VIVALDI
From Concept to Reality: Key Technical Achievements

https://www.vivaldi-h2020.eu/

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PUBLIC

The novel CO_2-based industry

- Novel carbon capture and utilisation strategies for CO_2 valorisation are needed to achieve the European Union's target of reducing emissions by at least 80% by 2050.
- The yearly increasing industrial CO_2 emissions should not only be reduced or mitigated but should also be adopted as a novel feedstock: the era of the CO_2-based chemicals.
- Industries should abandon the conventional linear structure (i.e. fossil-based reagents are transformed into products and wastes to be disposed or treated) and switch to a circular concept where the (gaseous or liquid) wastes are transformed into novel sustainable compounds to be reused in the plant flowchart or to be sold externally.
- Bio-based products are shown to provide GHG savings (15% to 66%) if we assume that they will replace 20% of their fossil counterparts in the midterm future

VIVALDI : innoVative bIo-based chains for CO_2 VALorisation as aDded-value organIc acids

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Turns CO_2 emissions into sustainable bioproducts

Start date:
1.6.2021

Funded under:
H2020-EU 3.2.

Duration:
4 years

16 partners

Budget:
7 M€

Project partners

The multidisciplinary and international consortium is formed by **16 partners**, including:

- biobased Industries
- technology developers
- end-user
- knowledge hubs

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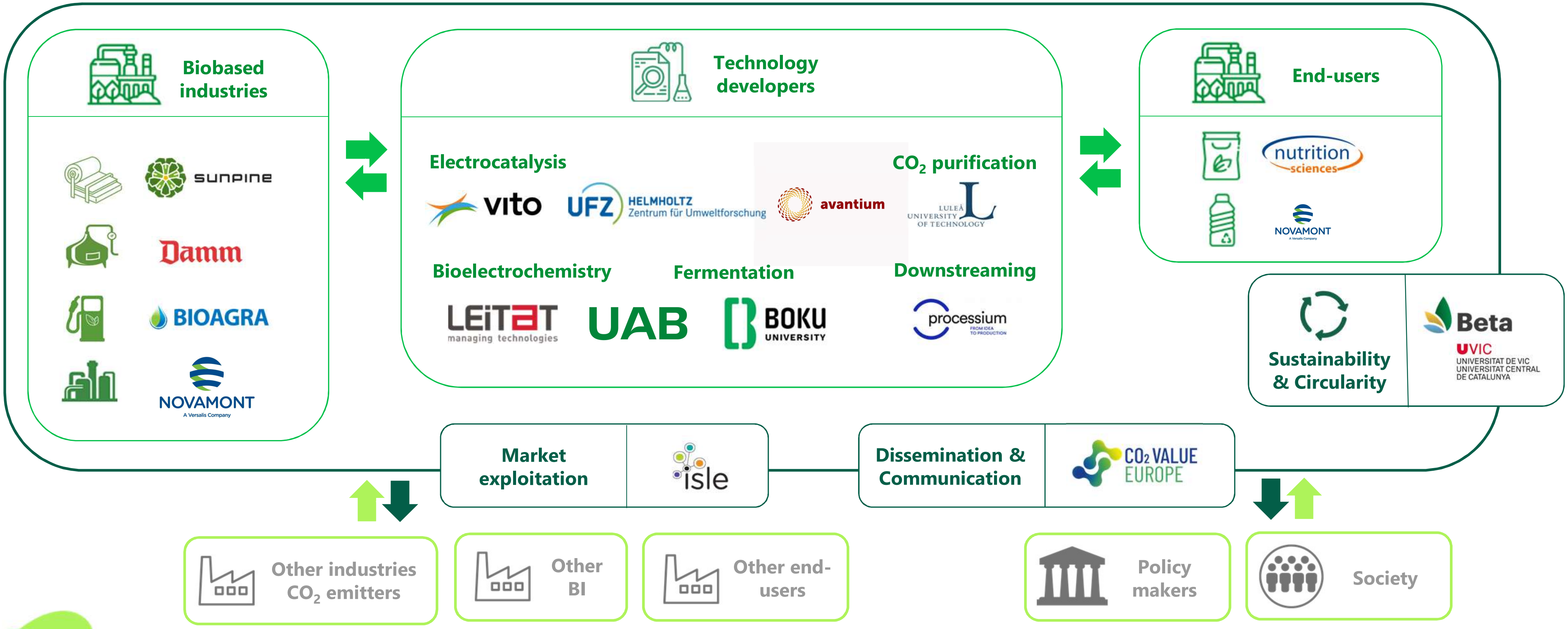
Turns CO2 emissions into sustainable bioproducts

Methodology



Biobased industries

Technology developers

Electrocatalysis

CO_2 purification

Bioelectrochemistry

Fermentation

Downstreaming

End-users

Sustainability & Circularity

Market exploitation

Dissemination & Communication

Other industries CO_2 emitters

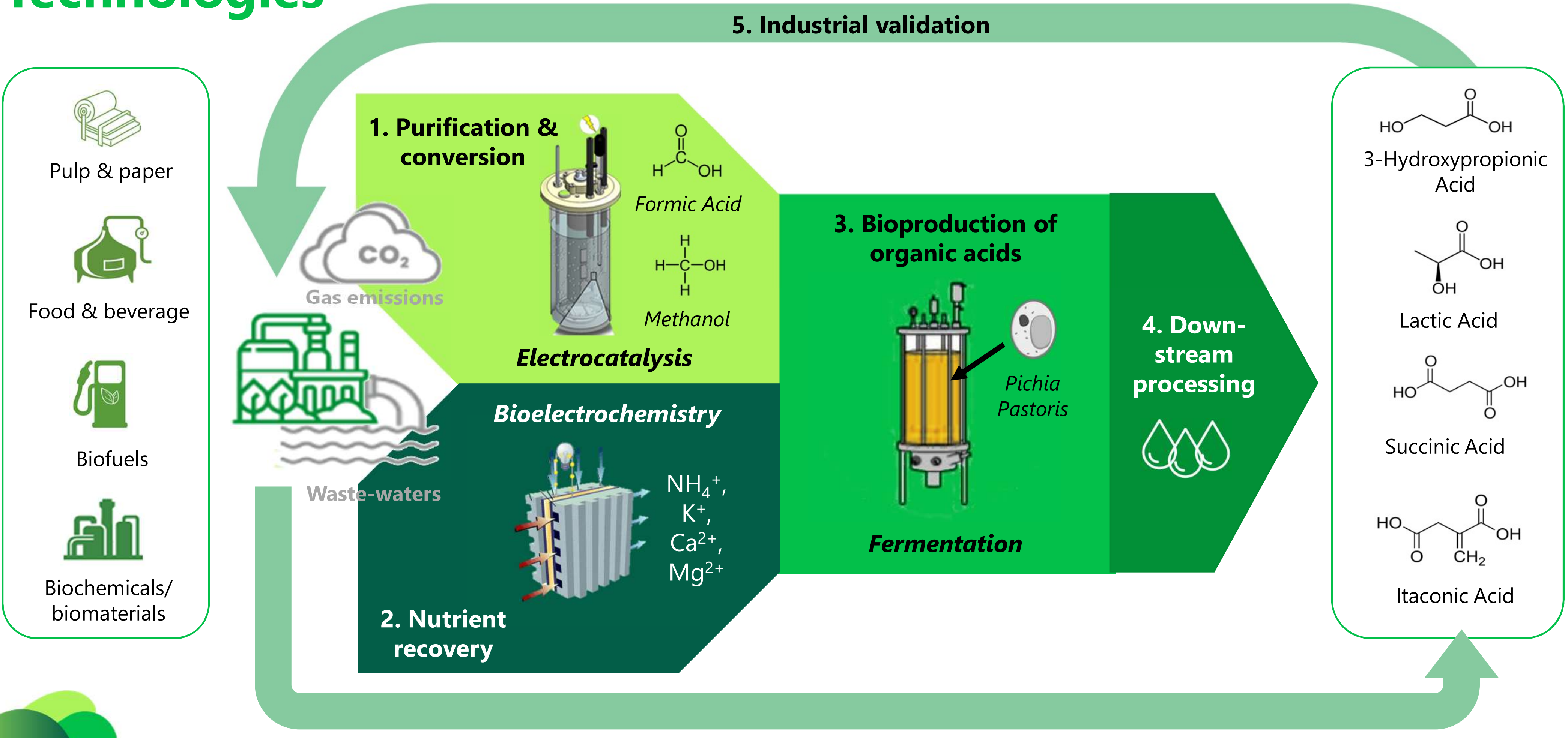
Other BI

Other end-users

Policy makers

Society

Technologies



5. Industrial validation

Pulp & paper

Food & beverage

Biofuels

Biochemicals/ biomaterials

Gas emissions

Waste-waters

1. Purification & conversion

Formic Acid

Methanol

Electrocatalysis

Bioelectrochemistry

NH_4^+, K^+, Ca^{2+}, Mg^{2+}

2. Nutrient recovery

3. Bioproduction of organic acids

Pichia Pastoris

Fermentation

4. Down-stream processing

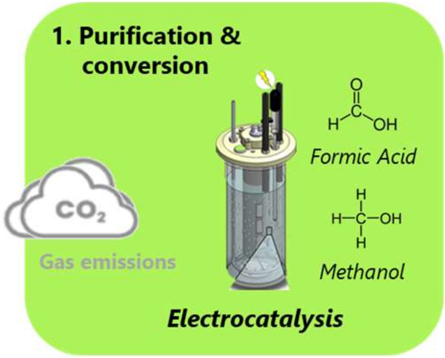
3-Hydroxypropionic Acid

Lactic Acid

Succinic Acid

Itaconic Acid

CO_2 capture, purification and conversion to Formic acid and methanol



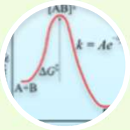
Why MDEA-based absorption with the enzyme carbonic anhydrase ?

it enables economic, efficient and selective CO_2 purification for:

- Large amounts of CO_2
- Low energy use
- Possibility of H_2S removal
- Lower Heat of Regeneration

Potential drawback: slow CO_2 absorption rate

Why CO_2 electroreduction?



CO_2 transformation is limited by thermodynamic and kinetic inertness. To overcome the high energy barriers of CO_2 activation, catalysts are required.

It can be produced at biocompatible conditions (neutral pH, ambient temperature and pressure, physiologic salinity and under presence of components of microbial media).

Depending on the conditions and electrode materials, different products can be obtained. Understanding ECO_2R opens a plethora of novel possibilities of CO_2 valorisation as microbial feedstock.

ECO_2R provides a pathway for the utilization and (temporary) storage of electric energy. Electricity from photovoltaic cells, wind turbines, or off-peak grid power sources can be used to drive CO_2 reduction.

Why Formic Acid (FA) and Methanol (MeOH)?

i. CO_2 reduction to added-value chemicals (i.e. FA) leads to short-term economic feasibility to **a higher market price** and (MWh/tC) among similar **higher energy content** products.

ii. **Biomethanol** from wastes has a higher value (400–450 €/ton) than its cost of production 200 €/ton

iii. The **energetic efficiency** of converting FA/MeOH into biomass aerobically can reach 50%, while for other C1-feedstocks it lies in a range of 20–40%.

iv. Microbial utilisation of FA and MeOH as C-source needs a **minimal media and simple nitrogen sources**

v. Cultivation of microorganisms on C1-gases (e.g. CH_4, CO, and H_2/CO_2) has several drawbacks: low water solubility, limited mass transfer (due to phase boundaries), issues with storage and transportation, low yield and low microbial productivity.

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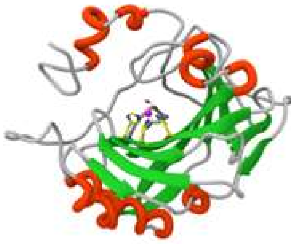
CO_2 capture and purification

CHEMO-ENZYMATIC CO_2-CAPTURE

Tertiary-amine based solvent + Carbonic anhydrase (CA)

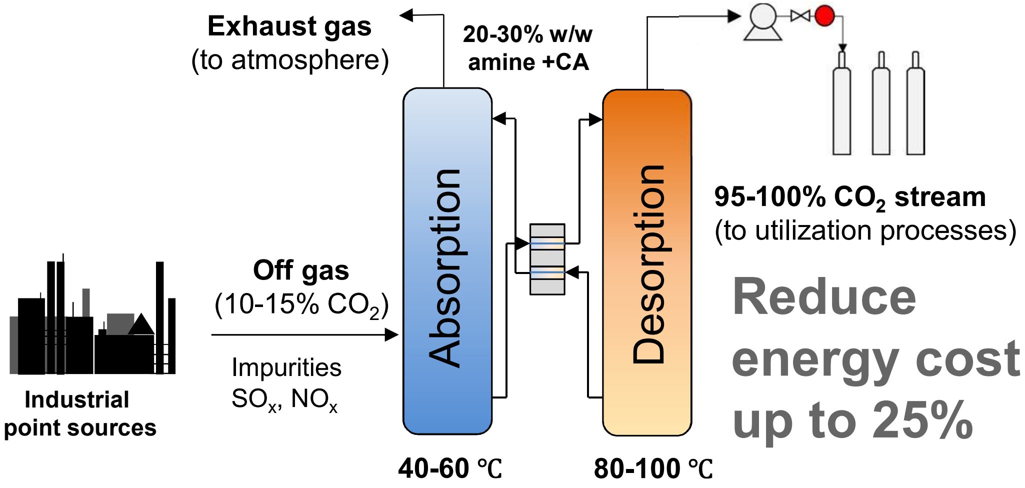
- was first discovered in vertebrate erythrocytes in the 1930s
- can be found in many organisms (humans, animals, bacteria…)
- is one of the fastest enzymes in nature (turnover up to 10^7 s^{-1})



Predominant reactions:

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

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



Exhaust gas
(to atmosphere)

20-30% w/w amine +CA

Industrial point sources

Off gas
(10-15% CO_2)

Impurities
SO_x, NO_x

Absorption

Desorption

95-100% CO_2 stream
(to utilization processes)

40-60 ℃

80-100 ℃

Reduce energy cost up to 25%

Higher absorption rates than MDEA only

Low energy for solvent regeneration

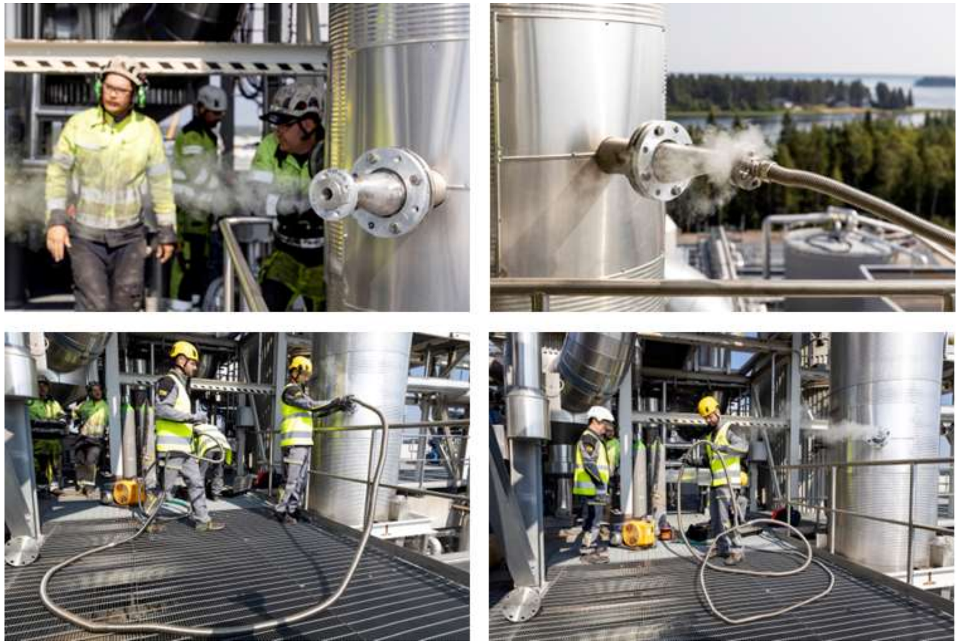
Mild conditions (pH 8.0)

Ayanne de Oliveira Maciel, et al., *Chemosphere*, (2022) p. 134419.

CO_2 capture and purification

Flue gas sampling campaign

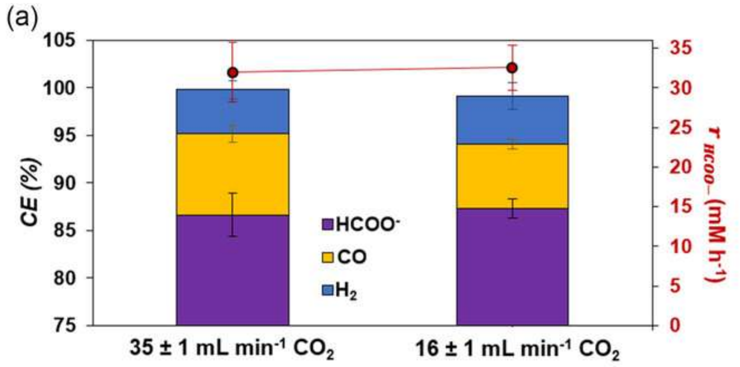
SunPine (Piteå, Sweden) - 2022

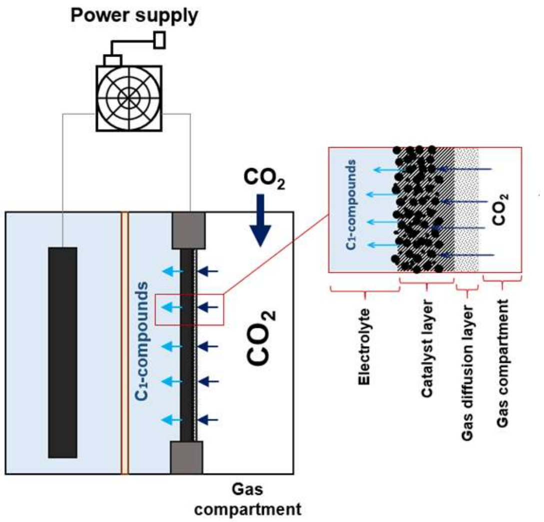


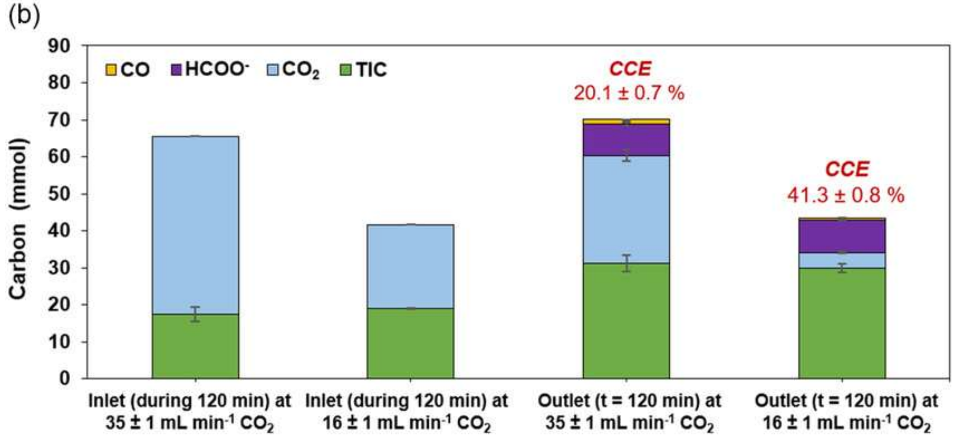
Component	Bottle 1 – before scrubber	Bottle 2 – after scrubber	Bottle 3 – after scrubber
CO_2 %	11.9	11.8	11.8
CO (ppm)	0	0	0
SO_x (ppm)	5	0	0
NO_x (ppm)	0	0	0
C_xH_y (ppm)	1370	480	510
O_2 %	5.7	5.6	5.7

CO_2 conversion to Formic Acid

- **Engineering electrochemical CO_2 reduction reaction using gas diffusions electrodes to the optimum efficiency in terms of**
- Electrons - Coulombic efficiency (*CE*): Limit is 100%
- Carbon (CO_2) - Carbon conversion efficiency (*CCE*): Limit is 50%

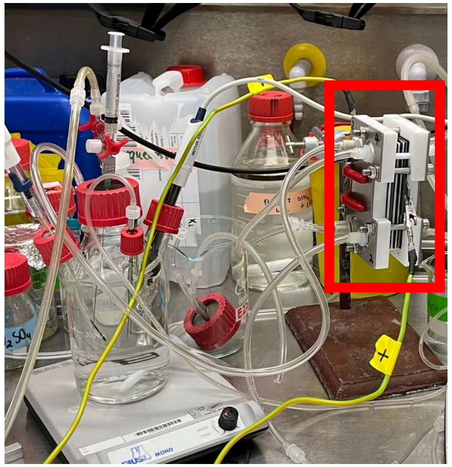






Izadi et al., *Advanced Energy and Sustainability Research*, (2024) p.2400031.
Izadi and Harnisch, *Joule,* 6 (5), 935 - 940

Scale up of eCO_2RR to formate

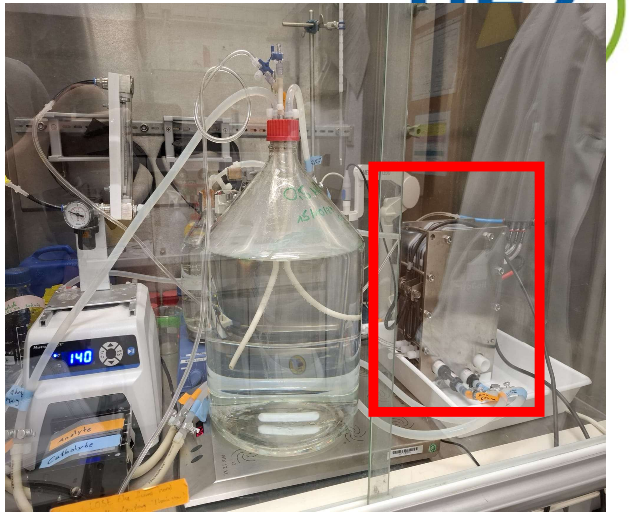


0.5 L
10 cm^2 electrode

→ 10 times →

5 L
100 cm^2 electrode

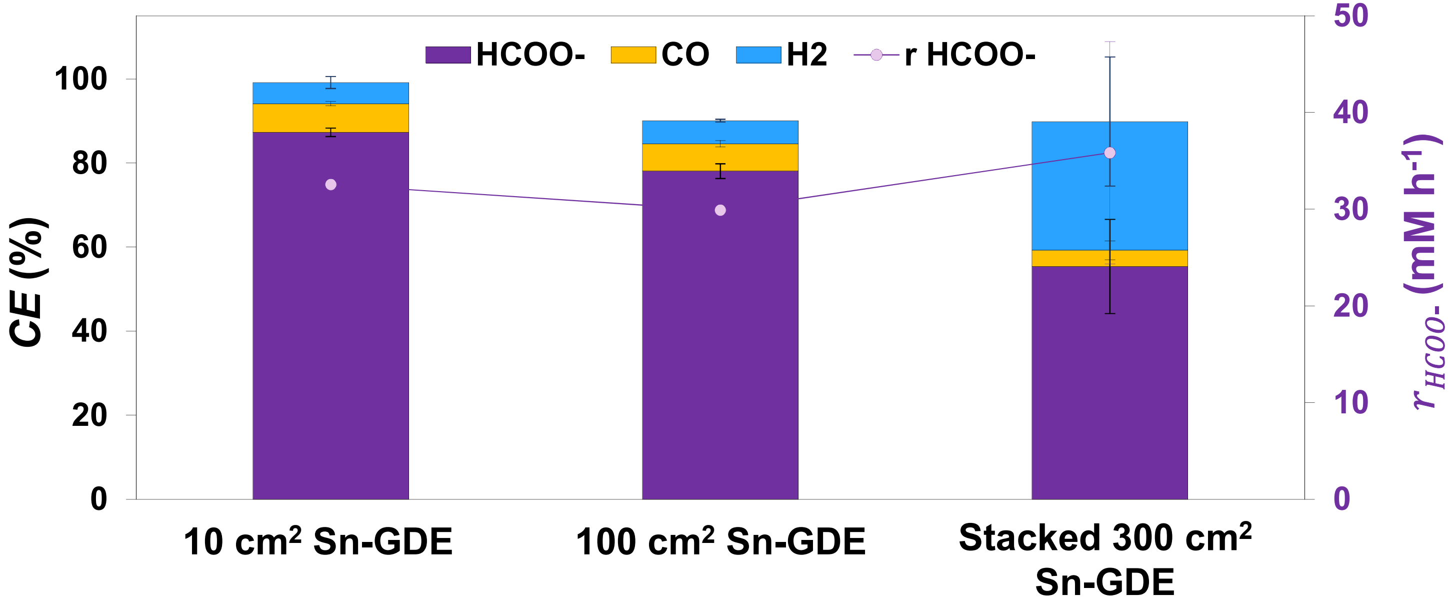
→ 3 times →



15 L
Stack 300 cm^2 electrode

Izadi*, Varhade, Schneider, Haus, Singh, Guruji, Pant, and Harnisch, Industrial Chemistry & Materials,
Under review (collaboration of UFZ and VITO)

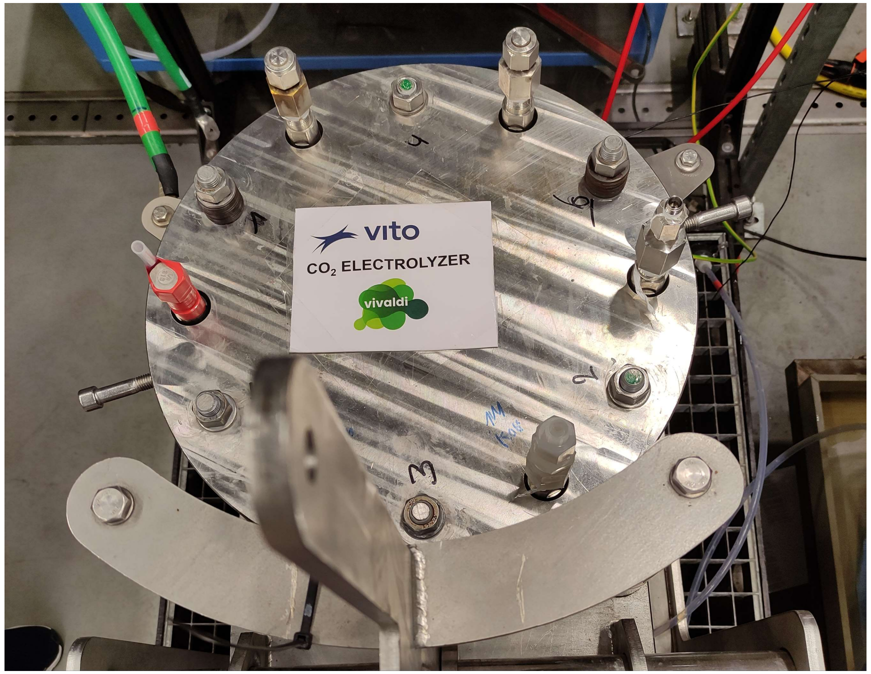
Scale up of eCO_2RR to formate



Izadi*, Varhade, Schneider, Haus, Singh, Guruji, Pant, and Harnisch, Industrial Chemistry & Materials, Under review (collaboration of UFZ and VITO)

Scale up of eCO_2RR to formate

A flow cell set up with scaled up Sn and Bi electrode (400 cm^2)



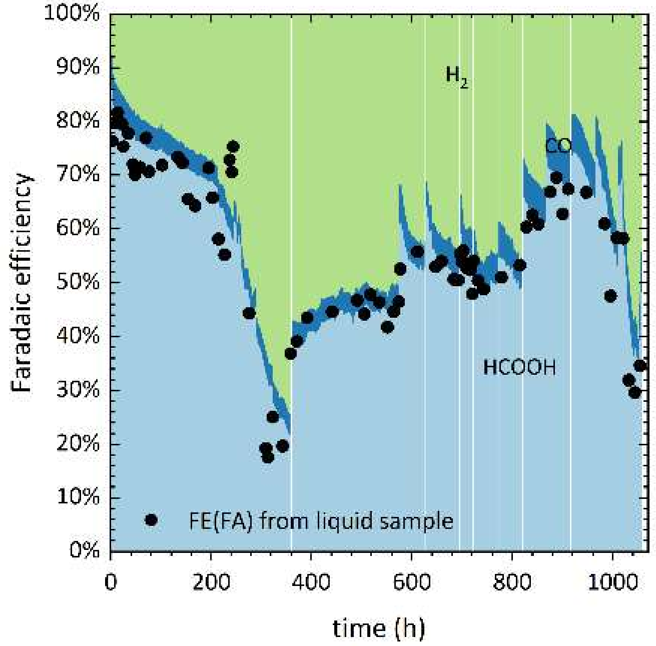
- 2 M KOH as electrolyte
- CO_2 800-1000 mL/min in a flow-through mode of operation.
- Fumasep® FKB-PK- 130 Membrane (AEM)
- Cell operated at galvanostatic condition at 40 A (j=100 mA/cm^2)
- Formate concentration measured using HPLC technique by periodically collecting samples from both anolyte and catholye.

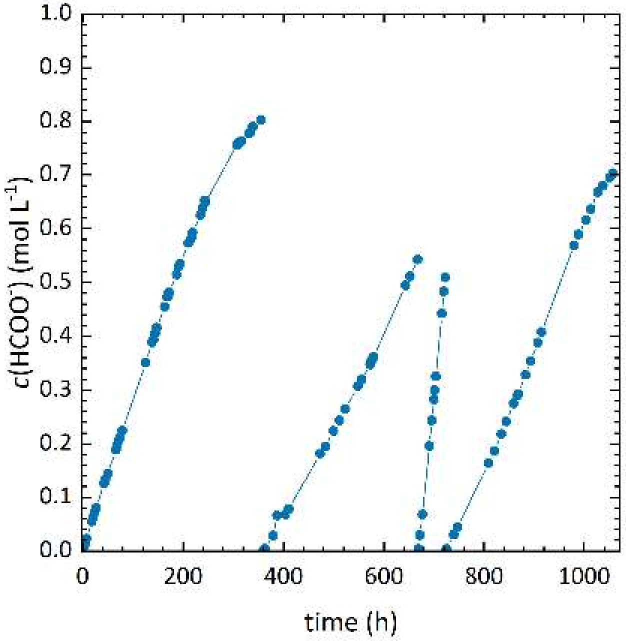
Chandani SINGH *et al.* RE-ACTIVATION PROCESS OF GAS DIFFUSION ELECTRODE. WO2024251664A1; PCT/EP2024/065202 (filed June 3, 2023).

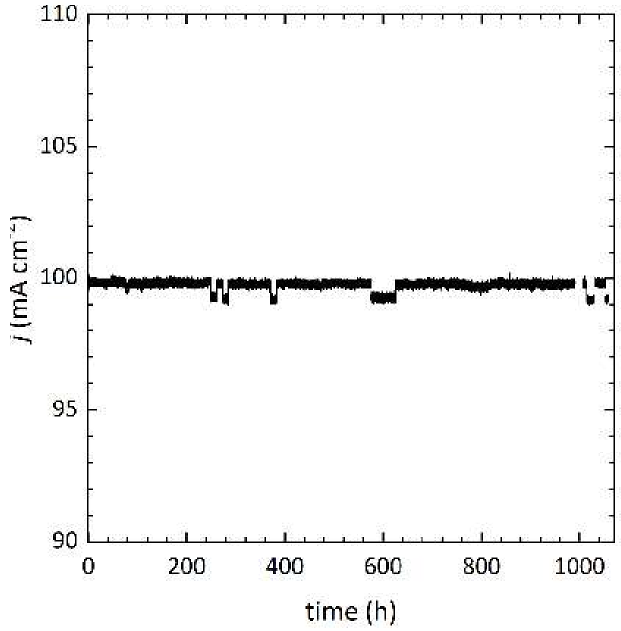
Scale up of eCO$_2$RR to formate

- 1000-hour test of Sn GDE

- Effect of changing process conditions (K$^+$ migration, Formate build up)
- Recovery of selectivity towards formate → patent filed (**2023016EP01**)



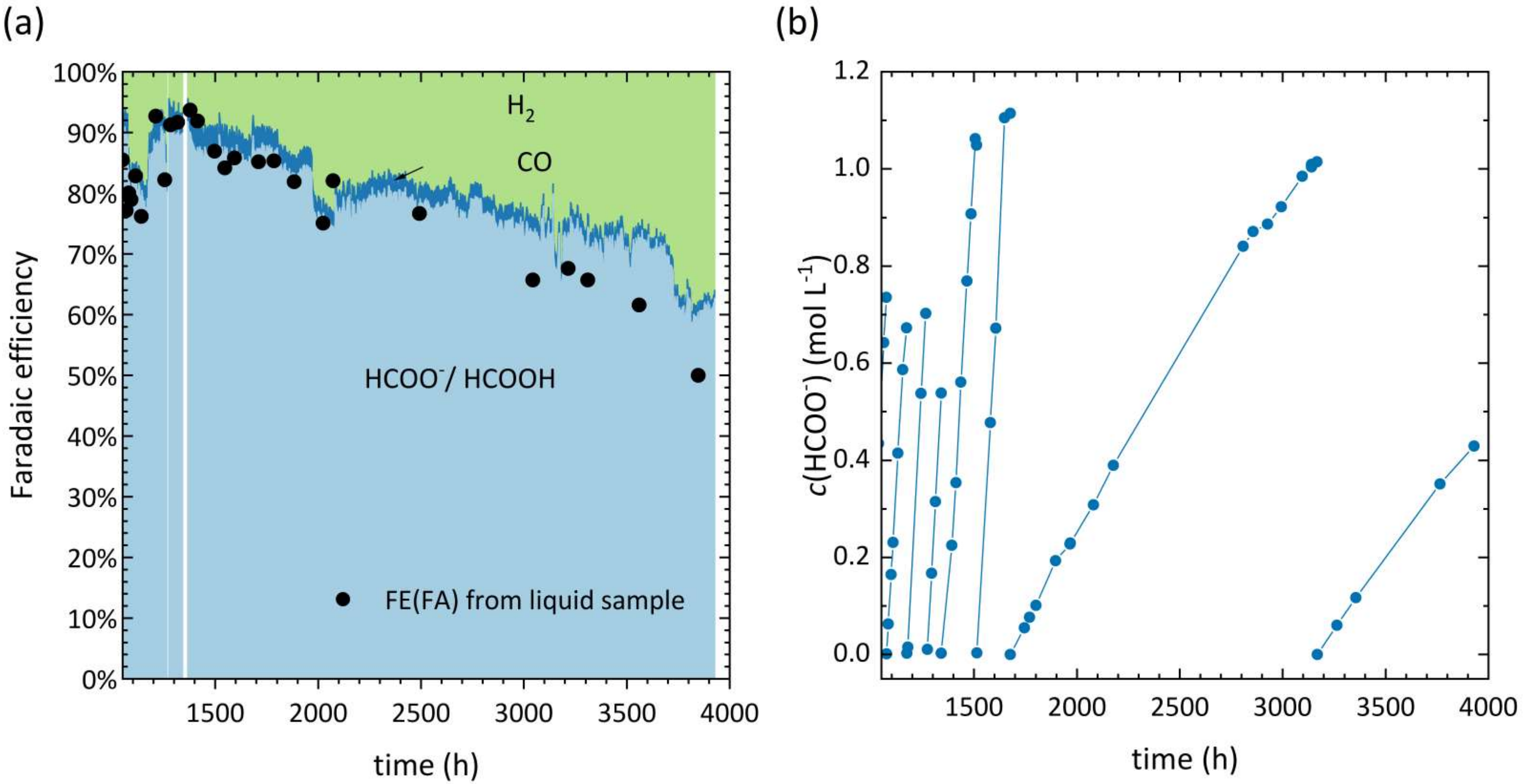




Chandani SINGH *et al.* RE-ACTIVATION PROCESS OF GAS DIFFUSION ELECTRODE. WO2024251664A1; PCT/EP2024/065202 (filed June 3, 2023).

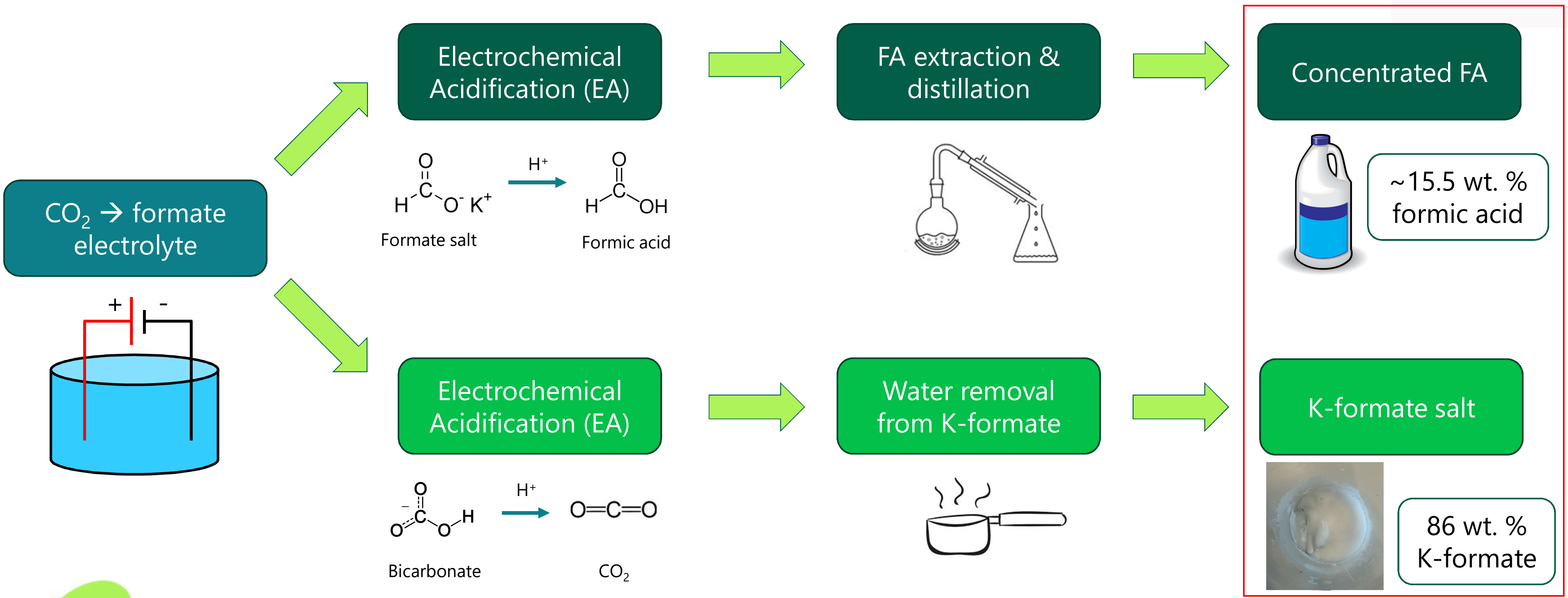
Scale up of eCO_2RR to formate

- 4000 Hours operation with Bi-GDE



Formic Acid purification

Used in fermentation



CO_2 → formate electrolyte

Electrochemical Acidification (EA)

FA extraction & distillation

Concentrated FA

~15.5 wt. % formic acid

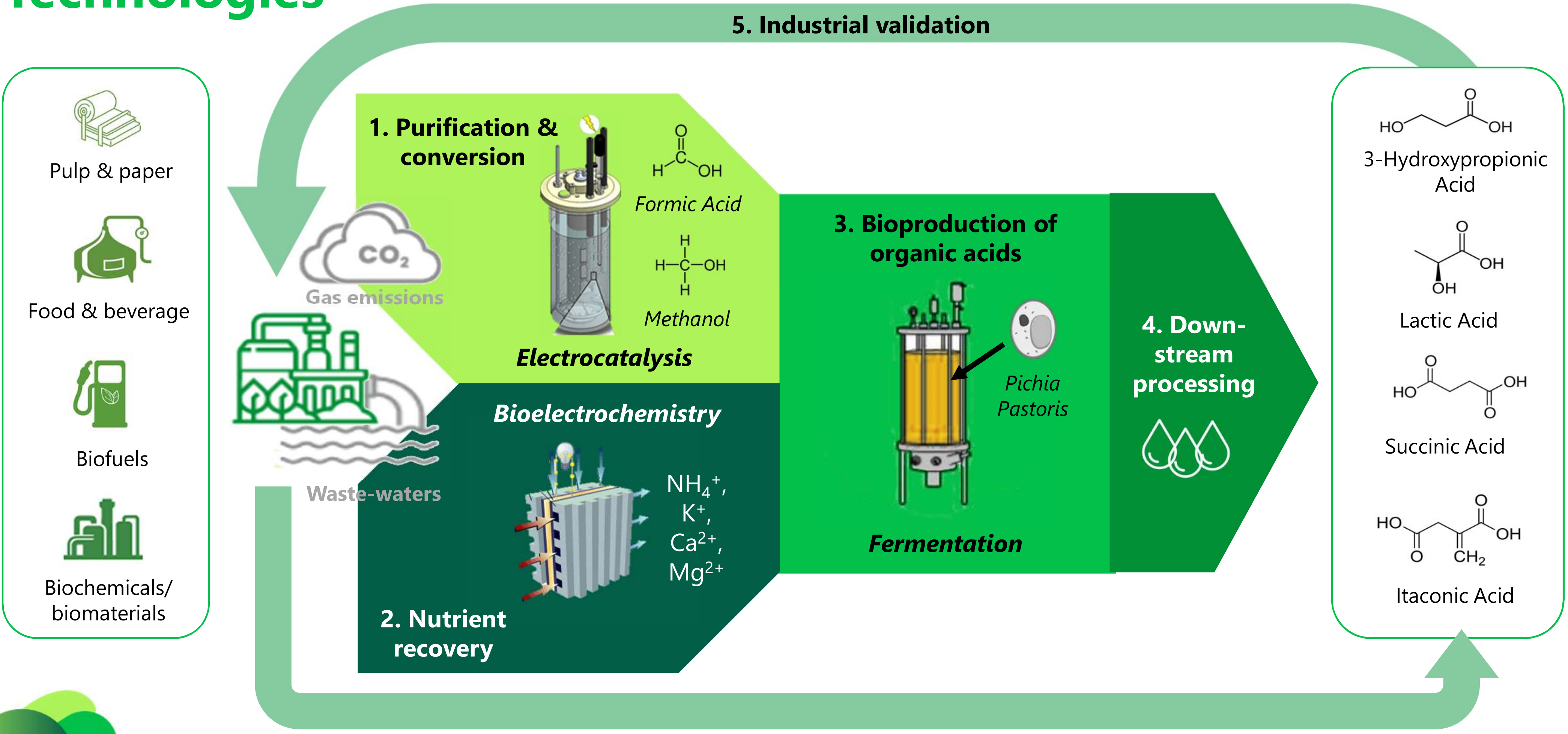
Electrochemical Acidification (EA)

Water removal from K-formate

K-formate salt

86 wt. % K-formate

Technologies



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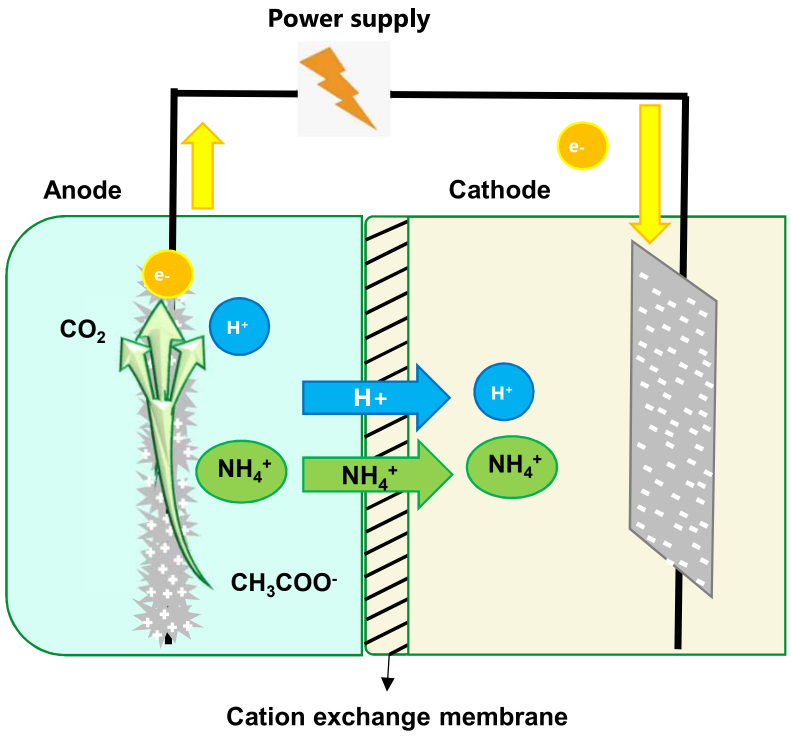
Bioelectrochemical ammonium recovery

UAB



Organic matter is oxidised at the anode side and electrons flow from the anode to the cathode since a **potential is applied** in the cell

The charge balance due to the electron transport is balanced by **cation transport over the cation exchange membrane (CEM)** to maintain electroneutrality

Therefore, ammonium and other cations are concentrated in the cathode compartment

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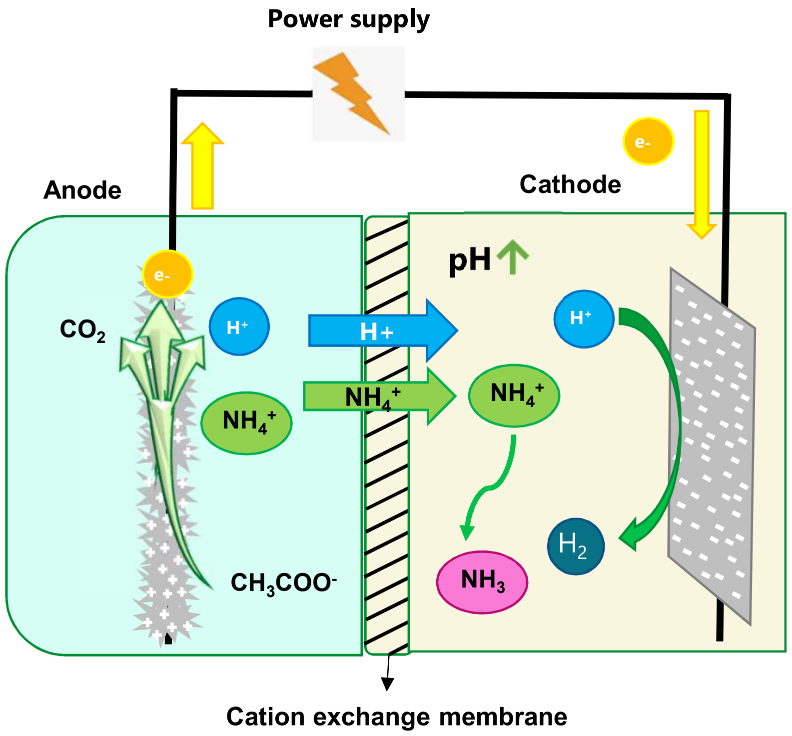
Turns CO₂ emissions into sustainable bioproducts

Bioelectrochemical ammonium recovery

UAB



The **NH_4^+** cations, once transported into the catholyte, are converted into **NH_3** molecules because H_2 production increases pH of the catholyte

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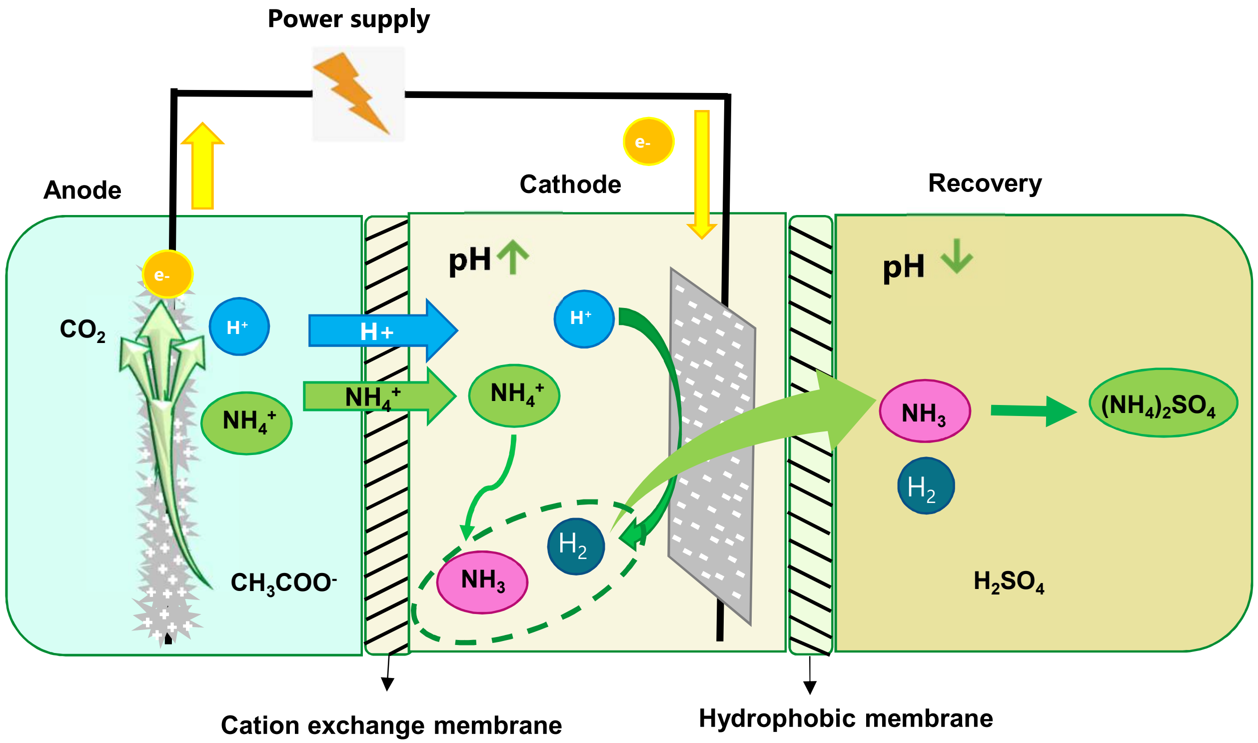
Turns CO₂ emissions into sustainable bioproducts

Bioelectrochemical ammonium recovery

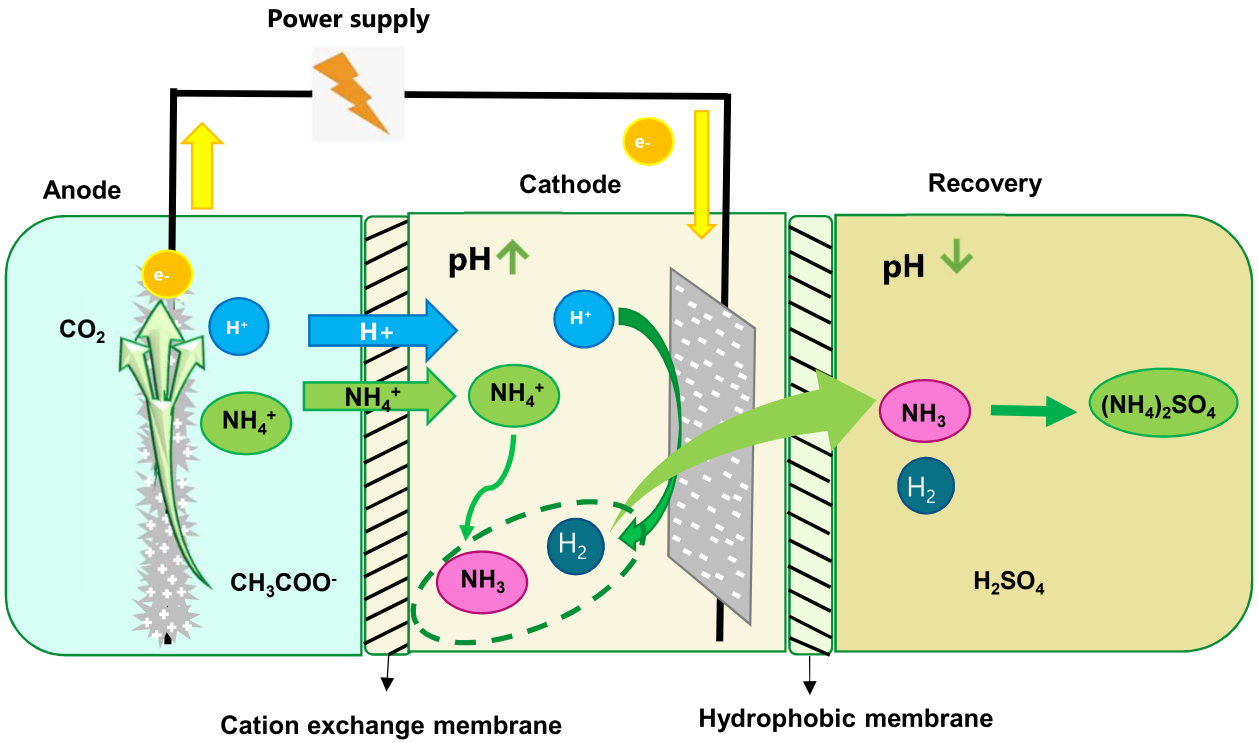


NH_3 can pass through the pores of the hydrophobic membrane and is absorbed by sulphuric acid on the other side to produce **ammonium sulphate**

The **hydrophobic membrane** prevents the permeation of other ions, enhancing ammonia purity in the recovery solution

Galeano M, Sulonen M,Ul Kausar Z, Baeza M, Baeza JA and Guisasola A. Bioelectrochemical ammonium recovery from wastewater: A review
Chemical Engineering Journal Volume 472, 15 September 2023, 144855

Bioelectrochemical ammonium recovery



Power supply

Anode

Cathode

Recovery

e^-

e^-

CO_2

H^+

NH_4^+

CH_3COO^-

$H+$

NH_4^+

pH ↑

H^+

NH_4^+

NH_3

H_2

pH ↓

NH_3

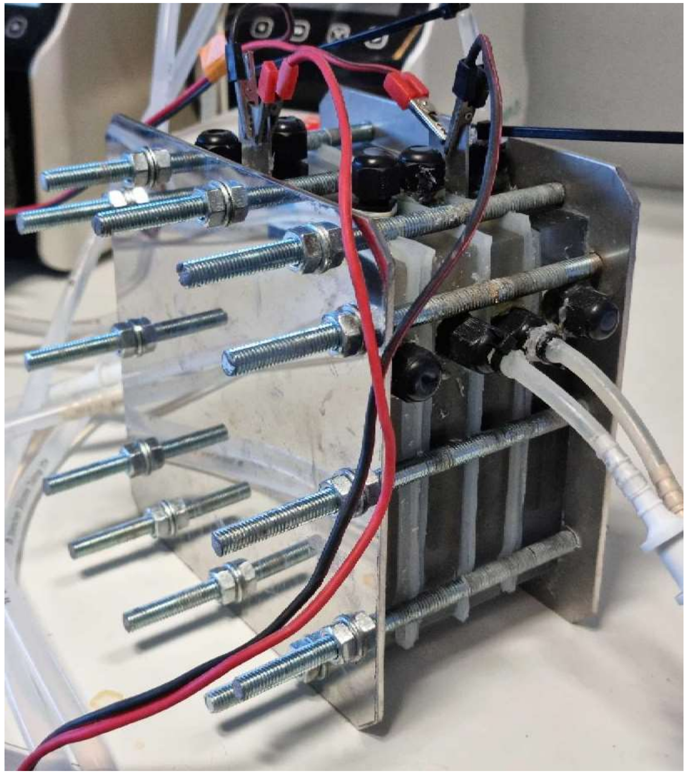
H_2

$(NH_4)_2SO_4$

H_2SO_4

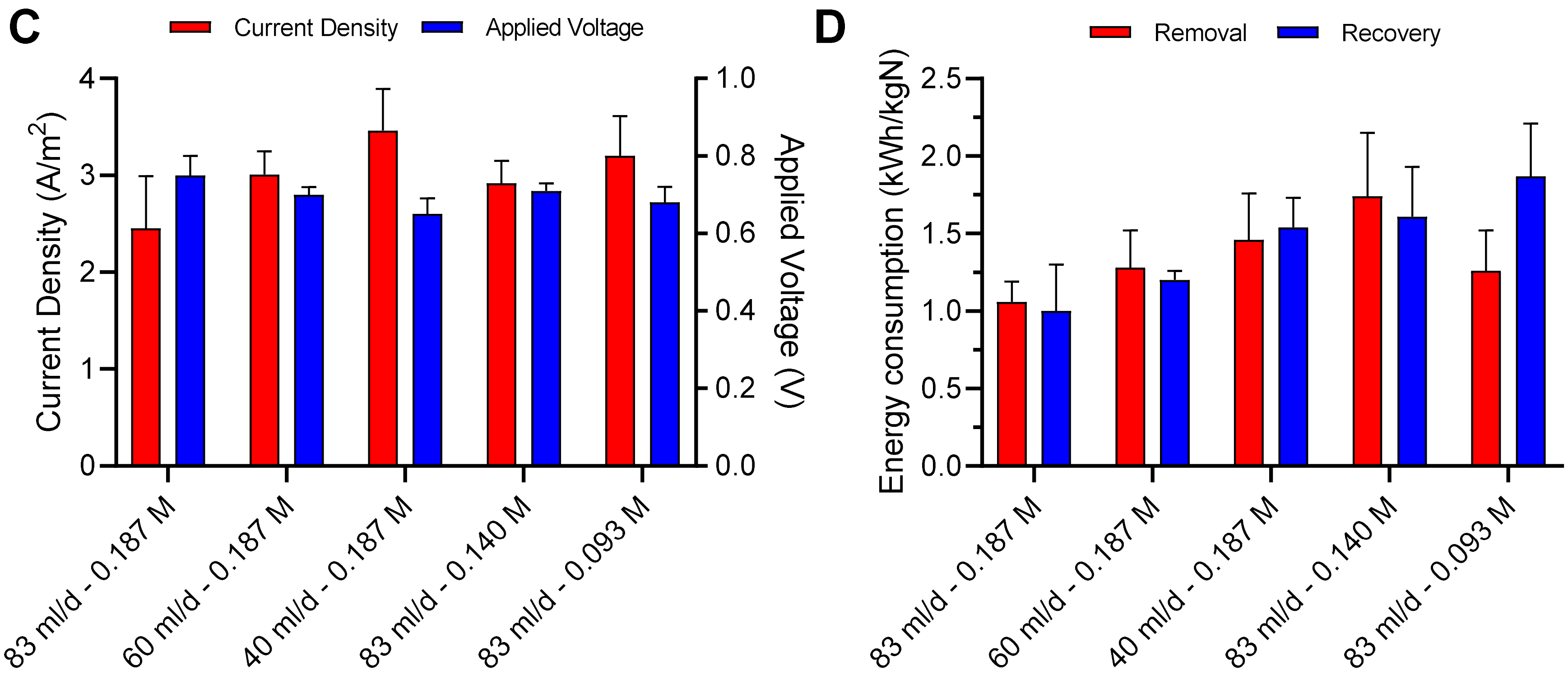
Cation exchange membrane

Hydrophobic membrane



moving to continuous conditions: energy demand

UAB



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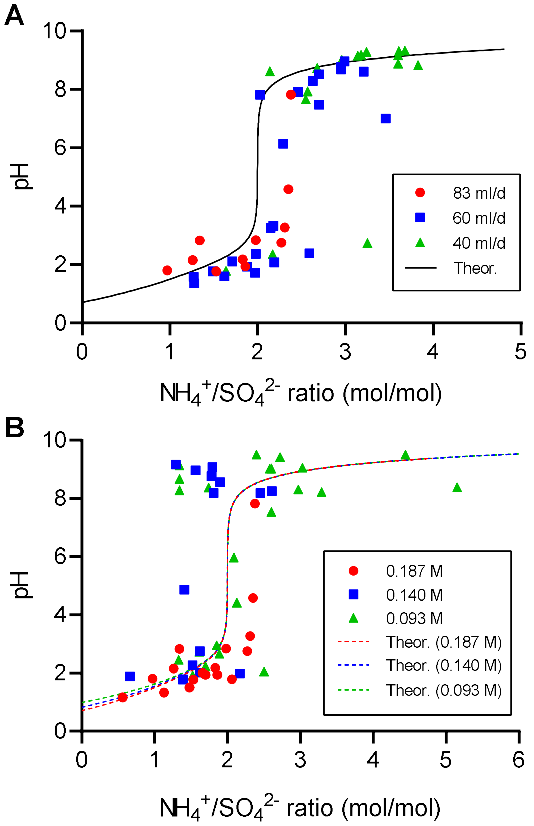
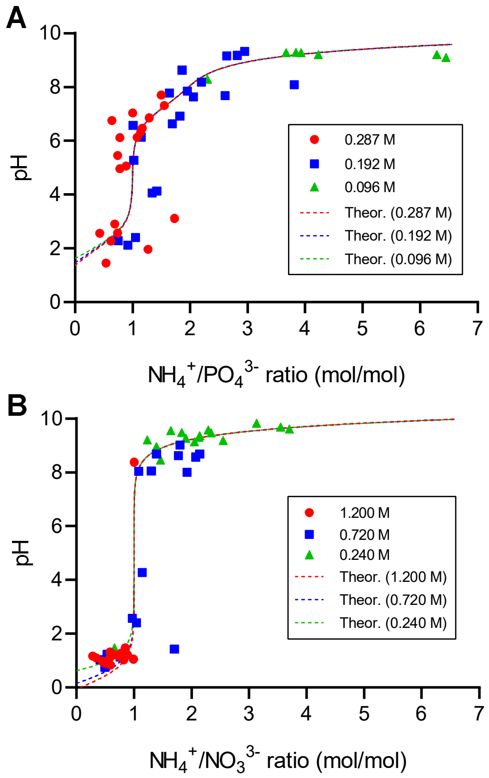
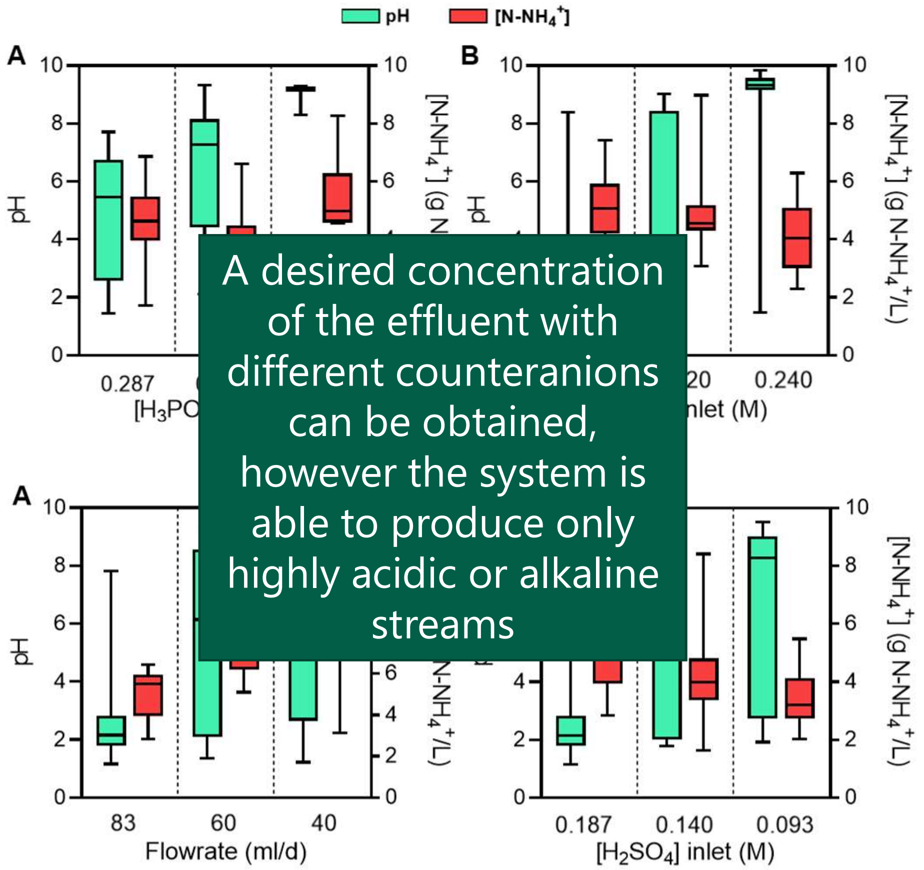
Customizing ammonium recovery effluents (pH, concentration, counter-anion)







A desired concentration of the effluent with different counteranions can be obtained, however the system is able to produce only highly acidic or alkaline streams

Fernández-Verdejo D, Galeano M, Ul Kausar Z, Baeza JA, Guisasola JA. Customizing bioelectrochemical ammonium recovery to produce effluents with different characteristics (under preparation)

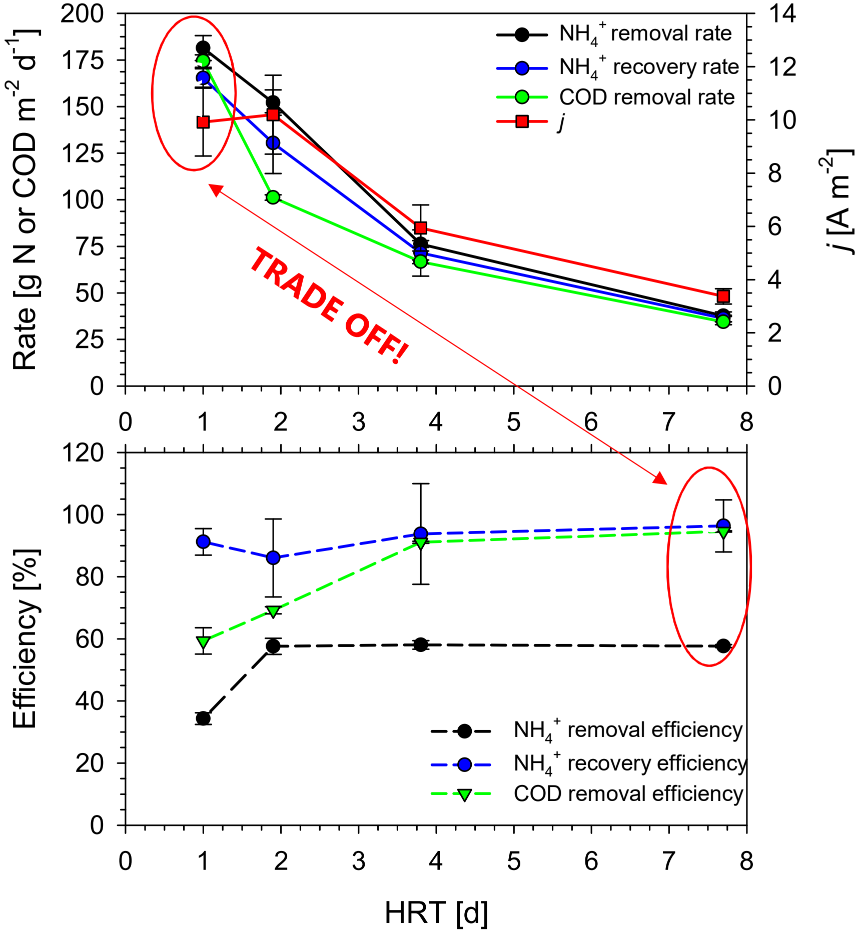
Implementation of a pH control in the recovery chamber

Optimising ammonium recovery rate:

- Evaluation of different Hydraulic Retention Times (HRTs) was carried out to test the robustness of the pH control and to identify optimal operating conditions for ammonium recovery.

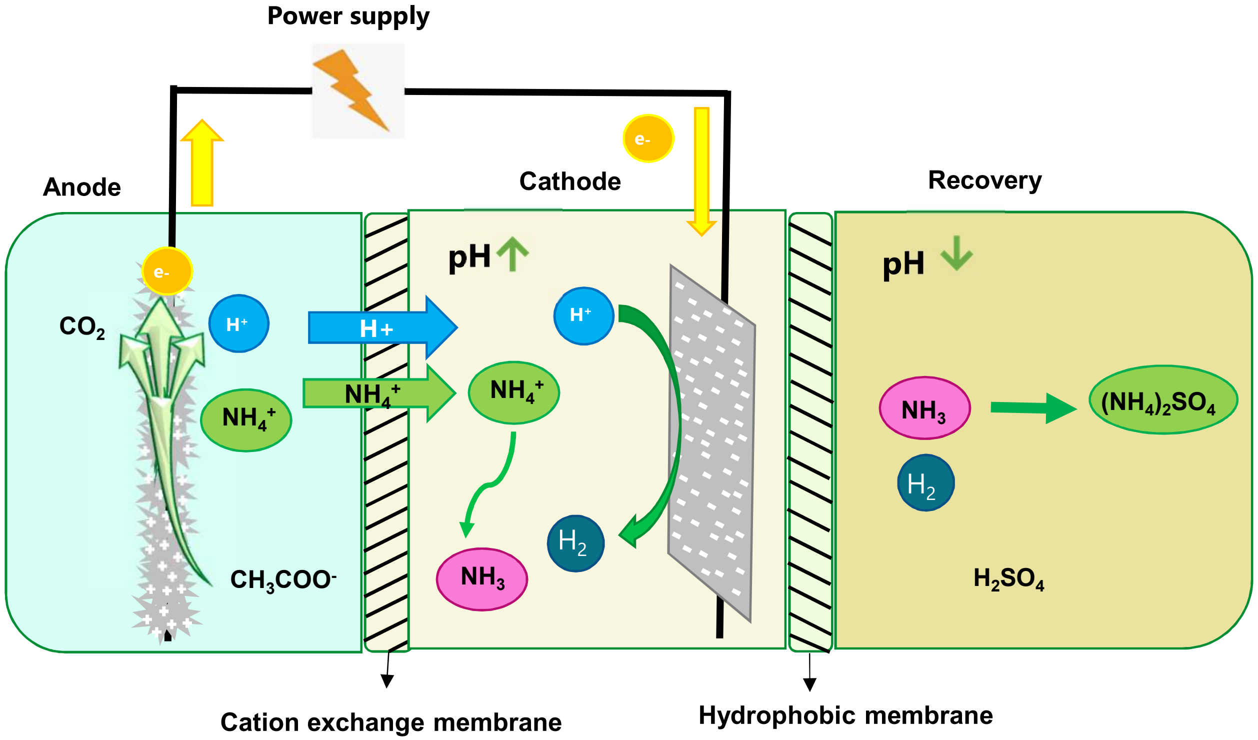
- Peak performance was achieved at HRT = 1.9d:
  - **>11 A/m²**
  - **>150 g N/m²/d recovered**
  - **>180 g N/m²/d removed**
  - **<1.5 kWh/kg N recovered**
  - **>90% recovery efficiency**
  - **>60% COD removal**
  - **>1.26 m^3 H_2/m^3 reactor/d (if r_{CAT} = 100%)**

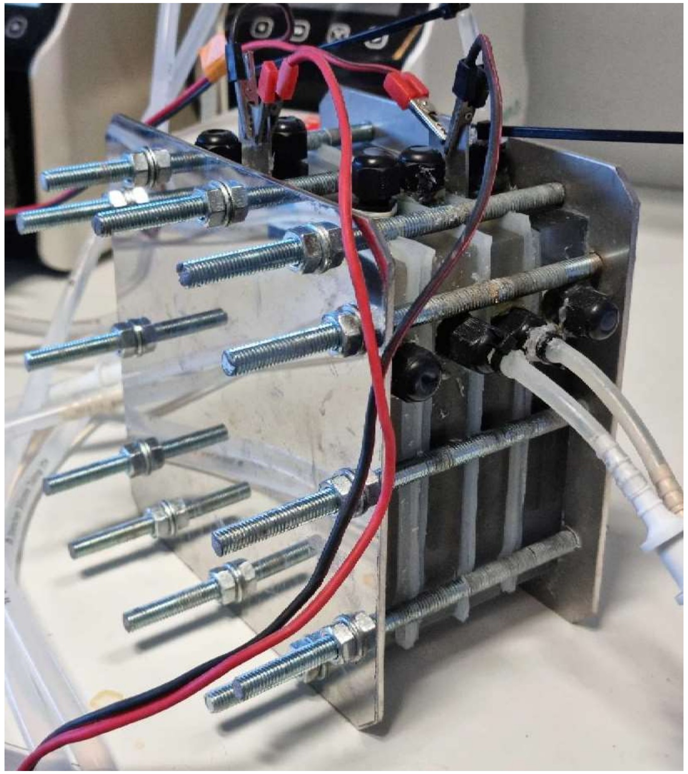
- However, at and HRT<1d, the ammonium concentration in the anolyte was excessive, causing a decrease in performance and destabilizing the pH in the recovery chamber (possible inhibition by free ammonia).



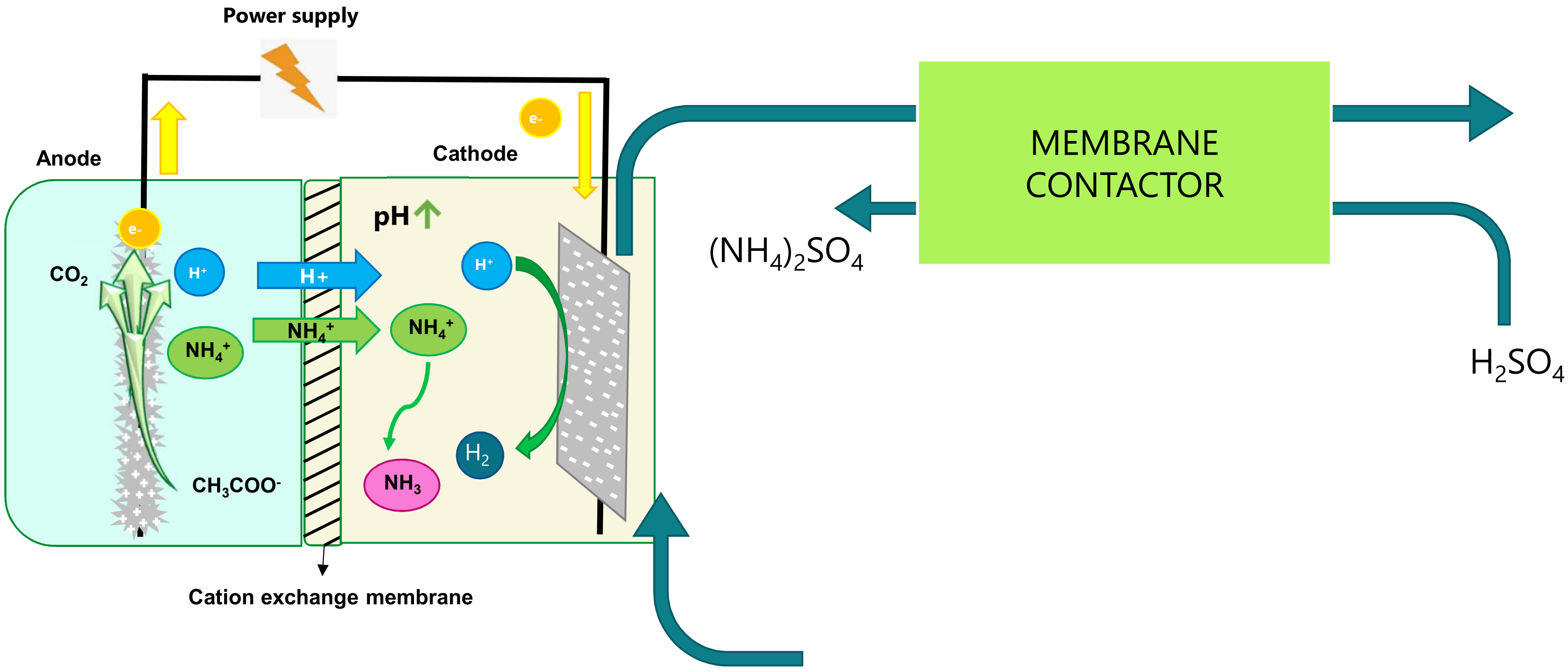
Bioelectrochemical ammonium recovery

UAB



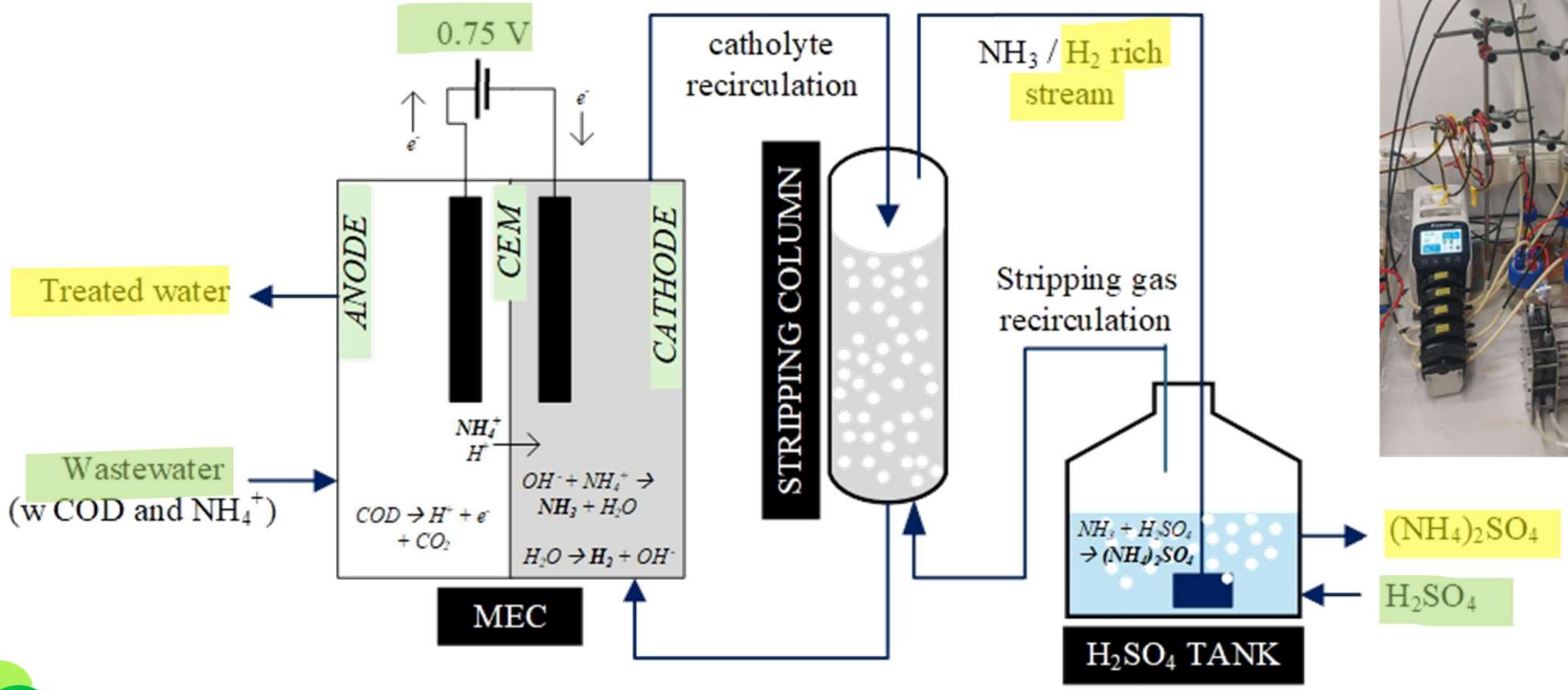


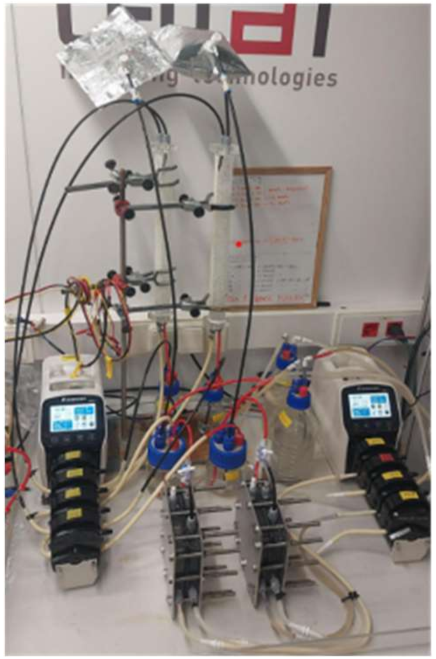
Bioelectrochemical ammonium recovery



Bioelectrochemical ammonium recovery

MEC reactor for nitrogen (NH_4^+) removal and recovery (NH_3 or NH_4^+)



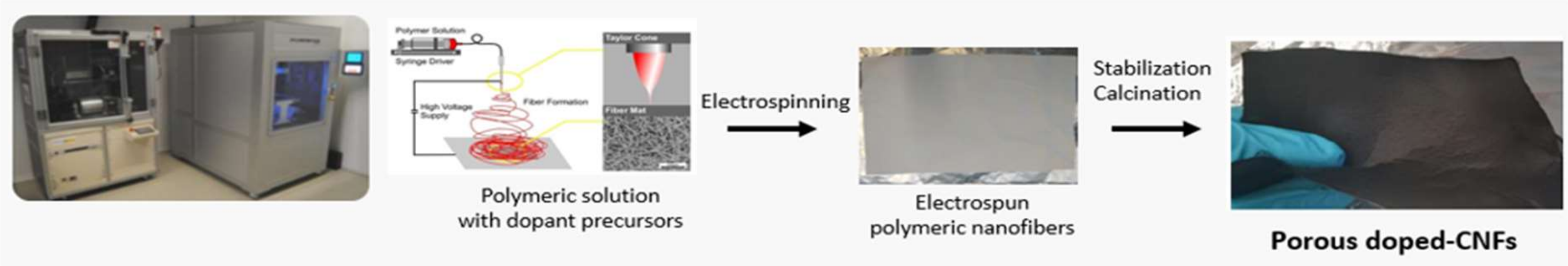


Bioelectrochemical Ammonium Recovery

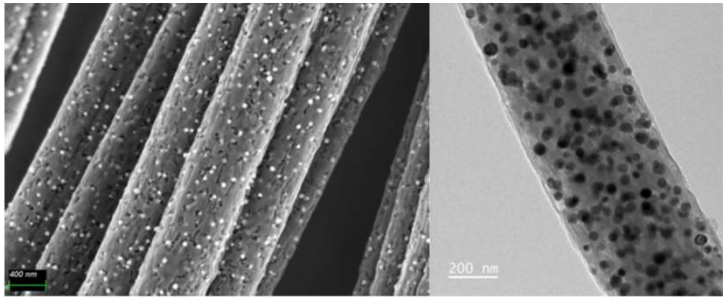
Free-Standing Carbon Nanofiber Films with Cobalt Phosphide Nanoparticles as Cathodes for Hydrogen Evolution Reaction in a Microbial Electrolysis Cell

- ### Fabricated by electrospinning

Pérez-Pi, Gerard, et al. "Free-Standing Carbon Nanofiber Films with Supported Cobalt Phosphide Nanoparticles as Cathodes for Hydrogen Evolution Reaction in a Microbial Electrolysis Cell." Nanomaterials 14.22 (2024): 1849.

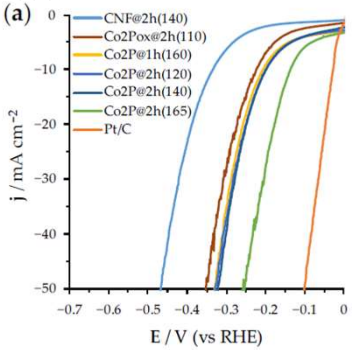


- ### HRSEM and TEM images of the sample Co2P@2h(165)

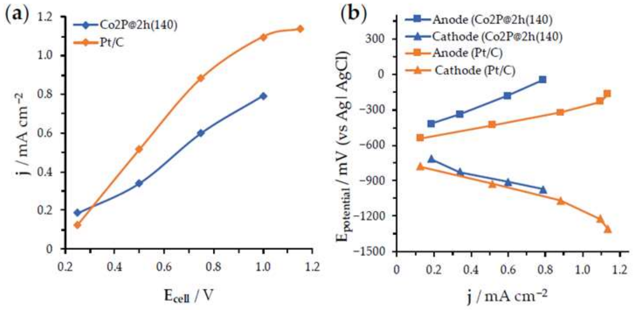


- ### LSV curves of developed materials,

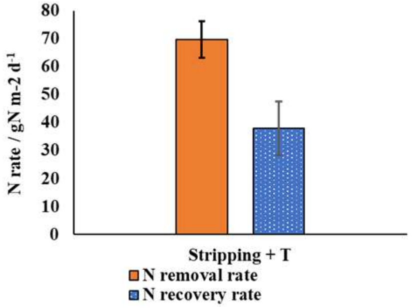
the best results were found for Co2P@2h(165), with overpotential η10 = 137 mV, which is significant good for free Pt cathode.



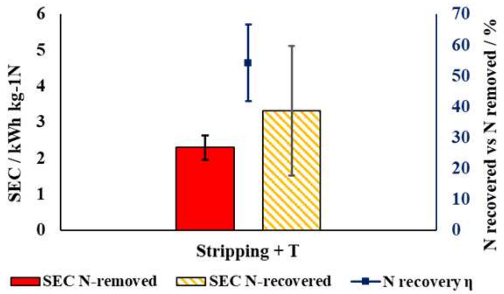
- ### Good performance comparison of Co2P@2h(140) versus Pt/C cathodes in MEC reactors.



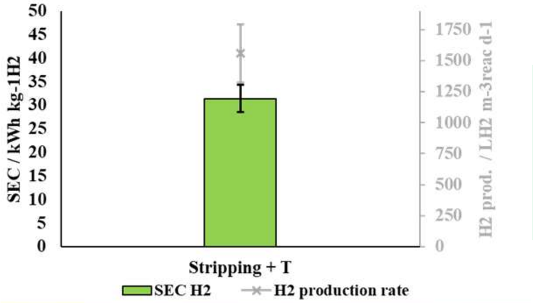
Bioelectrochemical Ammonium Recovery



High removal (efficient treatment) and hight recovery rates of NH_4^+

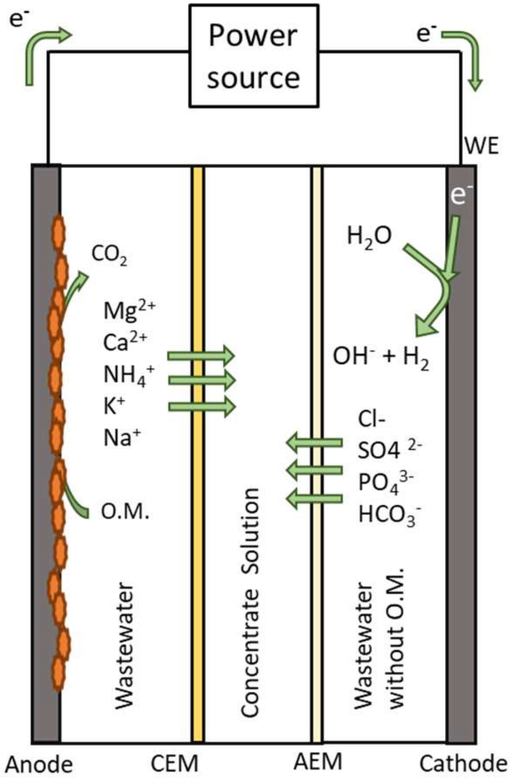


High energy efficiency, vs. other NH_4^+ removal approaches and fertilizer production through Haber-Bosch (8 kWh $kgNH_3^{-1}$)



Also, H2 is produced with high energy efficiency, less than 35 vs 55 KWh $kg^{-1}H_2$ used by electrolyzers

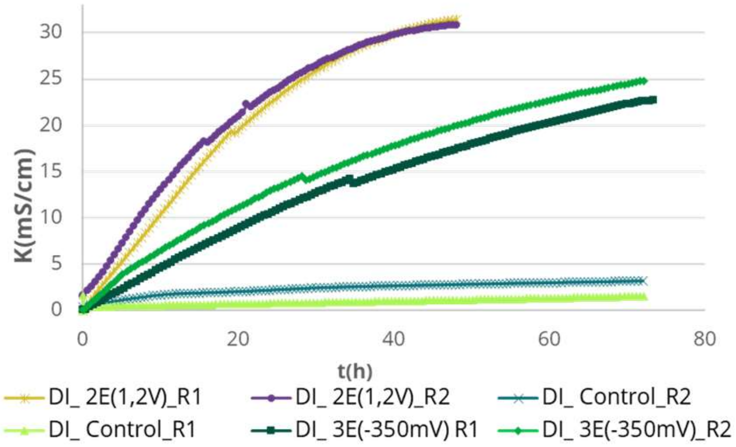
Nutrient Bioelectroconcentration (BEC)



Using a three-chamber bioelectrochemical reactor the anions and cations are concentrated in the saline (middle) chamber obtaining a nutrient rich stream

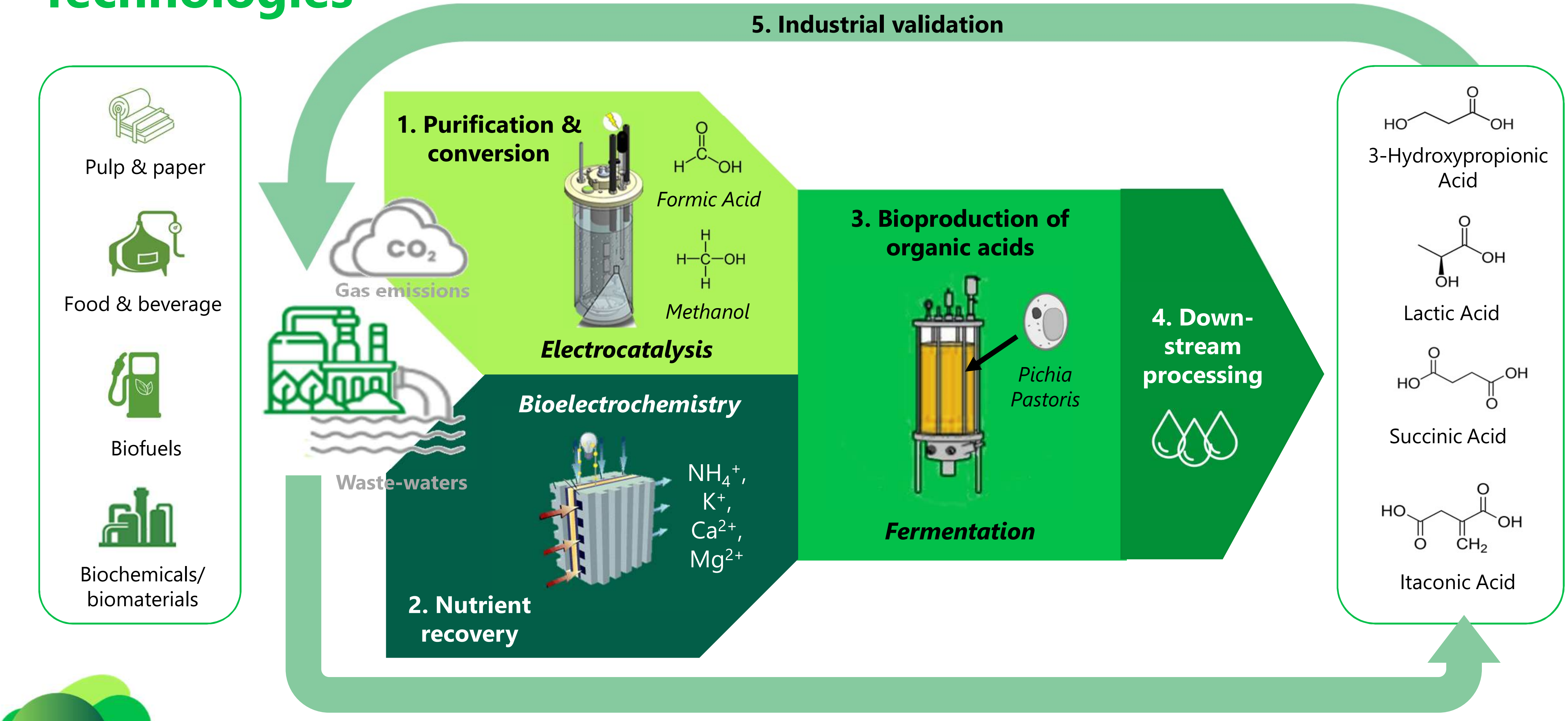
		time	Na	Mg	K	Ca	NH_4^+	Cl^-	SO_4^{2-}	PO_4^{3-}
		h	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
DI_2E	2 electrodes 1.2V	0	8	1,0	<1	<1	0,0	0,90	<1	<1
		48	10023	139,9	172	42	7,4	5555	7,92	8,51

High Na^+ and Cl^- concentration may hinder selectivity of targeted cations as NH_4^+,Mg^{2+}, K^+ or Ca^{2+}



- Concentration capacity operating the BEC in 2 and 3 electrodes configuration vs control (no applied voltage)
- Electric conductivity evolution of concentrate solution chamber indicate a nutrient recovery in this stream (as table shows)

Technologies



5. Industrial validation

Pulp & paper

Food & beverage

Biofuels

Biochemicals/ biomaterials

Gas emissions

Waste-waters

1. Purification & conversion

Formic Acid

Methanol

Electrocatalysis

Bioelectrochemistry

NH_4^+, K^+, Ca^{2+}, Mg^{2+}

2. Nutrient recovery

3. Bioproduction of organic acids

Pichia Pastoris

Fermentation

4. Down-stream processing

3-Hydroxypropionic Acid

Lactic Acid

Succinic Acid

Itaconic Acid

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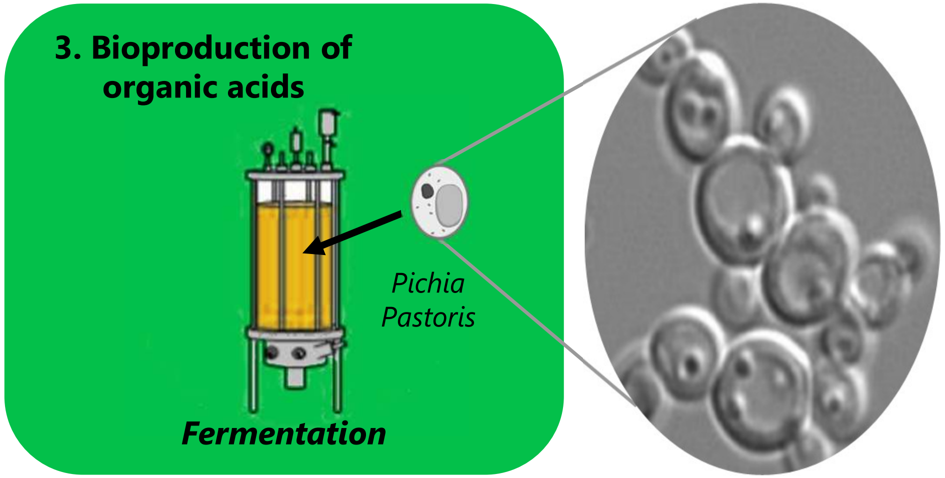
Turns CO₂ emissions into sustainable bioproducts

Fermentation



Why *Komagataella phaffii (aka Pichia Pastoris)*?

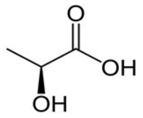
i. Grows at optimal conditions for recovery of free organic acids: low extracellular pH and high product concentration

ii. Grows on MeOH and can use FA as auxiliary substrate

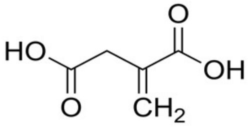
iii. Can grow and produce on simple mineralic media

iv. Industrial scale fermentation is established

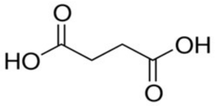
v. Genetics and metabolisms are well studied, a genome scale metabolic model and synthetic biology tools are established



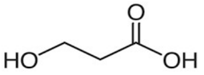
Lactic Acid



Itaconic Acid



Succinic Acid



3-Hydroxypropionic Acid

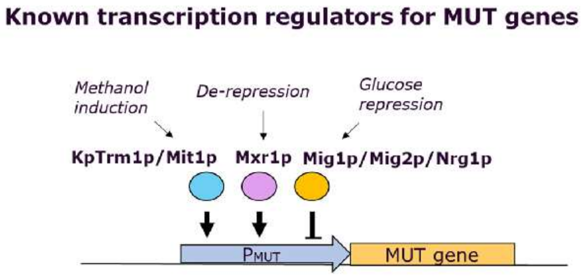
Bioproduction of Lactic Acid

Expression of a **Lactate dehydrogenase L** LdhL in *K. phaffii*

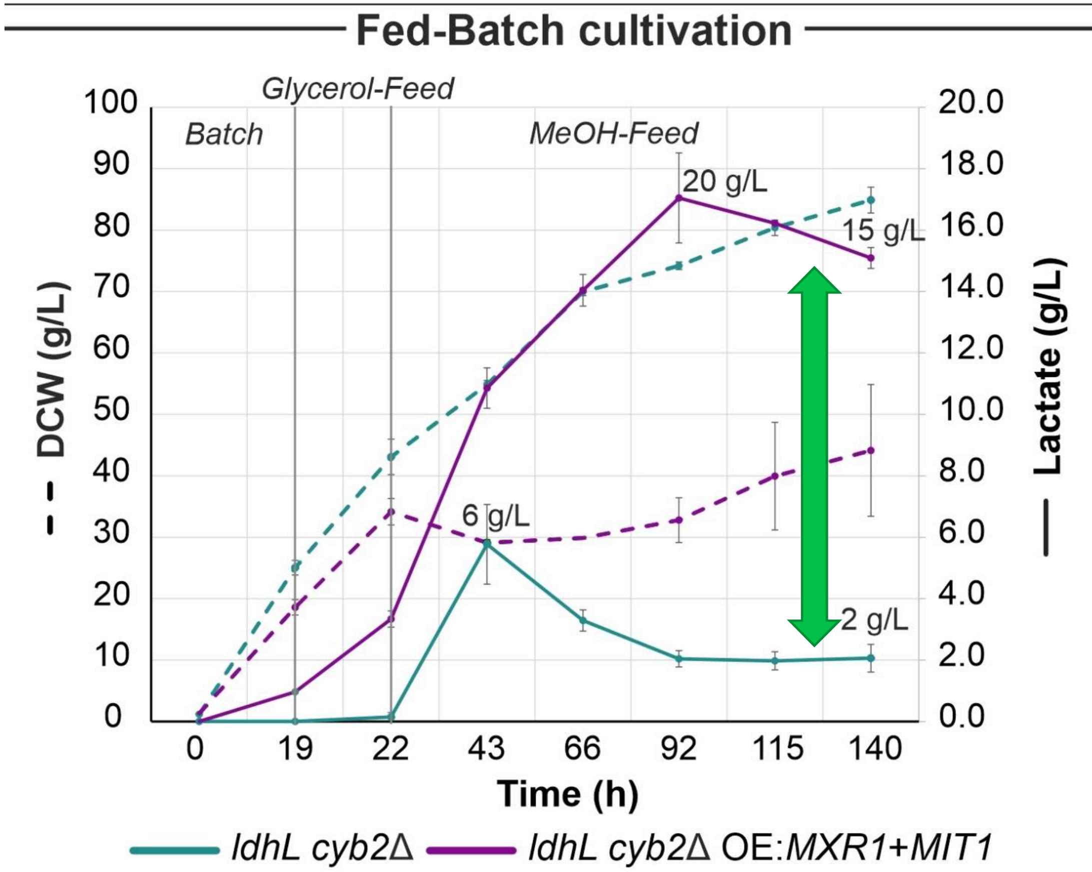
- Very low titers
- Consumption of the product when MeOH is used as a carbon source
- Additional *CYB2* deletion boosted LA titers (300 mg L^{-1}) but did not prevent consumption

Methanol utilization pathway is impacted by the **presence of LA**

Engineering of **transcription factors of the methanol metabolism** lead to elevated LA titers: 20 g/L

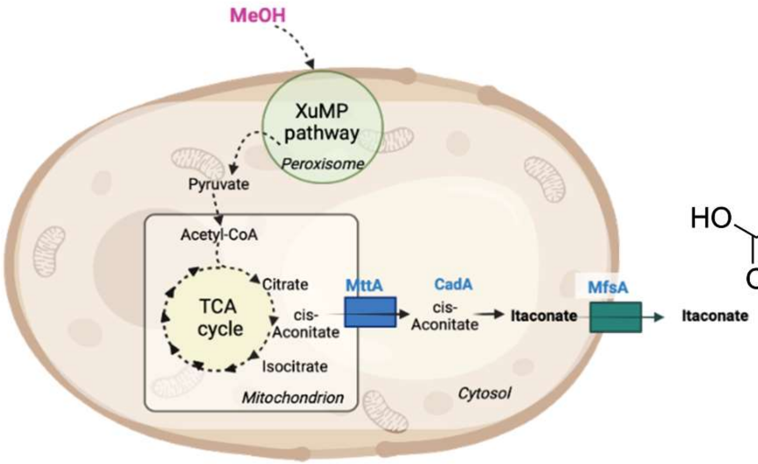


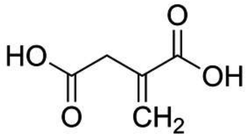
Takagi et al (2019)



Bachleitner et. al (2024)
Metab Eng. 85:133-144

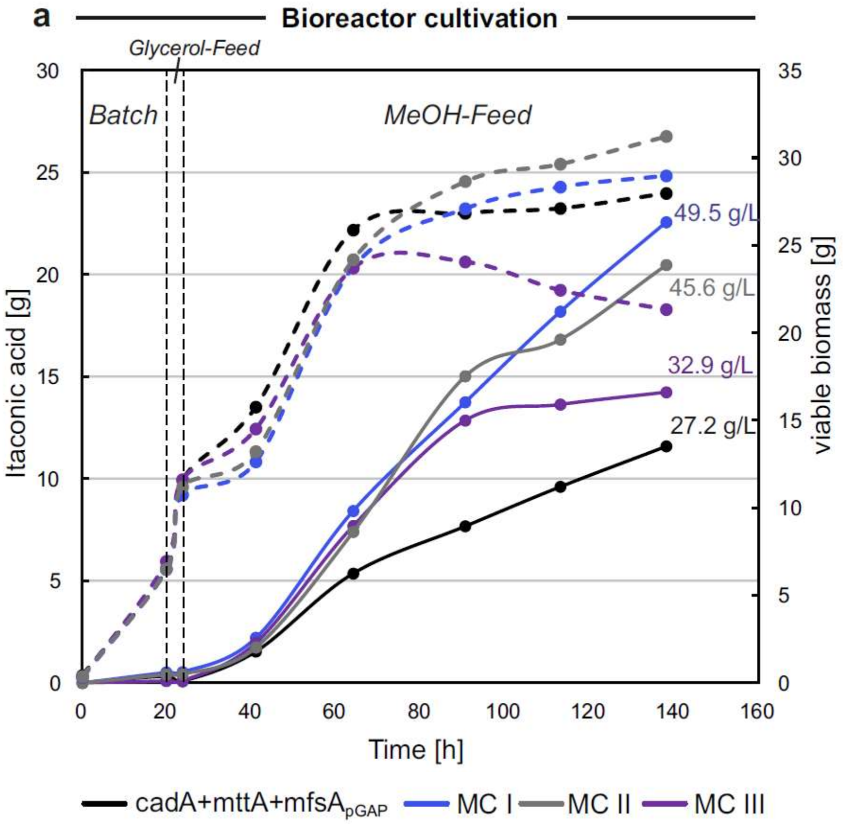
Bioproduction of Itaconic Acid





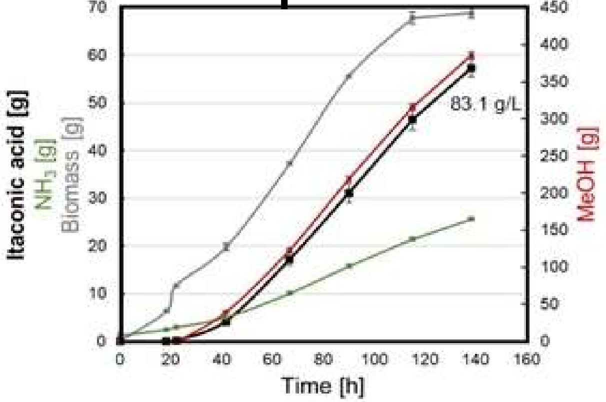
- cadA: cis-aconitate decarboxylase
- mttA: mitochondrial transporter
- mfsA: exporter

Integration of heterologous pathway and increasing the number of gene copies increased IA titers up to 50 g/L

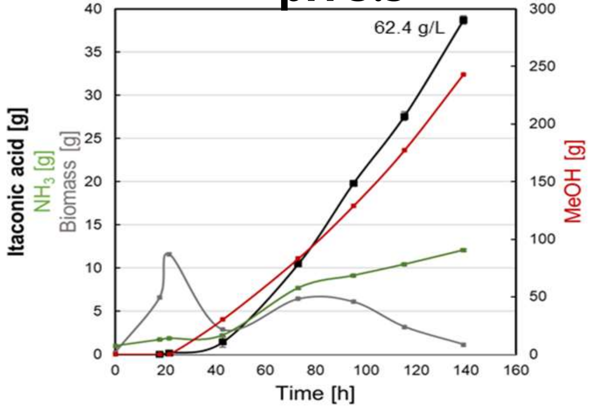


Bioproduction of Itaconic Acid

pH 5.5



pH 3.5



Insertion of the **Itaconic acid pathway** in *K. phaffii*

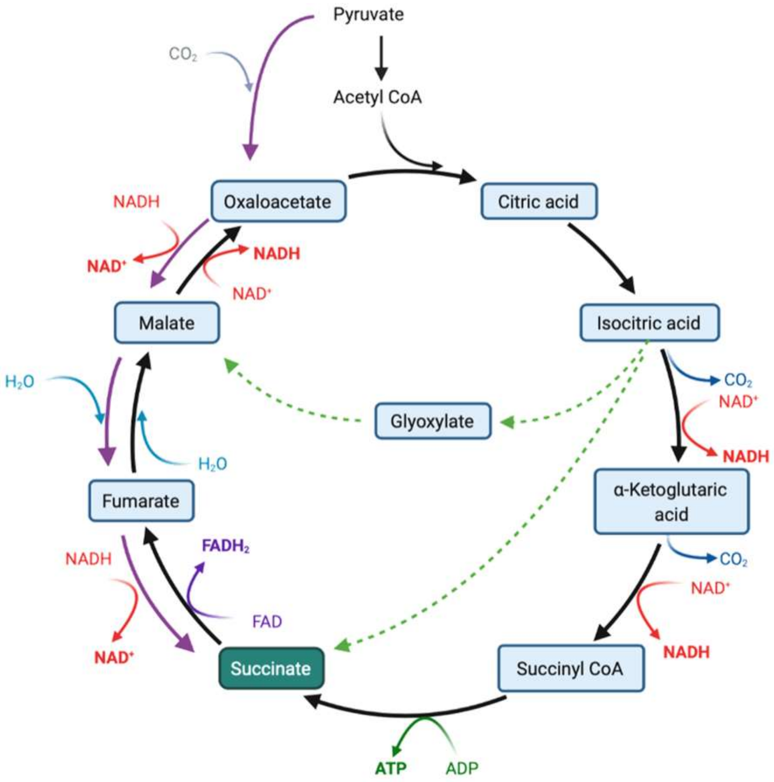
- **Optimization** of strains and the fermentation process (including media, temperature and MeOH feed) lead to **high titers** at pH 5.5 on MeOH
  - 83.1 g/L
  - $Y_{P/S}$ 0.15 g/g

Development of a fermentation process at **low pH**

- A low pH is desired by industries; it helps to **reduce downstream process costs** and is **less wasteful**
  - 62.4 g/L
  - $Y_{P/S}$ 0.15 g/g

Severinsen et al (2024)
Biotechnol Biofuels Bioprod. 17:98

Bioproduction of Succinic Acid



Succinic acid can be produced via

- Oxidative TCA pathway
- Reductive TCA pathway

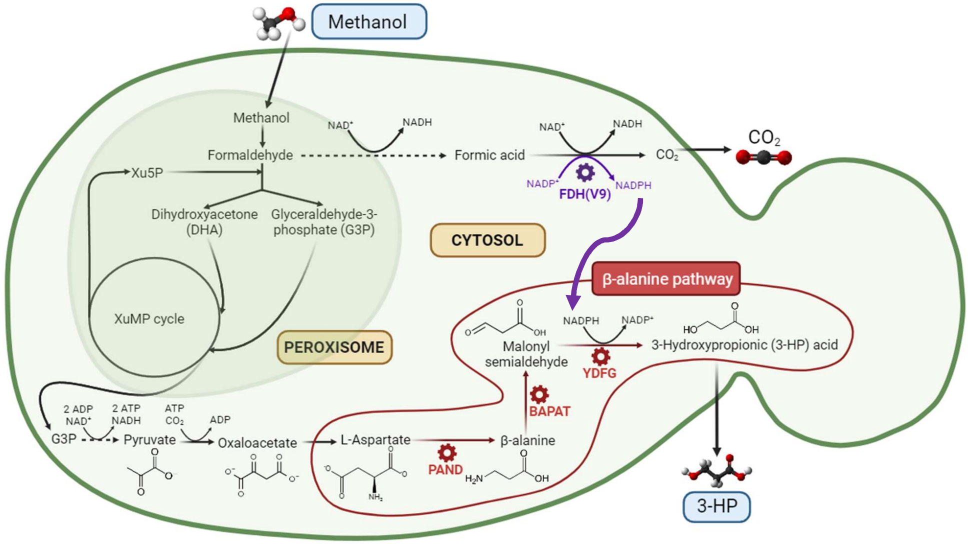
The TCA cycle plays an important role for **energy generation** when MeOH is used as a carbon source and is challenging to engineer in *K. phaffii*.

- Engineering of the oTCA cycle rendered cells **non growing** on MeOH (several enzymes are essential).
- Expression of a heterologous Flavin NADH oxidoreductase and further evolutionary engineering rescues growth on MeOH and succinic acid production.
- Engineering of the rTCA cycle in combination with transporters lead to high succinic acid production.
- Transporters are not specific to succinate but export also other dicarboxylic acids such as malate and fumarate.

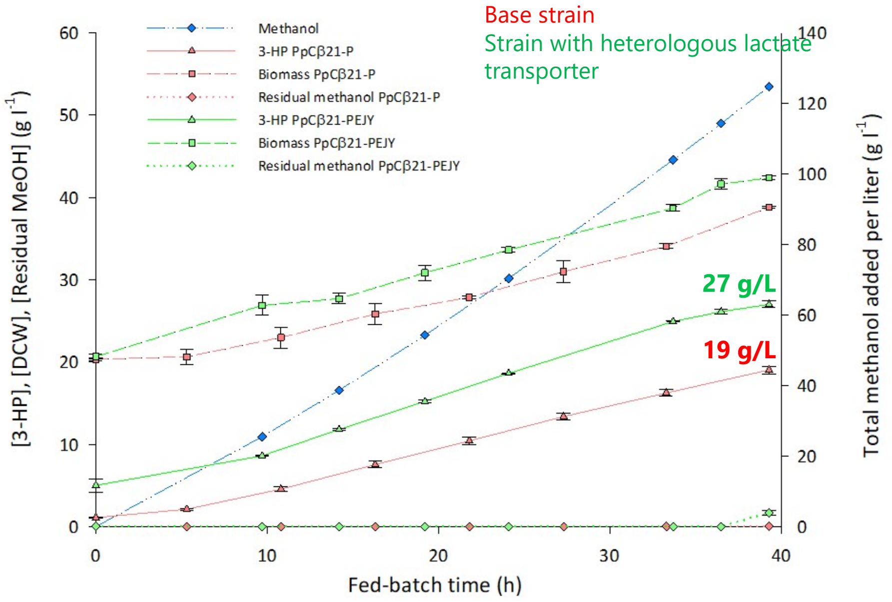
Bioproduction of 3 Hydroxypropionic Acid

UAB

- Introduction of the synthetic β-alanine pathway allows for 3-HP production
- Tuning NADP⁺/NADPH balance by introducing a heterologous NADP⁺-dependent Formate Dehydrogenase (FDH) improves strain performance.



Bioreactor cultivations (1-L scale): Fed-batch at a preprogrammed growth rate of 0.03 h^{-1} at pH 5



Base strain

Strain with heterologous lactate transporter

Introduction of a heterologous lactate transporter increased $Y_{P/S}$ by 27% (0.19 g/g), STY by 20% (0.56 g/(h·L)), and final 3-HP concentration by 42% (27 g/L) at 1-L fed-batch scale, **as well as strain robustness at pH=3.5**

Àvila-Cabré et al. Microb Cell Fact. 2023. 22(1):237. doi: 10.1186/s12934-023-02241-9.
Àvila-Cabré et al. J. Biol. Eng. 2025. 19(1):19. doi:10.1186/s13036-025-00488-x

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Turns CO_2 emissions into sustainable bioproducts

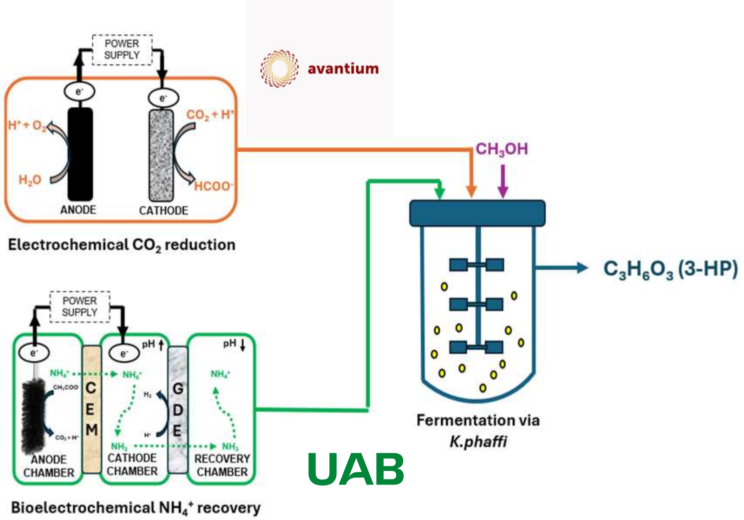
Combining biological and electrochemical processes

UFZ

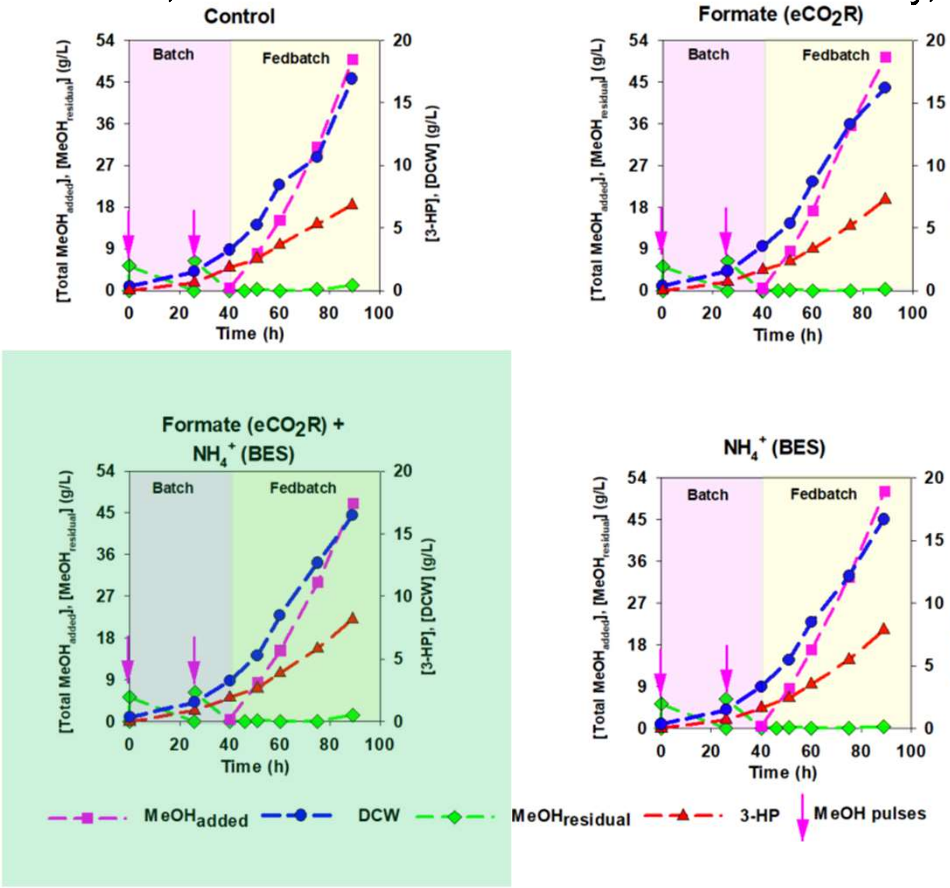
UAB

BOKU UNIVERSITY

3-step strategy: Integrating electrochemical CO_2 reduction, bioelectrochemical ammonium recovery, and fermentation for 3-HP production.

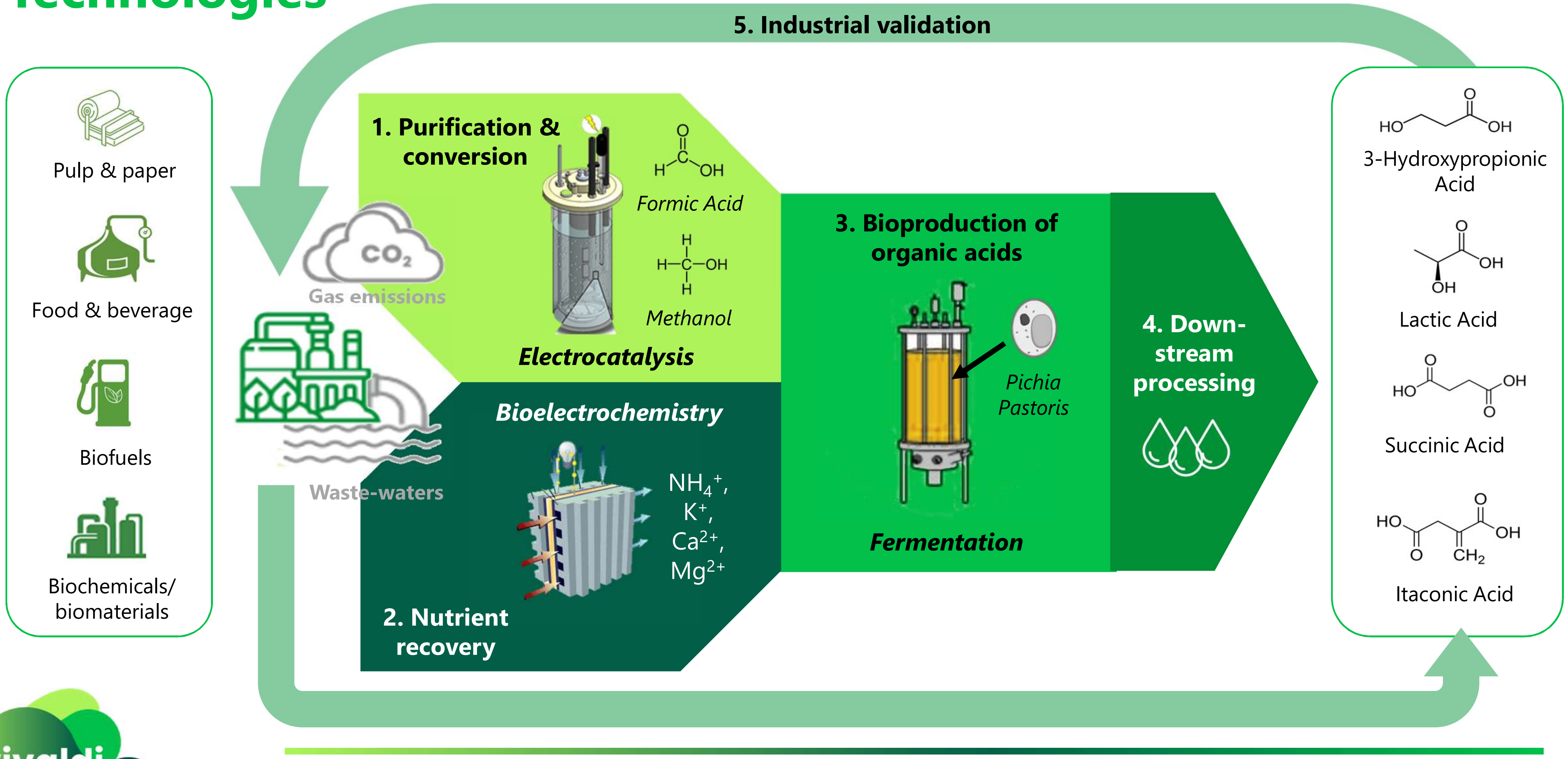


UAB



3-HP yield per methanol increased by **18% with full integration** (0.26 g/g vs. 0.22 g/g in control).

Technologies



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NH_4^+, K^+, Ca^{2+}, Mg^{2+}

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Lactic Acid

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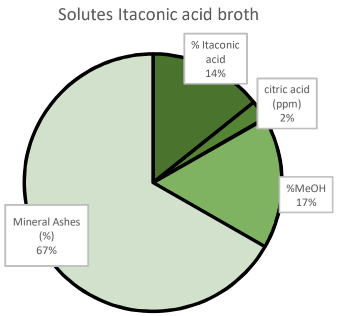
Downstream processes

Process synthesis

Goals

- Achieve product specification
- Minimize energy consumption
- Minimize effluent production

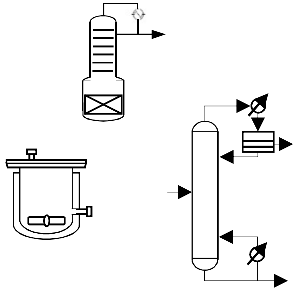
Characterization of broth composition → Determination of physical properties → Identification of driving forces for separation → Identification of separation technologies → Process Flowsheeting

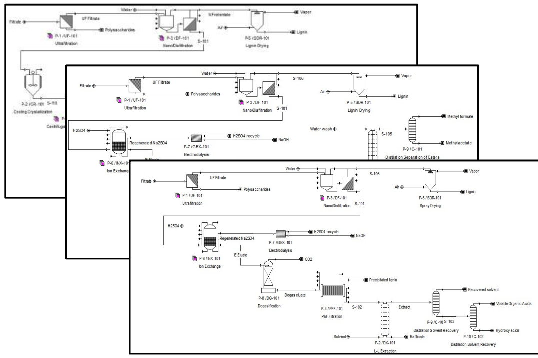


Component	MW (g/mol)	Density (kg/m3)	pKa (-)	Tboil (°C)
3-HPA	90,08	1252	4,51	162
Lactic	90,078	1200	3,86	227,6
Formic	46,06	1214,5	3,75	101
Acetic	60,05	1044,3	4,756	117,9
Citric	192,124	1665	3,13	
Methanol	32,042	787,2	15,5	64,5
Glycerol	92,094	1258,2	14,1	289
Ethanol	46,069	784,8	15,9	78,24
Amino acids	149,11		2,28	
Proteins	-	-	-	-

…

…

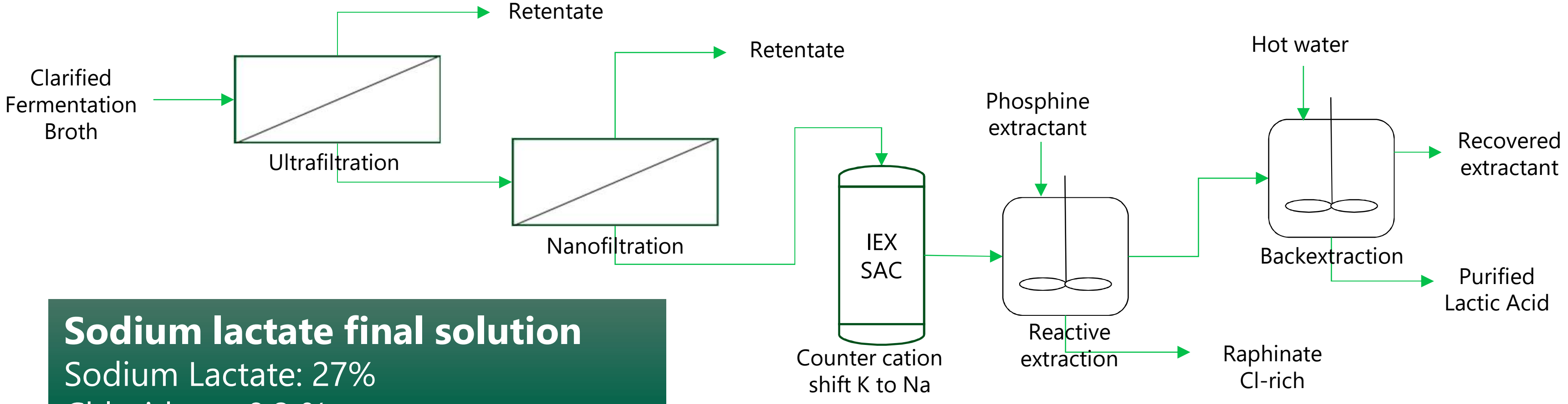




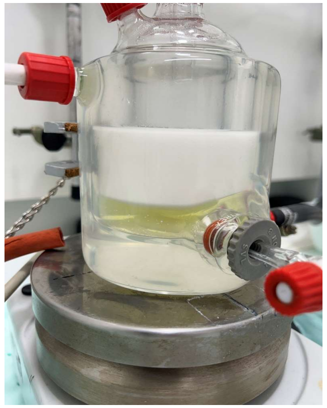
Downstreaming processes

Downstream steps for the recovery of purified sodium lactate

- Pre-purification by Ultra and nanofiltration (removal of broth impurities)
- Shift of counter-cation from K to Na by cationic ion exchange (final user prefered form)
- Reactive extraction for removal of mineral acids (chlorides and sulfates)
- Main challenge: High content of chlorides in broth (~3000 ppm) and low initial titer (17 g/L)



Sodium lactate final solution
Sodium Lactate: 27%
Chlorides < 0.2 %
Sulfates < 0.1%
Final purity > 95%

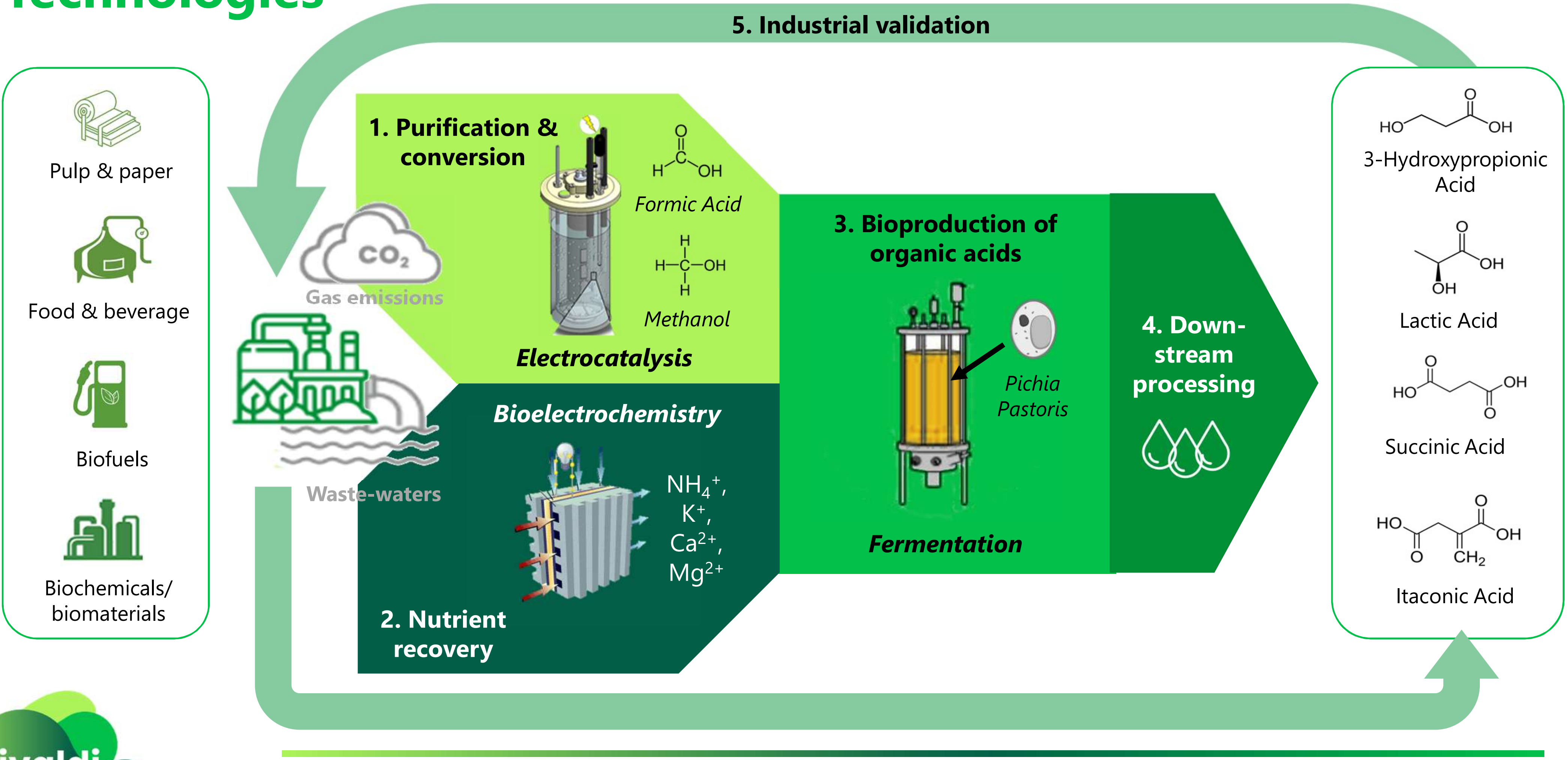

Reactive Extraction

A medium that rules them all…

When combining electrochemical and biological processes, the medium has to be sufficiently simple to ensure efficient electrochemical performance, yet complex enough to support biological activity….

…. on top of that, it has to be again "simple" enough for a technoeconomically feasible downstreaming process

Technologies



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NH_4^+, K^+, Ca^{2+}, Mg^{2+}

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3-Hydroxypropionic Acid

Lactic Acid

Succinic Acid

Itaconic Acid

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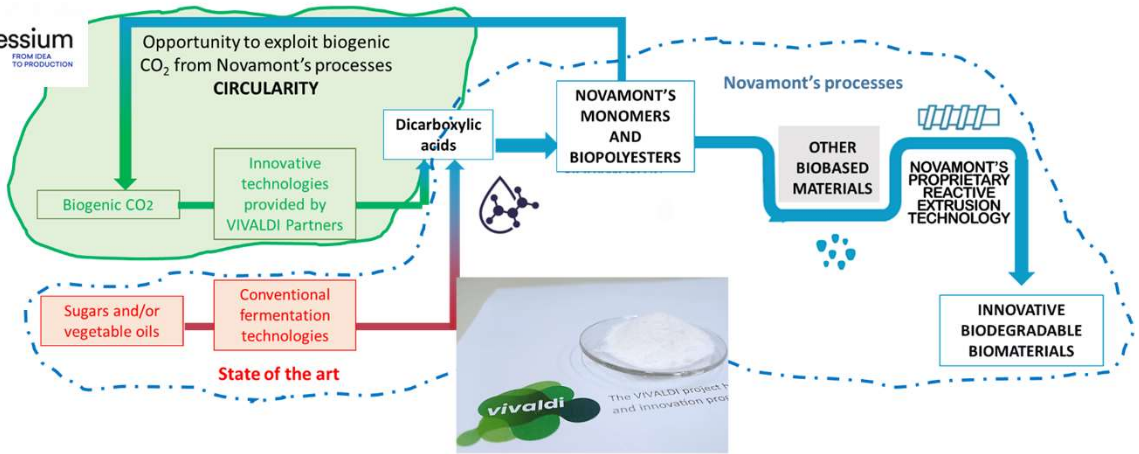
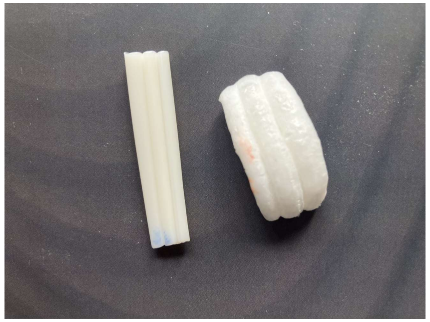
Turns CO_2 emissions into sustainable bioproducts

Succinic acid utilisation



Foaming

Bio IA based



Bio SA based

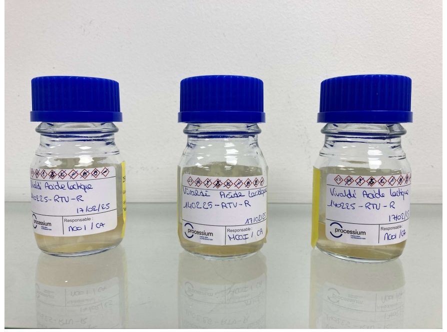
Injection moulding bioplastic
Bio SA based material

Processability	Regular
Melt thermal stability (ASTM D4440)	Excellent
Rheology (ASTM D4440)	Compatible with injection moulding and foaming applications
Film biodegradability (ISO 17556)	Compatible with OK Compost certification
Mechanical properties (ASTM D882)	Comparable with similar materials not based on biogenic CO_2 based monomers
Recyclablity	100% recyclable (mechanical recycling)

Biolactic acid utilisation

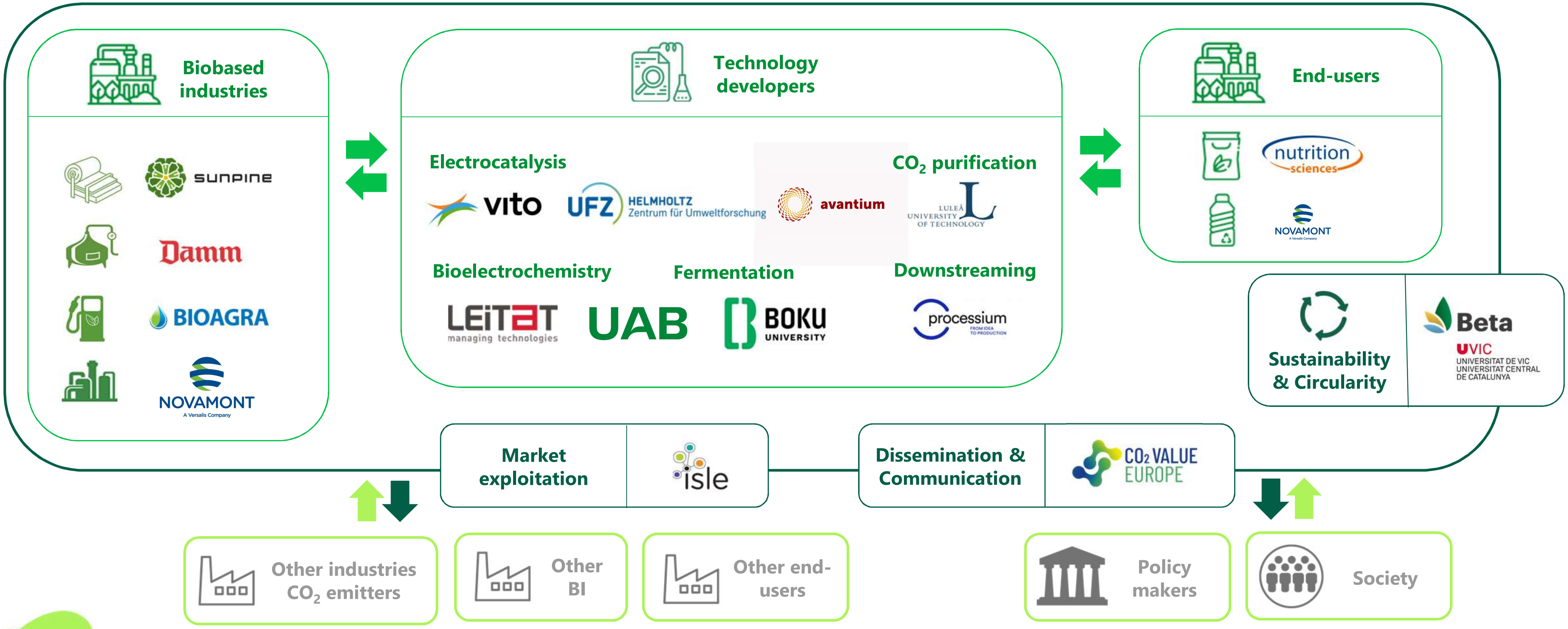
Different levels of validation

- Level 1: Specifications → active ingredient and impurities
- Level 2: Buffering capacity
- Level 3: Functionality: antimicrobial potential



- BioLA is NaLA while commercial sources are KLA
- BioLA has lower concentration of LA
- Market price BioLA ? Compared to conventional (K)LA
- BioLA is compliant with legal requirements (excl. EFSA ?)
- BioLA has a good buffering capacity
- BioLA has similar antimicrobial potential compared to conventional LA

Methodology



Biobased industries

SUNPINE

Damm

BIOAGRA

NOVAMONT
A Versalis Company

Technology developers

Electrocatalysis

vito

UFZ HELMHOLTZ Zentrum für Umweltforschung

avantium

CO_2 purification

LULEÅ UNIVERSITY OF TECHNOLOGY

Bioelectrochemistry

LEITAT managing technologies

UAB

Fermentation

BOKU UNIVERSITY

Downstreaming

processium FROM IDEA TO PRODUCTION

End-users

nutrition sciences

NOVAMONT
A Versalis Company

Sustainability & Circularity

Beta

UVIC UNIVERSITAT DE VIC UNIVERSITAT CENTRAL DE CATALUNYA

Market exploitation

isle

Dissemination & Communication

CO2 VALUE EUROPE

Other industries CO_2 emitters

Other BI

Other end-users

Policy makers

Society

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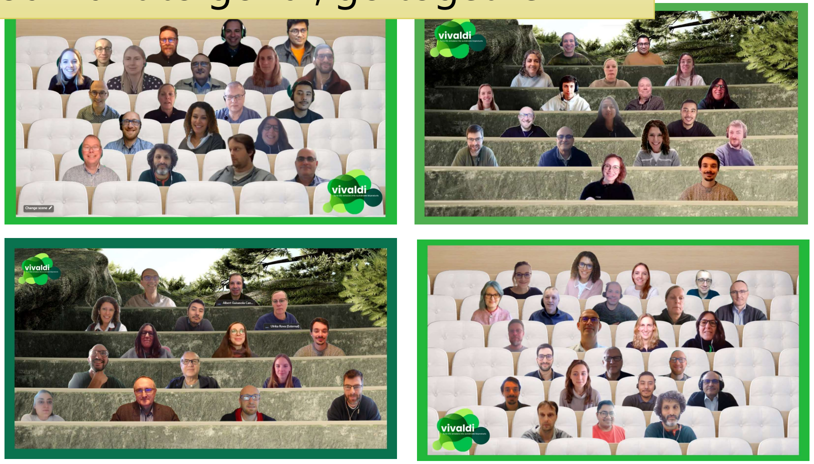
A massive team effort

“If you want to go fast, go alone. If you want to go far, go together”



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THANK YOU

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