



Engineering sustaining Bio-CCU: Solubilisation, reactor design, downstreaming

Webinar from the BIOCON-CO₂ Consortium

Thursday, 17th March 2022

14:00 - 15:30 CET

Online

[Register here:](#)

biocon-co2.eu/news/



This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement no. 761042 (BIOCON-CO₂). This output reflects the views only of the author(s), and the European Commission cannot be held responsible for any use which may be made of the information contained therein.

Welcome

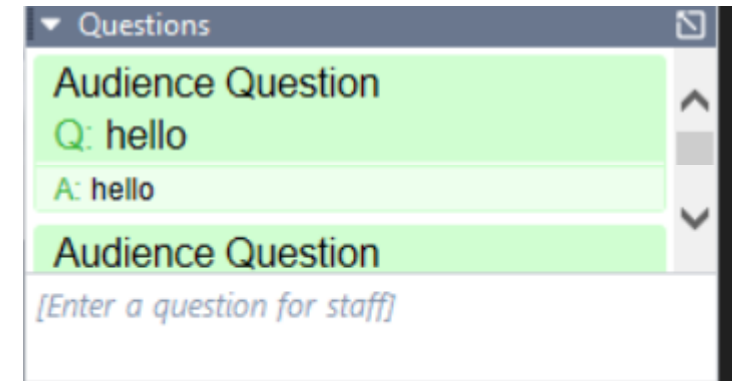


- Purpose of webinar series
 - To increase community outreach, helping to establish long-term partnerships between consortium and future users
 - Each webinar is dedicated to a specific aspect of the project, with a special focus on further development, upscaling, and industrial uptake
- Past webinars (videos on <https://biocon-co2.eu/>)
 - “*Bio-CCU: potentials & opportunities*” - 9th Dec. 2020 - Context & introduction to BIOCON-CO2 project
 - “*CCU Biocatalysts: How to get them out of the lab?*” - 24th March 2021 - R&T focus on challenges of increasing yield for industrial relevance
- Upcoming events:
 - *Policy and economic perspectives webinar* – date TBD
 - *Final Symposium*: Ghent, Belgium – 14 & 15 June 2022
 - Registered participants will receive email invitation

Webinar logistics



- This webinar is recorded and will be made public via the project website.
- All attendees are muted. Please ask questions at any time through the chat window. We will be happy to answer questions after each presentation.
- For the panel discussion at the end of the webinar, we will open discussion with attendees. “Raise your hand” and unmute yourself to ask a question.



Program



Timing	Topic	Panellist
14:00-14:05	Welcome and introduction	Montse Bosch, LEITAT
14:05-14:20	Trickle-bed reactors for CO ₂ fixation	Rubén Rodríguez-Alegre & Mari Carme Royo Reverter, LEITAT
14:20-14:35	Advances in small-scale process development for fermentative CO ₂ utilization	Aline Hüser, RWTH Aachen University, AVT
14:35-14:50	Decision making tool for downstream processing	Carlos Andecochea Saiz, LEITAT
14:50-15:05	Pervaporation and its application to the downstream of alcohols	Ilse Lammerink, PERVATECH
15:05-15:20	Nanofiltration and reactive extraction, and its application to the downstream of formic acid	Tomás Roncal Martínez, TECNALIA
15:20-15:30	Q&A session and conclusion	Round table



BIOCON-CO2 webinar series

BIOCON-CO2 project overview

17th March 2022

Montse Bosch, LEITAT

Technical coordinator BIOCON-CO2



BIOCON-CO₂ at a Glance



Programme: EU Horizon 2020 – (BIOTEC-05-2017) Microbial platforms for CO₂ re-use processes in the low-carbon economy

Duration: January 2018 – June 2022 (54 months)

Budget: €6.9 million

Coordinator: Acondicionamiento Tarrasense Asociación (LEITAT), Spain

Consortium: 18 partners in 8 countries

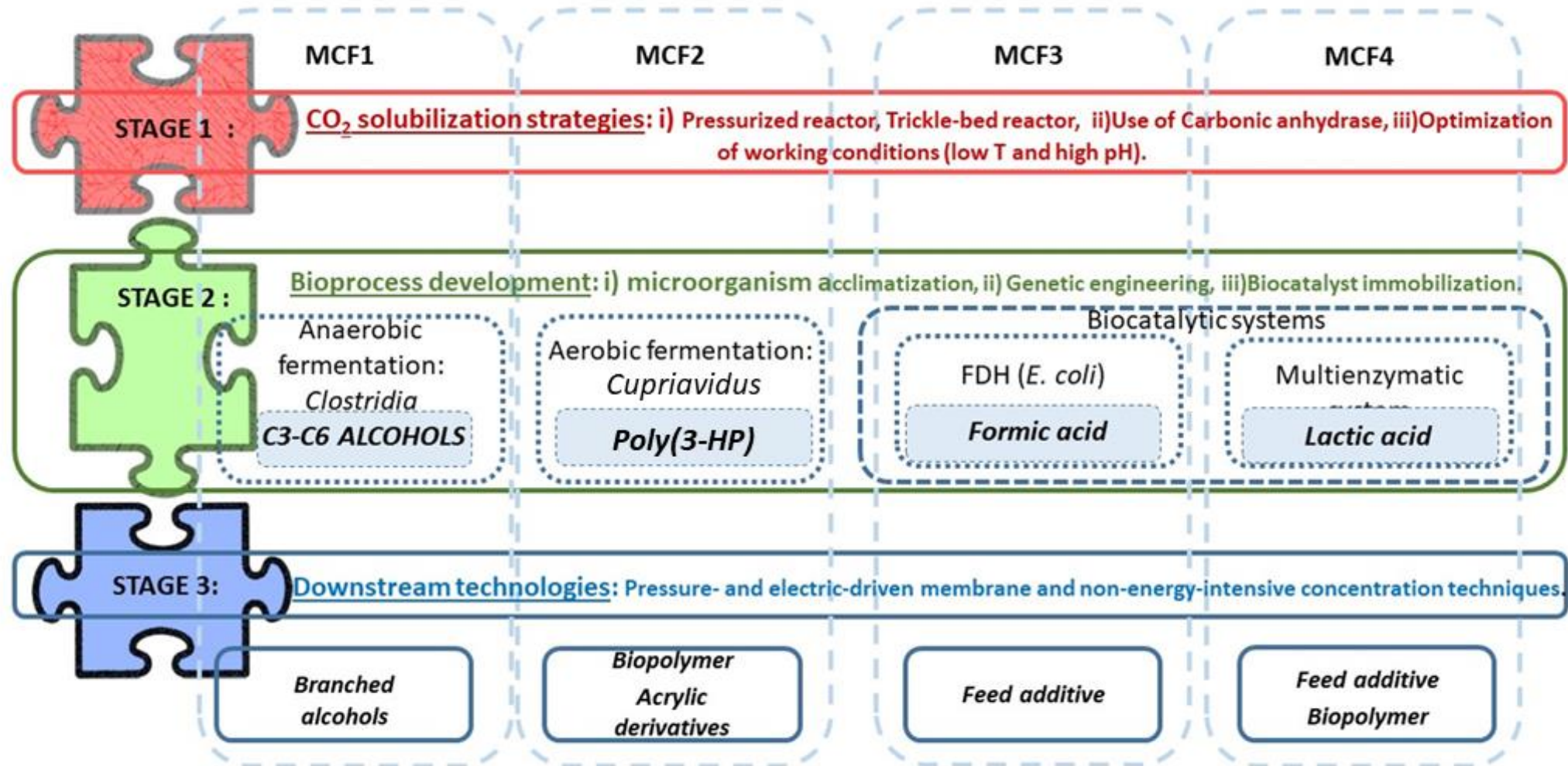
Transforming raw CO₂ waste from the iron, steel, cement and electric power industries into value-added chemicals and plastics

Why? To reduce greenhouse gas emissions and avoid overexploitation of natural resources

How? Developing and validating a flexible strategy to biologically transform CO₂ into value-added chemicals and plastics

What for? To increase sustainability of the chemical industry, providing support for European leadership in biological CO₂ re-use technologies

BIOCON-CO₂ platform



Consortium

BIOCON-CO₂: 18 partners based in 8 countries



Large industries:



RTOs:



Universities:

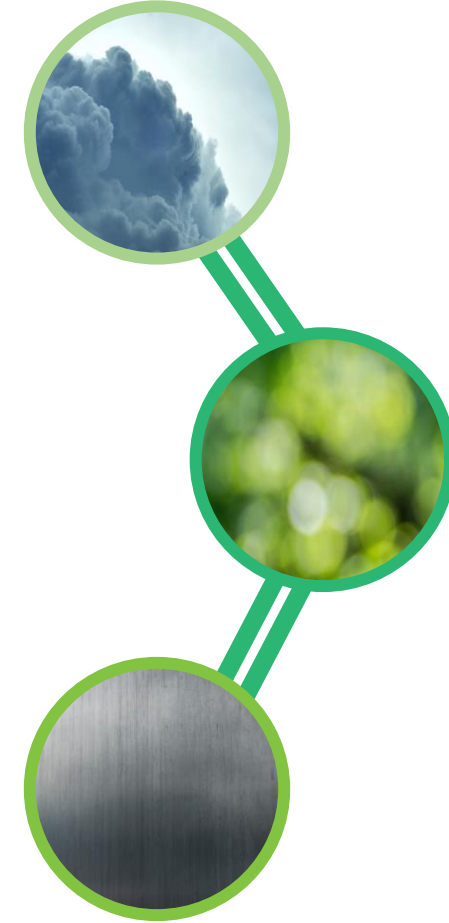


SMEs:



Expected Results

- Assessment and validation of **three low-energy microbial processing systems** capable of converting CO₂ emissions from the iron and steel industry into valuable industrial products
- Production of **four chemical building blocks** produced using CO₂ re-use technologies that have application in the food/feed, chemical (acrylates, polymers, surfactants) and plastic industries
- **Pilot installation** in an industrial setting upon project completion which demonstrates and validates the effectiveness of four chemical building blocks produced using CO₂ re-use technologies
- **Improved public perception** of CO₂ re-use technologies through transparent and responsible communication, knowledge transfer and exploitation of project outcomes





Trickle-bed reactors for CO₂ fixation

Webinar #3: Engineering sustaining Bio-CCU

Rubén Rodríguez-Alegre

Mari Carmen Royo

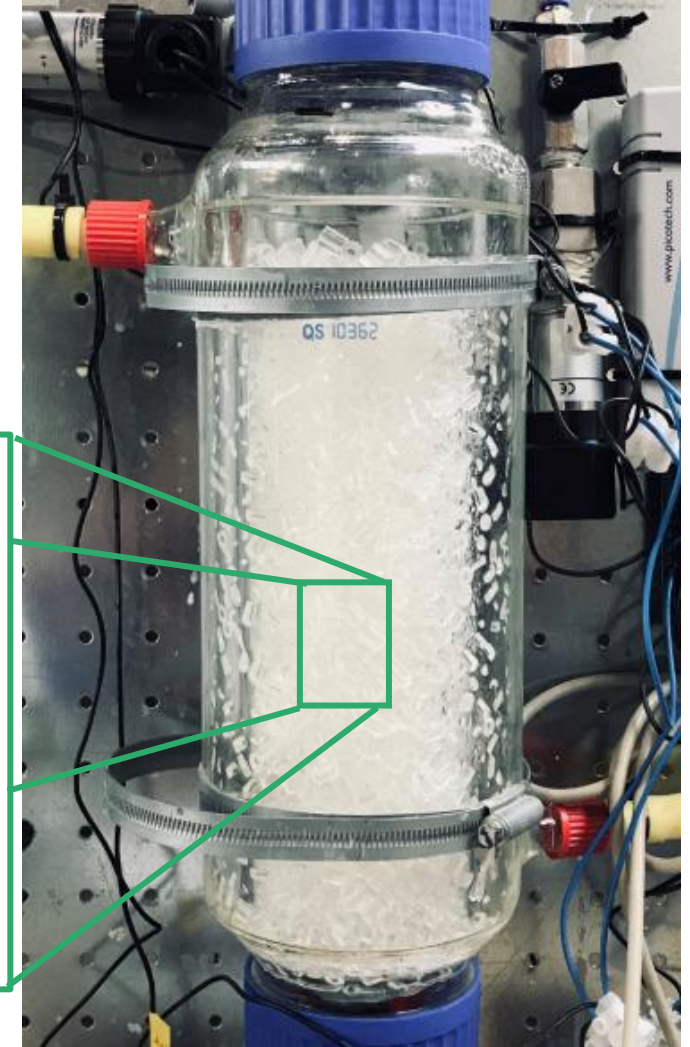
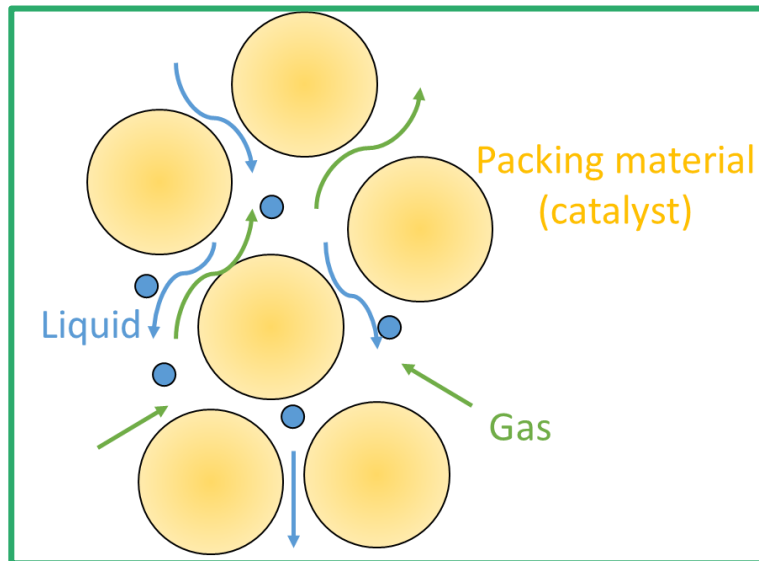
LEiT²T
managing technologies



Trickle-Bed Reactor

Chemical reactor that uses the downward movement of a **liquid** and the downward (co-current) or upward (counter-current) movement of **gas** over a packed bed of (**catalyst**) particles.

Hydrodynamics within the reactor is extremely complex. Due to this, studies on the field are being carried out and several publications are being appearing.



Basic Configurations and Operation of TBR



(a) Conventional trickle-bed reactors:

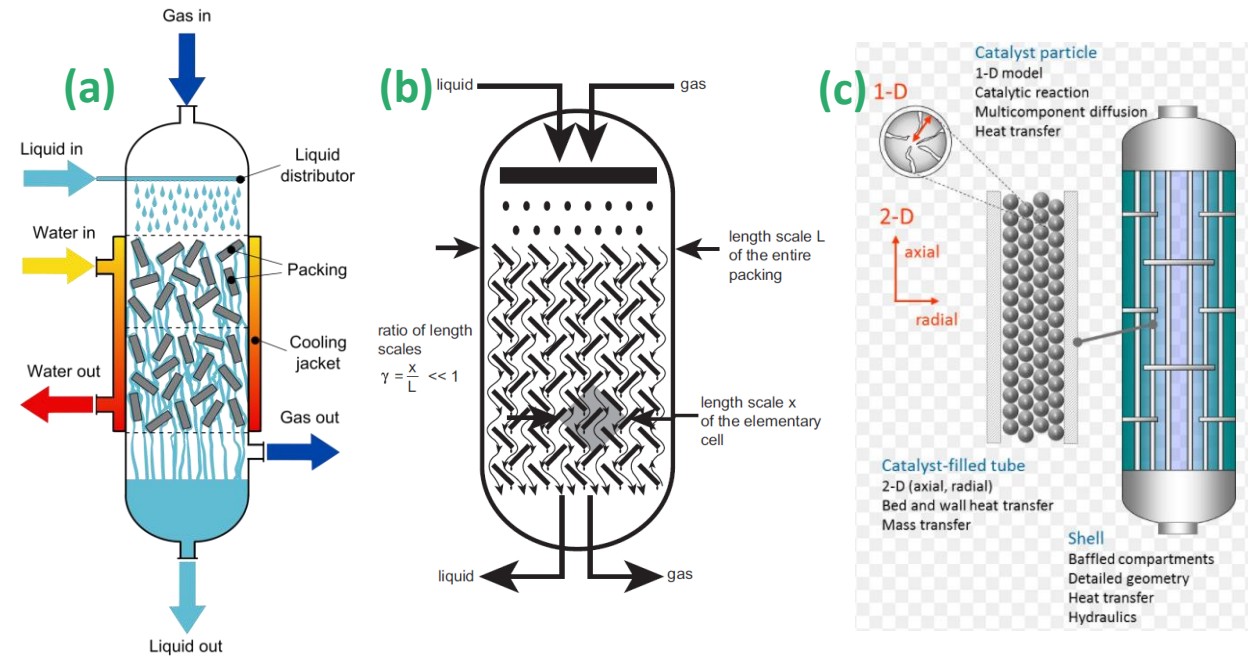
- Randomly packed beds of porous catalyst particles

(b) Semi-structures trickle-bed reactors:

- Structured packing catalyst
- Lower pressure drop and eliminates diffusion as a limiting factor to the reaction

(c) Micro trickle-bed reactors:

- Micro channels packed with catalyst particles
- Better control of reaction parameters and enhance process safety



TBR main points

Advantages

- Can be used for three - phase reactions
- Lower total energy consumption since solids are stagnant, not suspended in slurry
- Simple to operate under high temperatures and pressures
- Lower catalyst attrition
- High elimination capacity
- Large volume processing



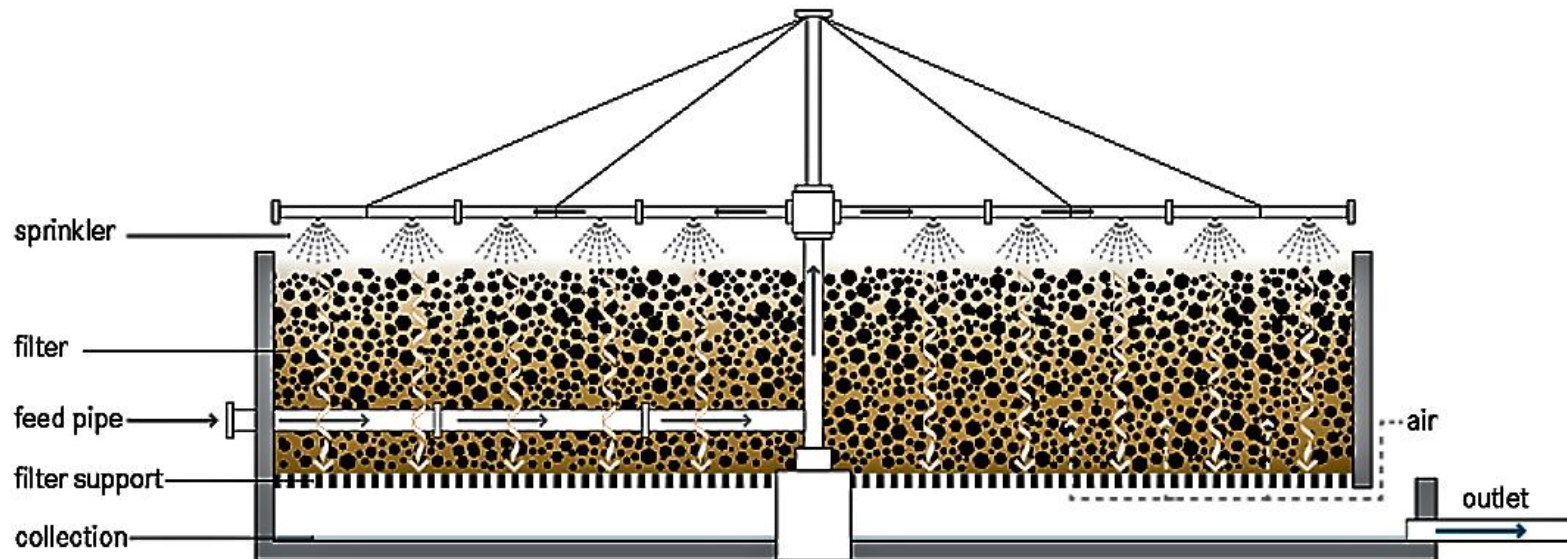
Disadvantages

- Hot spots may develop due to solvent evaporation
- Channeling may occur, leading to inefficiencies
- Difficult to control vessel parameters
- Lower performance when liquid not uniformly distributed
- Difficult to scale up due to dependence on fluid dynamics of system

Real applications



- Hydrodesulfurization of heavy oil stocks
- Hydro treating of lubricating oils
- Oxidation of harmful chemical compounds in wastewater
- Wastewater treatment where biomass resides on the packed material surface

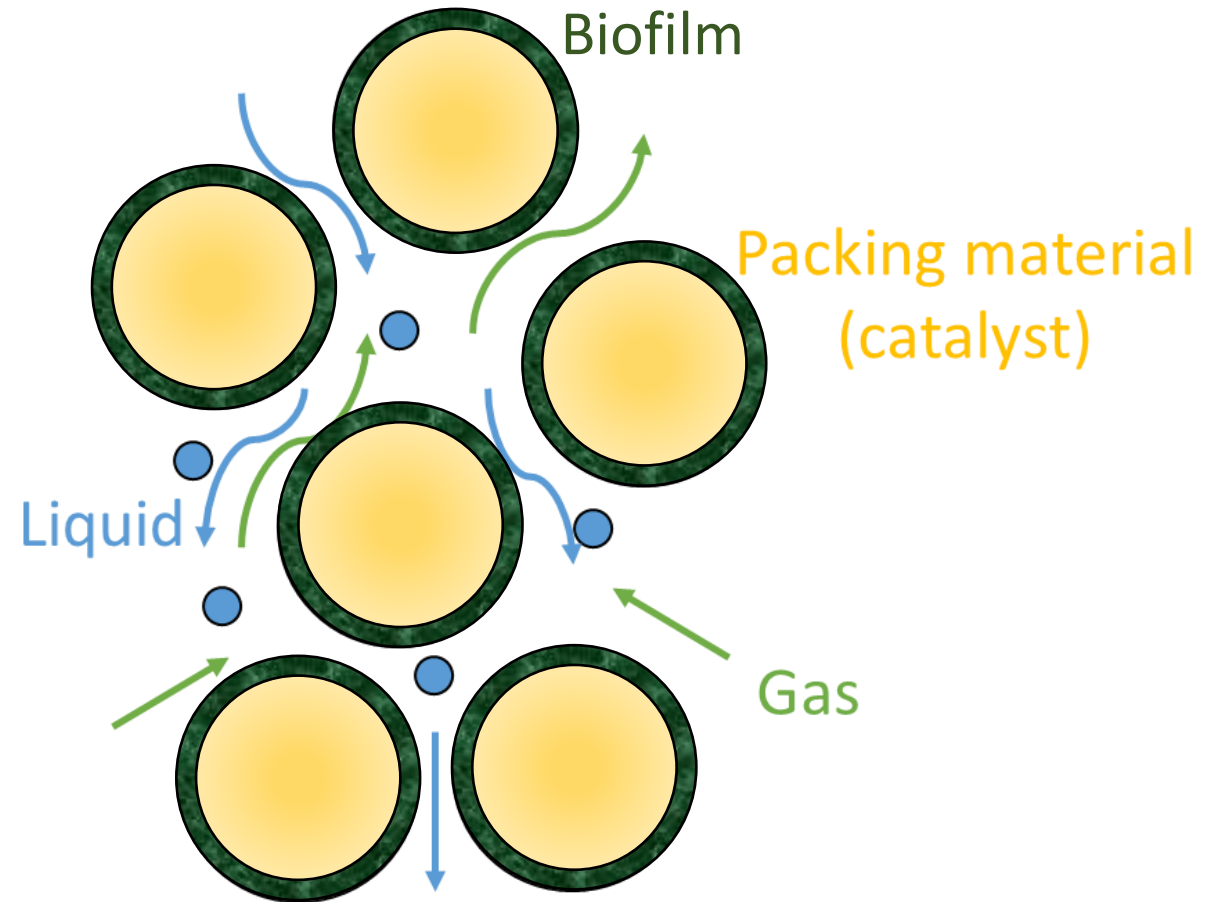


Trickle-bed bioreactor (TBBR)

- Improve the CO₂ capture efficiency
- CO₂ consumption by biofilm

project

- Adhesion of bacteria *Cupriavidus necator* and biofilm formation
- Adaptability of the packing material inside the reactor
- Degradation suffered by the packing materials over time



Packing materials in TBR



Packing materials are commonly used in TBR for adhesion and growth of bacteria

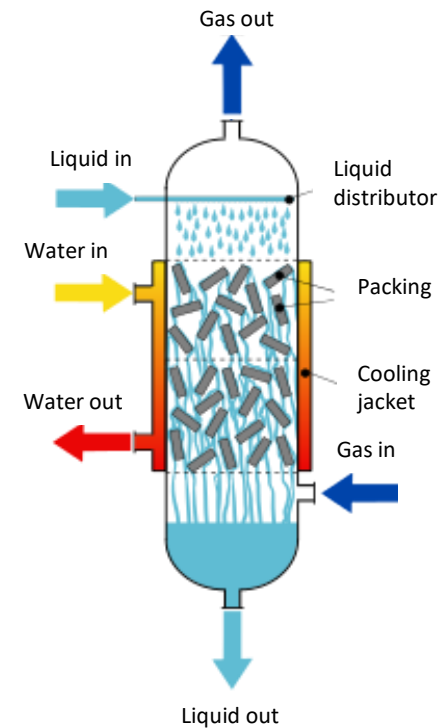
Parameters influencing the attachment, growth and biofilm formation:

- Electrostatic interaction between support and bacteria
- Surface area and surface roughness of the support
- Size and shape of the bacteria
- Hydrophobic or hydrophilic nature of the support and bacteria
- Availability of nutrients
- Shear forces in the bioreactor



RASCHIG RINGS – CONVENTIONAL PACKING MATERIAL

- Provide a large surface area within the reactor
- Random packing
- High economic cost
- Petroleum-based material

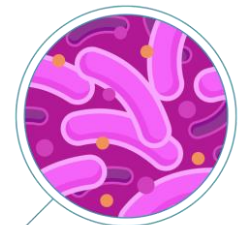


Trickle bed reactor

STAGE 1



STAGE 2



Cupriavidus necator
on packing material.

TARGET COMPOUND

Advanced packing materials

The aim of this research is to study innovative, efficient, environmentally friendly and low-cost packing materials, by analyzing their characteristics, bio-adhesion properties and growth of bacteria

POLYURETHANE FOAMS



Hard PU foam



Soft PU foam



*Polyisocyanurate
(PIR) foam*

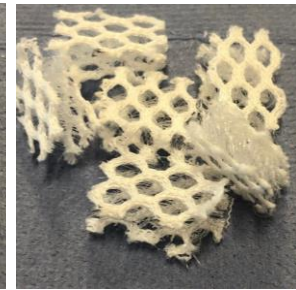
FIBROUS MATERIALS (PES TEXTILES)



Woven



Non-woven



3D

HARDWOOD CHIPS



Beech wood



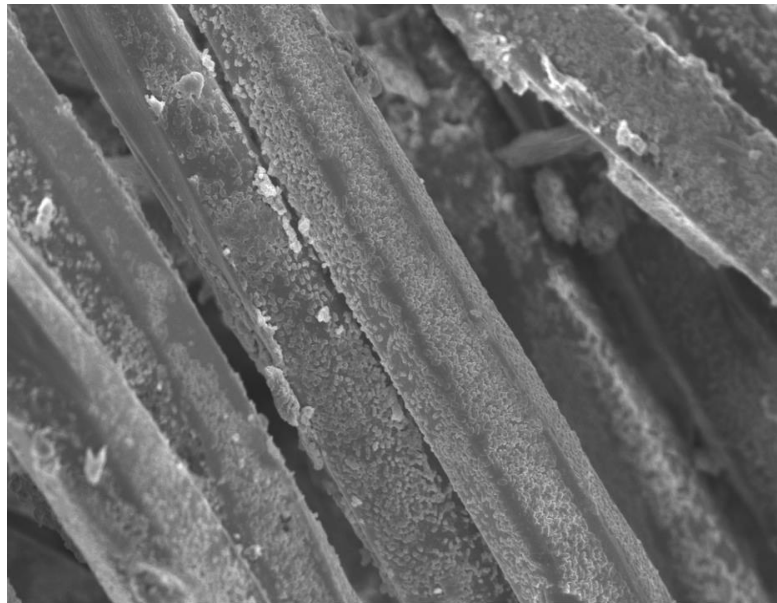
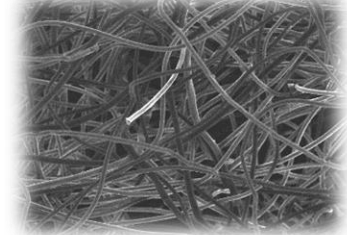
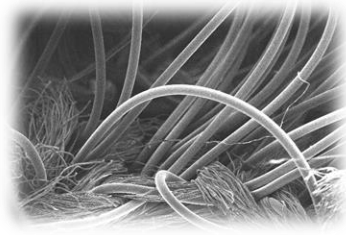
Eucalyptus wood

POLYPROPYLENE PELLETS



**REUSE AND WASTE
MANAGEMENT:** Materials from
industrial pre-consumer waste.

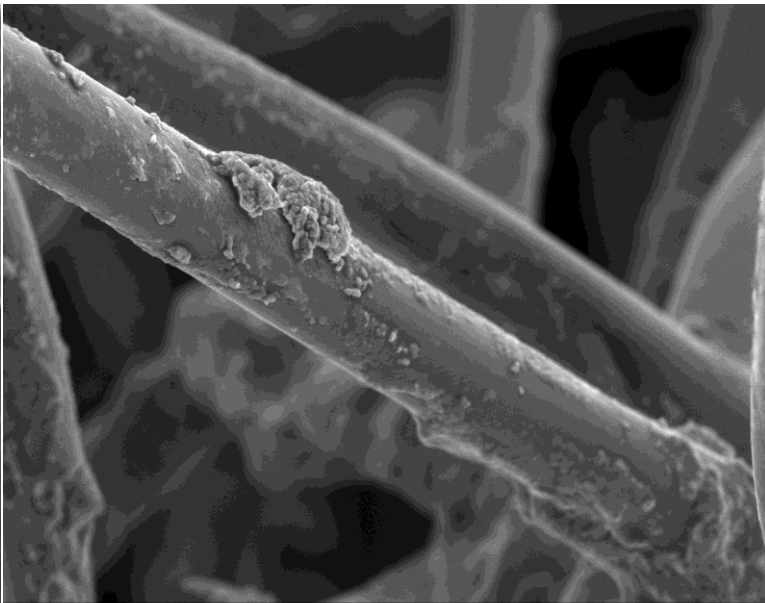
Bacterial adhesion and growth



SEI 10kV WD14mm SS50
LEITAT

x1.000

10µm



SEI 10kV WD12mm SS50
LEITAT

x1.000

10µm



Plasma technology



Plasma is a partially ionized gas composed of electrons, ions, photons, atoms and molecules, with negative global electric charge

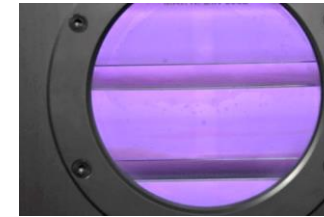
Surface phenomena could **promote biofilm formation**:

- Surface cleaning without modification of intrinsic properties
- Increased fibre surface roughness and surface area
- Increased surface energy to promote wetting
- Deposition of functional groups onto the surface (-OH, -COOH, -SiO₂, -NH₂)
- Functional nano-coatings deposition (PECVD)

Advantages of plasma technology:

- Neither water consumption nor wastewater effluents;
- No chemical consumption;
- Drying and curing processes are not necessary;
- Well-controlled and reproducible technique.

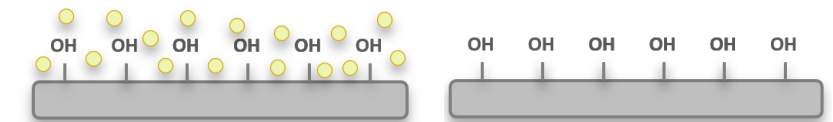
Low pressure plasma



Atmospheric pressure plasma



Surface cleaning process:



Surface functionalization with PECVD:

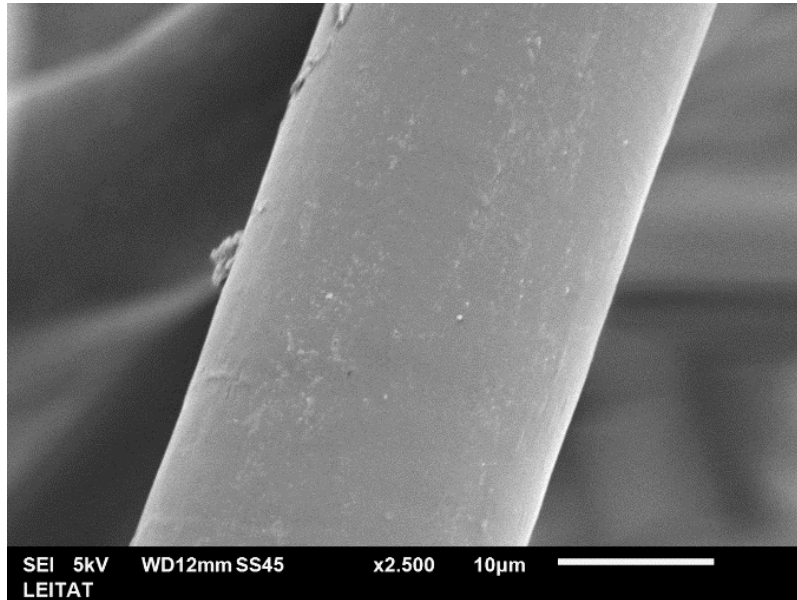


Plasma technology

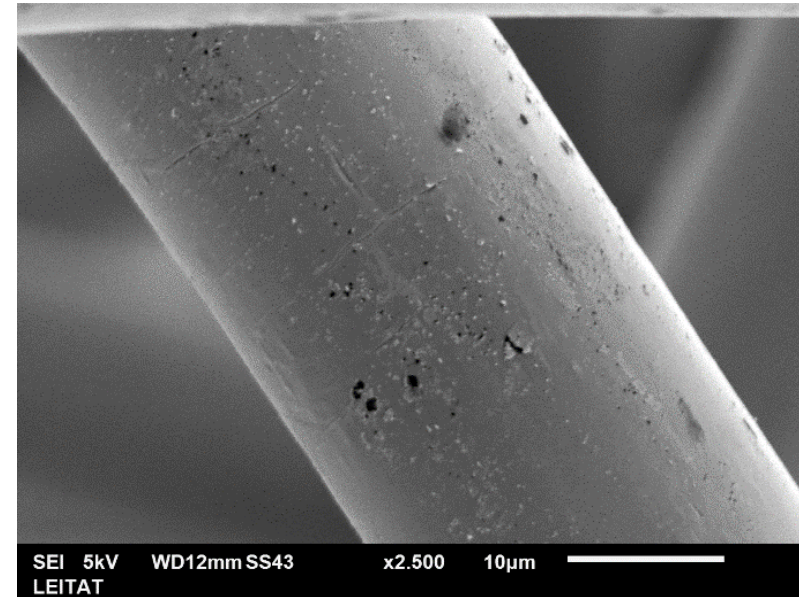


- Surface treatments to improve biofilm formation on textile materials using **AIR (generation of polar functional groups and roughness)**:

Untreated packing material



Treated packing material

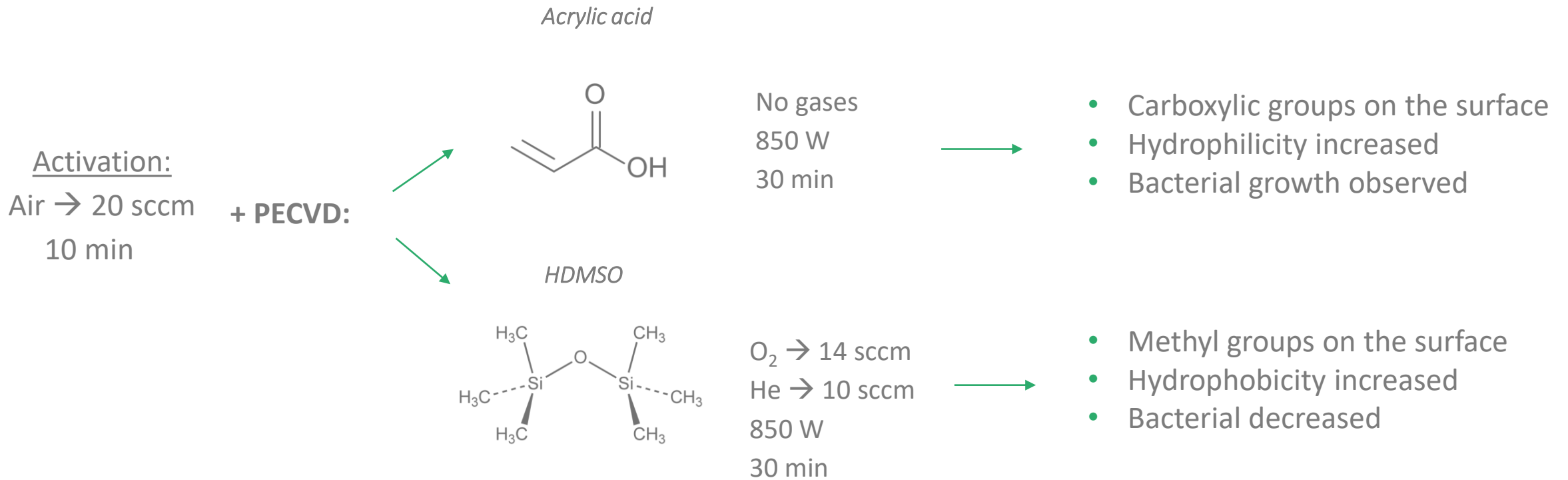


- Optimized plasma conditions (electrode distance, gas and power) → 2 cm, 21 KHz, Air, 1 m/min
- Roughness increased
- Bacterial growth maintained

Plasma technology



- Surface treatments to improve biofilm formation on textile materials using **PECVD (Acrylic acid and HDMSO)**:



Conclusions



- BIOCON-CO₂ project has demonstrate the viability of TBR uses in CO₂ capture
- 10 different packing materials have been evaluated by means of surface characterization, behaviour inside the reactor and biofilm adhesion and growth
- It was determined the capability of packing materials to create biofilms by *C. necator*
- Plasma treatments on selected textiles:
 - Atmospheric plasma using gases to increase the roughness of the surface
 - PECVD plasma to functionalise the surface with permanent functional groups
 - Surface properties and biofilm formation can be tuned changing plasma conditions
- It is expected to have a publication soon with more results



Thank you

Rubén Rodríguez-Alegre – rrodriguez@leitat.org

Mari Carmen Royo – mcroyo@leitat.org

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www.biocon-co2.eu



BIOCON-CO2@aquatt.ie



[@BIOCON_CO2](https://twitter.com/BIOCON_CO2)



Advances in small scale process development for fermentative CO₂ utilization

BIOCON-CO2 Webinar 3: Engineering sustaining Bio-CCU

17th March 2022

Aline Hüser, Marcel Mann & Prof. Dr. Jochen Büchs

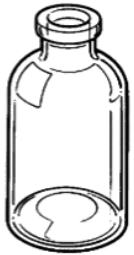
Chair of Biochemical Engineering, RWTH Aachen University



State of the art process development for gas fermentation



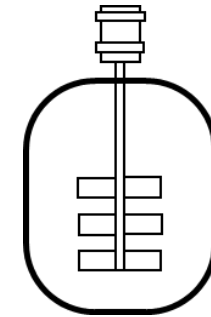
Serum bottle



Is there something to
fill the gap?



Fermenter



No online monitoring

Batch gas supply

High throughput

Online monitoring

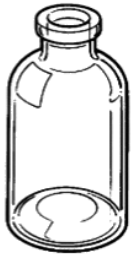
Continuous gas supply

Limited throughput

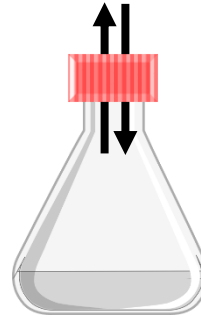
State of the art process development for gas fermentation



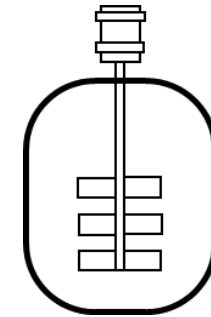
Serum bottle



Gas shaker



Fermenter



No online monitoring

Batch gas supply

High throughput

Online monitoring

Continuous gas supply

High throughput

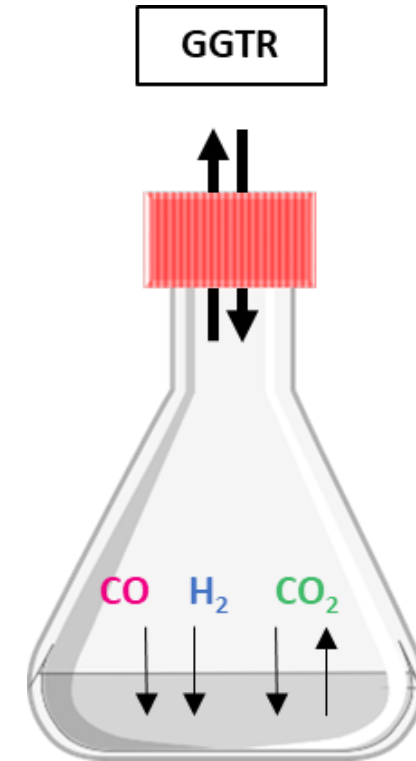
Online monitoring

Continuous gas supply

Limited throughput

Measurement principle

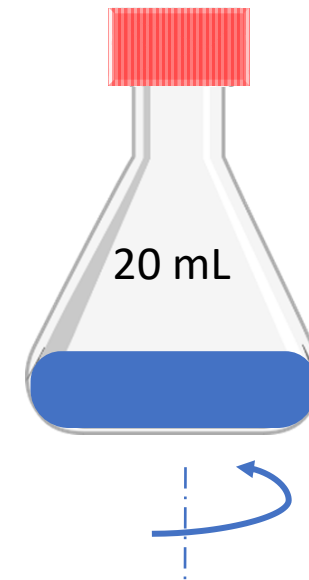
- Gross Gas Transfer Rate (**GGTR**) calculation
 - Determined via a pressure sensor
 - Represents the total gas transfer into and out of the liquid phase
- Carbon dioxide transfer rate (**CO₂TR**) calculation
 - Measured via a CO₂-Sensor
 - Represents the transfer of consumed or produced carbon dioxide



Case study - Gas fermentation using *C. ljungdahlii*



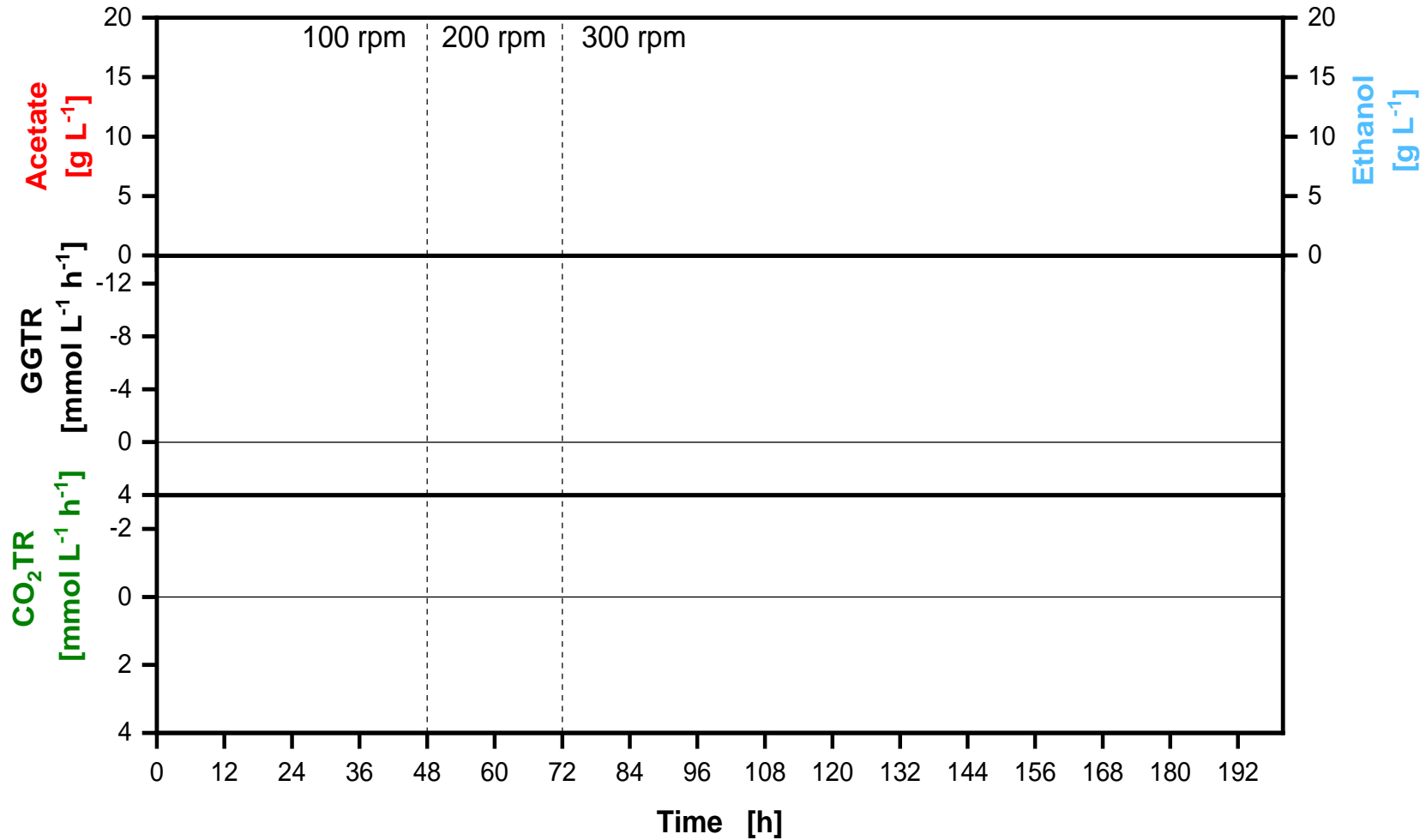
- Investigation of different gas transfer rates
 - Effect on gas consumption and carbon dioxide conversion?
 - Enhanced product formation?
- Stepwise increase of shaking frequency
 - 100 rpm
 - 200 rpm
 - 300 rpm



→ Higher shaking frequencies result in higher gas transfer rates

Effect of increased gas transfer rates

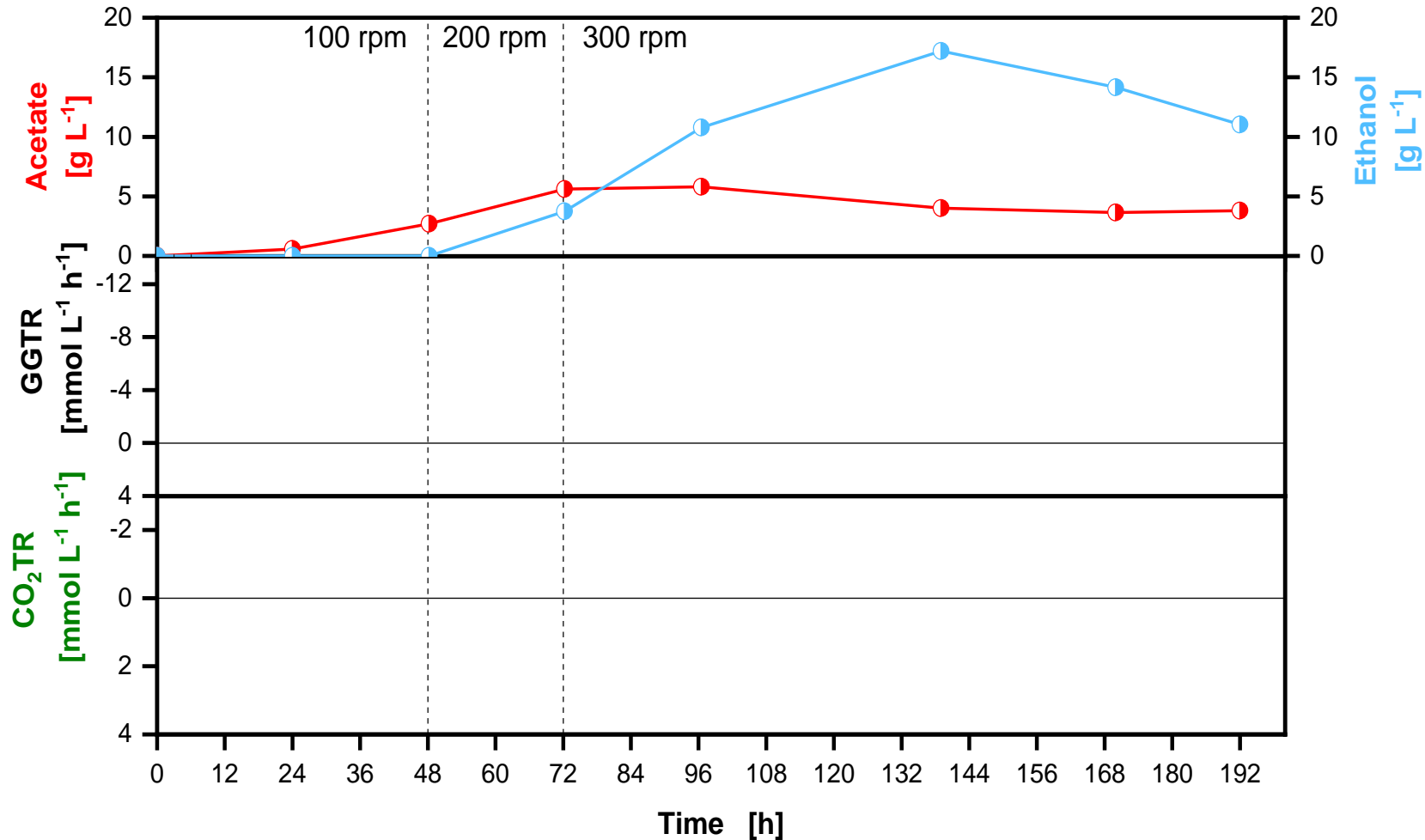
C. ljungdahlii wildtype, ATCC media, T = 37°C, pH 7, 100 mmol BisTris, n = 100 - 300 rpm,
 $d_0 = 50$ mm, $\dot{V}_{Gas} = 5$ mL min⁻¹, 10% CO / 20% CO₂ / 50% H₂ / 20% N₂



Effect of increased gas transfer rates

C. ljungdahlii wildtype, ATCC media, T = 37°C, pH 7, 100 mmol BisTris, n = 100 - 300 rpm,

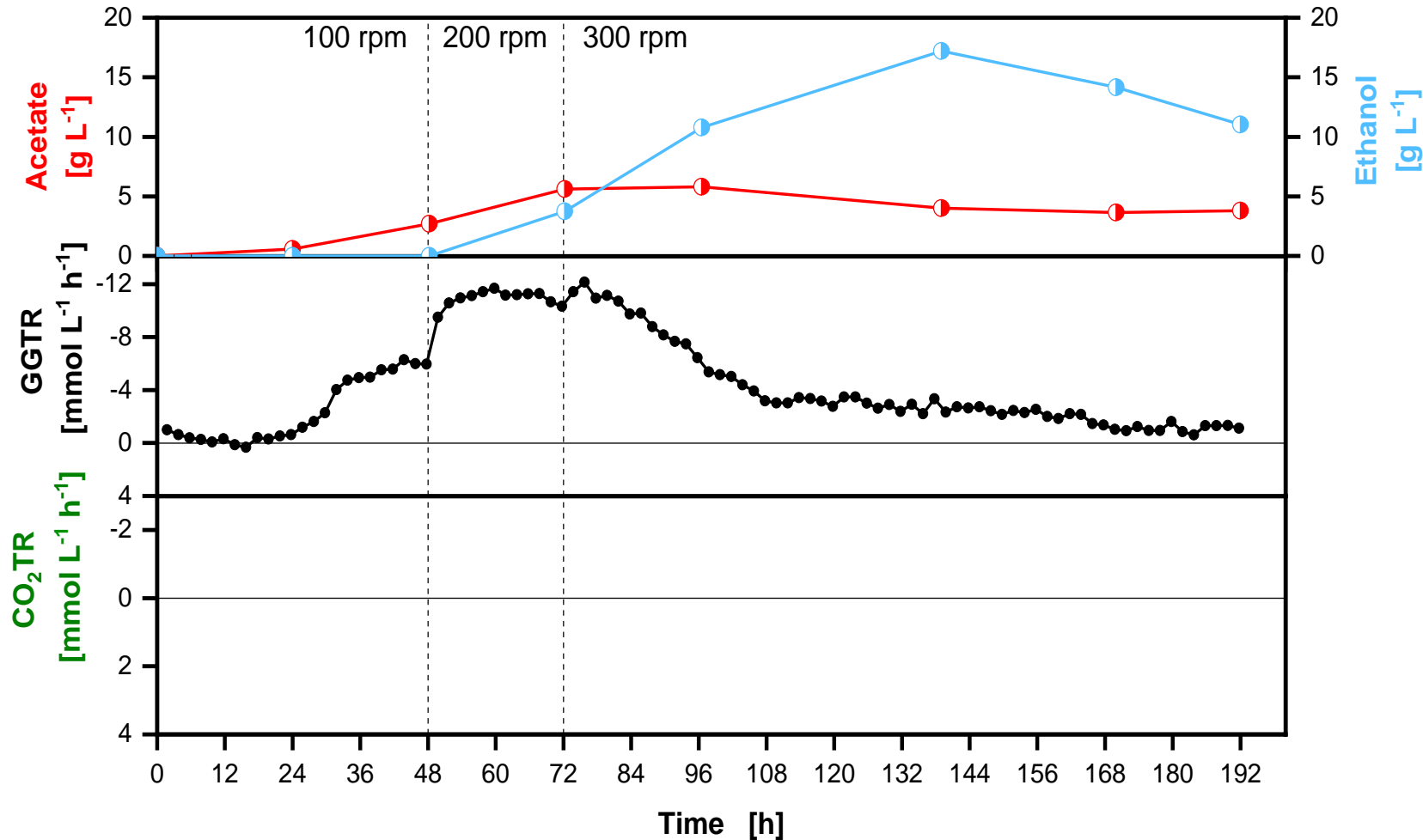
$d_0 = 50$ mm, $\dot{V}_{Gas} = 5$ mL min⁻¹, 10% CO / 20% CO₂ / 50% H₂ / 20% N₂



- Metabolic shift at 300 rpm
- Ethanol concentration of 15 g L⁻¹

Effect of increased gas transfer rates

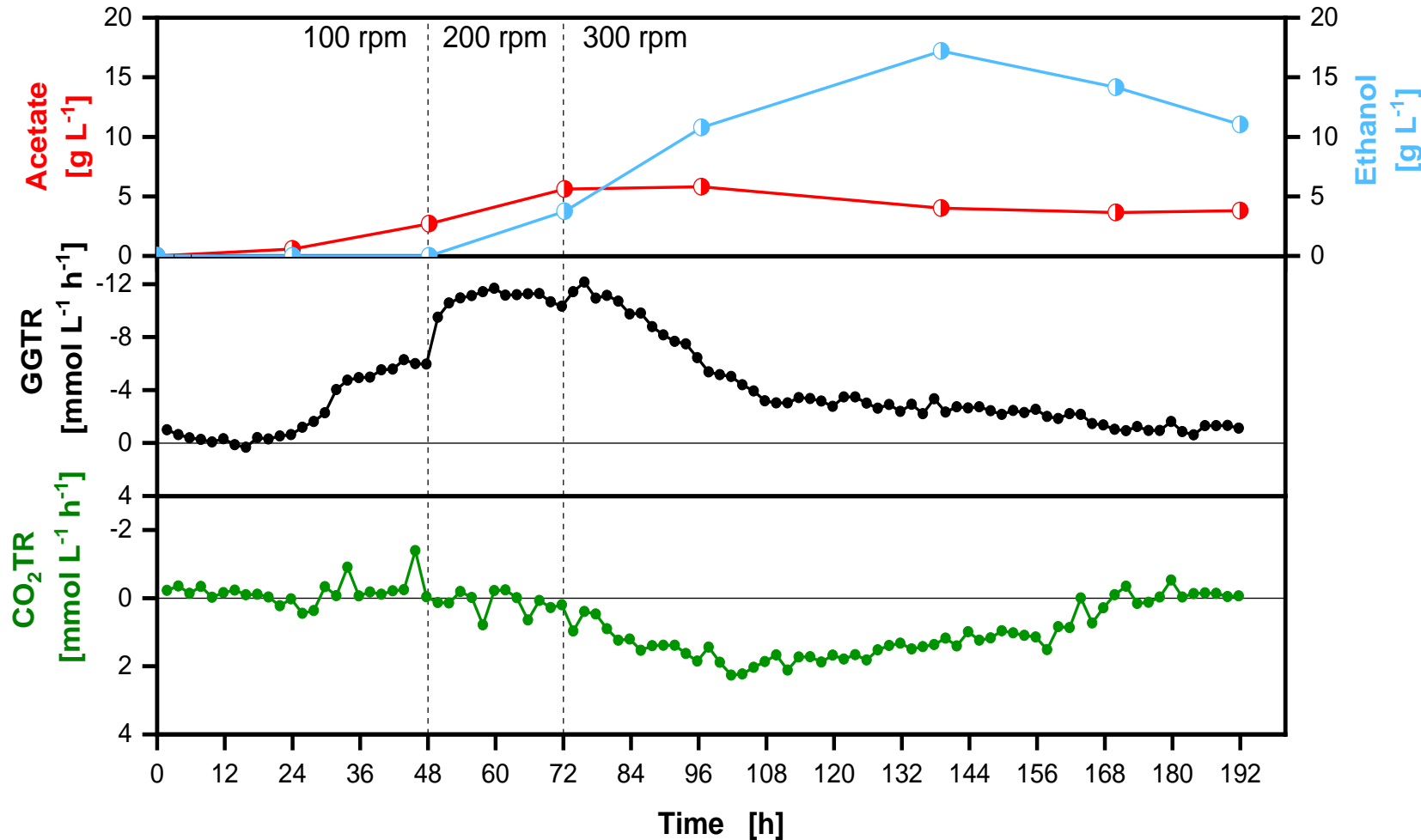
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- Metabolic shift at 300 rpm
- Ethanol concentration of 15 g L⁻¹
- Gas consumption increases with increasing shaking frequency
- GGTR drops after increase to 300 rpm

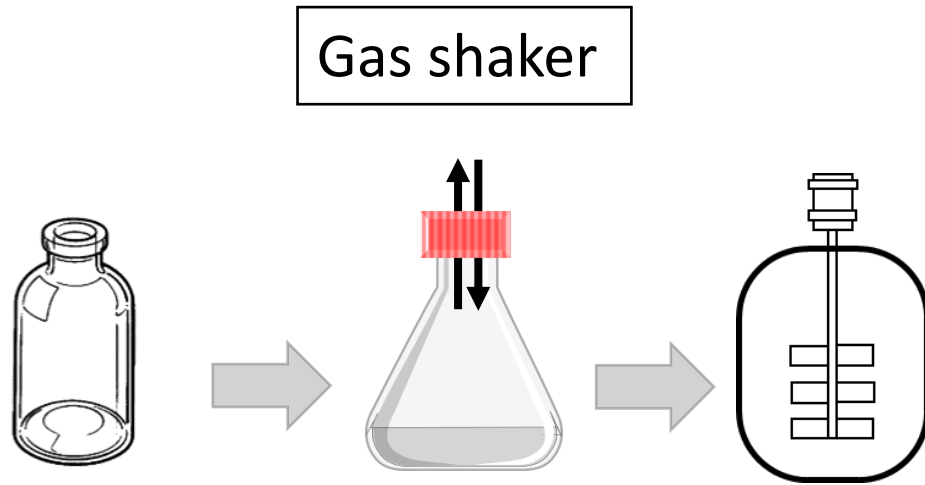
Effect of increased gas transfer rates

C. ljungdahlii wildtype, ATCC media, T = 37°C, pH 7, 100 mmol BisTris, n = 100 - 300 rpm,
 $d_0 = 50$ mm, $\dot{V}_{Gas} = 5$ mL min⁻¹, 10% CO / 20% CO₂ / 50% H₂ / 20% N₂



- Metabolic shift at 300 rpm
 - Ethanol concentration of 15 g L⁻¹
 - Gas consumption increases with increasing shaking frequency
 - GGTR drops after increase to 300 rpm
 - CO₂TR indicates excess CO₂ production after increase to 300 rpm
- ➔ Increasing gas transfer leads to hydrogenase inhibition

Summary



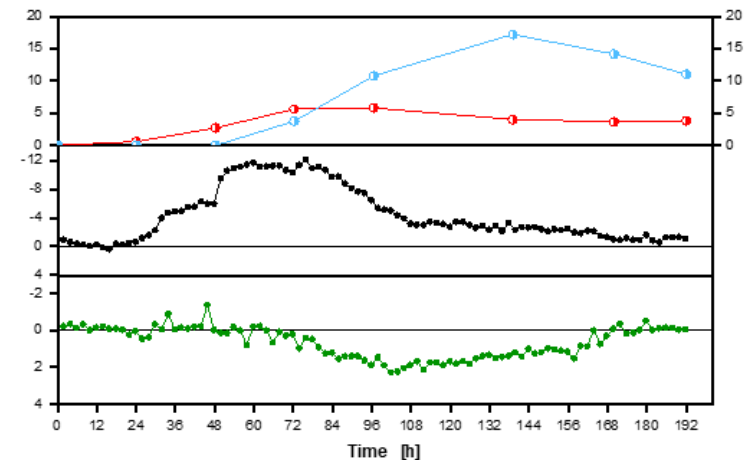
Novel shake flask system

Online monitoring of gas transfer rates

Applicable for process development

BIOCON-CO₂

Analyzing gas transfer rates



Online measurement of GGTR and CO₂TR
enables deeper insights into small scale
gas fermentation processes.



Thank you

aline.hueser@avt.rwth-aachen.de

marcel.mann@avt.rwth-Aachen.de

jochen.buechs@avt.rwth-aachen.de



www.biocon-co2.eu



BIOCON-CO2@aquatt.ie



[@BIOCON_CO2](https://twitter.com/BIOCON_CO2)



Development of a tool for optimum downstream processing

Webinar #3: Engineering sustaining Bio-CCU

Carlos Andecochea

LEITAT
managing technologies



Contents



- Tool Overview
- Introduction to DoE
- What is RSM
- Optimization
- Validation
- Summary

Tool overview



- Avoid problems related to the availability of software licenses
- User-friendly
- Design of experiments from 2 to 4 variables:
 - Directed design using circumscribed central composite (CCC)
 - Free design
- Based on Response Surface Methodology (RSM)
- Statistical model describing the process by regression analysis and lineal least square
- Optimal process conditions calculation using canonical analysis.
- Tailored statistical tool for optimization of downstream strategies for lactic acid, polyhydroxybutirate, and C₃-C₆ alcohol recovery

Decision making tool



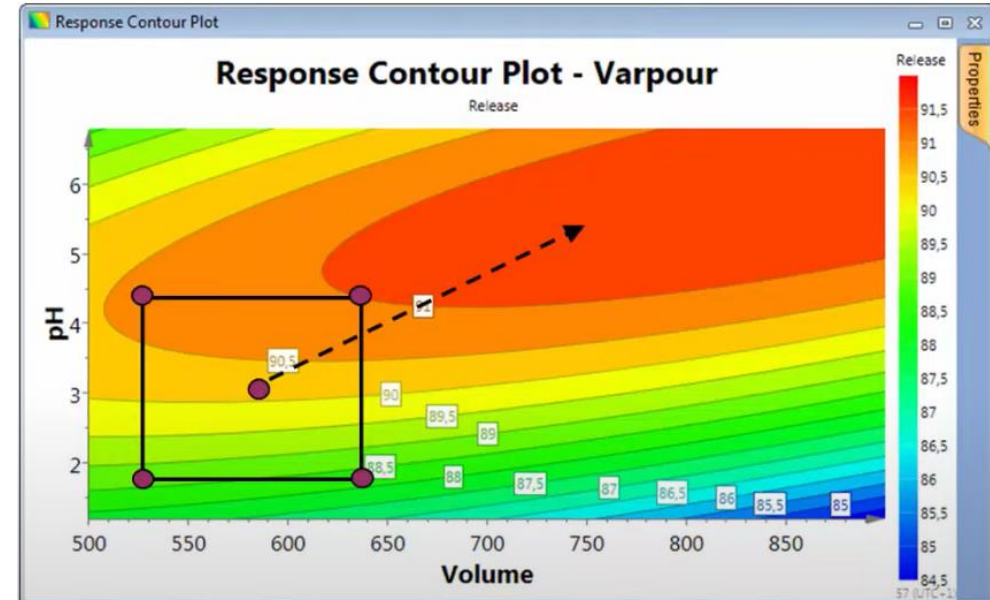
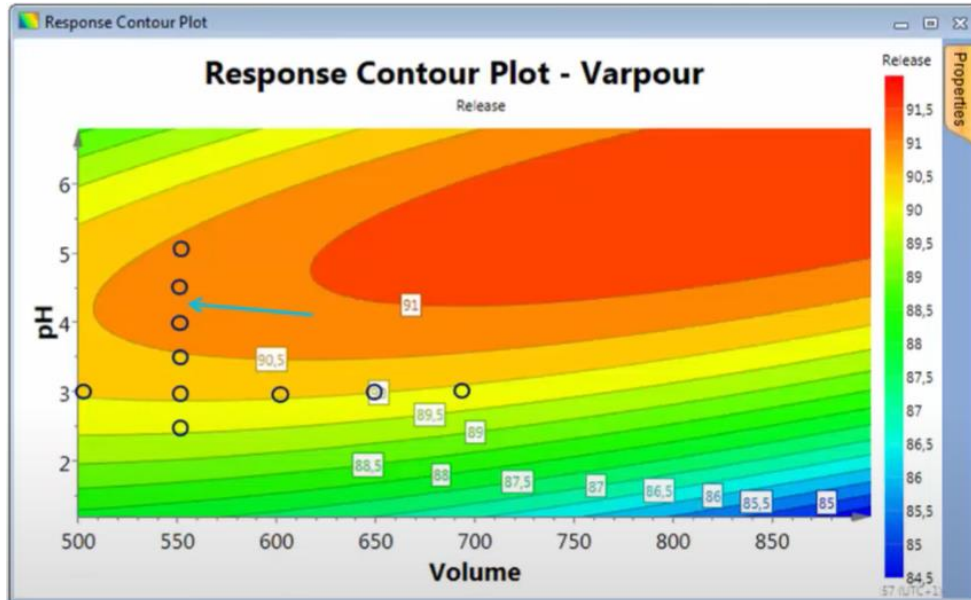
Part 1: Design of experiments

- DoE is the design of any task that aims to describe and explain the variation of information under conditions that are hypothesized to reflect the variation.
 - Usually applied to processes/experiments
- Prediction of responses based on few experiments
- Check multiple variables at the same time including interactions
- Important to select the right points for the DoE analysis
 - Constrained within reality.
 - Spread enough – experimental error.

Decision making tool



Part 1: Design of experiments



Decision making tool



Part 1: Design of experiments

1

Select the number of parameters

Choose an option

☐ 2 factors ☒ 3 factors ☐ 4 factors

Accept

2

3 factors: select type of design

Choose an option

☐ Free design ☒ Directed design

Accept

Circumscribed Central Composite design

3

Set the boundaries

Parameter 1

Name

Minimum

Maximum

Parameter 2

Name

Minimum

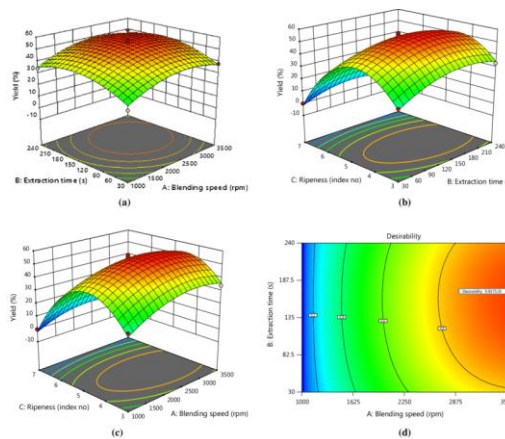
- In first step, the user set the design of experiment conditions
- Circumscribed Central Composite design request information outside the boundaries
 - If boundaries cannot be exceeded, limits can be transformed
- 4 parameters design only as free design option

Decision making tool



Part 2: Surface response

- RSM evaluates the effects of multiple factors and their interactions on a process response, establishing the relationship between input and output variables.
- Allows for predictive response of the process at given conditions.
- Analyzing the response surface topography by looking for local maximum or minimums, and ridgelines, the optimal conditions zones might be found.
- Tends to be limited to 3 factors due to its spacial representation.



Decision making tool



Part 2: Surface response

4

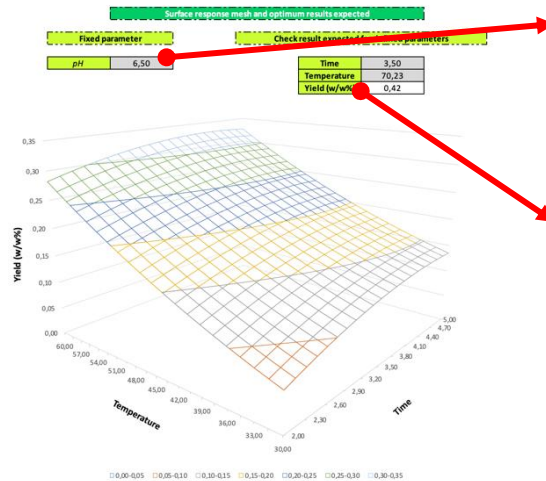
Three factors

Defined limits

	Minimum	Maximum
pH	3	10
Time	2	5
Temperature	30	60

Experimental conditions

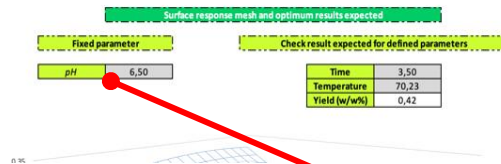
Experiment	pH	Time	Temperature	Yield (w/w%)
1	10,0	5,0	60,0	
2	10,0	5,0	30,0	
3	10,0	2,0	30,0	
4	3,0	2,0	30,0	
5	3,0	5,0	60,0	
6	3,0	2,0	60,0	
7	3,0	5,0	30,0	
8	10,0	2,0	60,0	
9	6,5	3,5	45,0	
10	6,5	3,5	45,0	
11	12,4	3,5	45,0	
12	6,5	1,0	45,0	
13	6,5	6,0	45,0	
14	6,5	3,5	19,8	
15	6,5	3,5	70,2	



- Fixed parameters must be set before displaying the surface response
- There is an option to check the result expected at given conditions

- Direct design give a list of experiments to be carried out
- Results must be introduced to display the surface response
- Free design conditions must be included between the limits set

Decision making tool



Part 3: Optimal values

5

Maximum/Minimum search

Maximum Minimum

Optimum values and result expected

pH	
Time	
Temperature	
Yield (w/w%)	No max. found

Optimum conditions may be found:
decreasing pH
increasing Time
increasing Temperature

*Suggestion of best conditions if
optimal is not found*

- Two buttons has been enabled to calculate maximum or minimum conditions if any
- Optimum search must be done after setting the fixed parameters
- If there is no maximum/minimum found, the tool will suggest where might be found the best conditions

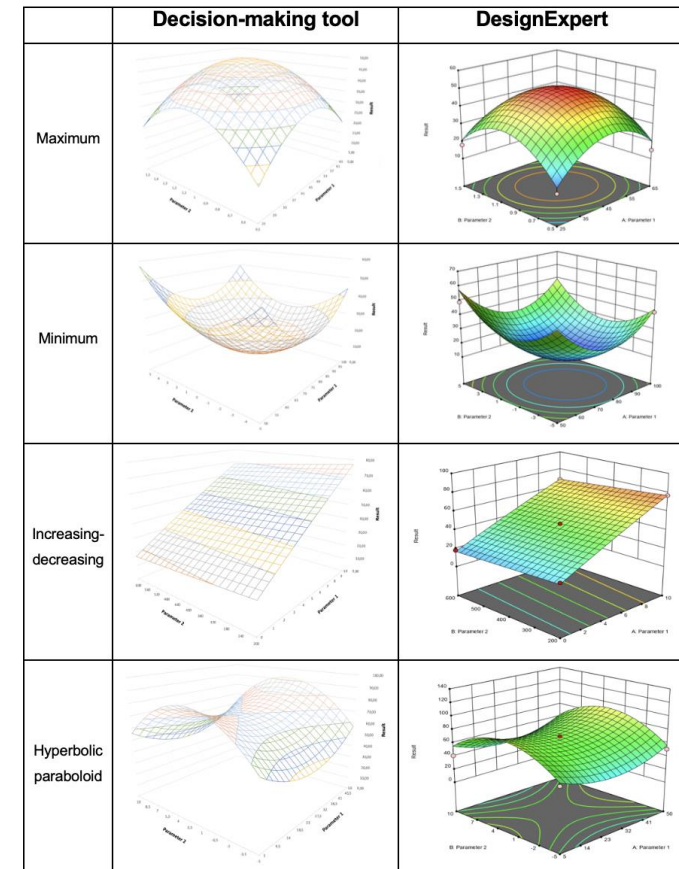
Decision making tool



Part 3: Validation

- Utility and viability of the decision-making tool
- Mathematical model - Simplifications
- Selection of suitable KPIs for downstream processes
 - User dependent
- Validation comparing responses with conventional software (DE)
 - Great results compared with commercial alternatives.

Process indicator		Ponderation	Scores		
			Process A	Process B	Process C
KPI ₁	Product quality	60%	100	90	40
KPI ₂	Separation effectiveness	20%	80	100	60
KPI ₄	Energy consumption	20%	70	100	35
Total		100%	90	94	43



Decision making tool



Part 4: Summary



- User-friendly
- Up to 4 variables with RSM and optimal conditions search.
- Open source – Available in Zenodo
- Tutorial of tool usage
- Validated against conventional softwares (DE)



Thank you

Carlos Andecochea— candecochea@leitat.org



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LEiTAT
managing technologies

BIOCON-CO2@aquatt.ie



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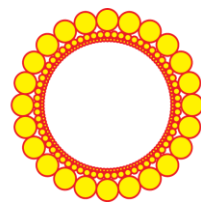
BIOCON-2

Pervaporation and its application to the downstream of alcohols

Engineering sustaining Bio-CCU

Ilse Lammerink

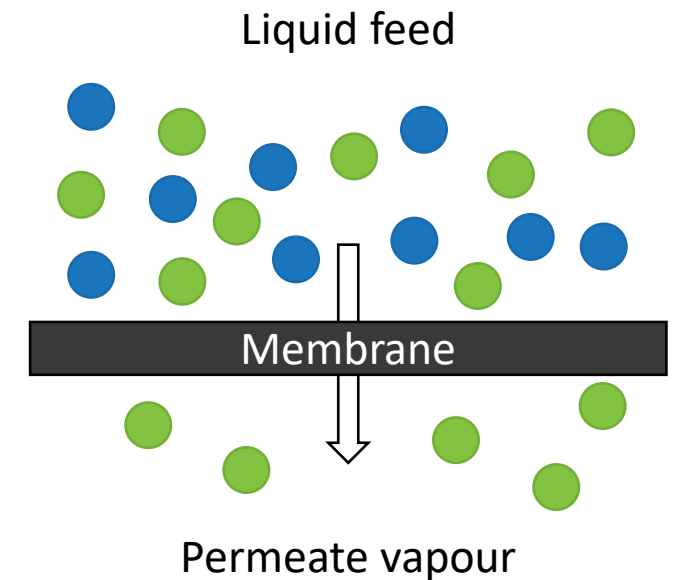
PERVATECH



Introduction to Pervaporation



- Membrane separation technology
- Separation of liquid mixtures using a dense membrane
- Pervaporation = permeation and evaporation:
 - Adsorption of material onto membrane surface
 - Diffusion through membrane
 - Desorption and evaporation into vapour phase



R. Castro-Muñoz, „Pervaporation: The emerging technique for extracting aroma compounds from food systems,” *Journal of Food Engineering*, vol. 253, pp. 27-39, 2019. DOI: 10.1016/j.jfoodeng.2019.02.013

G. Liu and W. Jin, „Pervaporation membrane materials: Recent trends and perspectives,” *Journal of Membrane Science*, vol. 636, 2021. DOI: 10.1016/j.memsci.2021.11955

Types of pervaporation processes



- Two classes of pervaporation depending on the membrane surface:

Hydrophilic

Selective permeation of water

- Membrane types:
 - Organosilica, e.g. HybSi® AR
 - Zeolites, e.g. NaA
 - Polymeric, e.g. PVA
- Applications
 - Solvent dehydration
 - Breaking of azeotropes
 - In-situ water removal

Hydrophobic/Organophilic

Selective permeation of organic molecules

- Membrane types:
 - Polymeric, e.g. PDMS, PEBA, POMS
- Applications
 - Recovery of products from fermentation broths
 - In-situ removal of toxic products (e.g. butanol)

R. Castro-Muñoz, „Pervaporation: The emerging technique for extracting aroma compounds from food systems,” *Journal of Food Engineering*, vol. 253, pp. 27-39, 2019. DOI: 10.1016/j.jfoodeng.2019.02.013

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H. Azimi, H. Tezel and J. Thibault, „Optimization of the in situ recovery of butanol from ABE fermentation broth via membrane pervaporation,” *Chemical Engineering Research and Design*, vol. 150, pp. 49-64, 2019. DOI: 10.1016/j.cherd.2019.07.012



Principles of pervaporation



- Two phenomena needed for pervaporation: separation + driving force
- Separation based on solution-diffusion interaction
 - Permeating material should have an affinity towards the membrane
 - Separation in hydrophilic pervaporation: difference in diffusion
 - Rigid pore structure → molecular sieving:
 - E.g. HybSi® AR (organosilica) $\varnothing_{\text{pore}} = 4.5 \text{ \AA}$
 - Kinetic diameter $\text{H}_2\text{O} = 2.96 \text{ \AA}$ and 2-propanol = 4.7 \AA
 - Separation in organophilic pervaporation: difference in solution

Membrane	H_2O contact angle (°)	Separation factor (-)	
		EtOH/ H_2O	ButOH/ H_2O
PDMS	110-120	7-8	40
PEBA	60-70	3-4	20



R. Castro-Muñoz, „Pervaporation: The emerging technique for extracting aroma compounds from food systems,” *Journal of Food Engineering*, vol. 253, pp. 27-39, 2019. DOI: 10.1016/j.jfoodeng.2019.02.013

G. Liu and W. Jin, „Pervaporation membrane materials: Recent trends and perspectives,” *Journal of Membrane Science*, vol. 636, 2021. DOI: 10.1016/j.memsci.2021.11955

Principles of pervaporation



- Two phenomena needed for pervaporation: separation + driving force
- Driving force needed to permeate material through membrane
- Driving force is a partial pressure gradient across the membrane:

$$\Delta p_i = p_i^F - p_i^P > 0$$

Increased by higher feed temperature

Decreased by decreasing vacuum pressure

R. Castro-Muñoz, „Pervaporation: The emerging technique for extracting aroma compounds from food systems,” *Journal of Food Engineering*, vol. 253, pp. 27-39, 2019. DOI: 10.1016/j.jfoodeng.2019.02.013

L. M. Vane, „Review: membrane materials for the removal of water from industrial solvents by pervaporation and vapor permeation,” *Journal of Chemical Technology and Biotechnology*, vol. 94, pp. 343-365, 2018. DOI: 10.1002/jctb.5839



Advantages and disadvantages



- Advantages

- Decreased energy consumption
- Breaking of azeotropes w/o entrainers
- Increase in yield, productivity and use of reactants for in-situ removal

- Disadvantages

- Hydrophilic membranes: relatively high costs for membranes
- Organophilic membranes: limited feed temperature (70 °C)

R. Castro-Muñoz, „Pervaporation: The emerging technique for extracting aroma compounds from food systems,” *Journal of Food Engineering*, vol. 253, pp. 27-39, 2019. DOI: 10.1016/j.jfoodeng.2019.02.013

G. Liu and W. Jin, „Pervaporation membrane materials: Recent trends and perspectives,” *Journal of Membrane Science*, vol. 636, 2021. DOI: 10.1016/j.memsci.2021.11955

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Pervaporation in BIOCON-CO₂



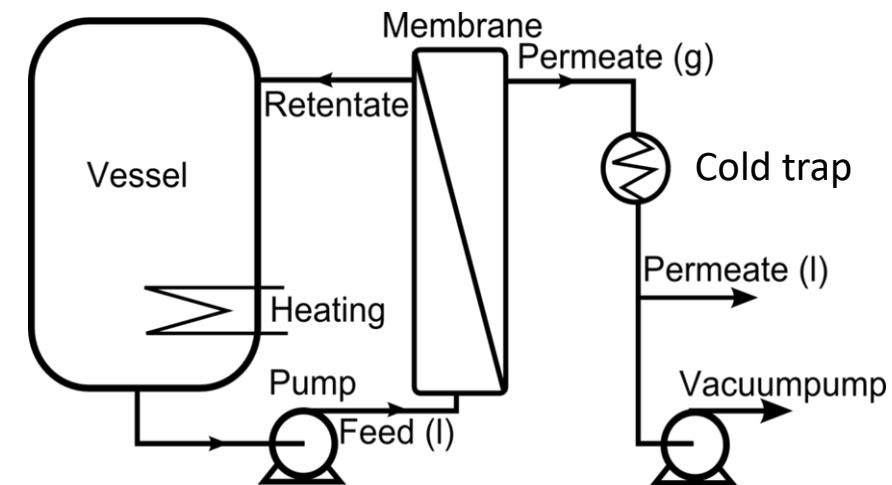
- Recovery of C3-C6 alcohols from effluent of *Clostridium ljungdahlii*
- Membrane: polydimethylsiloxane (PDMS)
- Performance measured using:

- **Recovery efficiency** (RE%, in %)

The percentage of recovered product

- **Flux** (J, in g·m⁻²·s⁻¹)

Mass of permeating material permeating per membrane area and per unit of time



R. Castro-Muñoz, „Pervaporation: The emerging technique for extracting aroma compounds from food systems,” *Journal of Food Engineering*, vol. 253, pp. 27-39, 2019. DOI: 10.1016/j.jfoodeng.2019.02.013

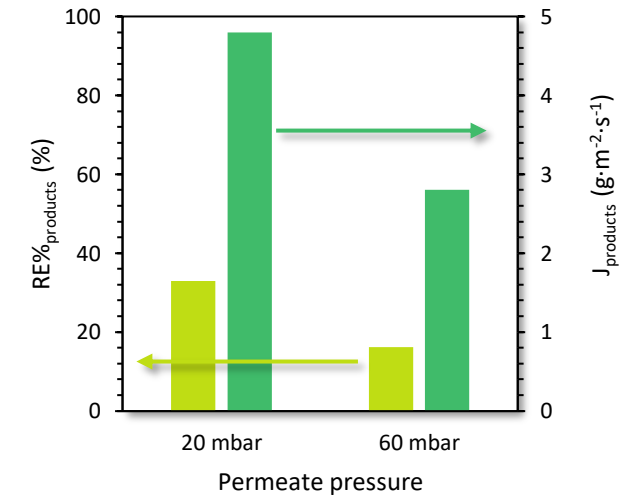
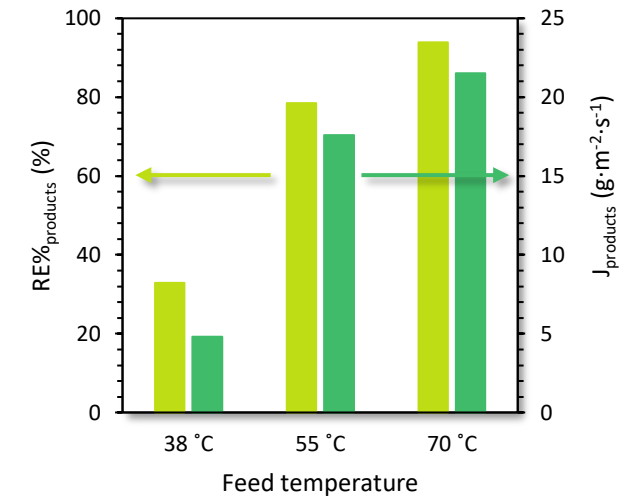
„Polydimethylsiloxane,” ACS, 14 April 2014. [Online]. Available: <https://www.acs.org/content/acs/en/molecule-of-the-week/archive/p/polydimethylsiloxane.html>. [Accessed on 16 January 2020].



Pervaporation in BIOCON-CO₂



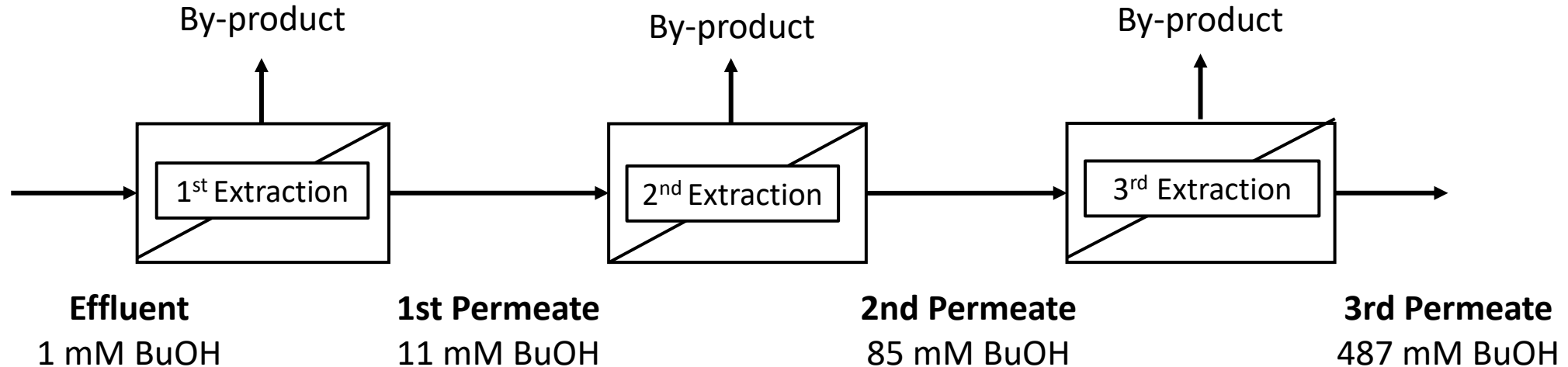
- Optimization of pervaporation parameters
- Increase in feed temperature
 - Three temperatures: 38, 55, 70 °C
 - Increase in T_{feed} leads to increase in p_{feed}
 - In turn, leads to higher driving force
- Decrease in permeate pressure
 - From 60 to 20 mbar
 - Decrease vacuum pressure leads to decrease in p_{permeate}
 - In turn, leads to higher driving force



Pervaporation in BIOCON-CO₂



- Multiple stage to increase butanol concentration to 400 mM
- Pervaporation parameters:
 - Feed temperature: 70 °C
 - Permeate pressure: 20 mbar



$$RE_{1-\text{BuOH}} = >90\%$$

Summary

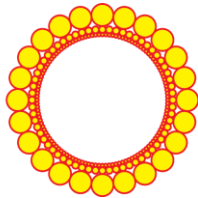


- Pervaporation is used for the separation of liquid mixtures.
- Hydrophilic and organophilic pervaporation.
- Separation occurs based on preferential solution and diffusion.
- Driving force is a partial pressure difference.
- Within BIOCON-CO₂: organophilic pervaporation to recover C3-C6 alcohols.



Thank you

PERVATECH



Ilse.Lammerink@Pervatech.nl

www.pervatech.com



www.biocon-co2.eu



BIOCON-CO2@aquatt.ie



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BIOCON-2

Nanofiltration and reactive extraction, and its application to the downstream of formic acid

Engineering sustaining Bio-CCU - 17th March 2022 - Webinar

Tomás Roncal, PhD.

Tecnalia, *Basque Research and Technology Alliance (BRTA)*



Downstream processing (DSP)

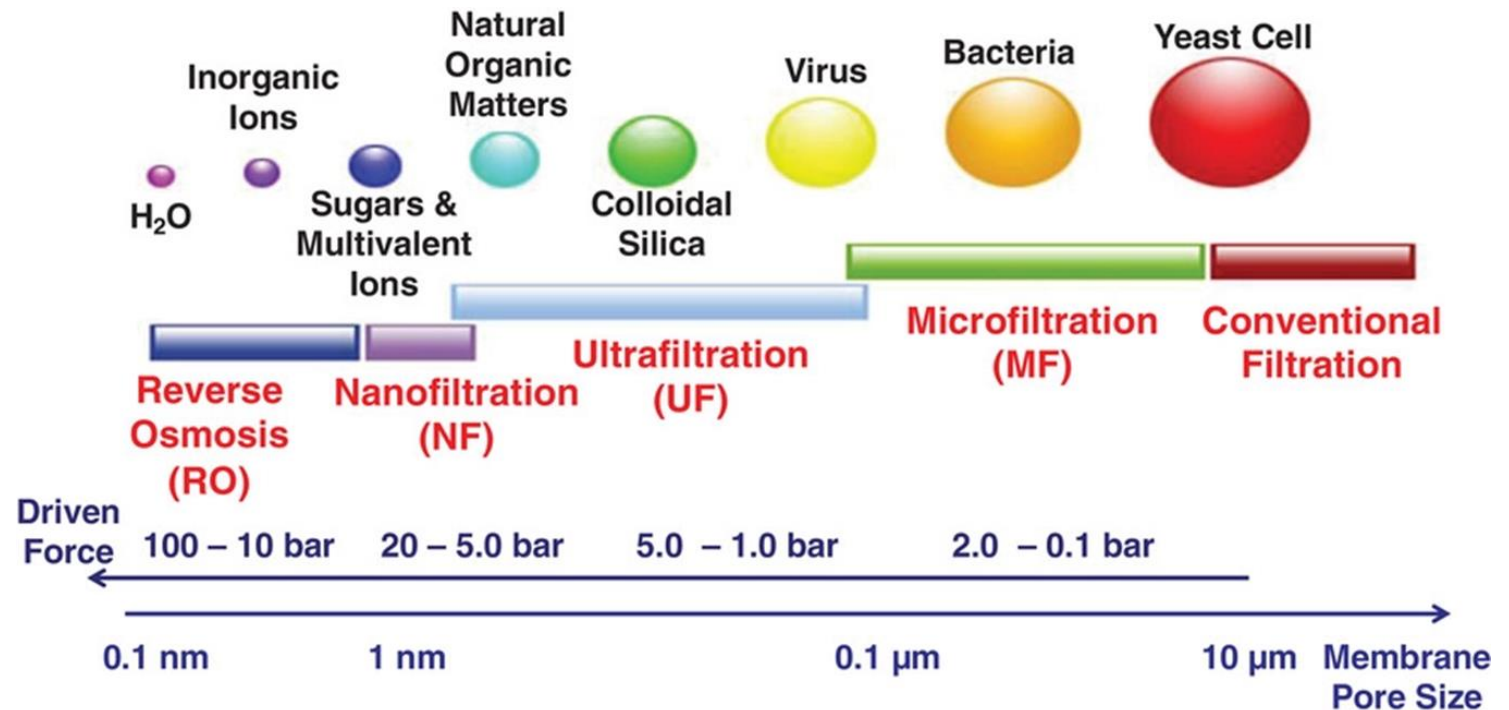


- Bio-based products must be efficiently recovered and purified from the media where they are produced to be used in their final applications.
- Product recovery and purification, known as **downstream processing**, is often a complex task accounting for a significant share of the process costs (up to 75%).
- CO₂ (gas)-derived products usually are present at one to two orders of magnitude lower than their sugar-derived counterparts.
- Necessary **efficient, cost-effective and non-energy intensive** downstream processes for industrial feasibility.



Nanofiltration (NF)

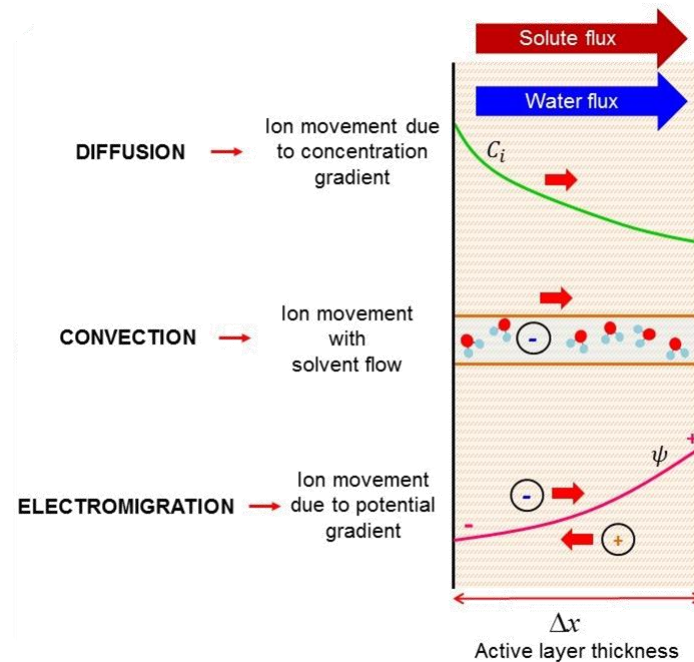
- Pressure driven membrane-based separation, between RO and UF.
- Separation of inorganic salts and small organic molecules.
- Energy efficient and environment-friendly.
- Membranes characterized by **structural** (pore size) and **electrical** (charge) parameters.
- **Pore size** of NF membranes in the order of nanometers and nominal molecular weight cut off (MWCO) in the range of 100–1000 Da.



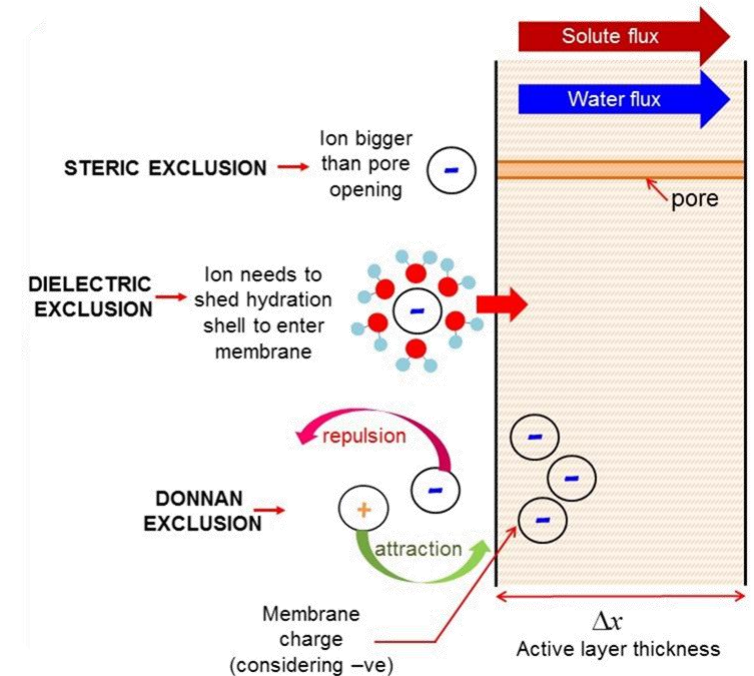
Nanofiltration (NF)

- Separation of solutes involves both **steric** (sieving) and **electrical** (Donnan) effects.
- Transport mechanisms:**
 - 1) diffusion
 - 2) convection
 - 3) electromigration
- Exclusion mechanisms:**
 - 1) steric exclusion
 - 2) Donnan effect
 - 3) dielectric exclusion

Solute transport mechanisms



Solute exclusion mechanisms

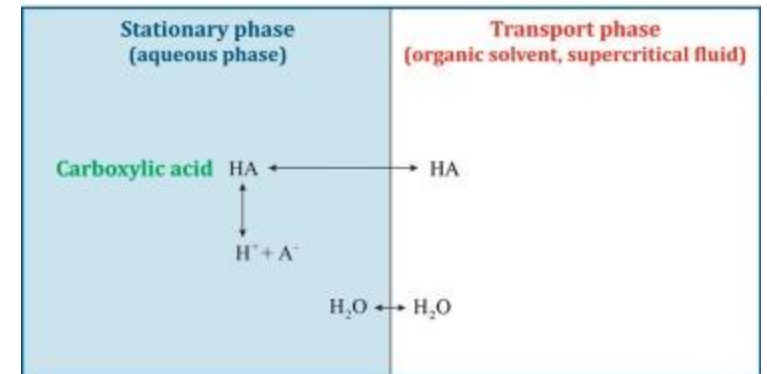


Reactive liquid-liquid extraction (R-LLE)

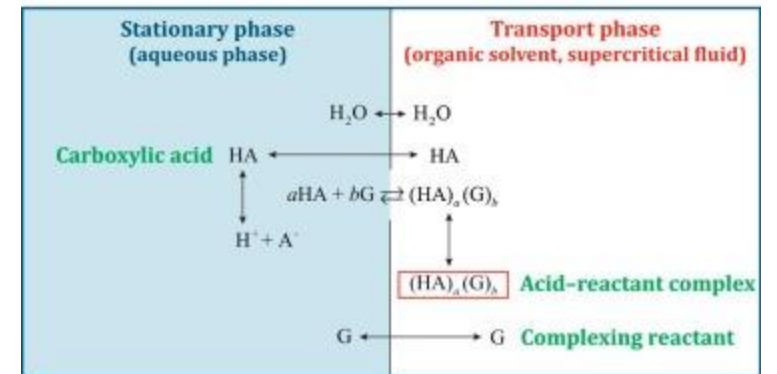


- **Physical extraction:** extraction of a solute into an inert non reacting solvent; only based on the different physical properties of solute and solvents, such as polarity.
- **Reactive extraction:** reversible reaction between the extractant in the organic phase and the solute in the aqueous phase, and the complexes formed are then solubilized in the organic phase.
- Reactive extraction is a **clean process**, since the energy demand is low and the extractant can be completely recovered and reused.

Physical extraction



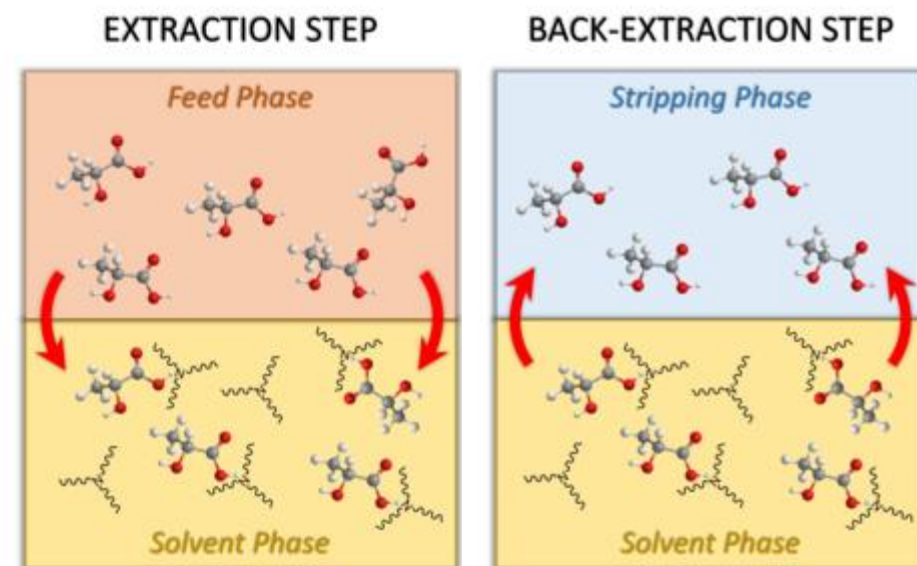
Reactive extraction



Reactive liquid-liquid extraction (R-LLE)



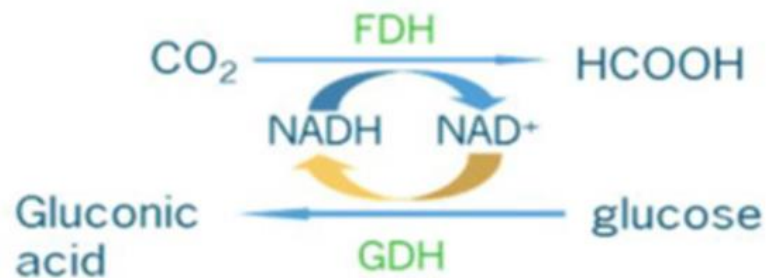
- Reactive extraction suitable for **recovery of carboxylic acids**.
- **Extractants**: aliphatic tertiary amines and alkyl phosphates.
- Extractants usually mixed with **diluents**, which affect the physical properties of the organic phase and the extraction.
- The **undissociated** form of carboxylic acids is the only one that can be extracted, so the pH of the aqueous phase should be kept at a value lower than the pK_a of the acid.
- There are **two steps** in reactive extraction:
 - 1) Extraction** of the solute from the aqueous phase to the organic phase.
 - 2) Back-extraction** of the complexed solute from the organic phase to recover the extractant-free solute in a new aqueous phase and, simultaneously, to regenerate the extractant for reuse.



Case study: DSP of formic (& gluconic) acid in BIOCON-CO₂



- Synthesis of formic acid from CO₂ by a coupled biocatalytic reaction (WFBR - Wageningen Food & Biobased Research).



- As a result of this reaction, aqueous effluents are produced characterized by the presence of equimolar concentrations of formic and gluconic acids.

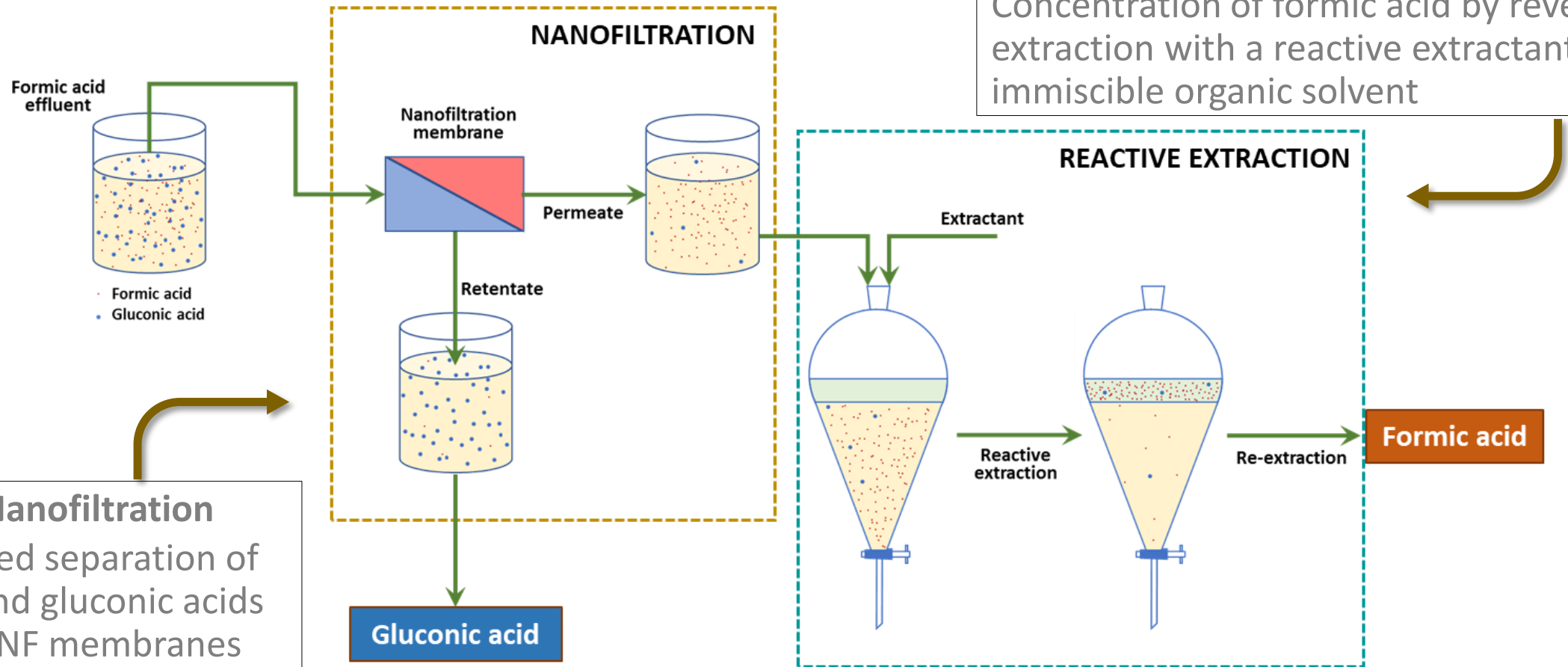
Formic acid effluent composition	
Compound	Concentration
Formic acid	2 g/L
Gluconic acid	9.8 g/L

Outline of formic and gluconic acids downstream



Step 2: Reactive extraction

Concentration of formic acid by reversible extraction with a reactive extractant in an immiscible organic solvent



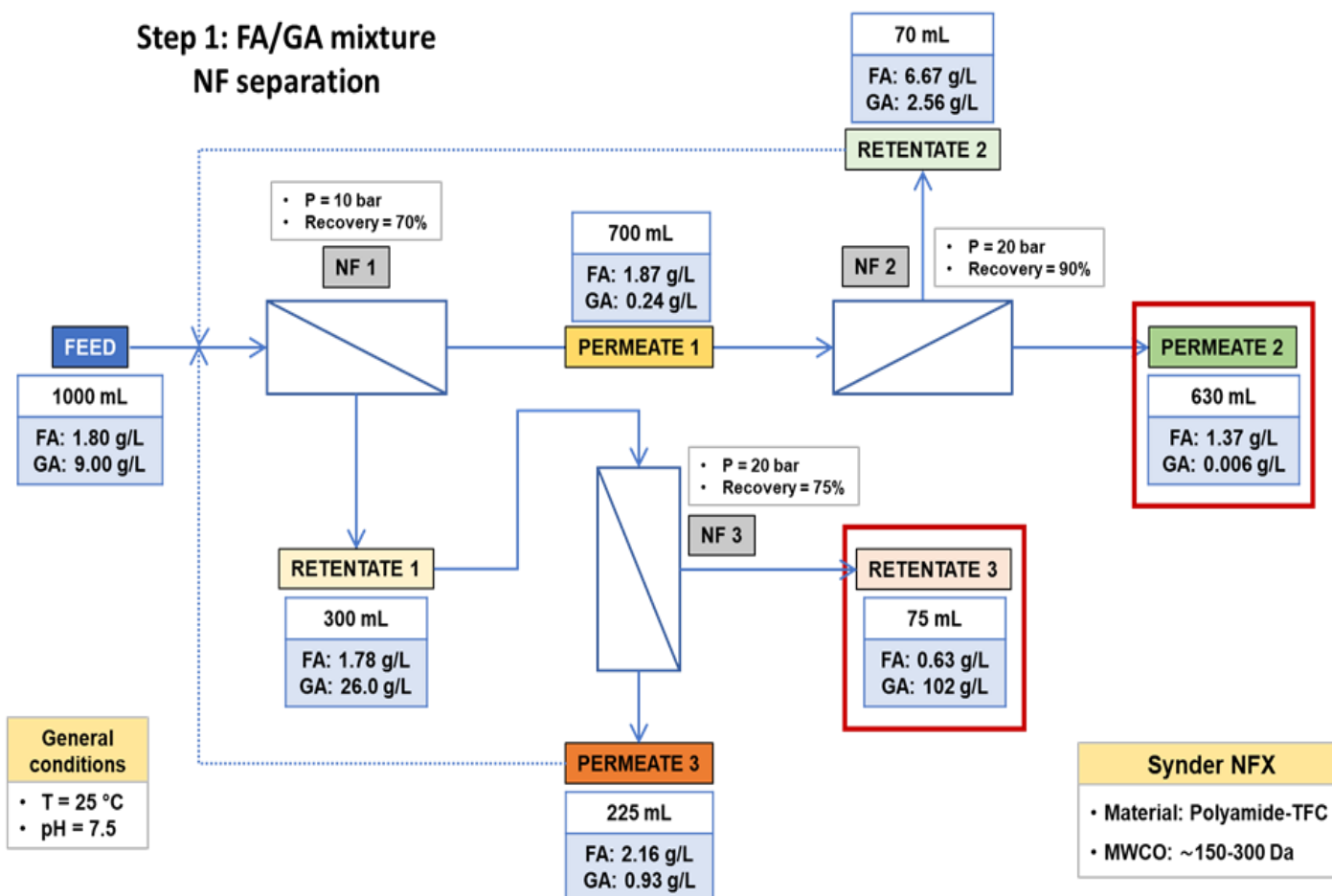
Step 1: Nanofiltration

MW-based separation of formic and gluconic acids through NF membranes

Step 1: Nanofiltration



Step 1: FA/GA mixture NF separation



Permeate pathway

Fraction	[F]	[G]	Y(F)	Y(G)	EF(F)	SF(F)	Purity (F)
Feed	1.80	9.00	100%	100%	1	1	16.7%
Permeate 1	1.87	0.24	72.5%	1.89%	38.4	112	88.5%
Permeate 2	1.37	0.006	47.6%	0.03%	1202	3515	99.6%

Retentate pathway

Fraction	[F]	[G]	Y(F)	Y(G)	EF(G)	SF(G)	Purity (G)
Feed	1.80	9.00	100%	100%	1	1	83.3%
Retentate 1	1.78	26.0	29.6%	86.5%	2.95	113	93.6%
Retentate 3	0.63	102	2.38%	77.2%	32.7	1257	99.4%

Step 2: Reactive extraction



- Whole reactive extraction process.

FEED		EXTRACTION		RE-EXTRACTION		WHOLE PROCESS			
pH = 2.7 V = 1000 mL		TOA 877 mM (n-oct) TOA/FA (mol) = 18.3 V = 100 mL (twice)		NaOH 6 M NaOH/FA (mol) = 14 V = 10 mL (twice)		V decrease from 1000 to 10 mL			
[FA] (g/L)	Y (%)	[FA] (g/L)	Y (%)	[FA] (g/L)	Y (%)	[FA] (g/L)	Y (%)	C. factor	V. decrease
2.24	100	19.8	88.5	174.5	88.1	174.5	77.9	77.9	1/100

- Reuse of TOA/n-octanol organic phase.

TOA/n-octanol	[FA] (g/L)	Y (%)
Fresh	18.3	90.2
Used (as is)	17.7	89.2
Used (add. re-extr.)	17.7	89.1



Thank you

Tomás Roncal (Tecnalia)

tomas.roncal@tecnalia.com



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Round table





Thank you!

And see you at our next event:

Final Symposium 14-15 June



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