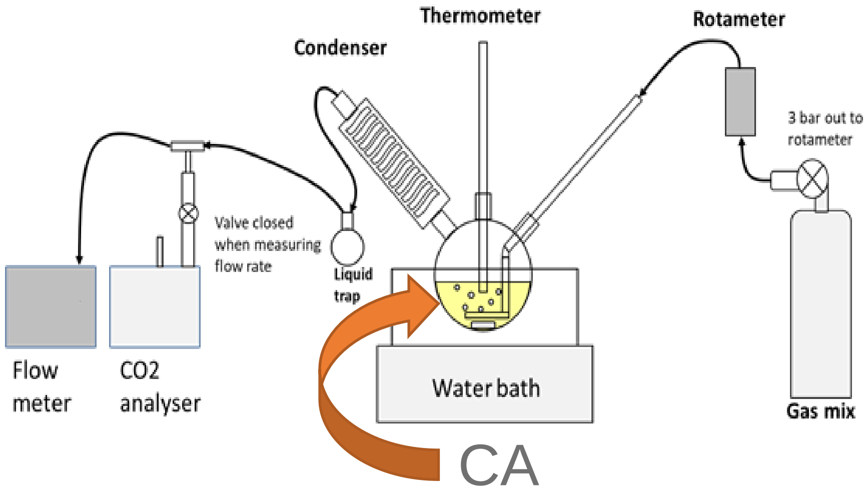
Solvent	Relative K_Ga (%)
25% MEA	100
25% MDEA	3
25% AAIL: amine blend	31

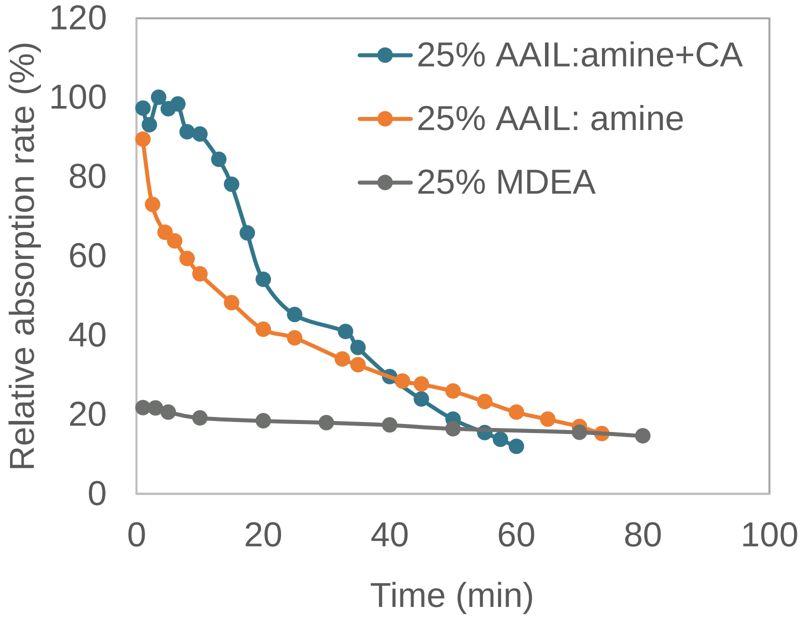
- **10-fold increase in mass transfer coefficient (K_GA) compared to MDEA**


1m (80mm ID) packed column (Raschig rings)

MDEA: Methyl diethanolamine; MEA: Monoethanolamine

Integration of Carbonic Anhydrase enzyme with novel hybrid solvent for efficient CO_2 capture



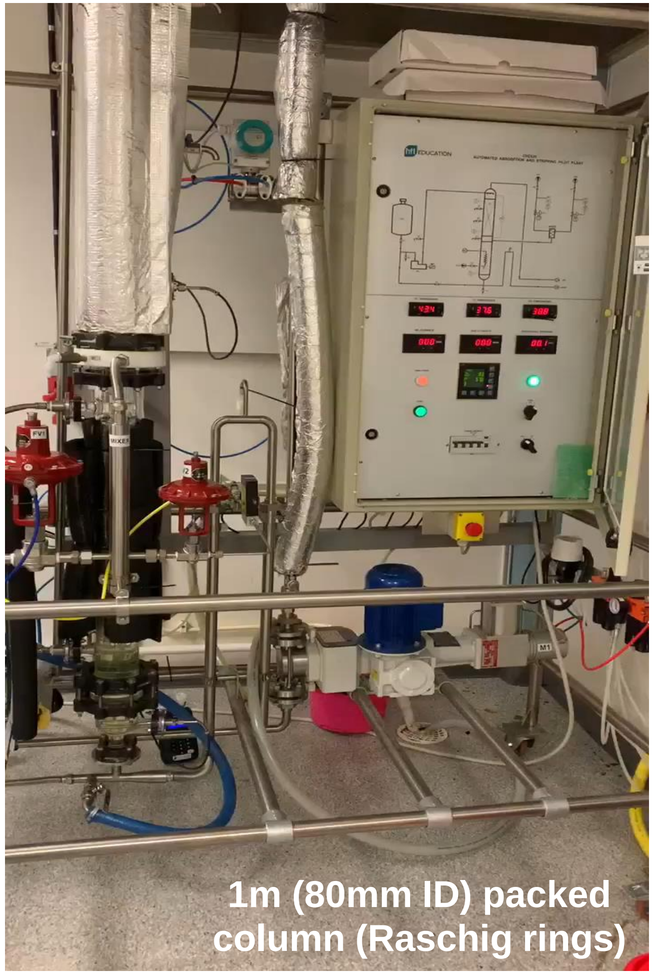


- **Reduced operation times by 25%**
- **32% increase in captured CO_2 compared to non-enzymatic reaction**

MDEA: Methyl diethanolamine

Upscaling of CO_2 capture: Experimental set-up for CO_2 absorption and stripping

CHE906-Hot water generator
(HFT Global Ltd, Derbyshire, UK)



CHE626-Automated absorption and stripping pilot plant
(HFT Global Ltd, Derbyshire, UK)

- **17% increase** in CO_2 load adding Carbonic Anhydrase in solvent
- **5 x higher** initial absorption rate than **MDEA**
- **82%** of that of **MEA**

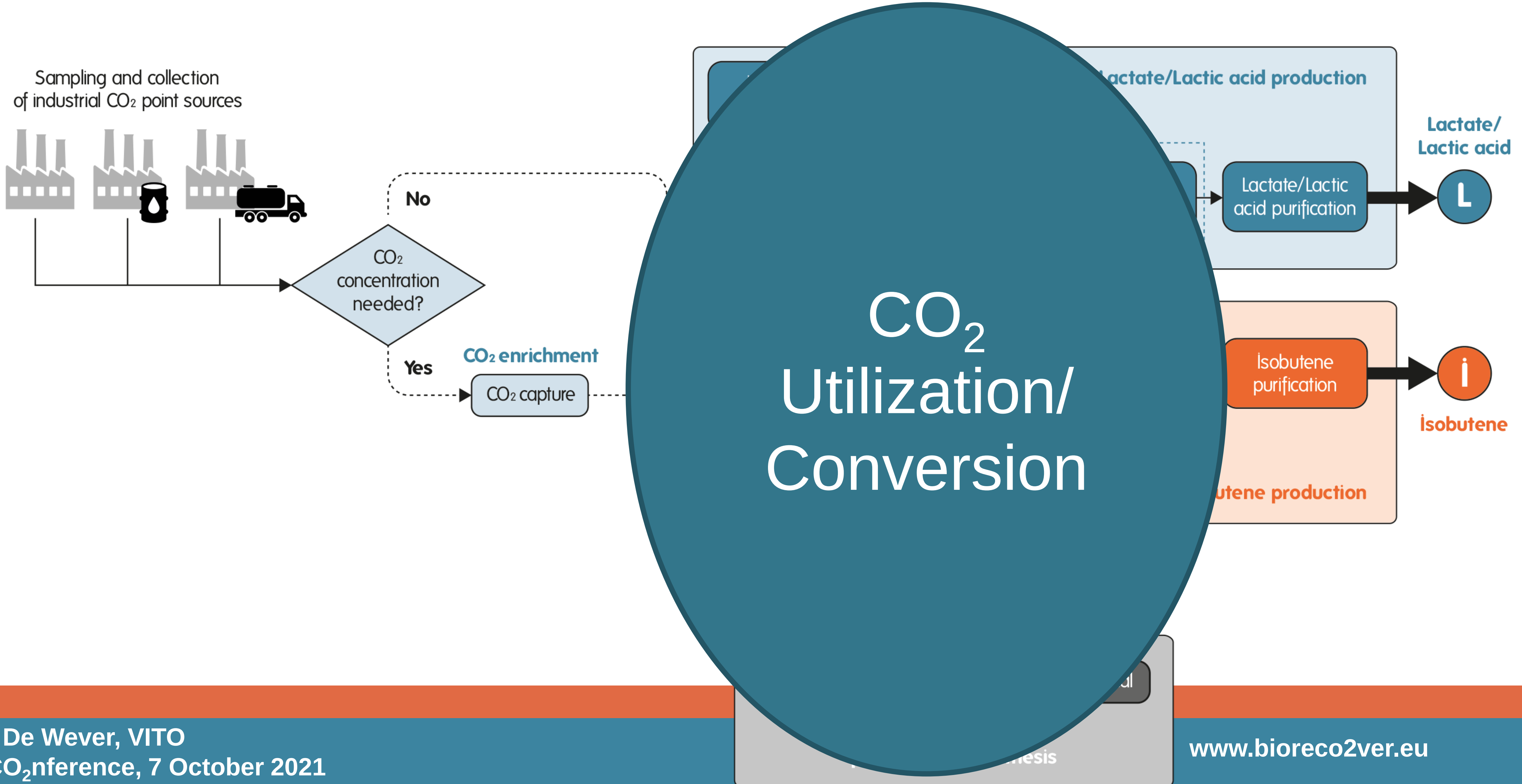
MDEA: Methyl diethanolamine; MEA: Monoethanolamine

CO_2 capture and pretreatment

Conclusions

- An ultrastable Carbonic Anhydrase enzyme was improved by protein engineering (and immobilization) for increasing stability towards harsh and high temperature environment
- An enzyme compatible novel hybrid solvent was developed with competitive absorption and desorption properties
- Large-scale Carbonic Anhydrase-aided CO_2 absorption was demonstrated

Overall project concept

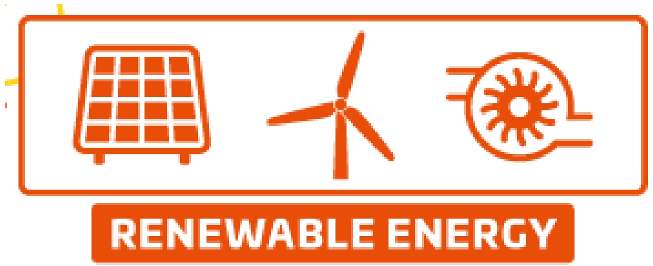


CO_2 conversion: process development

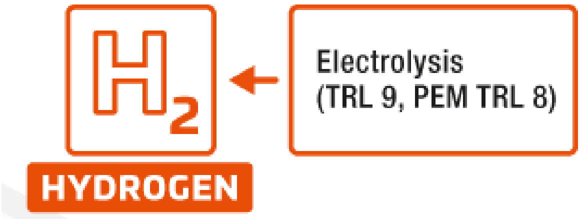
Microbial CO_2 conversion

- **2 technologies**

Bioelectrochemical systems



[High pressure] fermentors

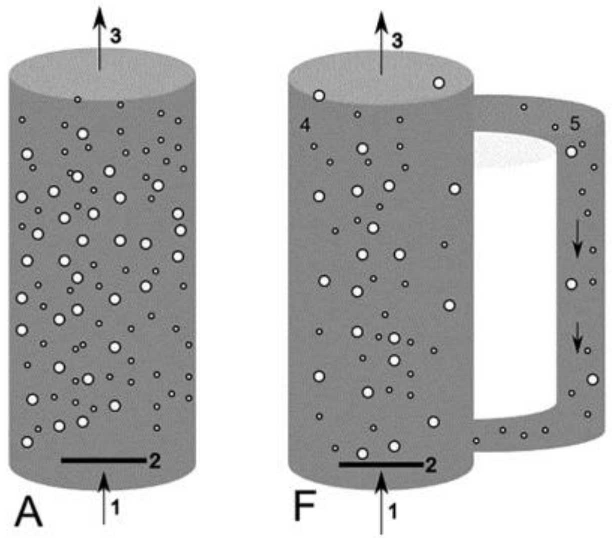


Gas (CO_2, H_2) solubility is low

- Gas-liquid mass transfer rate

$$\frac{dC_{i,L}}{dt} = K_L a_i * (y_i * P_R * H_i - C_{i,L})$$

  - K_L: overall mass transfer coefficient (based on liquid concentrations)
  - *a*: interfacial area between gas and liquid
  - K_L *a:* volumetric gas-to-liquid mass transfer coefficient
  - P_R: (absolute) reactor pressure
  - y_i: mole fraction of compound i in gas phase and
  - $C_{i,L}$: dissolved gas concentration of compound I
  - H_i : Henry's law coefficient for component i



- Can be improved by increase in pressure

Source: Van Hecke et al. (2019)


SIEMENS
MAXUM
edition II
Online GC


Fermentor skid

Operation at elevated pressure (5-10 bar)

Effects on microbial growth and product formation

- Variable threshold (either total pressure or partial pressure of specific substrate) above which microbial growth and metabolism is affected
- Inhibitory effects of increased partial pressure H_2 or of increased dissolved CO_2

Process operation and control

- Feedback control of dissolved gas concentration needed for reactor stability
- Process monitoring and determination of kinetic parameters complicated by lack of dissolved gas sensors (except for O_2) resistant to and accurate at broad P ranges

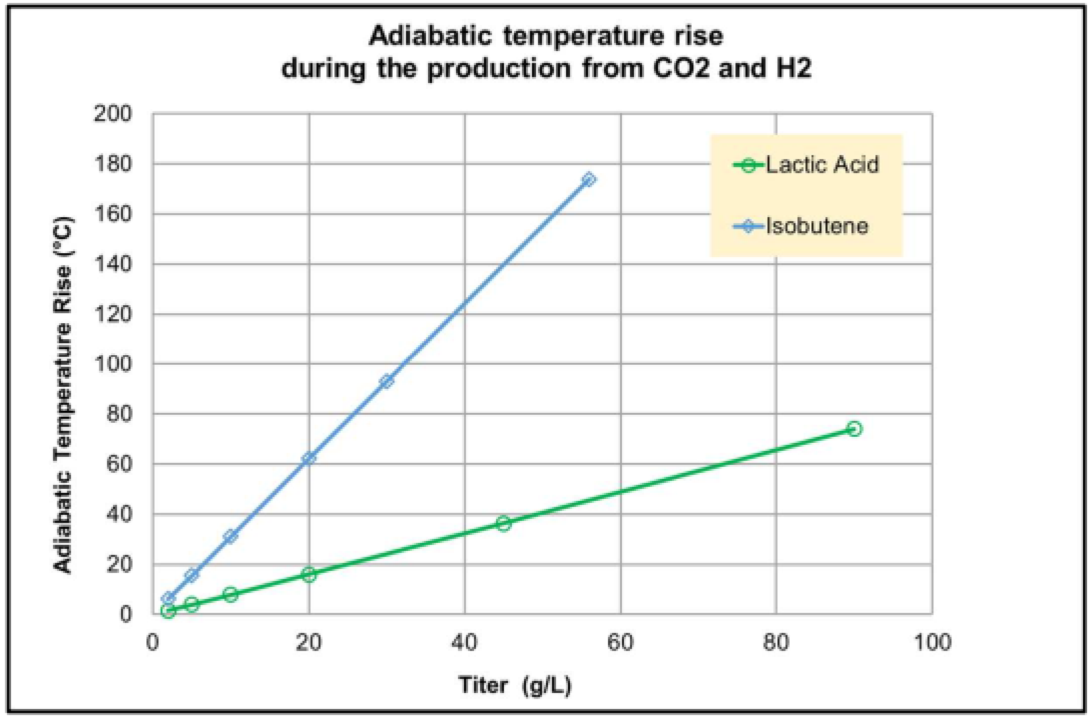
- Fermentations at moderately elevated pressures using C1 gases underexplored

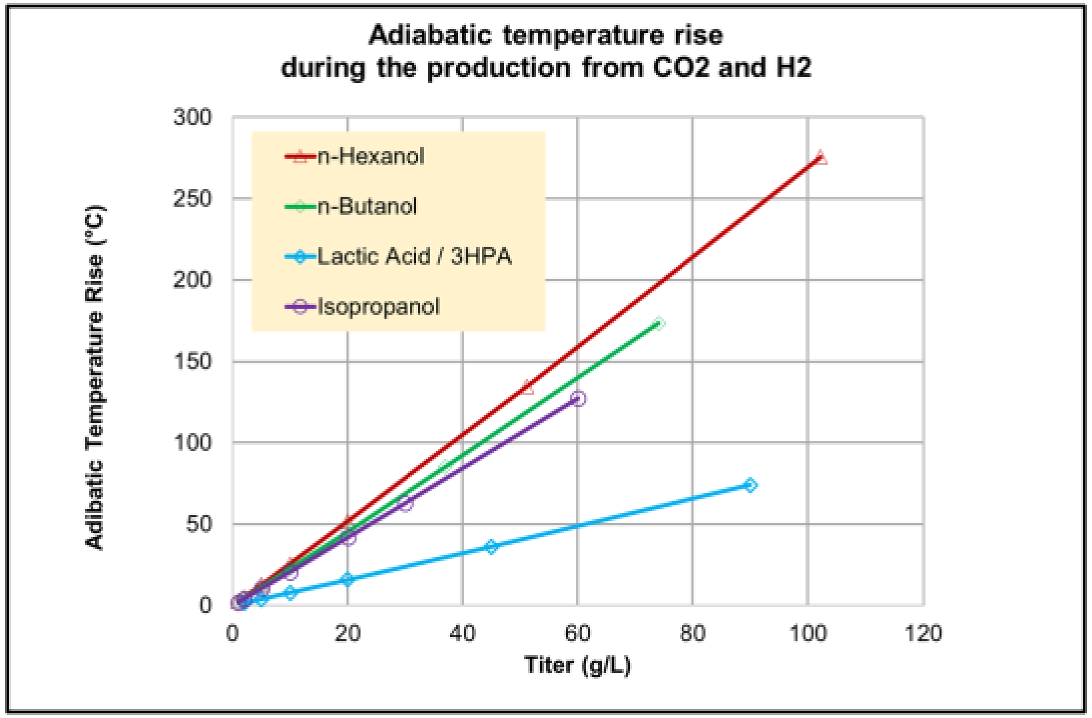
Source: Van Hecke et al. (2019)

Reaction at ambient conditions?

- Titer >10-20 g/L: need for cooling
- Heat losses not detectable at lab-scale, but substantial at industrial scale

- 100 kton lactic acid/yr
  - ≈ energy loss of 93 900 MWh/yr
  - ≈ energy consumption > 14 000 Europeans





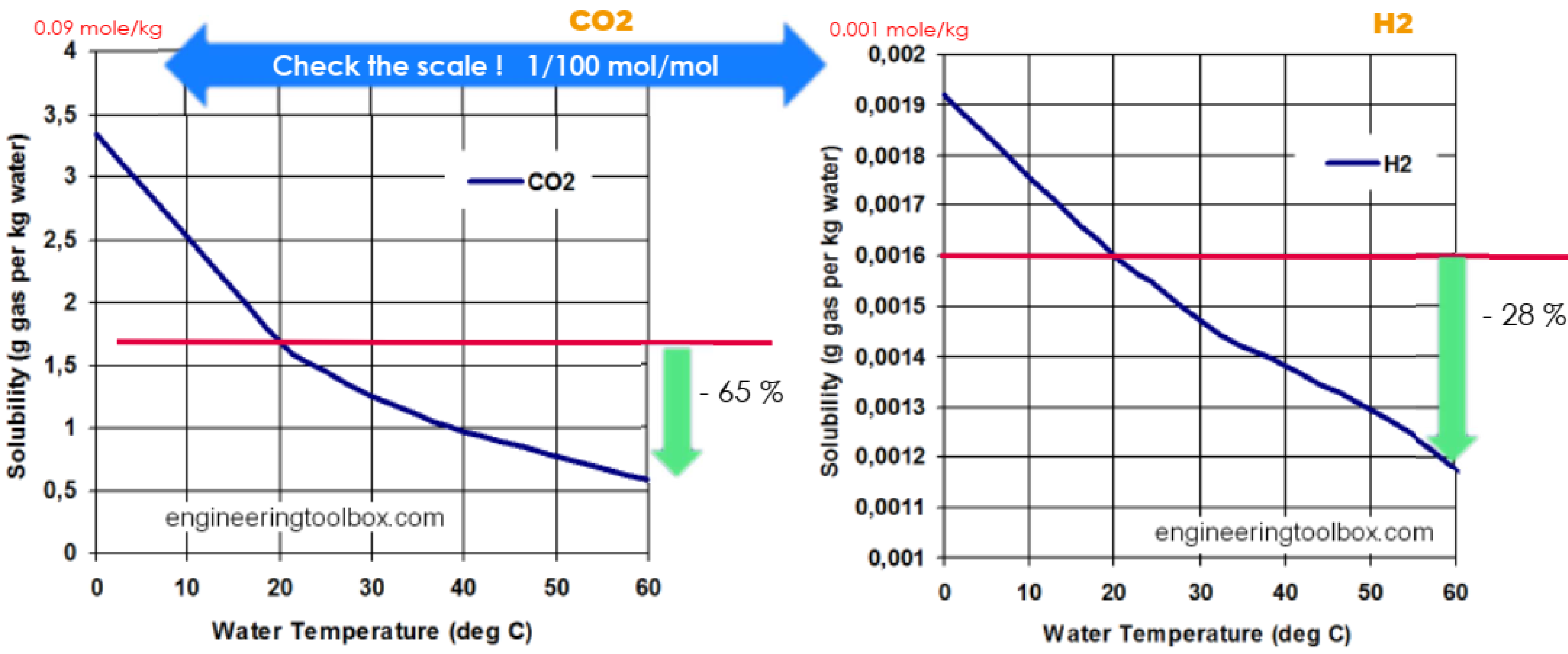
Heat management at (high) product titers

- Process solutions exist but come at a cost
- Lot of heat produced at low temperature: what to do with it?
  - Use for district heating? In greenhouses?

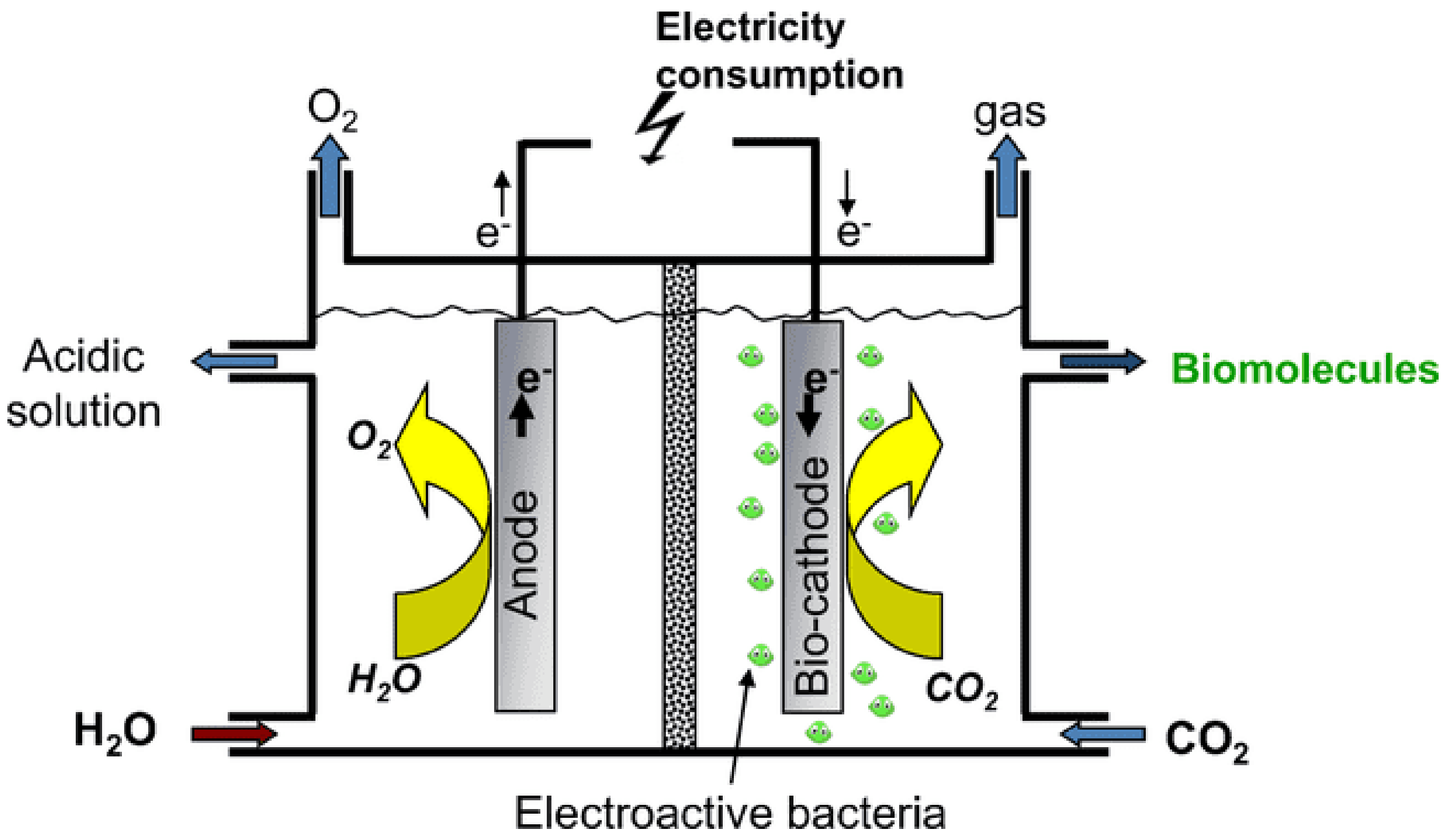
- Operation at higher T preferable for heat valorization

  →(hyper)thermophilic range
- Issue gas solubility

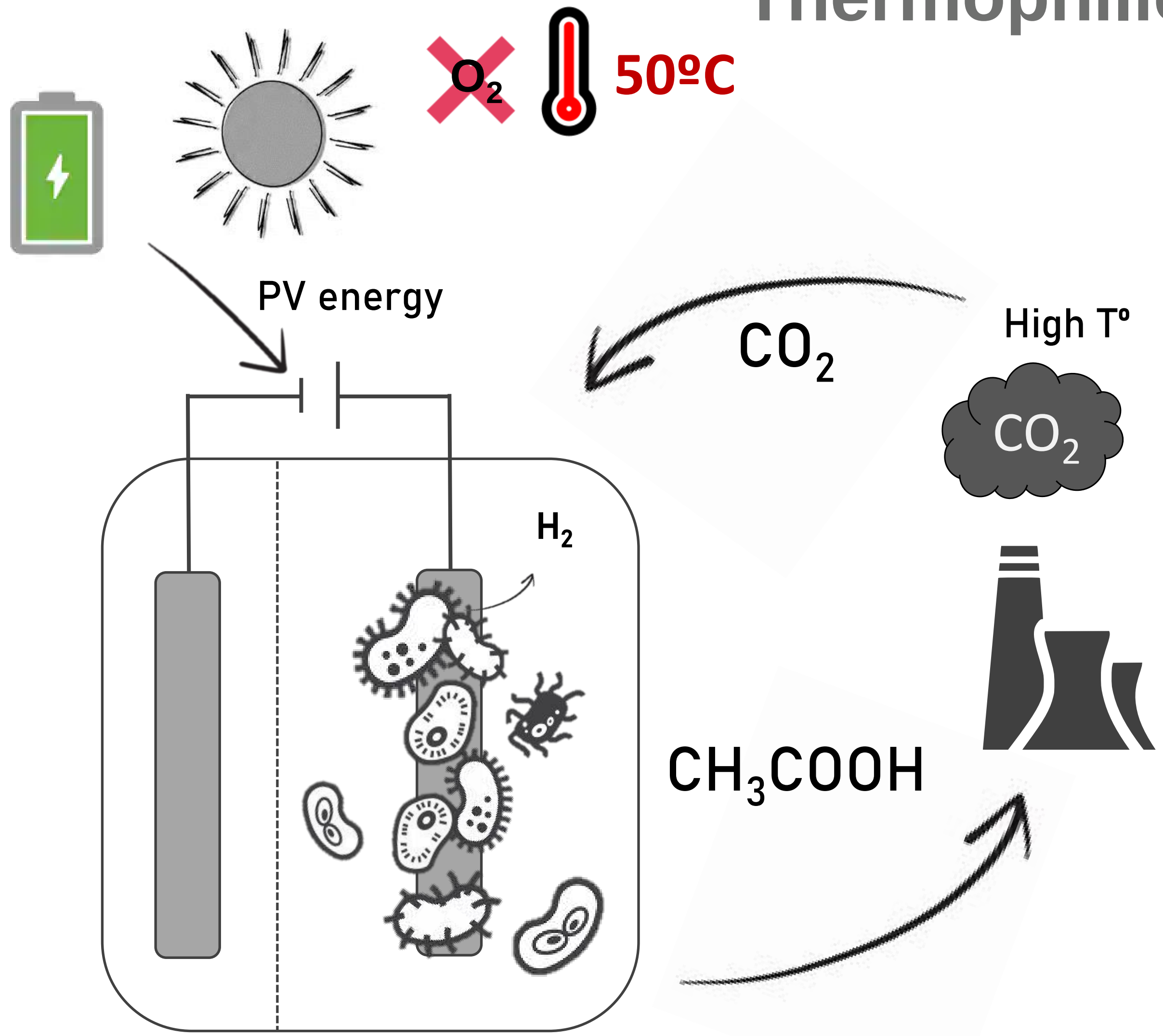
(source: Engineeringtoolbox.com)



Bioelectrochemistry

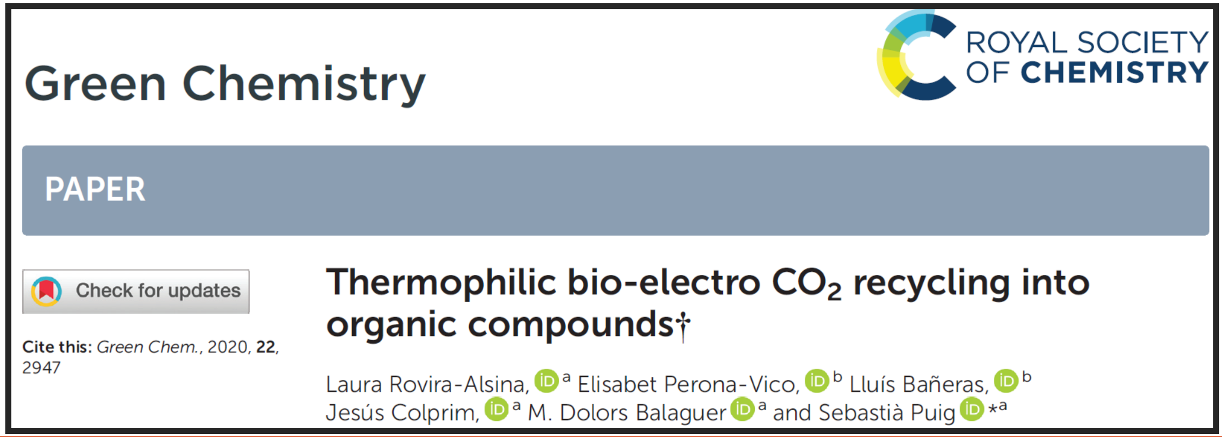


Thermophilic process



Thermophilic Microbial Electrolysis Cell

- Higher reaction rates
- Less risk of contamination
- More product specificity
- Heat management



Green Chemistry

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PAPER

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Cite this: *Green Chem.*, 2020, **22**, 2947

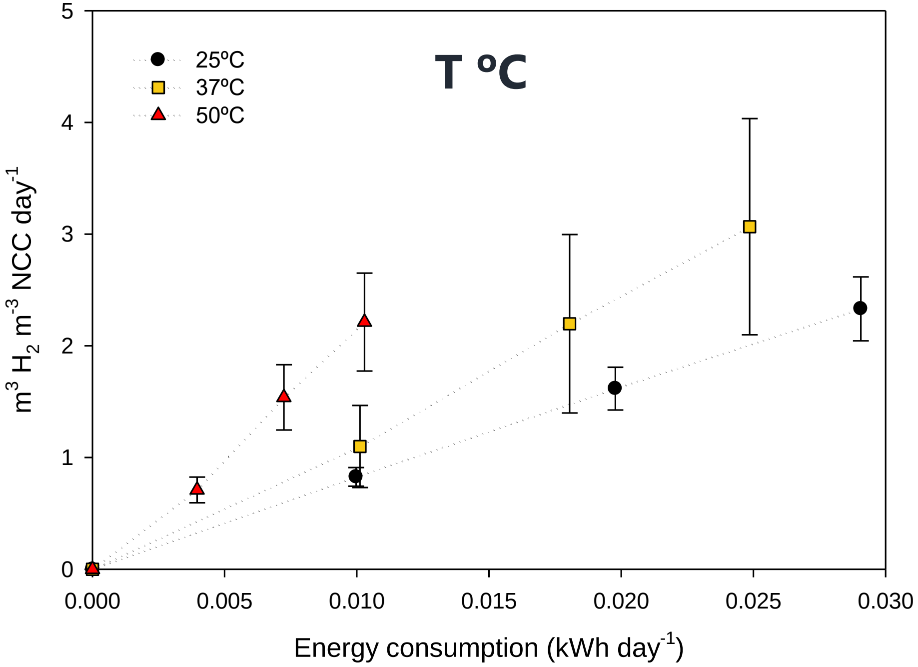
Thermophilic bio-electro CO_2 recycling into organic compounds†

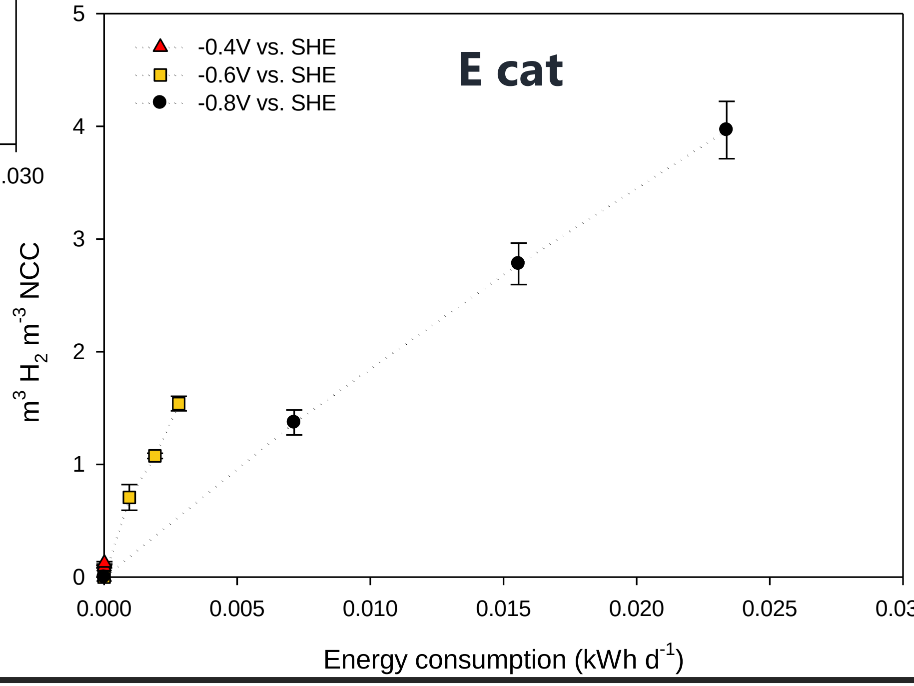
Laura Rovira-Alsina, [a] Elisabet Perona-Vico, [b] Lluís Bañeras, [b] Jesús Colprim, [a] M. Dolors Balaguer [a] and Sebastià Puig *[a]

Pre-characterization

Abiotic H_2 production

T (ºC)	E_{cat} (V vs. SHE)
25	-0.8
37	
50	
	-0.6
	-0.4





Operational conditions
- 50 ºC
- -0.6 V vs. SHE

Thermophilic process

Set-up of mild thermophilic systems

Chronology

Reactors 1 and 2 (280 d operation)

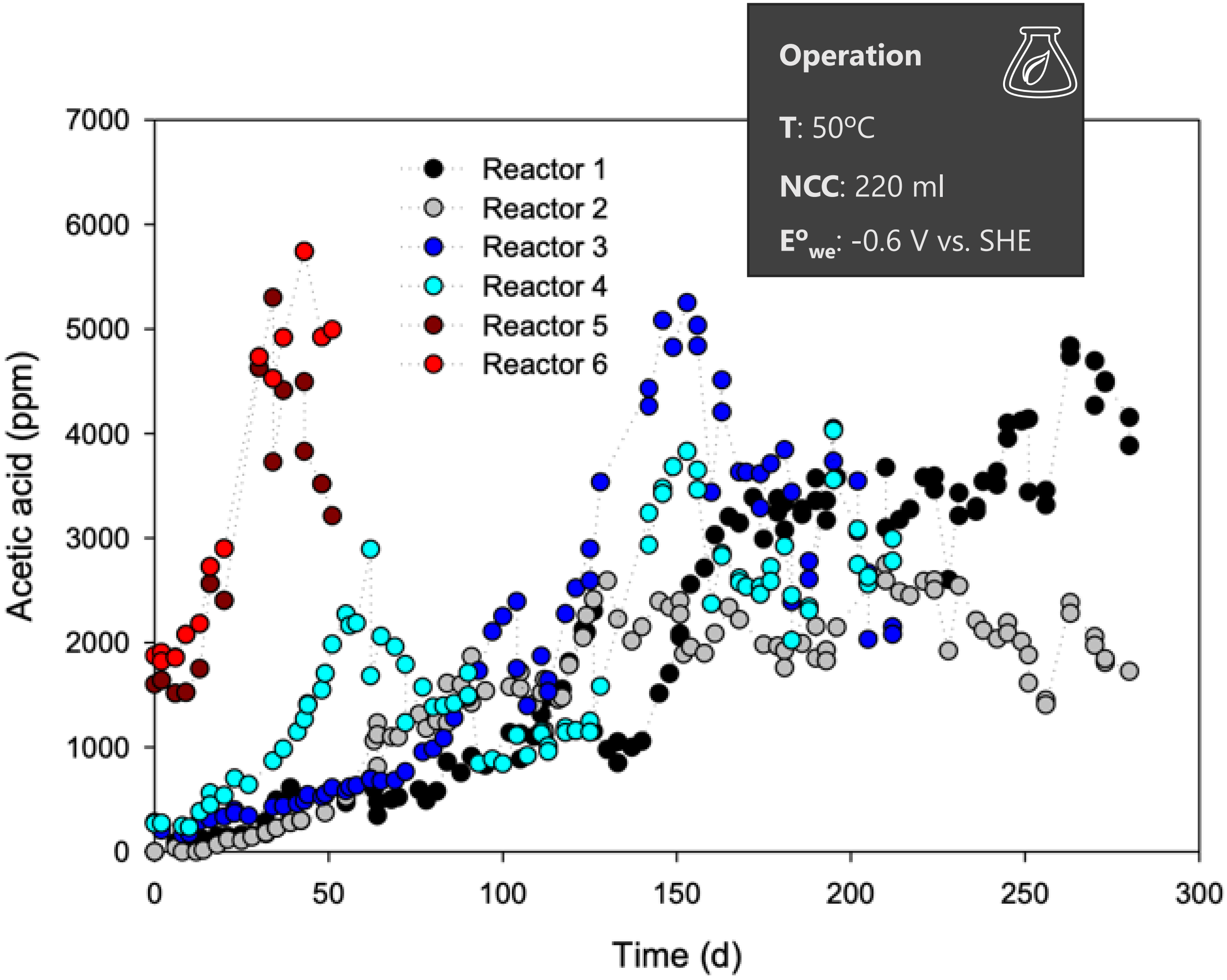
After 70 d, inoculation of

Reactors 3 and 4 (210 d operation)

After 160 d, inoculation of

Reactors 5 and 6 (50 d operation)

- Max production rate: 28 g acetate m^{-2} d^{-1}
- Coulombic efficiency: 80-90%



Scaling up

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CO_2 conversion: micro-organisms

Microbial CO_2 conversion

- 3 microbial platforms

Microbial platforms		T range	O_2 tolerance	Target product	Partner
Autotrophic	Clostridial strain	Mesophilic	Anaerobic	Isobutene	Global Bioenergies
	Cupriavidus necator	Mesophilic	Aerobic	Lactate	Enobraq
Capnophilic	*Thermotoga neapolitana*	Hyper-thermophilic	Strictly anaerobic	Lactate + H_2	Consiglio Nazionale delle Ricerche

Capnophilic lactate production (80°C)

Capnophilic Lactic Fermentation (CLF) pathway: *Thermotoga neapolitana*-based platform to gain value from CO_2 and waste by production of L-lactate & H_2

- Proof of concept net CO_2 fixation in lactic acid
- Engineered bacteria: 70% increase

UPTAKE

Wild type

CH_3CO_2Na + CO_2 → Sodium lactate

0.8 ± 0.02 g L^{-1}   **0.4 ± 0.01 g L^{-1}**   **1.1 ± 0.03 g L^{-1}**

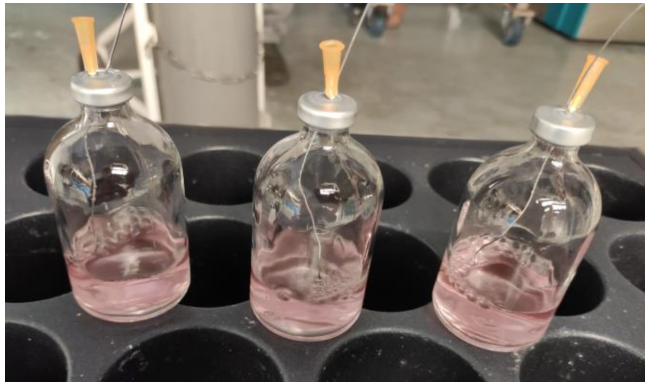
CL-11-AS

CH_3CO_2Na + CO_2 → Sodium lactate

1.4 ± 0.08 g L^{-1}   **0.7 ± 0.04 g L^{-1}**   **1.9 ± 0.1 g L^{-1}**

Capnophilic lactate production

- Tests with real offgas

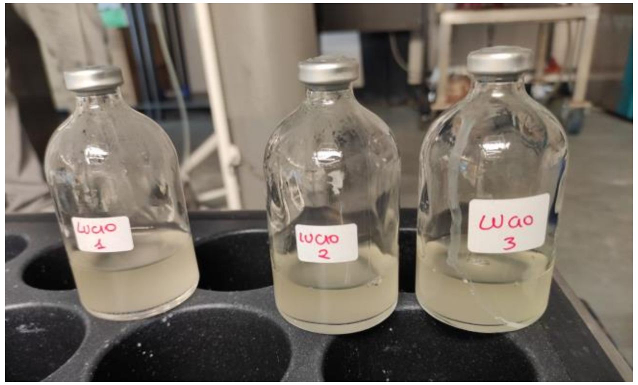


30’

80°

48 h

80°



Thermotoga neapolitana is tolerant to O_2 containing offgas (0.2%)

Thermotoga neapolitana is tolerant to offgas impurities without pretreatment

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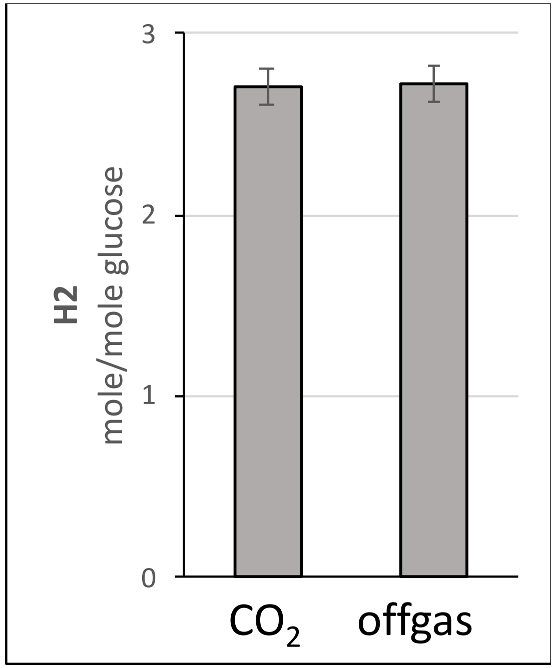
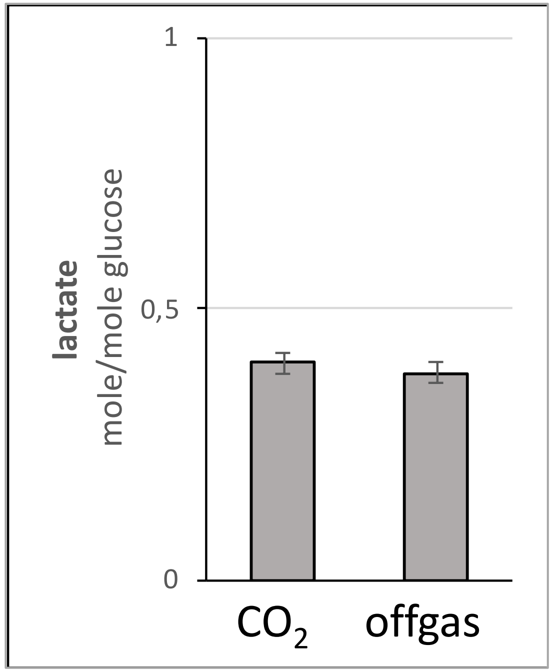
Capnophilic lactate production

- Tests with real offgas on 1-L scale: same performance as with pure CO_2

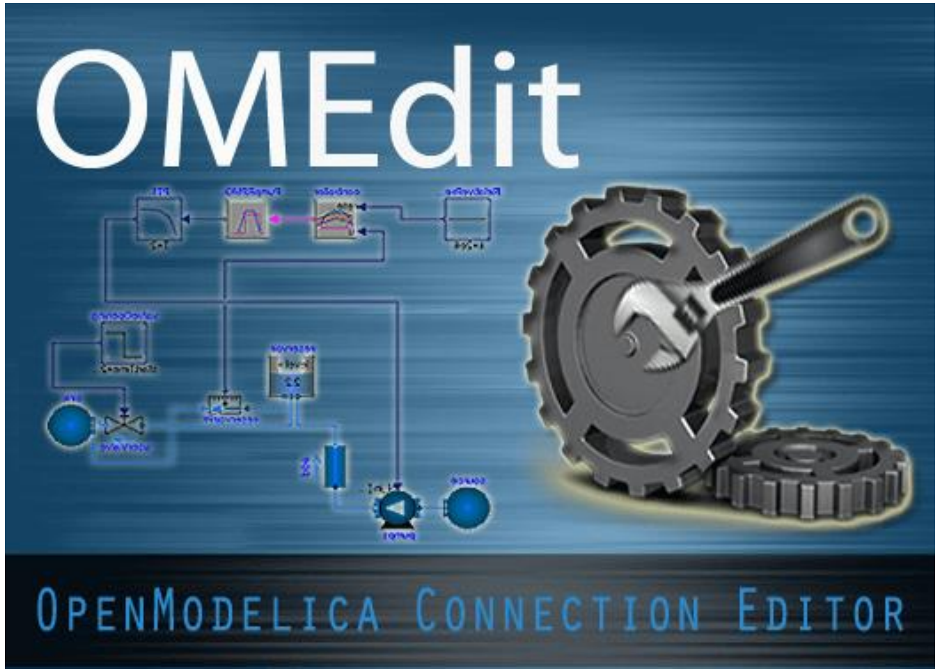




Modelling and simulation

Modelling and simulation

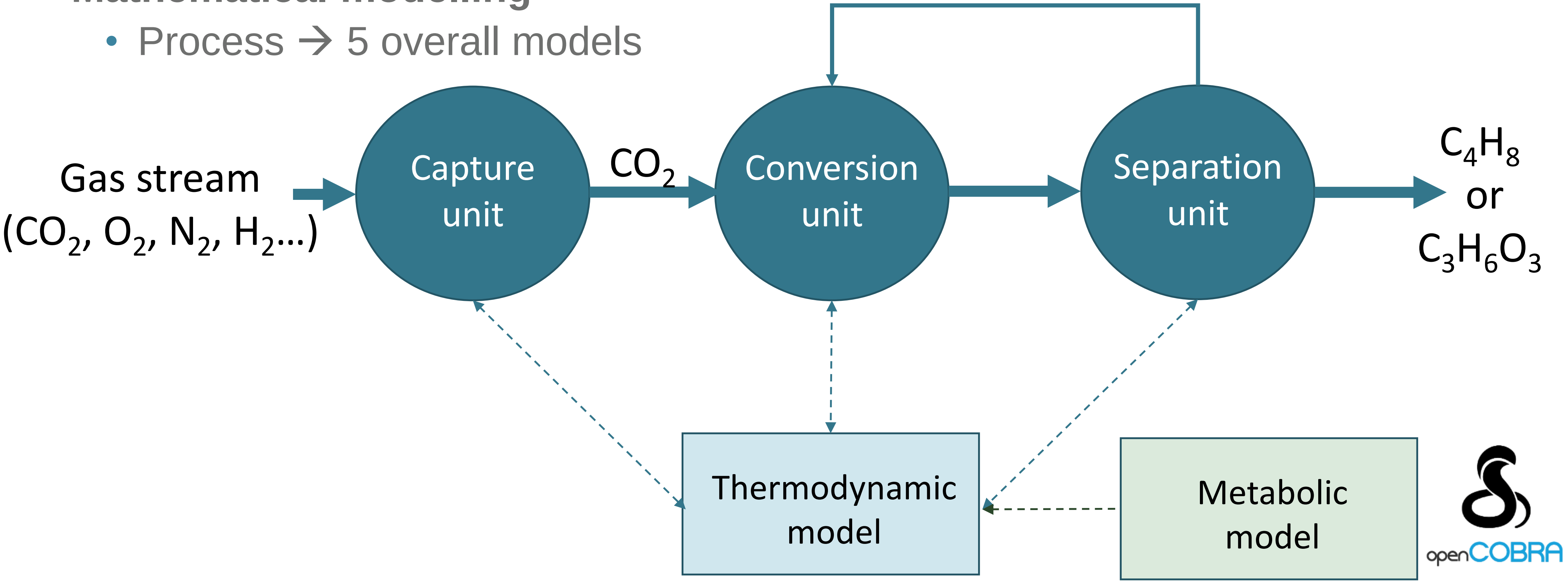
- **Mathematical modelling**
  - Development tool



- Modular models (overall solutions)
- Specialized solvers are available
- Feasible connection with python (for optimization & data recovery)
- **Open source**

Modelling and simulation

- **Mathematical modelling**
  - Process → 5 overall models



Modelling and simulation

- **Advances beyond State of the Art**
  - Thermodynamics for novel tailored made solvents for CO_2 capture process
  - Comprehensive modelling of each bioelectrochemical & biological system considering
    - Physical chemistry (mass transfer & equilibrium)
    - Microbiology (growth and production)
    - Electrochemistry (H_2 production by water electrolysis)
    - Bioelectrochemistry (H_2 production using biocathodes)
  - Simulation/optimization tool based on open source environment: openModelica
    - Noticeable reduction costs by optimizing design and operational parameters
  - Tool allowed to simulate hypothetical scenarios and state KPIs to reach a feasible operation at industrial scale, showing the way for upscaling developments

Conclusions

- Gas fermentation & microbial electrosynthesis emerging for fuel & chemical production
  - Productivities (and titers) need to be increased to allow industrialization
  - Heat management - Gas solubility / mass transfer
- Promising new/hybrid concepts including biotechnology
  - For CO_2 capture and conversion
  - Research and upscaling
- Accelerate developments through integrated approach (Bioprocess + Biological engineering)
- Modelling
  - Optimization tool developed and tested
  - Possibility to simulate hypothetical scenarios and point to objectives for future work

Acknowledgements

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Thank you for your attention!

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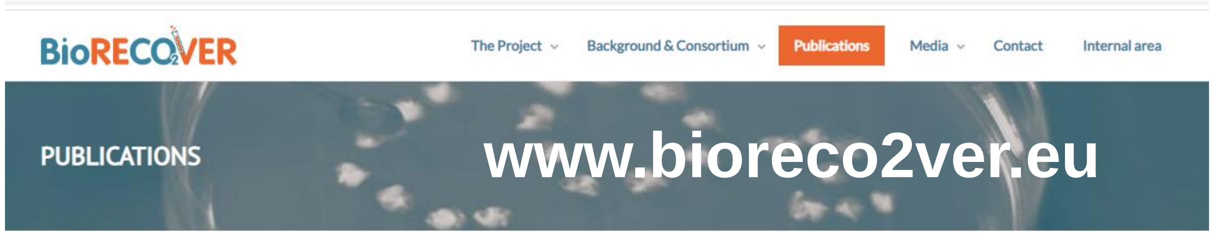

Publications

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-V. Luongo; A. Palma; E. R. Rene; A. Fontana; F. Pirozzi; G. Espositio; P. N.L. Lens (2018): Lactic acid recovery from a model of Thermotoga neapolitana fermentation broth using ion exchange resins in batch and fixed-bed reactors, DOI:10.1080/01496395.2018.1520727

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-N. Pradhan; G. d'Ippolito; L. Dipasquale; G. Esposito; A. Panico; P.N.L. Lens; A. Fontana (2019): Simultaneous synthesis of lactic acid and hydrogen from sugars via capnophilic lactic fermentation by Thermotoga neapolitana cf capnolactica, DOI: 10.5281/zenodo.3247821

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