BioRECO2VER

Heleen De Wever and project partners

BIOCON-CO_2 Final Symposium, 14 June 2022, Ghent, Belgium

Horizon 2020
European Union Funding
for Research & Innovation

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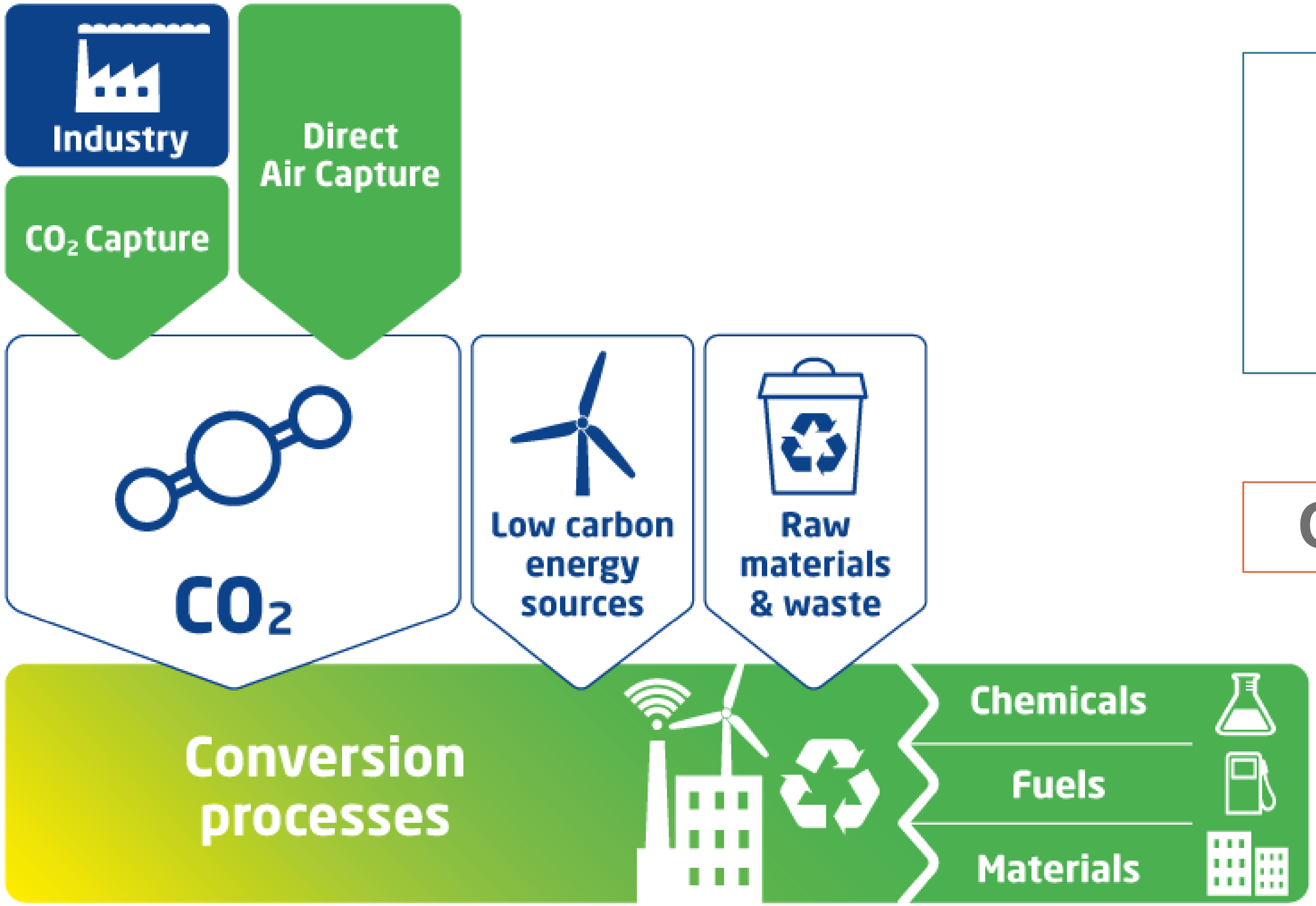
Carbon Capture and Utilization (CCU)



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

CO_2 <> CO

Research

Strong industrial involvement

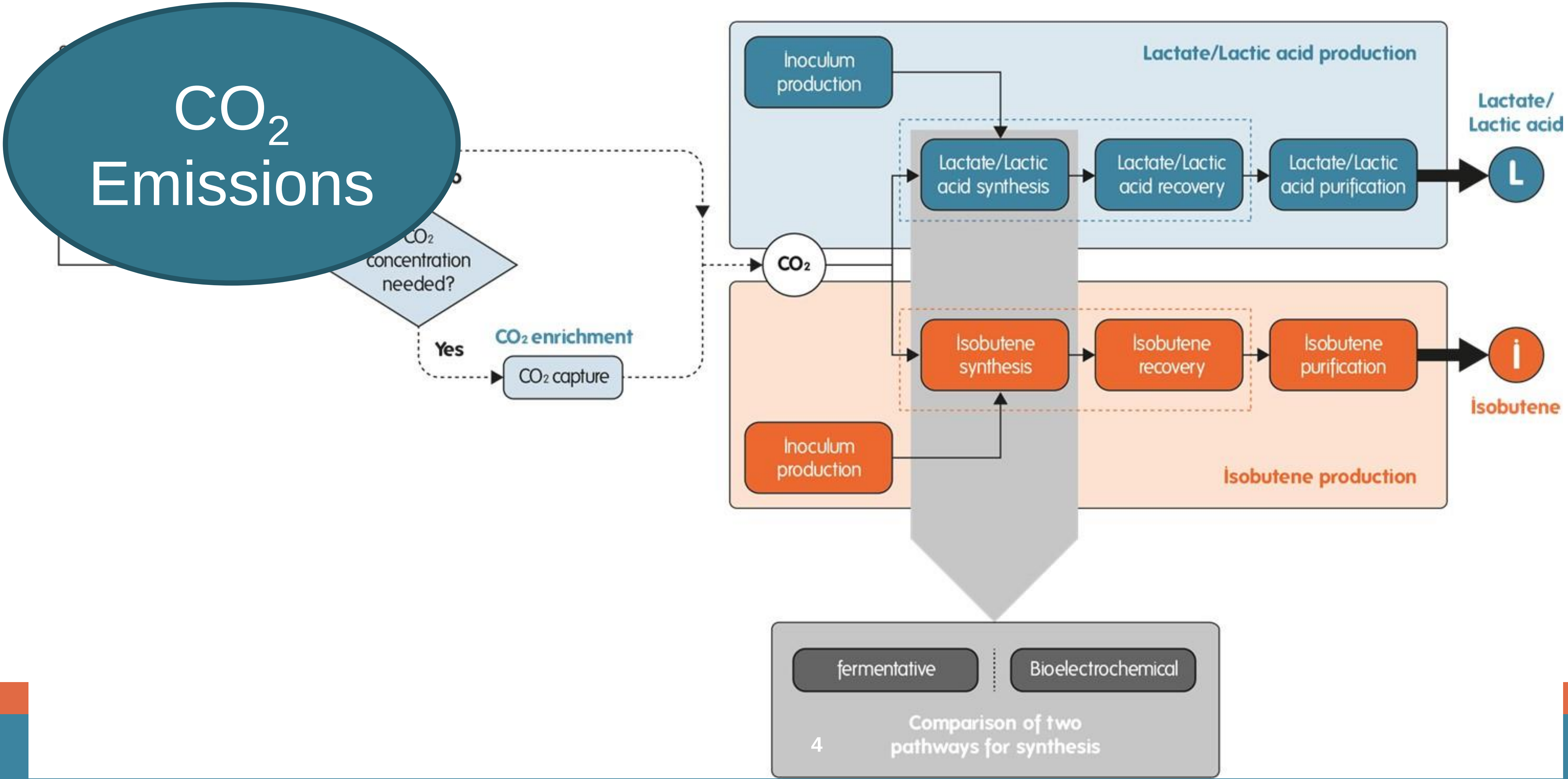
Source: https://www.co2value.eu/ccu/

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



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

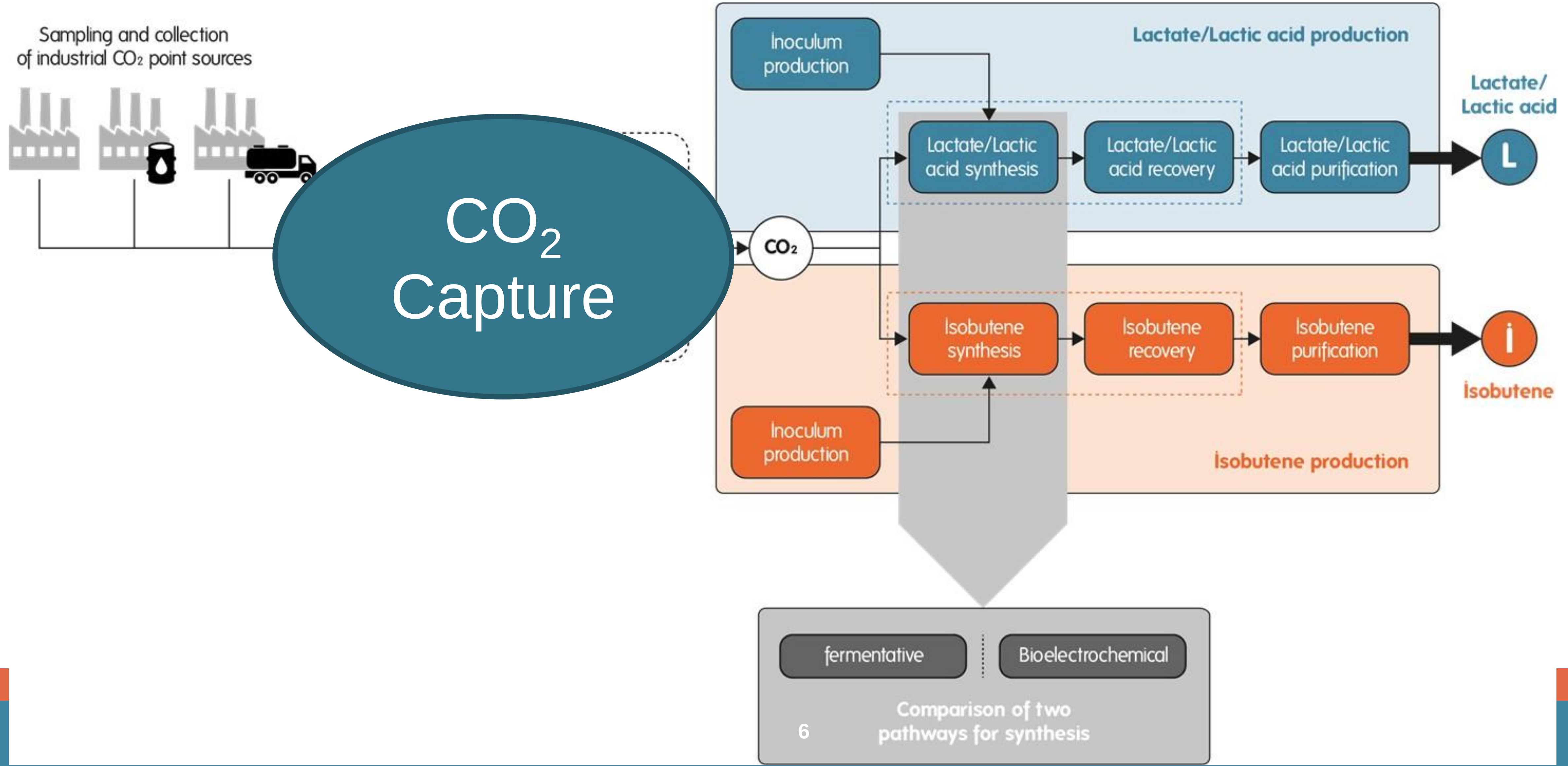
*Refineries have multiple sources of CO_2 and other air pollutants, but emissions are mainly connected with **energy production** needed for different refining processes. In general, **heaters, furnaces, gas turbines** etc. are responsible for ca. **60%** of the emissions.*

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

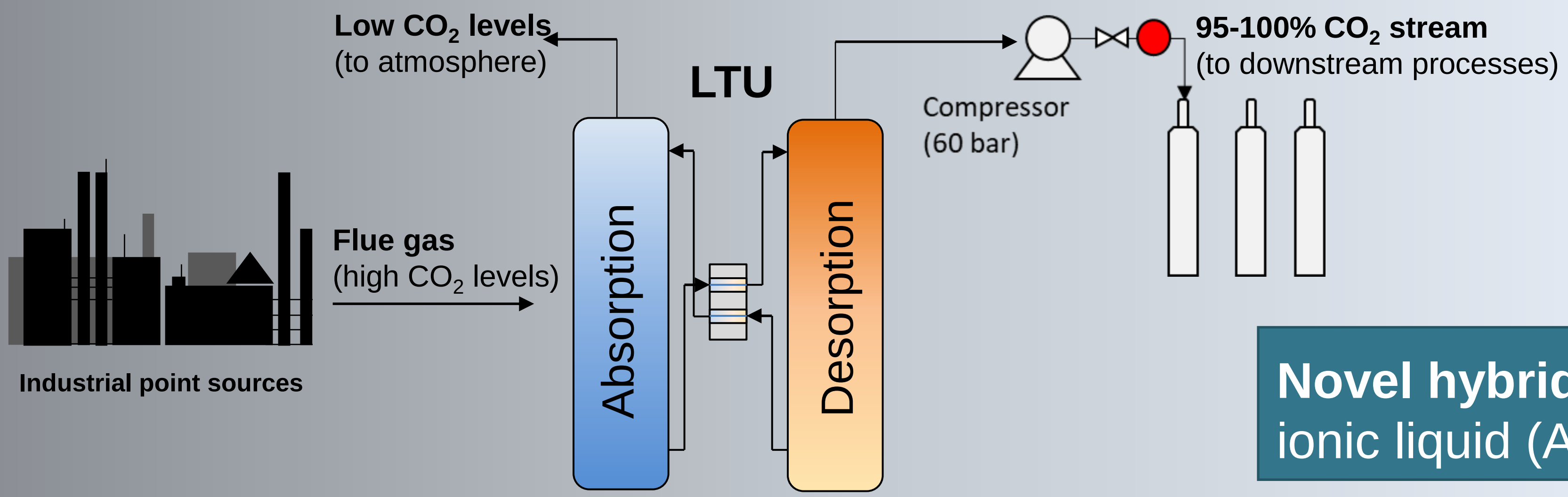
- **crude distillation unit (CDU)**
- **hydrogen production unit**
- **fluid catalytic cracking (FCC)**

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.

Overall project concept



CO_2 capture: novel hybrid chemo-enzymatic process



40-60 ℃,
Novel hybrid solvent + CA

Improved capture rates and reduced operation times

90-100 ℃, Novel hybrid solvent
(120-140 ℃, MEA)

Improved solvent regeneration at lower temperature

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

Improved biocatalyst:
Ultrastable Carbonic Anhydrase (CA)

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

MEA: Monoethanolamine

Enzyme improvement by directed evolution

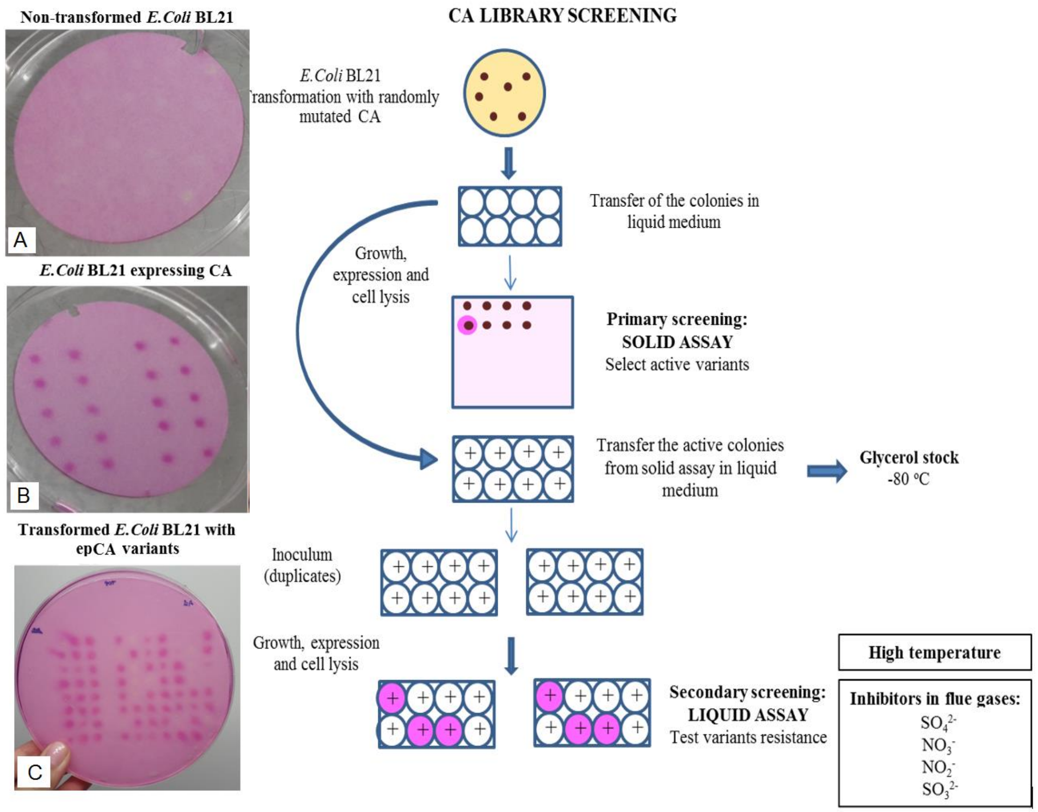
Library construction

Library screening

Scaled-up production of most promising variants

Sequencing for identification of mutations

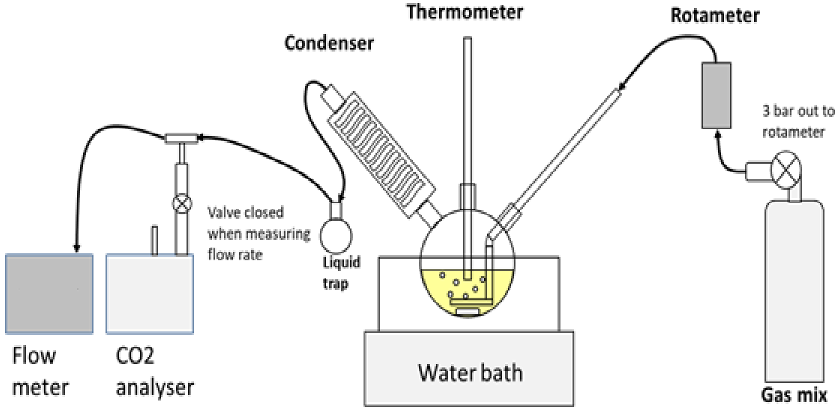
- **3 mutants showed 50% increased resistance to flue gas inhibitors**

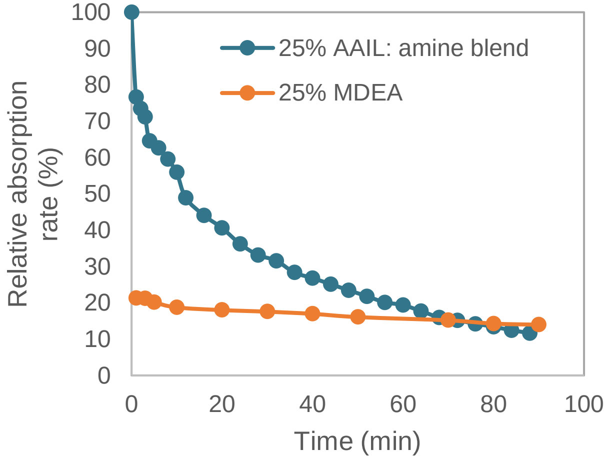


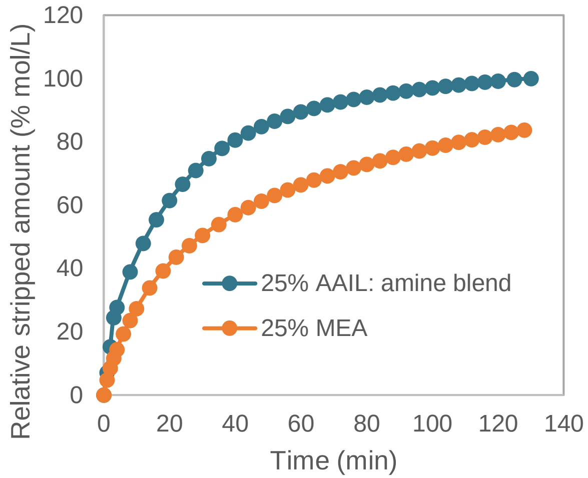
Novel hybrid solvent with competitive absorption and desorption properties

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 and pretreatment

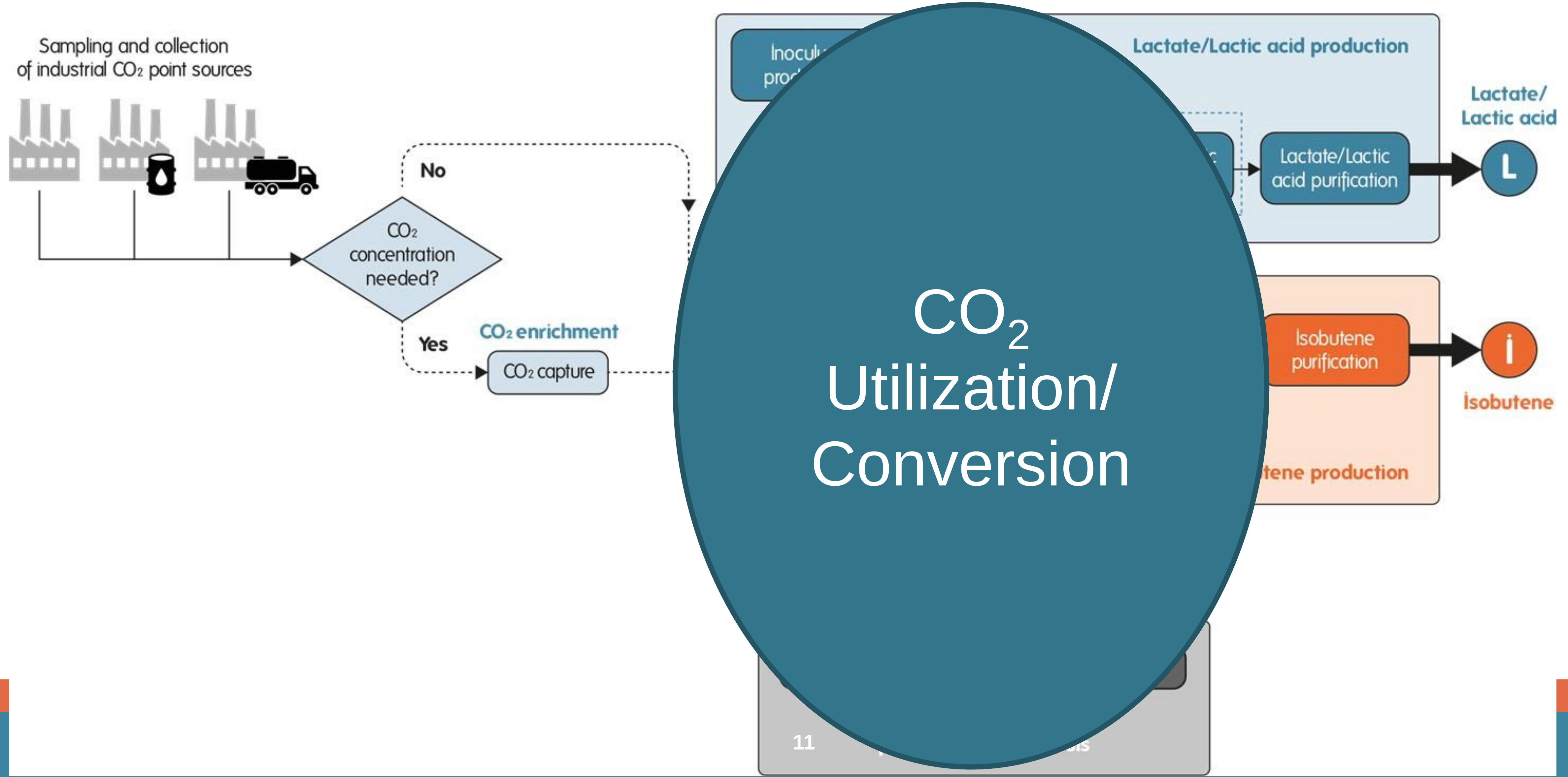
Highlights

- 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 (PEHAp-MDEA) was developed with competitive absorption and desorption properties
- Large-scale Carbonic Anhydrase-aided CO_2 absorption was demonstrated

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

MDEA: Methyl diethanolamine; PEHAp: pentaethylenehexamine prolinate; MEA: Monoethanolamine

Overall project concept



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

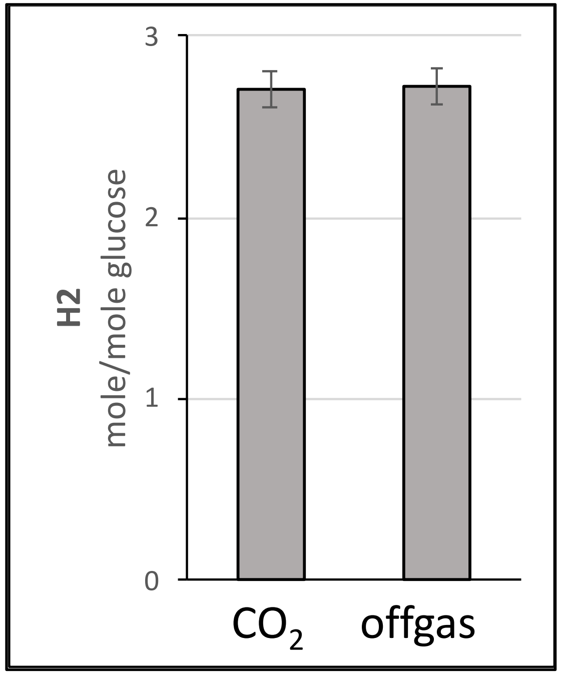
CO_2 conversion: 3 microbial platforms

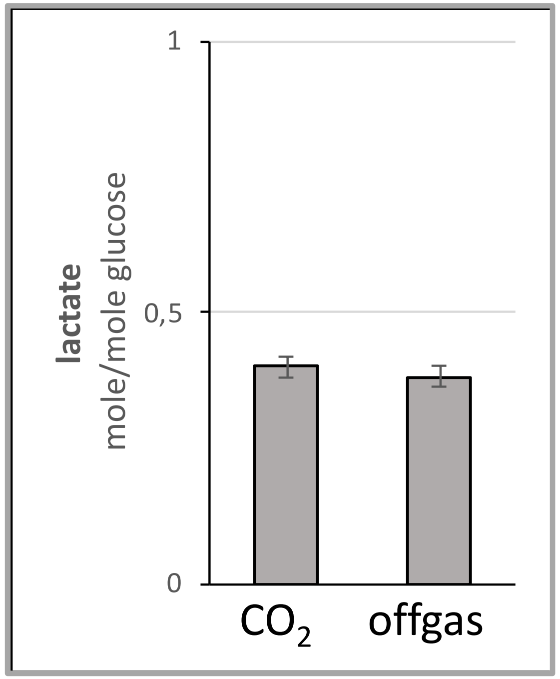
Highlights

- Established manipulation and genetic toolbox for *C. ljungdahlii* and implemented the isobutene pathway
- Isobutene production under autotrophic conditions
- Lactate re-consumption issue solved within *Cupriavidus* and lactate production improved by lactate dehydrogenase overexpression
- Selection of two model strains of *Thermotoga neapolitana*, DSM33003 and RQ7
  - Productivity (increase lactic acid molarity)
  - Genetic tools (transformable strains and amelioration of target steps)

CO_2 conversion: *Thermotoga* platform

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

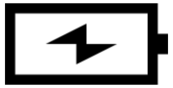




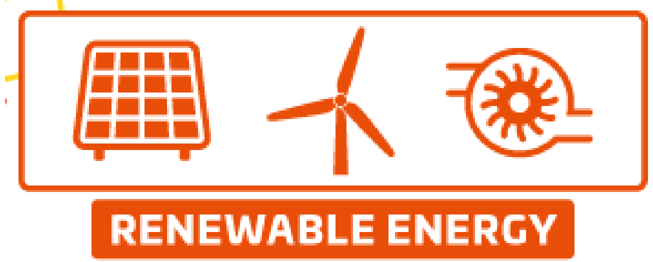
→ *Thermotoga neapolitana* is tolerant to offgas impurities without pretreatment

CO_2 conversion: 2 technologies

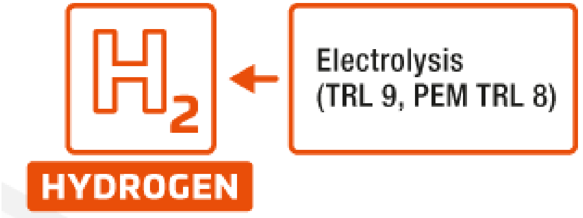
- **2 technologies**



Bio-electrochemical systems

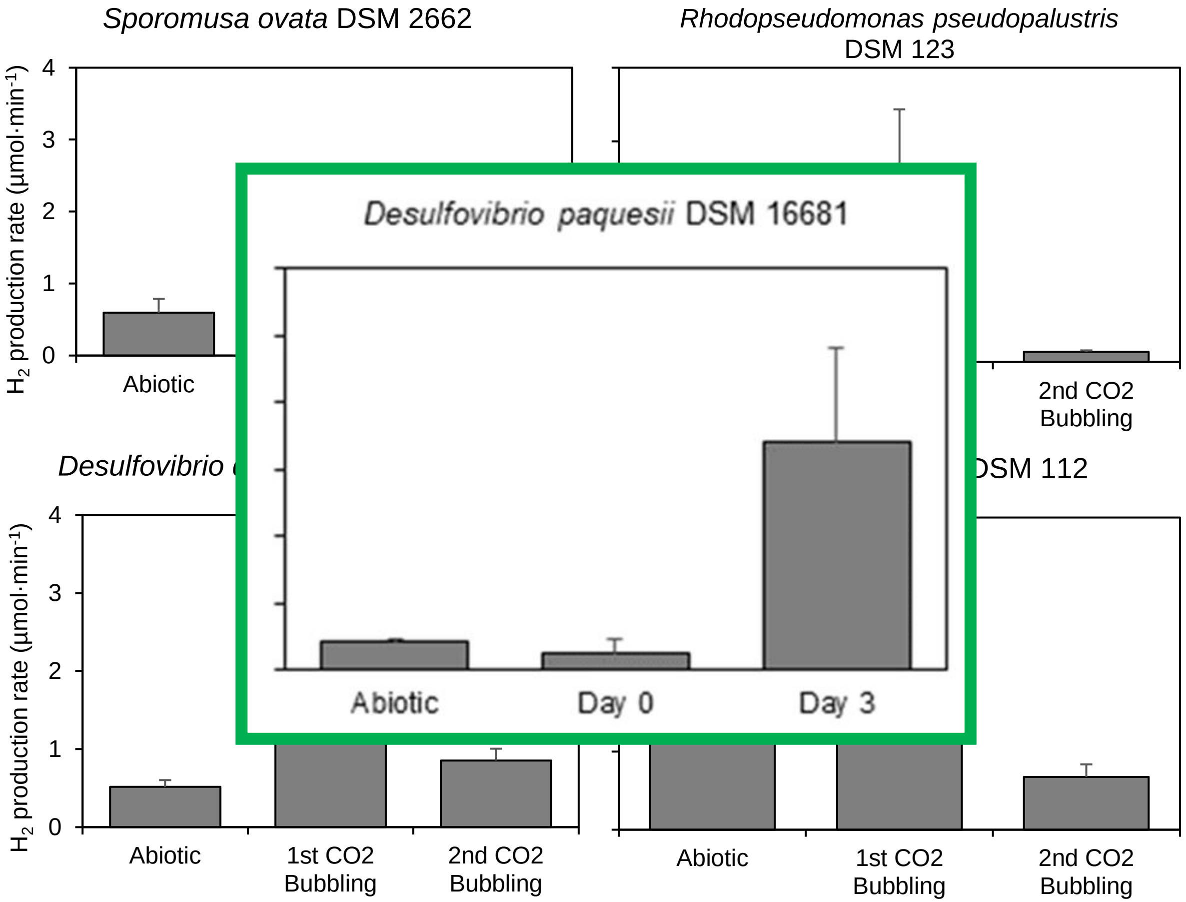


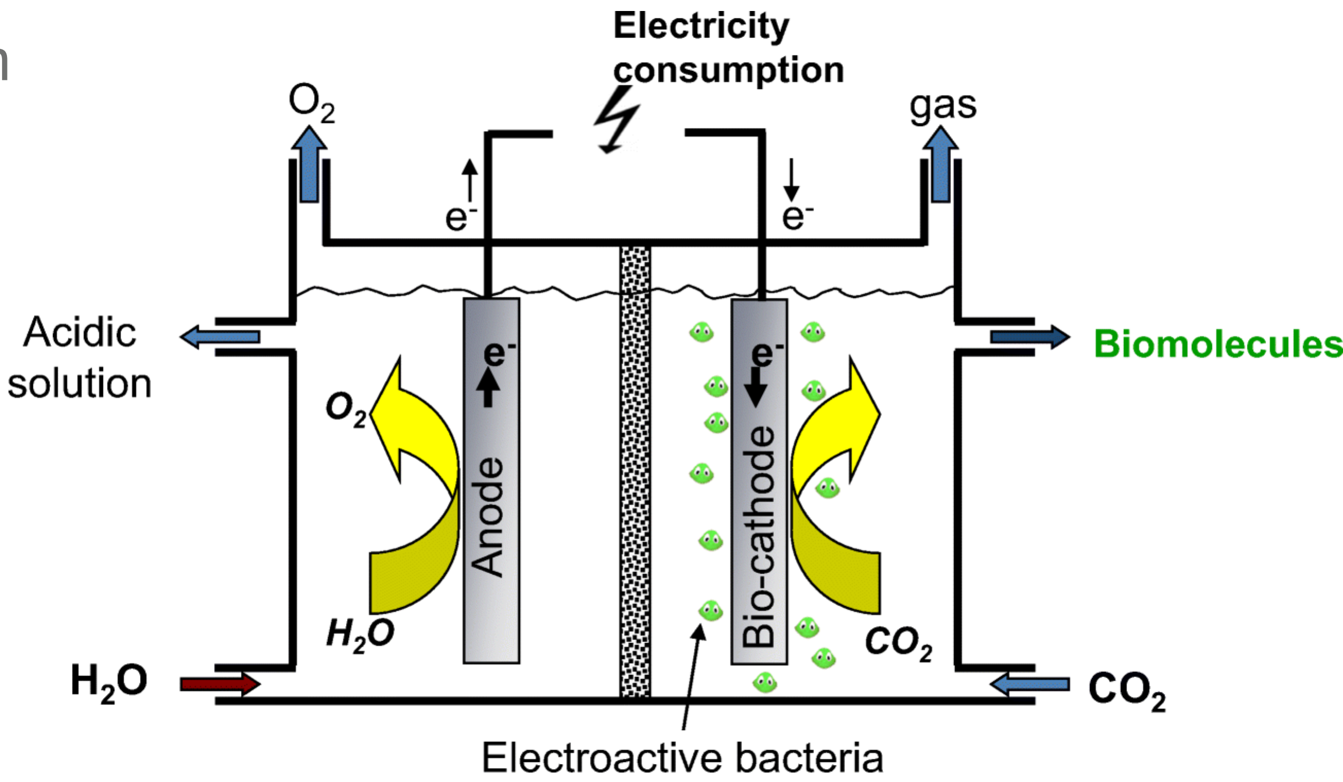
[High pressure] fermentors



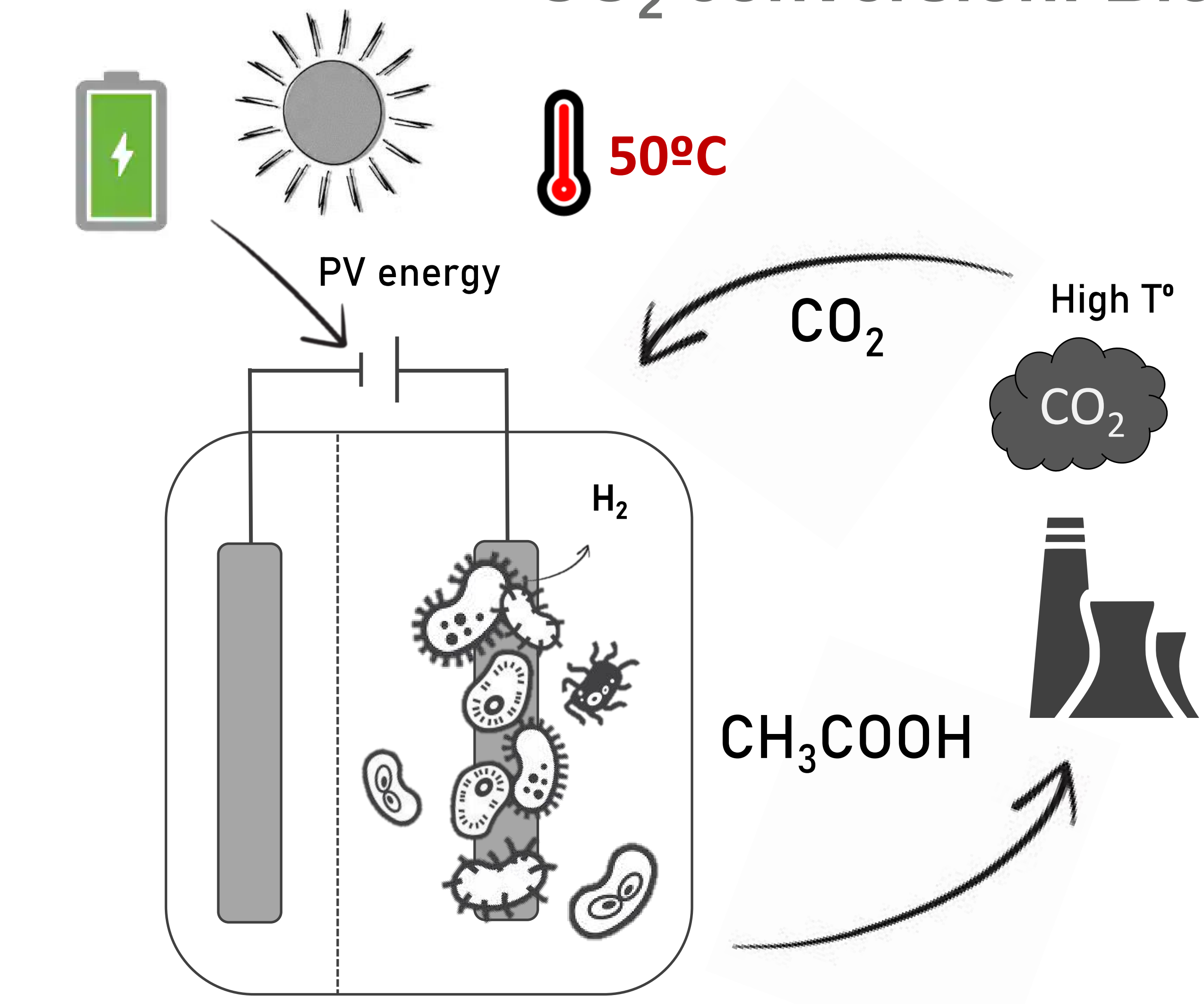
CO_2 conversion: Bio-electrosynthesis

- Maximize *in situ* H_2 production:
  Abiotic vs. **Biotic** mediated H_2 production



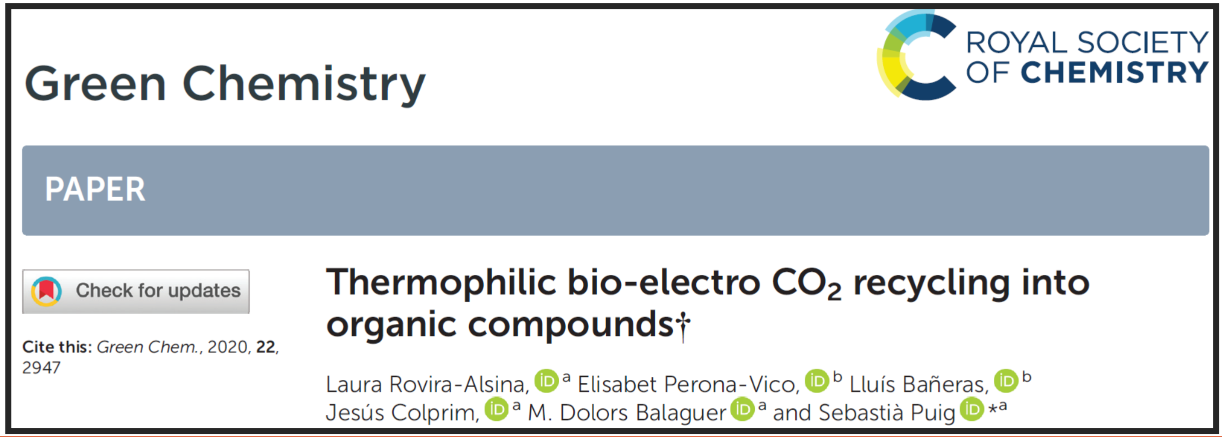


CO_2 conversion: Bio-electrosynthesis



Thermophilic Microbial Electrolysis Cell

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


Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

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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]

CO_2 conversion: Bio-electrosynthesis

50ºC

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)

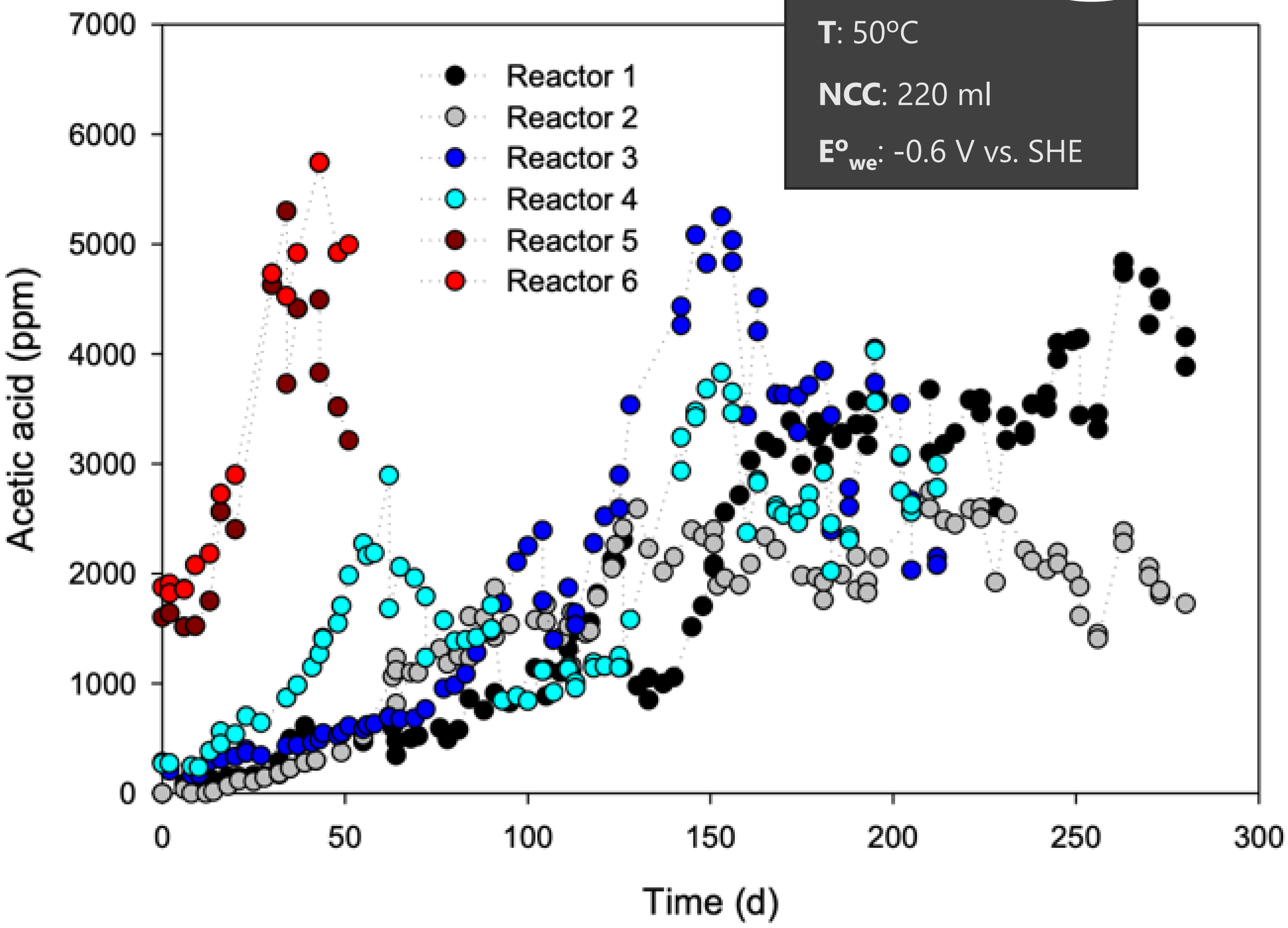
- Max production rate: 28 g acetate m^{-2} d^{-1}
- Coulombic efficiency: 80-90%

Operation

T: 50ºC

NCC: 220 ml

Eº$_{we}$: -0.6 V vs. SHE



Universitat
de Girona

nthesis

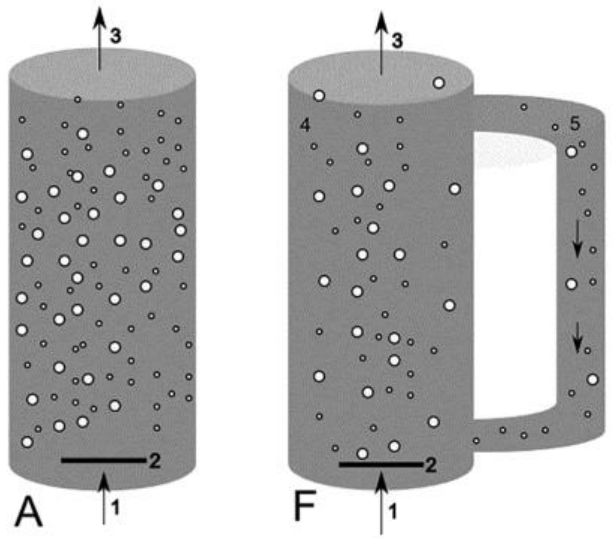
Gas (CO_2, H_2) solubility is low

- 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)

CO_2 conversion:
Pressurized fermentations (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

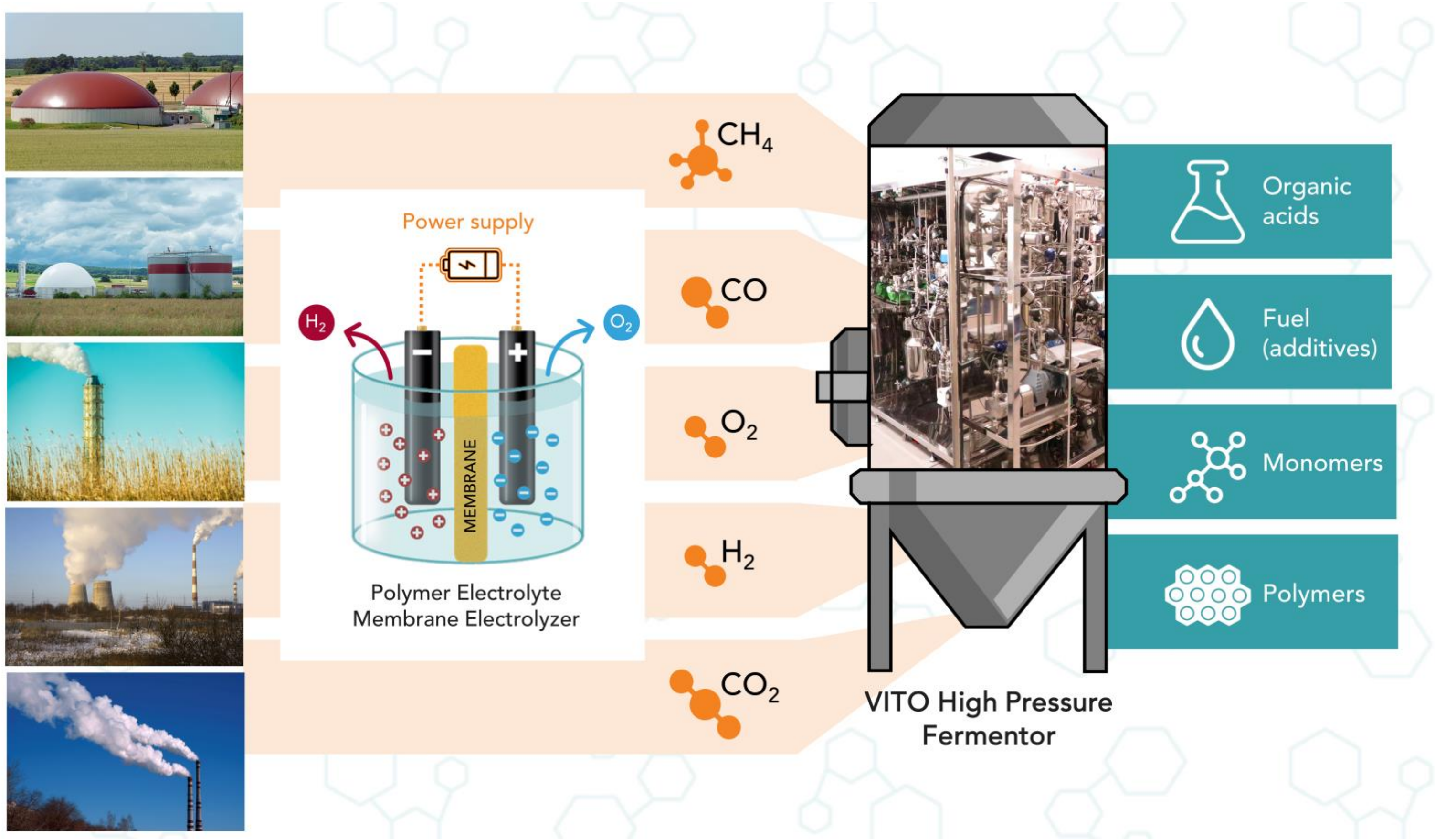
- Fermentations at moderately elevated pressures using C1 gases underexplored

Source: Van Hecke et al. (2019)


Fermentor skid


MAXUM
edition II
Online GC

Pressurized fermentor: main features



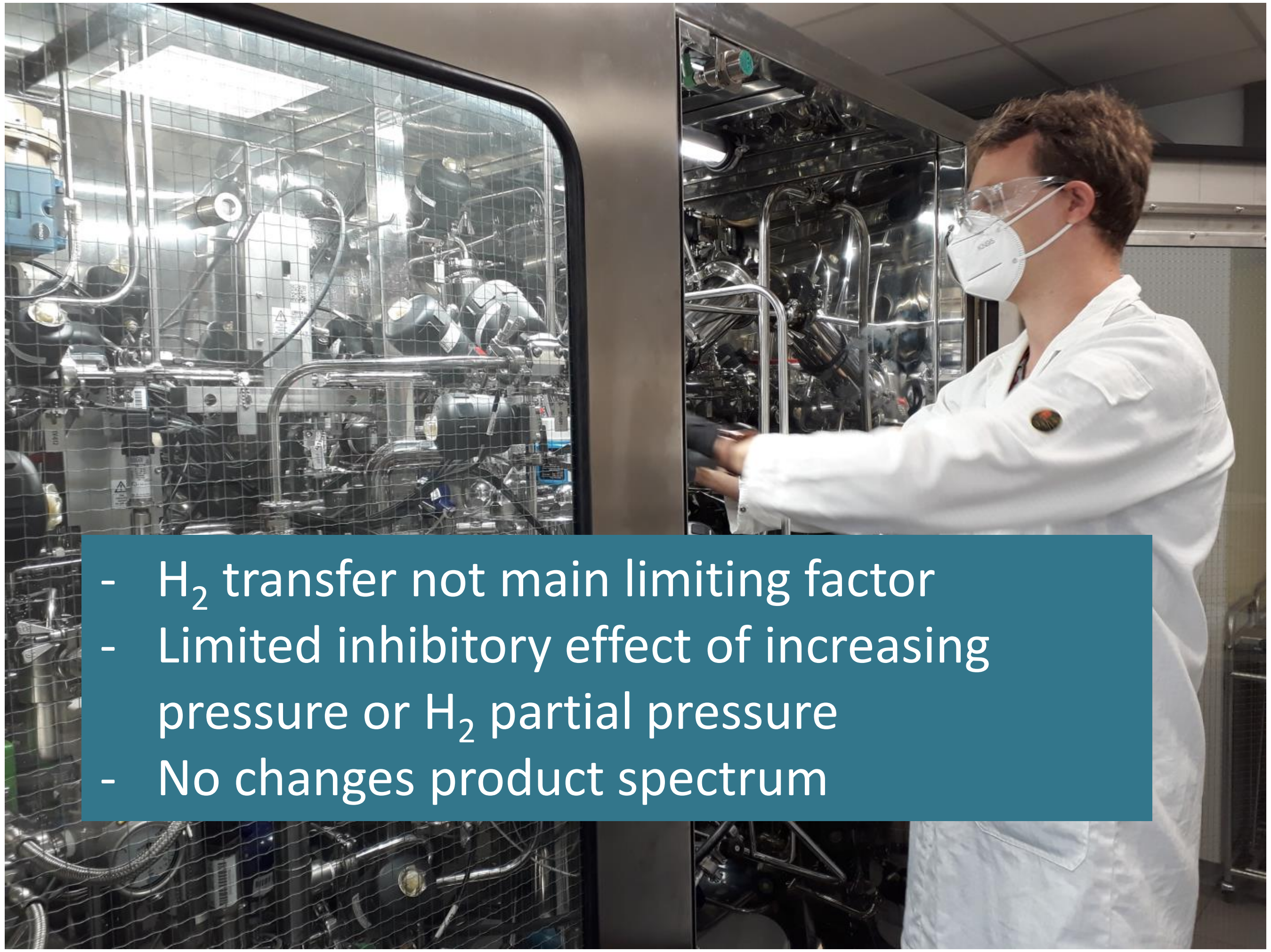
- In situ sterilizable bioreactor for gaseous fermentations
- CO_2, H_2, CO, O_2, N_2, gas mixtures such as syngas or real offgases
- Operation at constant or variable pressures up to 10 bara
- Food grade + ATEX (Ex II 2G) gas fermentation
- Online process monitoring and control
- Online gas analysis and control
- Integrated membrane filtration

Some experimental results

- Study effect of increasing pressure
- Compare at constant CO_2 partial pressure

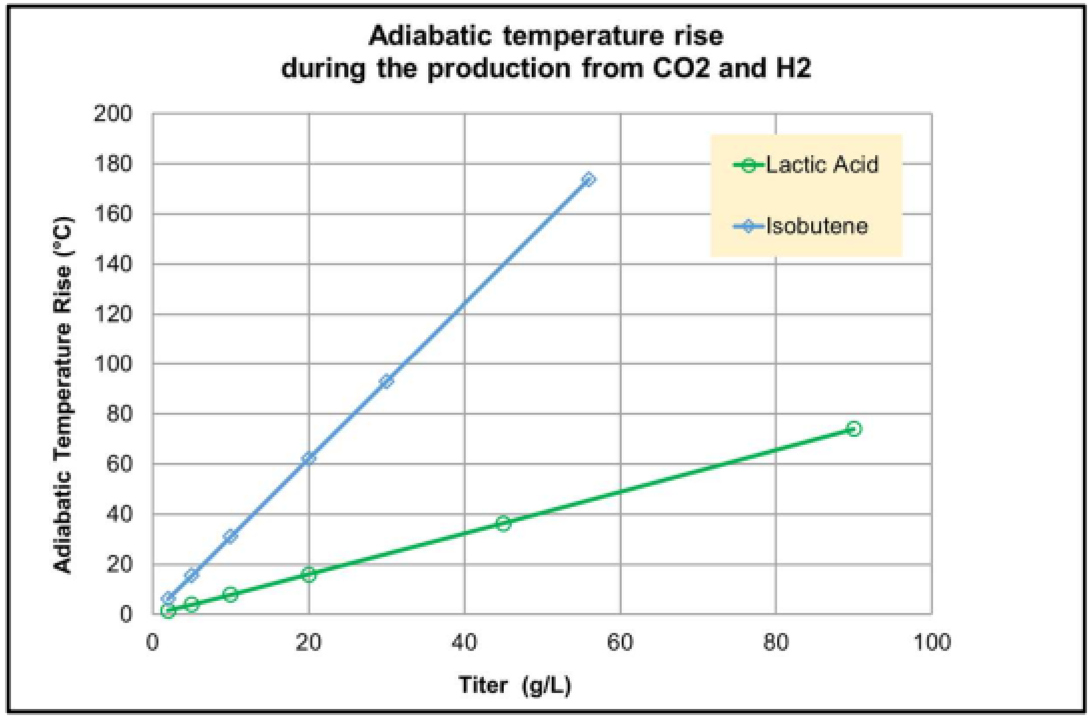
Pressure	Headspace H_2/CO_2 (vol%)	Main product (g/L)*	Productivity (g/L.h)
3 bar	80/20	25 (↑)	0,19
6 bar	88,5/11,5	21	0,21
9 bar	92/8	18 (↑)	0,17

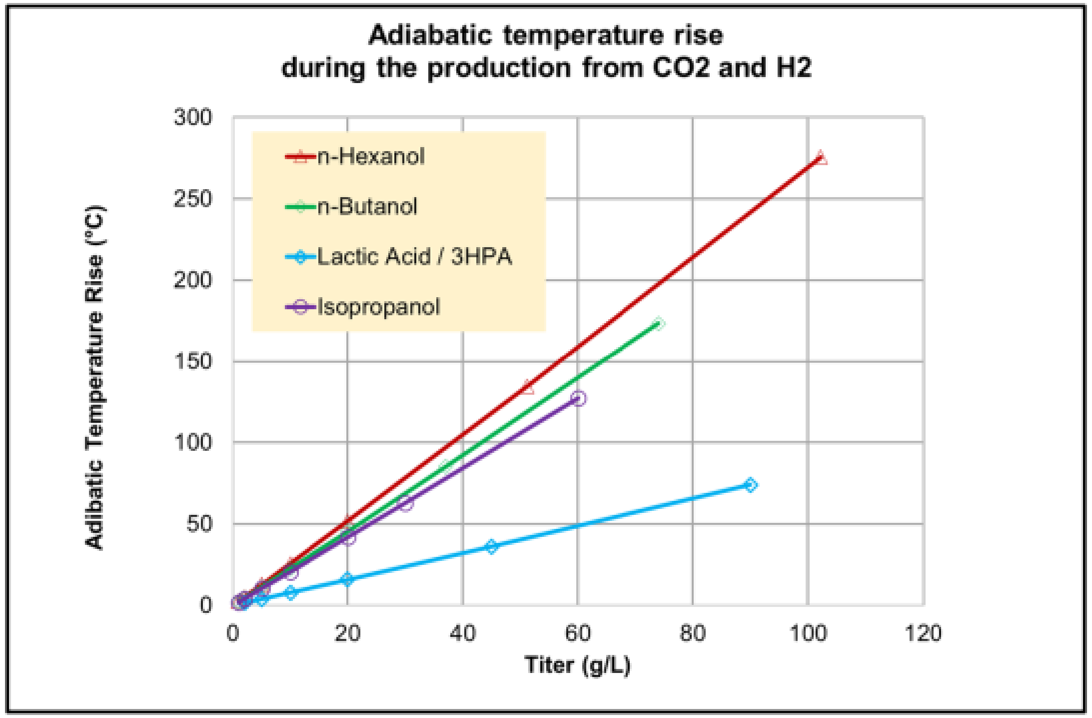
**at same fermentation duration*



- H_2 transfer not main limiting factor
- Limited inhibitory effect of increasing pressure or H_2 partial pressure
- No changes product spectrum

Need for high product titers





- 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

BioRECO2VER

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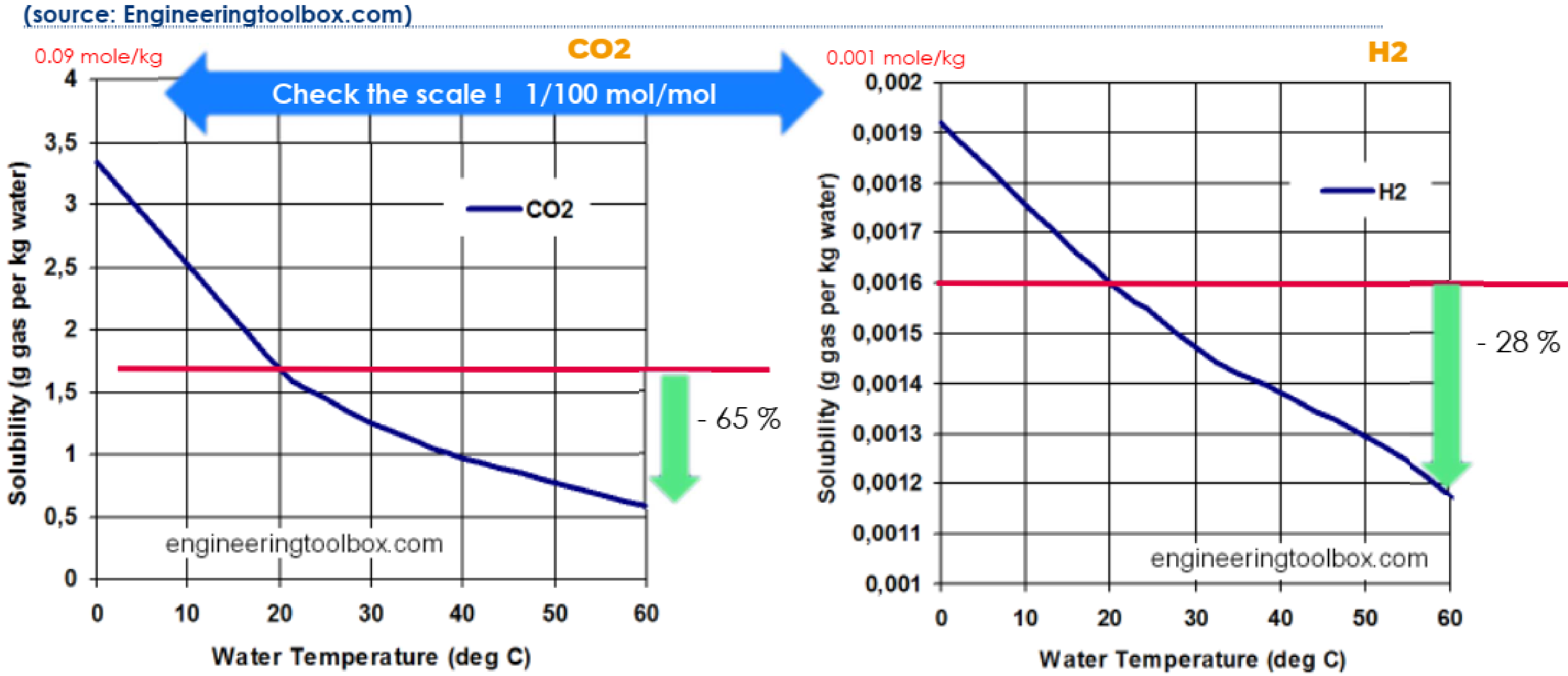
(High) product titers from CO_2 + H_2

- Lot of heat produced at low temperature: Use for district heating? In greenhouses?

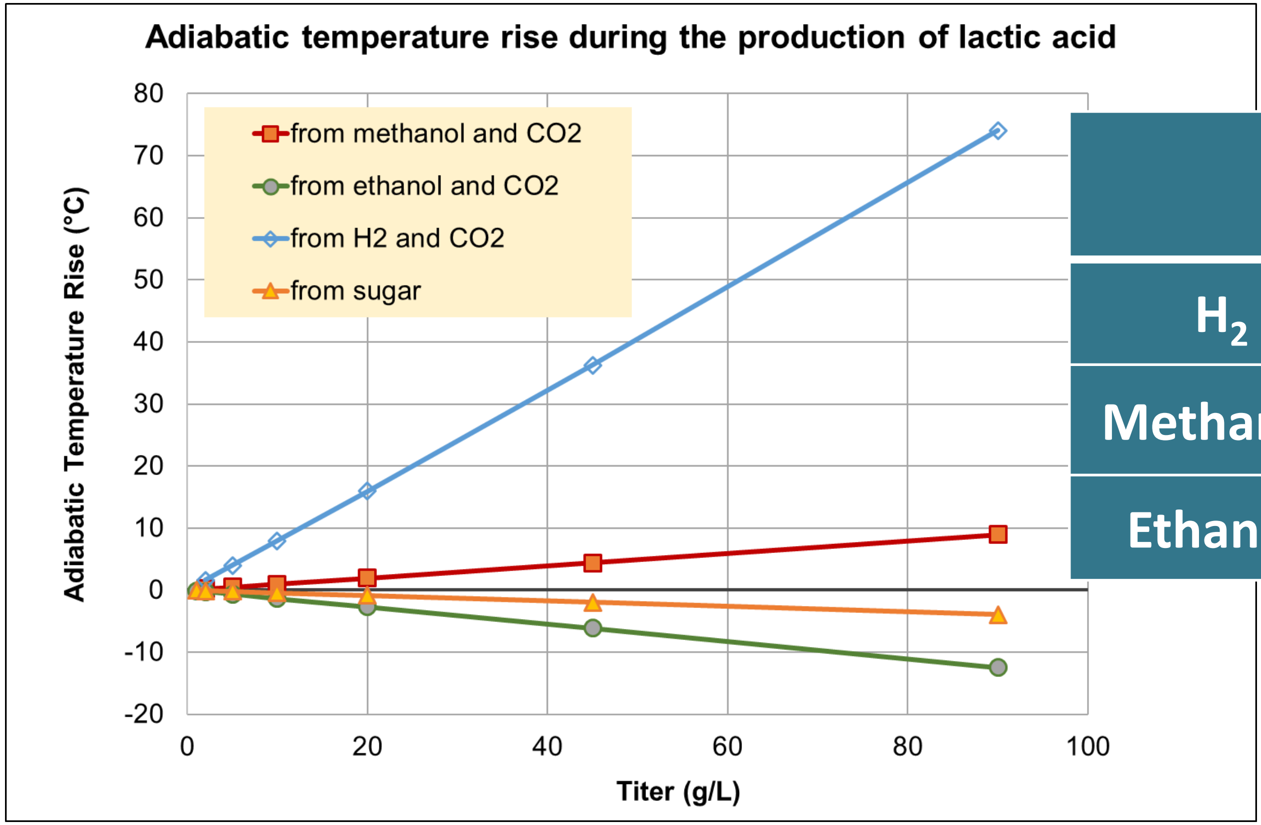
- Operation at higher T preferable for heat valorization

  →(hyper)thermophilic range

- Issue gas solubility



Use of alternative reducing agents?



	Reaction	$\Delta_r H°$ (kJ/mol)
$H_2 + CO_2$	$3\ CO_2 + 6\ H_2 \rightarrow C_3H_6O_3 + 3\ H_2O$	-298
Methanol + CO_2	$2\ CH_4O + CO_2 \rightarrow C_3H_6O_3 + H_2O$	-36
Ethanol + CO_2	$C_2H_6O + CO_2 \rightarrow C_3H_6O_3$	50

CO_2 conversion technologies

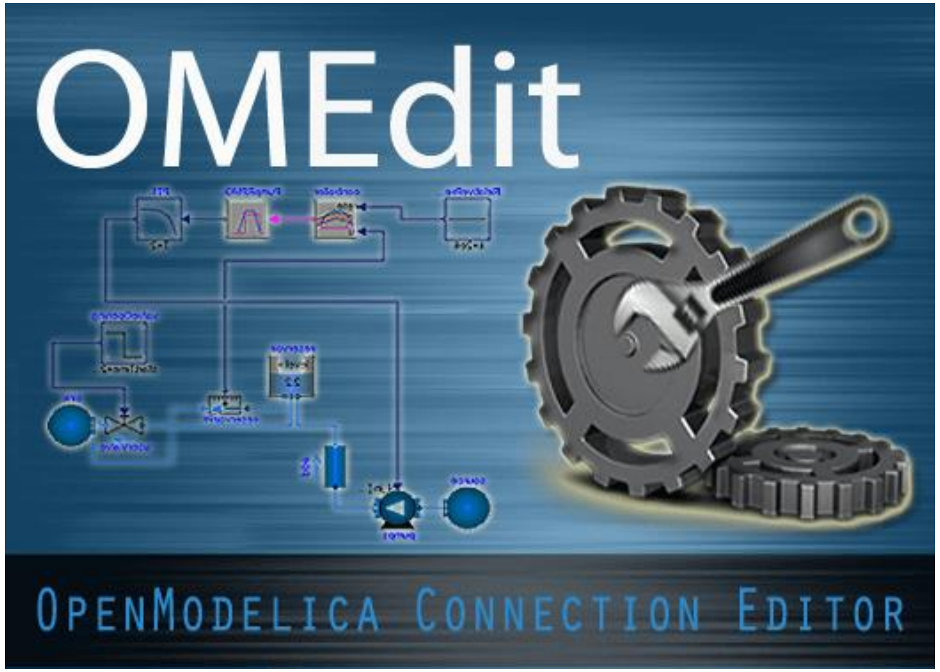
Highlights

- Flexible prototypes available as high tech research platforms

- Pressurized fermentor to study impact (partial) pressure on processes and optimize them prior to scale-up
- CO_2 conversion tested at pressures up to 10 bara and with real CO_2-rich offgases
- Challenging to have high product titers from CO_2/H_2 and good heat management

Modelling and simulation

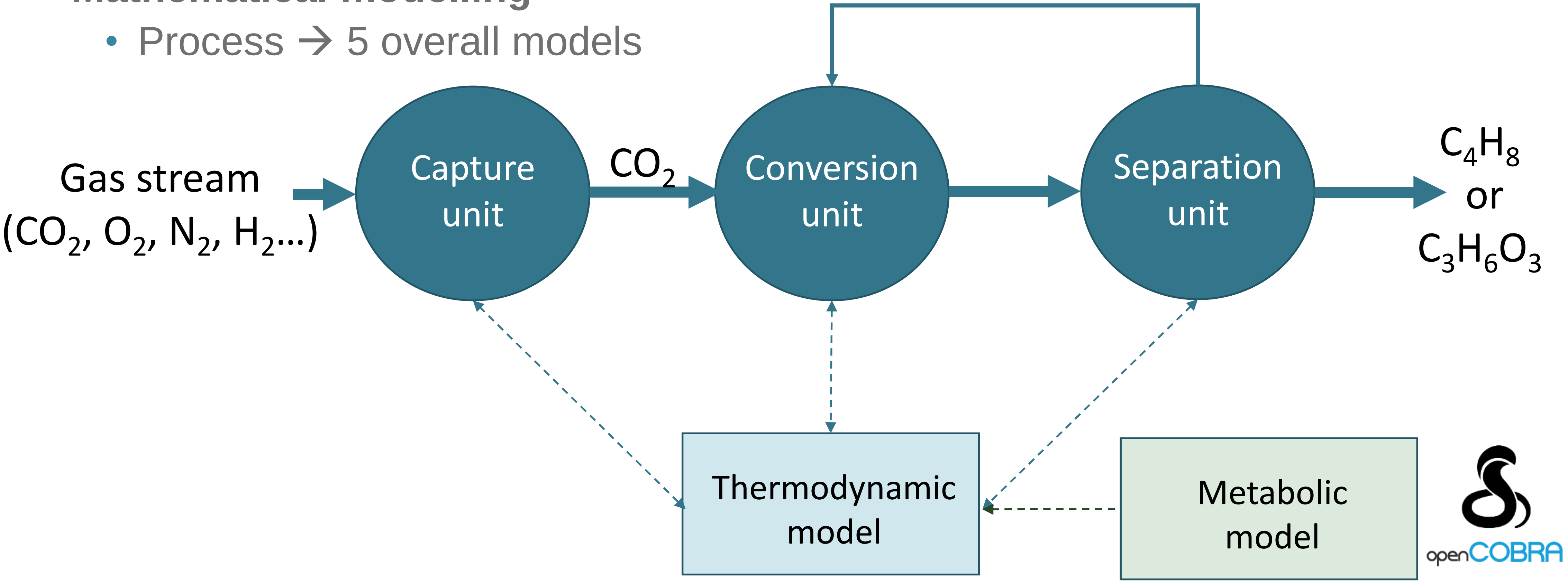
- **Mathematical modelling**
  - Development tool



- 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 bio-electrochemical & biological systems considering
  - Physical chemistry (mass transfer & equilibrium)
  - Microbiology (growth and production)
  - Electrochemistry (H_2 production by water electrolysis)
  - Bio-electrochemistry (H_2 production using biocathodes)
- Simulation/optimization tool (open-source environment: OpenModelica & Python)
  - Allowed to simulate hypothetical scenarios, showing the way for upscaling the project technology

Social acceptance of CCU

We wanted to look at two perspectives

- Industry
  - CCU industry about social acceptance by consumers regarding converted CO_2 in products
  - Companies that already have CO_2–based products on market about acceptance issues
- Consumers
  - How consumers feel about issue on converted CO_2 in their products
  - Which factors play a major role for acceptance

Methodology

- Literature research on consumer perception
- Online survey with 11 questions (n=93) circulated via our industry networks
- 4 expert interviews with companies who already launched CCU products
- 4 focus group discussions with 4-6 consumers each

Social acceptance of CCU

- Few studies have investigated the social acceptance of captured CO_2 in consumer products.
- Little is known about CCU as a technology among the wider population
  - Found positive correlations for people:
    - with regard to the attitude "environmental awareness"
    - with regard to a more technical background
    - with regard to the age of people (higher awareness when younger)
- Acceptance and trust in novel technologies like CCU are strongly dependent on the source of knowledge (knowledge provider)
  - → e.g. in Germany, the government and NGOs are considered trustworthy
- Difference between general agreement with a technology and having to interact personally → NIMBY effect (not-in-my-backyard effect)

Social acceptance of CCU

Main take-aways companies

- Difficult to market the concept of CCU
- Similar to bio-based, maybe use simpler terminology to get the message across
- Currently, brands are a stronger driver than regulation & policy for CCU
- Companies are largely convinced that a reliable label would be a strong tool for marketing

Main take-aways consumers

- No knowledge of CCU - positively surprised about CCU when they understand the concept
- Trust is strongly dependent on the source of information
- Issues can arise via the NIMBY-effect: If people perceive issue to personal health or other personal limitations (e.g. CCU plant in neighbourhood), they might oppose
- Best method to transfer information likely depends on the circumstances

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Contact:

heleen.dewever@vito.be

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