

BioRECO₂VER

(Pressurized) Fermentation for CO₂ conversion

Heleen De Wever (VITO) – Jean-Luc Dubois (Arkema)
Online webinar, 23 November 2021



Horizon 2020
European Union Funding
for Research & Innovation

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

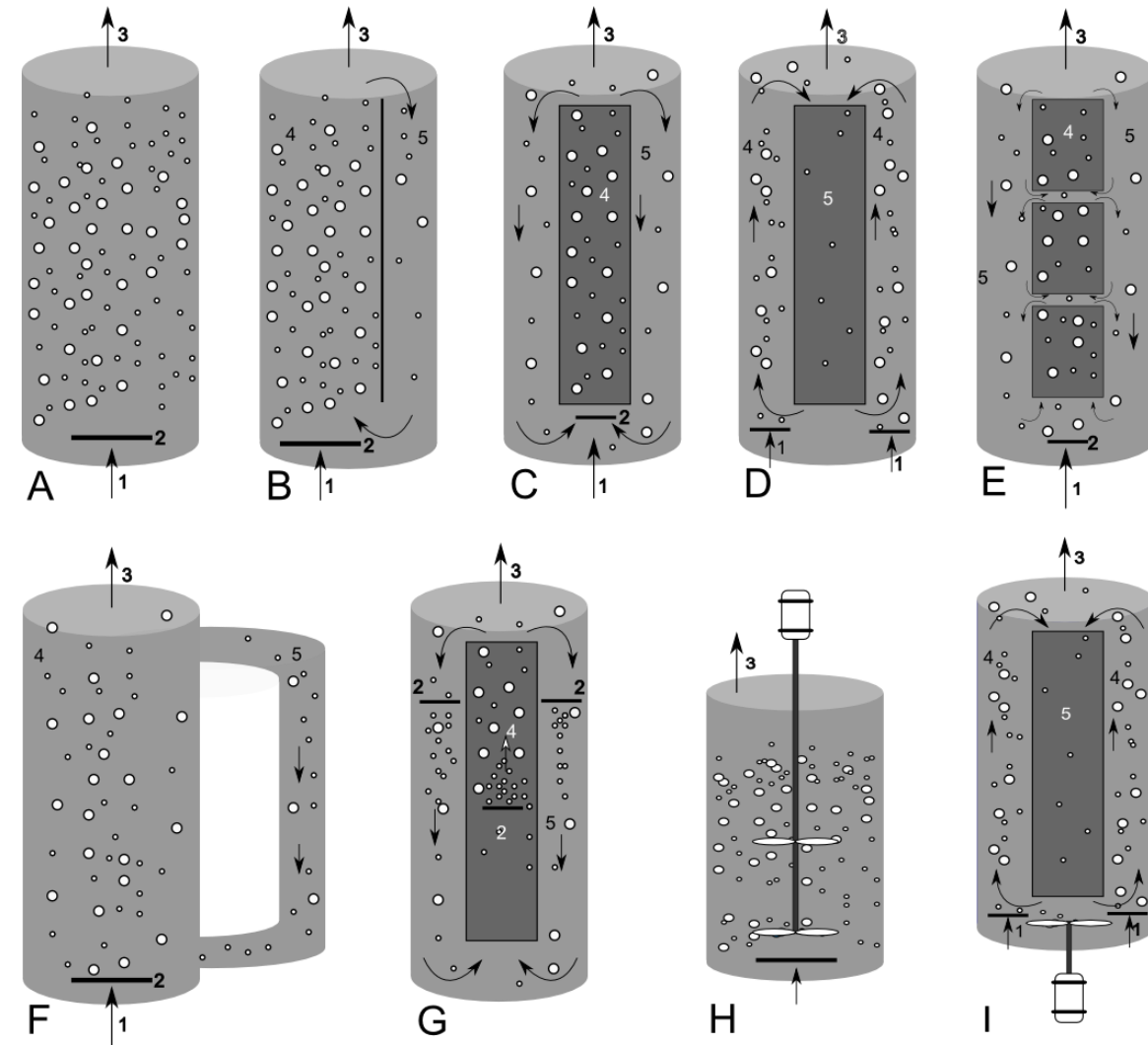
Gas fermentation

Microorganisms can use C1 gases as carbon and energy source or as electron acceptor

- Micro-organisms can only take up gaseous substrates in their dissolved form
- Series of mass transfer steps of substrate from gas bubble to reaction site inside the cell has to take place: gas-to-liquid mass transfer

Fermentor types in industrial settings:

- Bubble columns
- Airlift fermenters
- Stirred tank reactors
- Hybrids between airlift and stirred tank reactor



Source: Van Hecke et al. (2019)

Substrate availability in fermentations

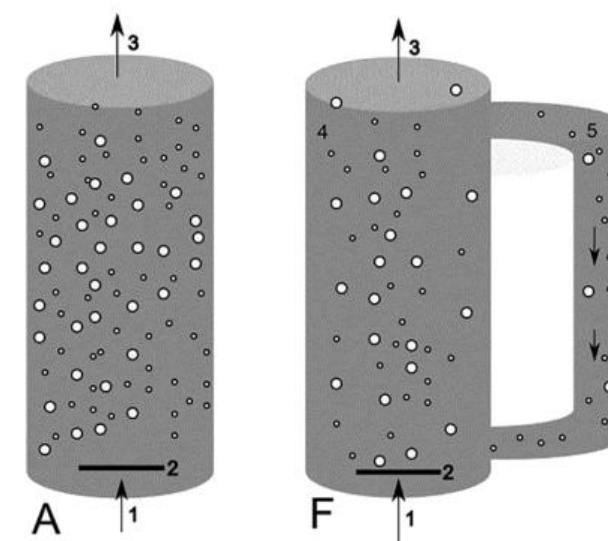
Table 2. Relative available molar substrate concentration of dissolved solid and gaseous substrates in the fermentation broth.

Substrate	Heat of combustion at 298.15 K and 1 atm [kJ mol ⁻¹]	Maximum solubility in water at 303.15 K and 1 atm [mmol L ⁻¹]	Common supply in media [g L ⁻¹] / gas feed [vol %]	Resulting available substrate [mmol L ⁻¹]	Ref.
Glucose	2820	2964	200 g L ⁻¹	1110	[137, 138]
CO	283	0.92	50 %	0.46	
CO ₂	–	29.99	CO ₂ + H ₂ + O ₂	14.99	[138, 139]
CH ₄	889	1.30		0.65	
H ₂	286	0.76		0.38	
O ₂	–	1.18		0.25	

Source: Geinitz et al. (2020)

Gas (CO₂, H₂) 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)

Operation at elevated pressure (5-10 bar)

Effects on microbial growth and product formation

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

Process operation and control

- Feedback control of **dissolved gas concentration** needed for reactor stability
- Process monitoring and determination of kinetic parameters complicated by **lack of dissolved gas sensors** (except for O_2) resistant to and accurate at broad P ranges
- Fermentations at moderately elevated pressures using C1 gases **underexplored**

Source: Van Hecke et al. (2019)

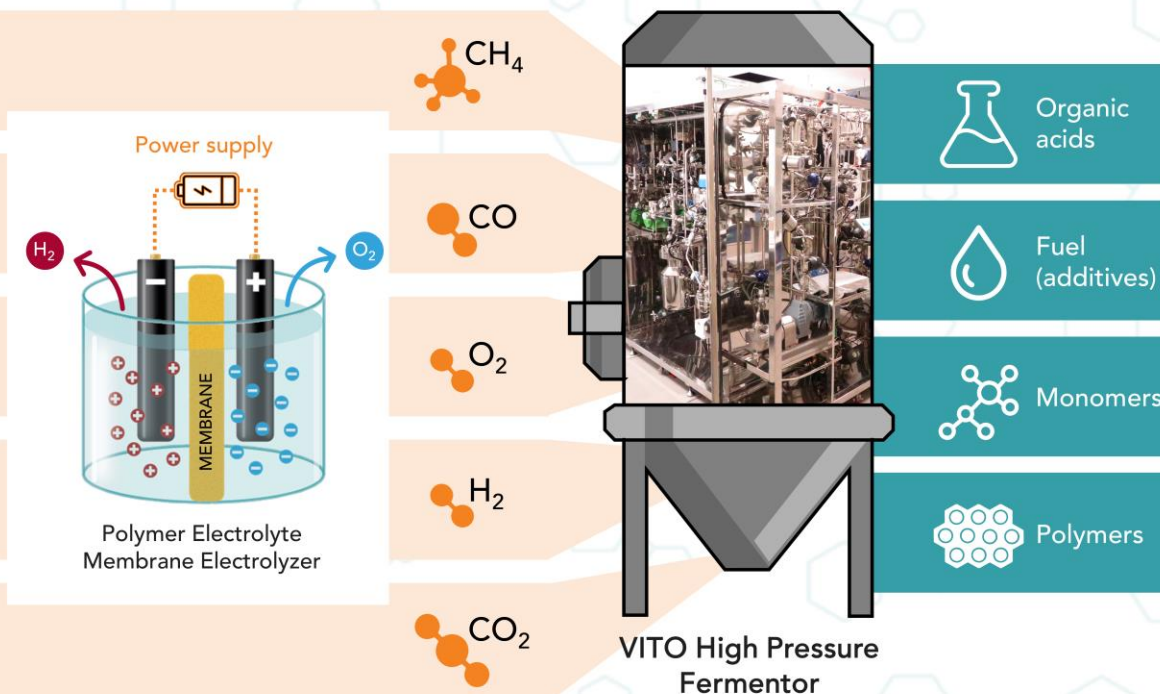



Fermentor skid



Online GC

Pressurized fermentor: main features



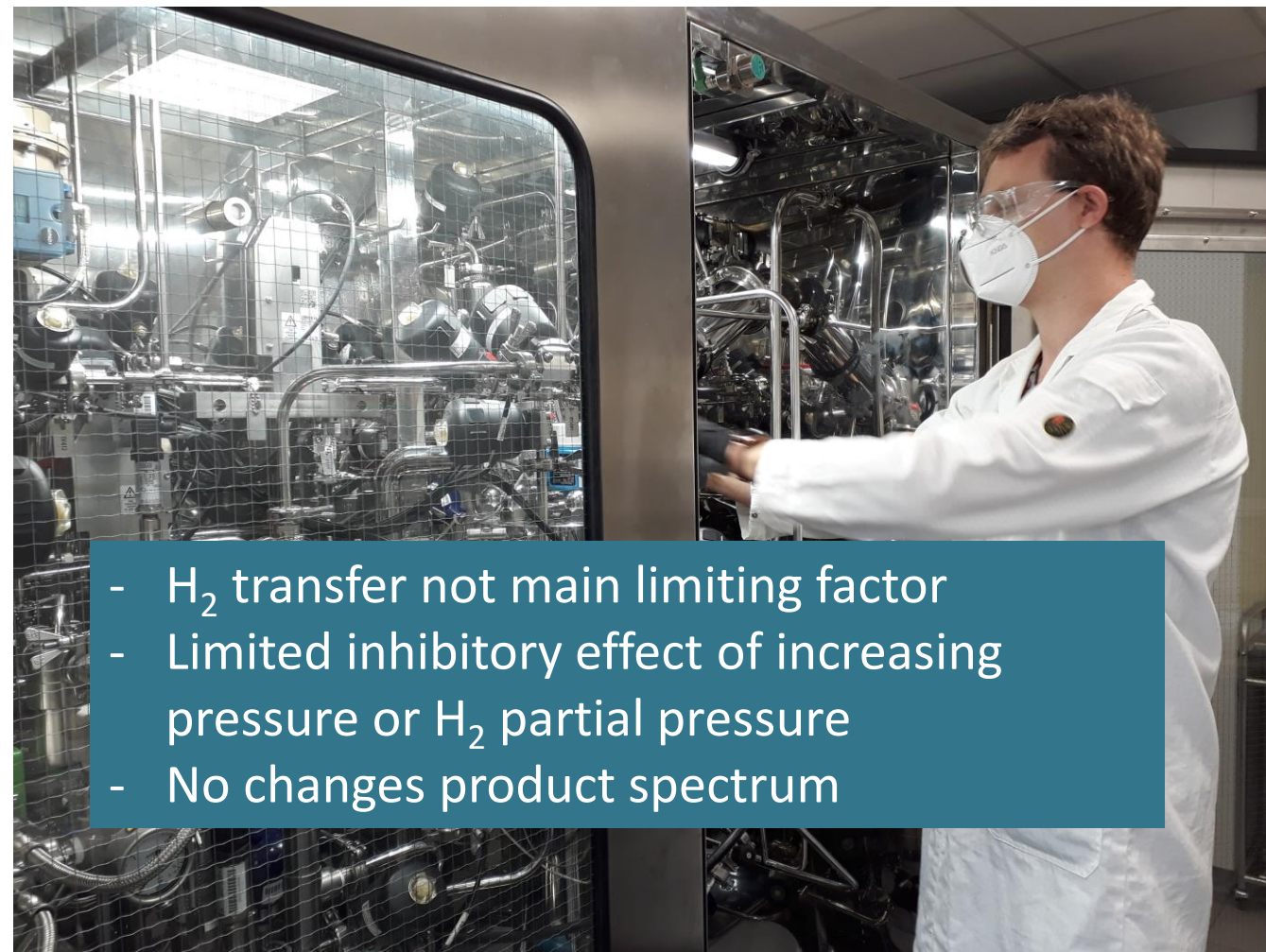
- In situ sterilizable bioreactor for gaseous fermentations
- CO₂, H₂, CO, O₂, N₂, gas mixtures such as syngas or real offgases
- Operation at constant or variable pressures up to 10 bara
- Food grade + ATEX ( II 2G) gas fermentation
- Online process monitoring and control
- Online gas analysis and control
- Integrated membrane filtration

Some experimental results

- Study effect of increasing pressure
- Compare at constant CO₂ partial pressure

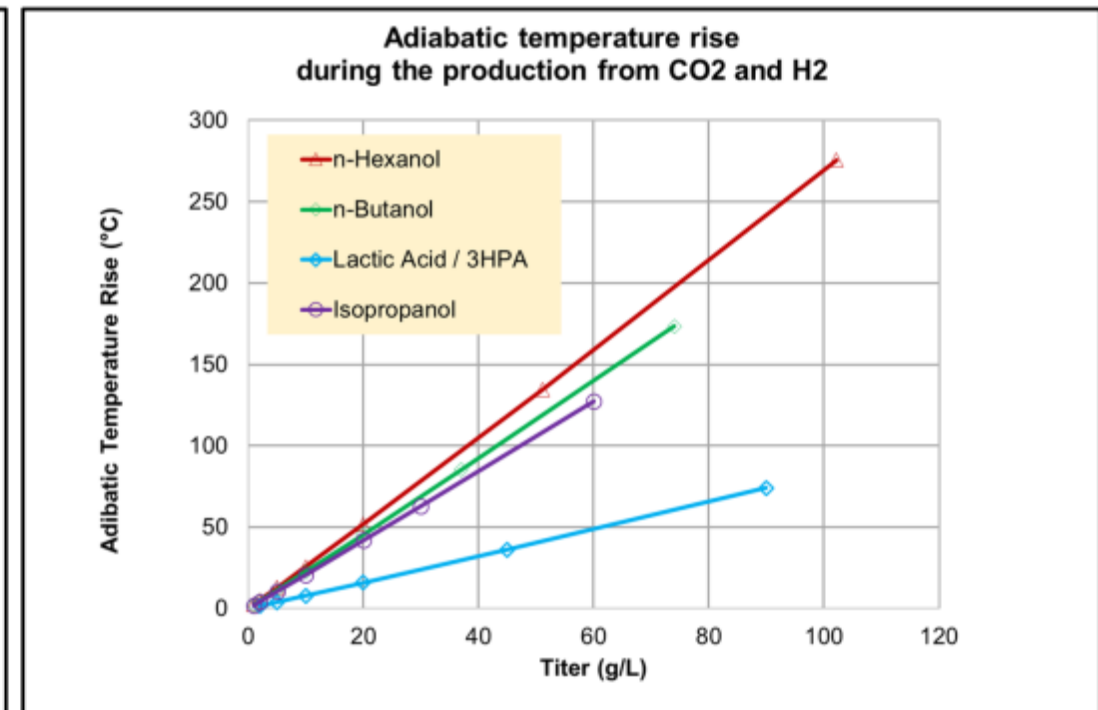
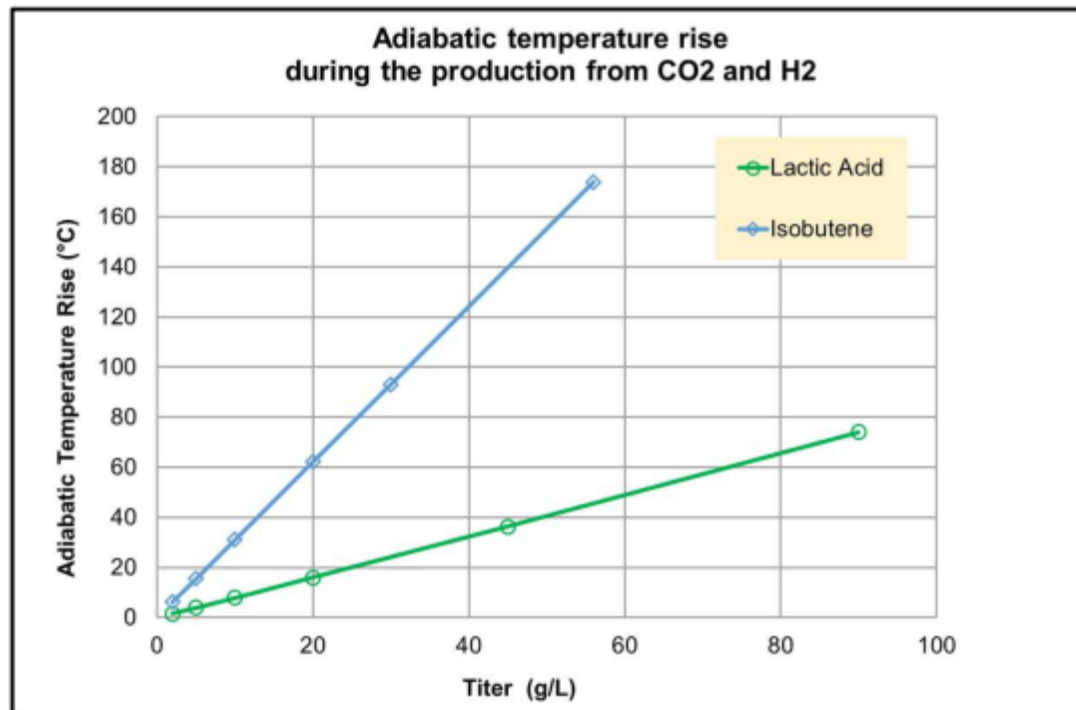
Pressure	Headspace H ₂ /CO ₂ (vol%)	Main product (g/L)*	Productivity (g/L.h)
3 bar	80/20	25 (↑)	0,19
6 bar	88,5/11,5	21	0,21
9 bar	92/8	18 (↑)	0,17

**at same fermentation duration*



- H₂ transfer not main limiting factor
- Limited inhibitory effect of increasing pressure or H₂ partial pressure
- No changes product spectrum

Need for high product titers



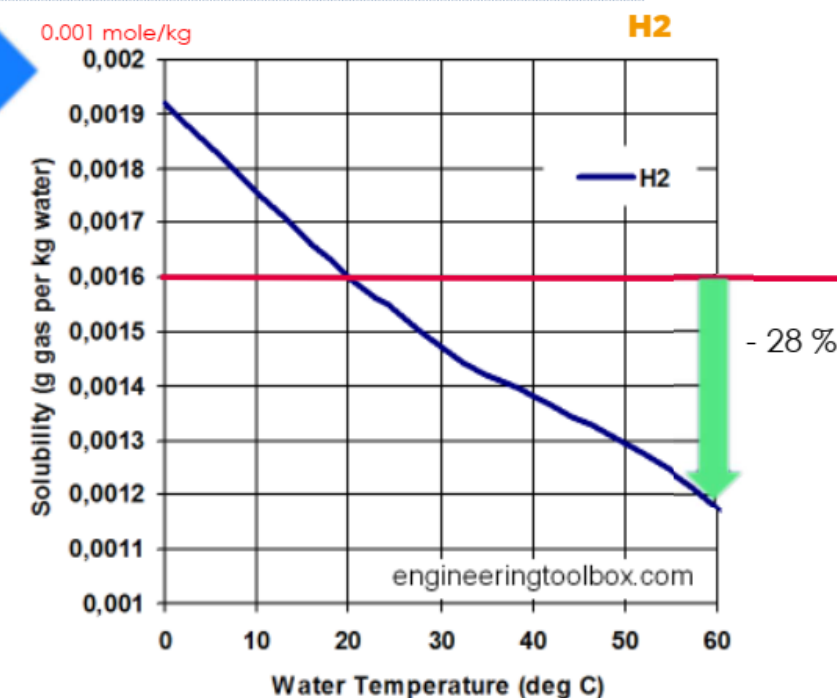
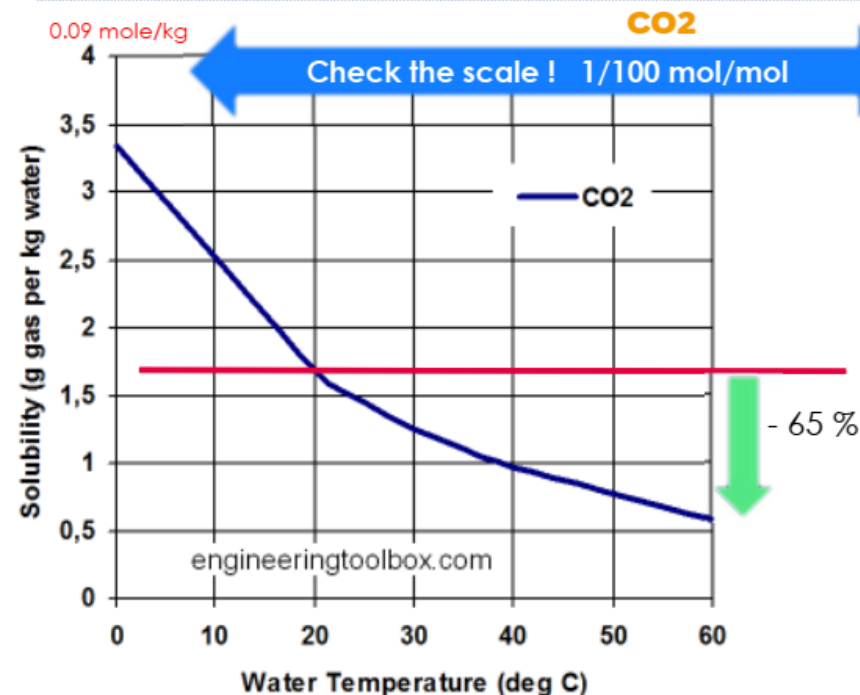
- Titer >10-20 g/L: need for cooling
- Heat losses not detectable at lab-scale, but substantial at industrial scale
- 100 kton lactic acid/yr
 - ≈ energy loss of 93 900 MWh/yr
 - ≈ energy consumption > 14 000 Europeans

Heat management at (high) product titers

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

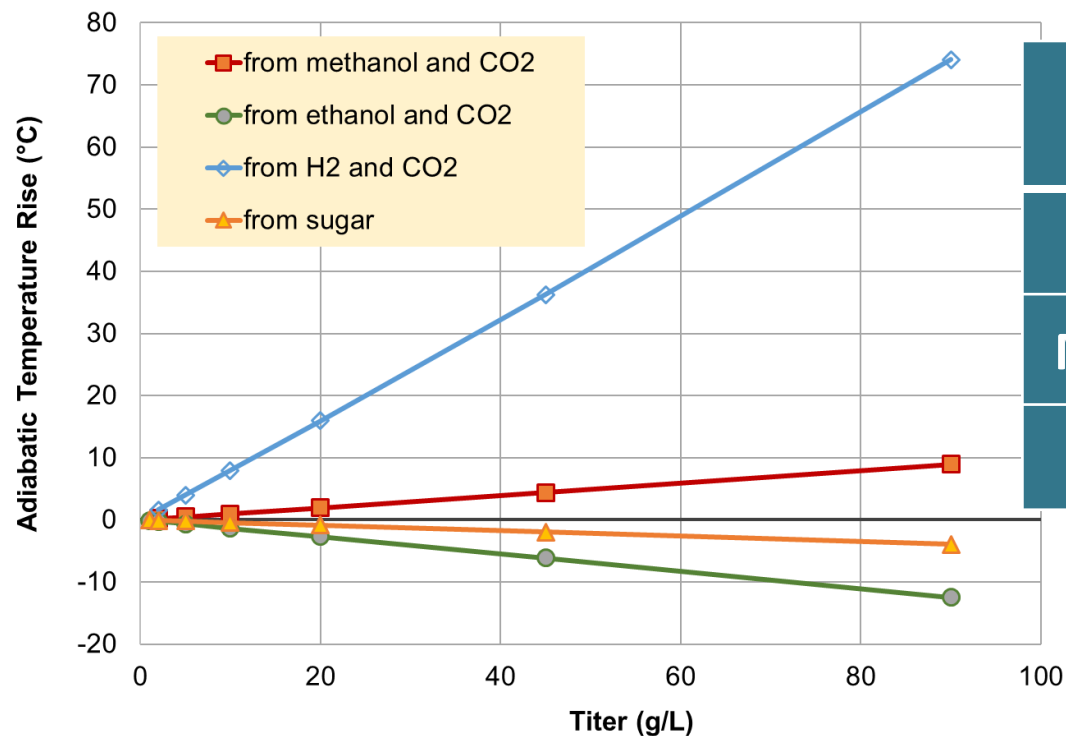
- Operation at higher T preferable for heat valorization
→ (hyper)thermophilic range
- Issue gas solubility

(source: Engineeringtoolbox.com)



Use of alternative reducing agents?

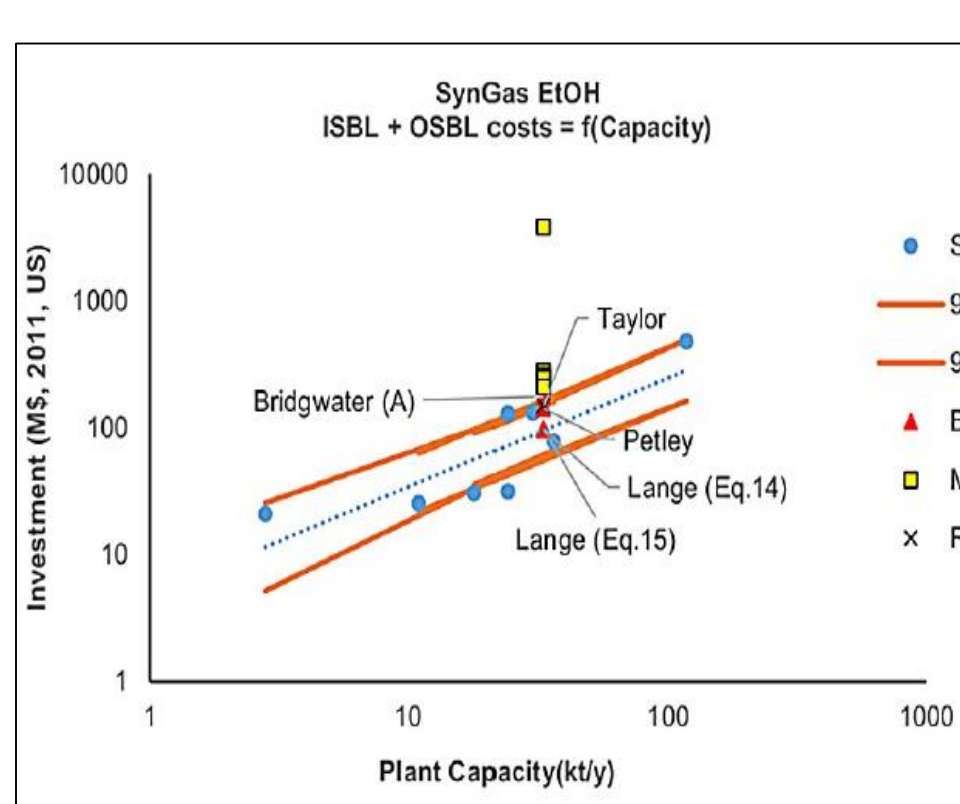
Adiabatic temperature rise during the production of lactic acid



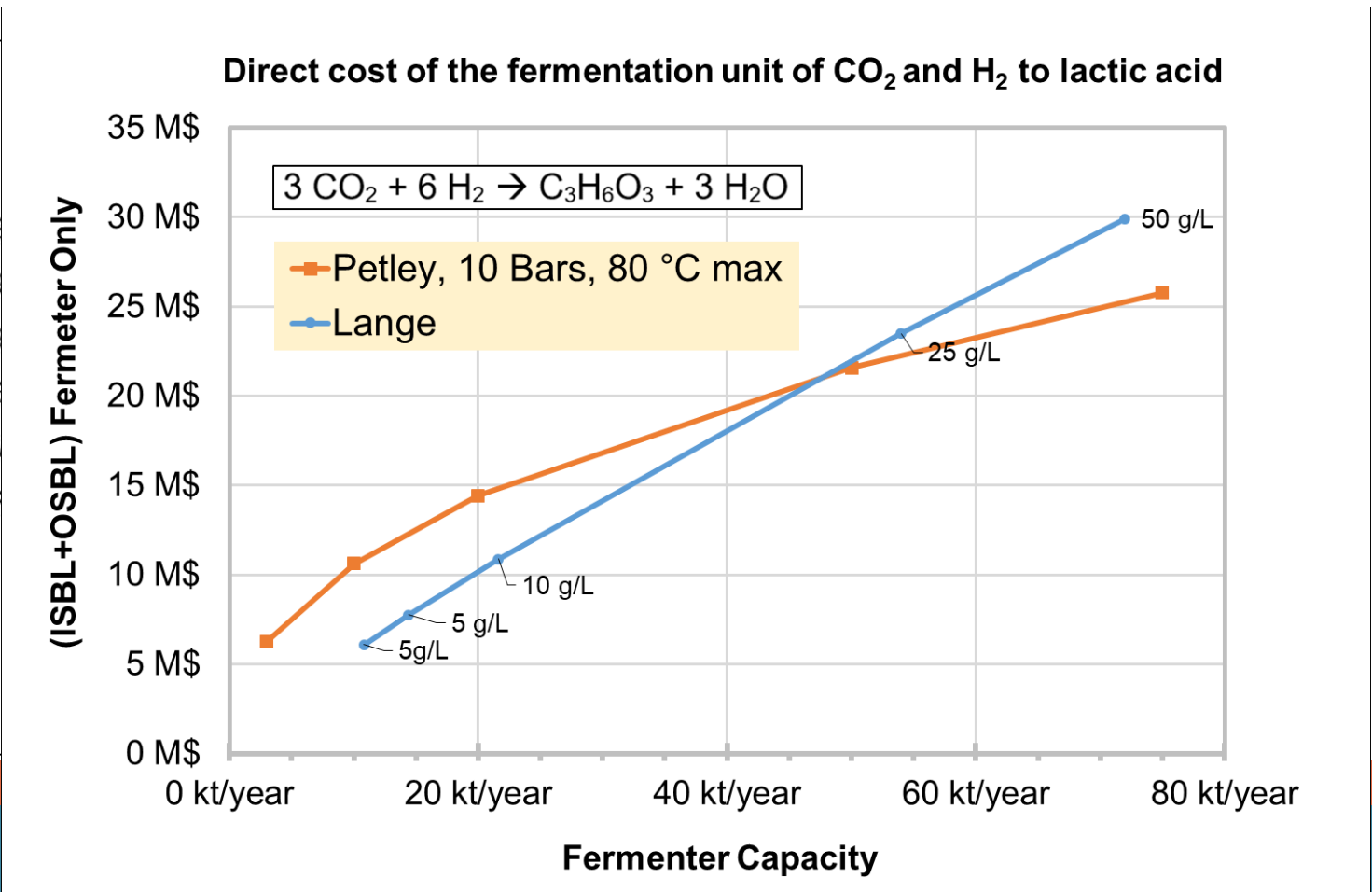
	Reaction	$\Delta_r H^\circ$ (kJ/mol)
H₂ + CO₂	$3 \text{ CO}_2 + 6 \text{ H}_2 \rightarrow \text{C}_3\text{H}_6\text{O}_3 + 3 \text{ H}_2\text{O}$	-298
Methanol + CO₂	$2 \text{ CH}_4\text{O} + \text{CO}_2 \rightarrow \text{C}_3\text{H}_6\text{O}_3 + \text{H}_2\text{O}$	-36
Ethanol + CO₂	$\text{C}_2\text{H}_6\text{O} + \text{CO}_2 \rightarrow \text{C}_3\text{H}_6\text{O}_3$	50

Rough Capital cost estimate for gas fermentors





- Petley: based on pressure and temperature - Lange: based on heat loss



Source: Tsagkari et al. (2016)



Industrial scale gas fermentation processes: 3 – 6000 \$/t product

	Ineos Bio	Calysta	Lanzatech	Unibio
Location	USA	China	Belgium	Russia
Product	Ethanol & Electricity	Proteins	Ethanol	Proteins
Feedstock	Biomass to Syngas	Methane	CO	Methane
Capacity product	24 kt/y - 8 MW	20 kt/y	63 kt/y	6 kt/y
CAPEX	130 M\$ (2011)	80 M\$ (2020)	180 M\$ (2020)	35 M\$ (2016)
Technology	Stirred tank/ Bubble column 	Loop reactor 	Jet Loop reactor 	U-loop 

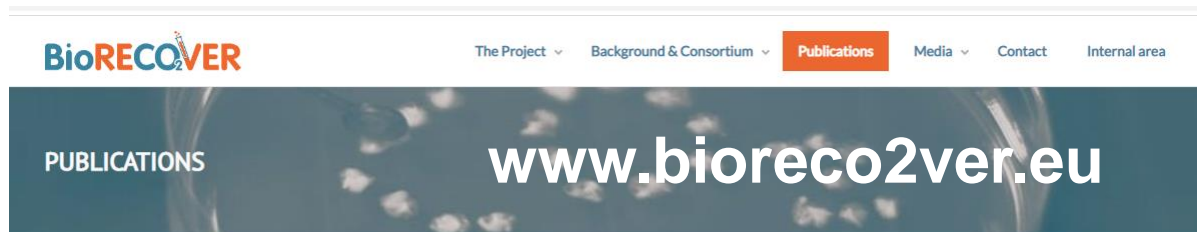
Summary

- Flexible prototype available as high tech research platform to study impact (partial) pressure on processes and optimize them prior to scale-up
- Fermentations at moderately elevated pressures using C1 gases underexplored
- CO₂ conversion processes tested at pressures up to 10 bara and with real CO₂-rich offgases
- Challenging to have high product titers from CO₂/H₂ and good heat management
 - Higher temperatures would be preferable
 - But gas solubility decreases at higher temperature
- Industrial scale gas fermentation processes:
 - Fermentor cost estimate: 500 \$/t product
 - Overall: 3 – 6000 \$/t product

Thank you for your attention!

Contact:

heleen.dewever@vito.be



Publications

-W. Van Hecke; R. Bockrath; H. De Wever (2019): *Effects of moderately elevated pressure on gas fermentation processes*, DOI: 10.1016/j.biortech.2019.122129

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

-G. Dreschke, G. d'Ippolito, A. Panico, P. N.L. Lens, G. Esposito, A. Fontana (2018): *Enhancement of hydrogen production rate by high biomass concentrations of Thermotoga neapolitana*, DOI: 10.5281/zenodo.3247830

-G. Nuzzo; S. Landi; E. Nunzia; E. Manzo; A. Fontana; G. d'Ippolito (2019): *Capnophilic Lactic Fermentation from Thermotoga neapolitana: A Resourceful Pathway to Obtain Almost Enantiopure L-lactic Acid*, DOI: 10.3390/fermentation5020034

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



Horizon 2020
European Union Funding
for Research & Innovation

BioRECO₂VER

The sole responsibility for the content of this dissemination and communication activity lies with the authors. It does not necessarily reflect the opinion of the European Union (EU) Horizon 2020. The EU is not responsible for any use that may be made of the information contained therein.