CO2 GAS FERMENTATION OPPORTUNITIES AND TECHNICAL CHALLENGES

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Arkema
238 PUBLICATIONS **3,919** CITATIONS

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CO_2 GAS FERMENTATION

OPPORTUNITIES AND TECHNICAL CHALLENGES

JEAN-LUC DUBOIS
SCIENTIFIC DIRECTOR
ARKEMA

9th Conference on CO_2 CO_2-based Fuels & Chemicals

2021
March
23-24

9th Conference on CO_2-based Fuels and Chemicals

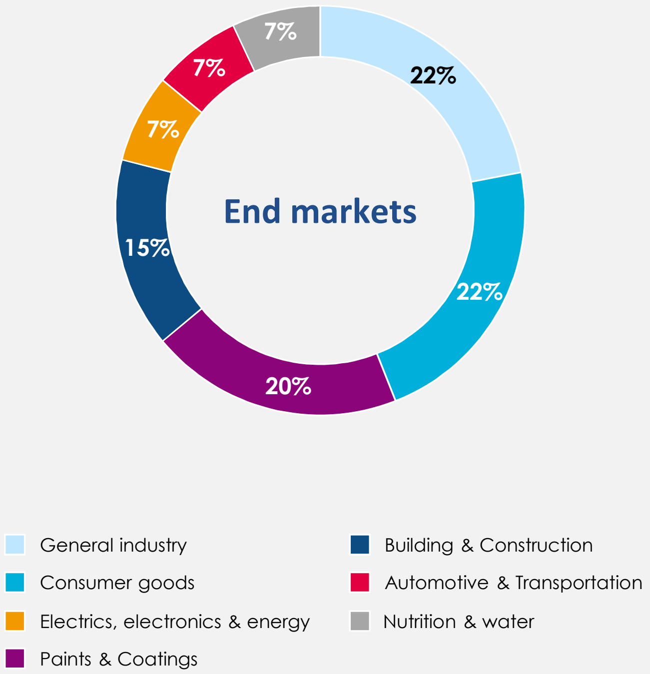
Online Event

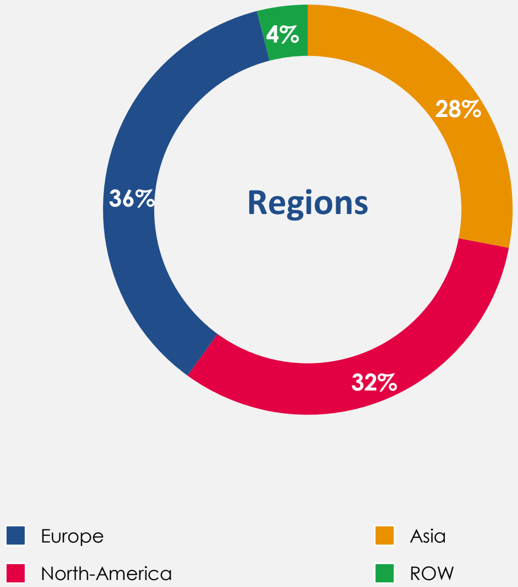
ARKEMA
INNOVATIVE CHEMISTRY

ARKEMA TODAY

2019 SALES SPLIT: €8.7bn

79 %
Specialty Materials





WOMEN AND MEN AT THE HEART OF OUR DEVELOPMENT

20,500
talents

11,200
in Europe

4,075
in North America

4,320 in Asia

905 in the rest of the world

Over
10,000
customers

Collaborations with the leading global brands

~2,000
new hires every year

Presence in
55 countries

144 plants
15 R&D centers

INNOVATIVE SOLUTIONS WITH A SIGNFICANT CONTRIBUTION TO THE UNITED NATIONS'S SUSTAINABLE DEVELOPMENT GOALS (SDG)

6 RESEARCH INNOVATIVE PLATEFORMS

New energies

Materials to develop solar power, wind power, and electric batteries

Biosourced materials

Solutions to replace fossil resources as raw materials

Water treatment

Materials for water filtration applications

Home efficiency and insulation

Solutions to reduce energy consumption of buildings

Lightweight materials

Materials for composites and 3D Printing

Consumer electronics

Solutions to bring electronics within everyone's reach

46*% PRODUCTS PORTFOLIO CONTRIBUTING TO UN SDG

SUSTAINABLE DEVELOPMENT GOALS

2 ZERO HUNGER
3 GOOD HEALTH AND WELL-BEING
6 CLEAN WATER AND SANITATION
7 AFFORDABLE AND CLEAN ENERGY
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
11 SUSTAINABLE CITIES AND COMMUNITIES
12 RESPONSIBLE CONSUMPTION AND PRODUCTION
13 CLIMATE ACTION
14 LIFE BELOW WATER
15 LIFE ON LAND

** 44% products portfolio assessed*

MANAGE OUR ACTIVITIES AS A RESPONSIBLE MANUFACTURER

CLIMATE

Climate plan : Commitment to Paris agreement and Science-based target trajectory **well below 2°C**

Greenhouse gas emissions (GHG) new target for 2030

-38%
vs 2015
≤ 2 950 kt eq. CO_2

ENVIRONMENT

New targets for 2030

AIR	WATER	ENERGY
-65% vs 2012	**-60%** vs 2012	**-20%** vs 2012
In volatile organic compounds (VOC) emissions intensity	In chemical oxygen demand (COD) intensity	In net energy purchases intensity

Performance 2019 (vs 2012)

AIR	WATER	ENERGY
-40%	**-50%**	**-9%**

SECURITY

To be among the best in the industry

SAFETY AT WORK[1]
Reduce injury frequency rate

2019	2025 target
1.3	< 1.2

SAFETY EVENTS[1]
Reduce safety events frequency rate

2019	2025 target
3.7	< 3

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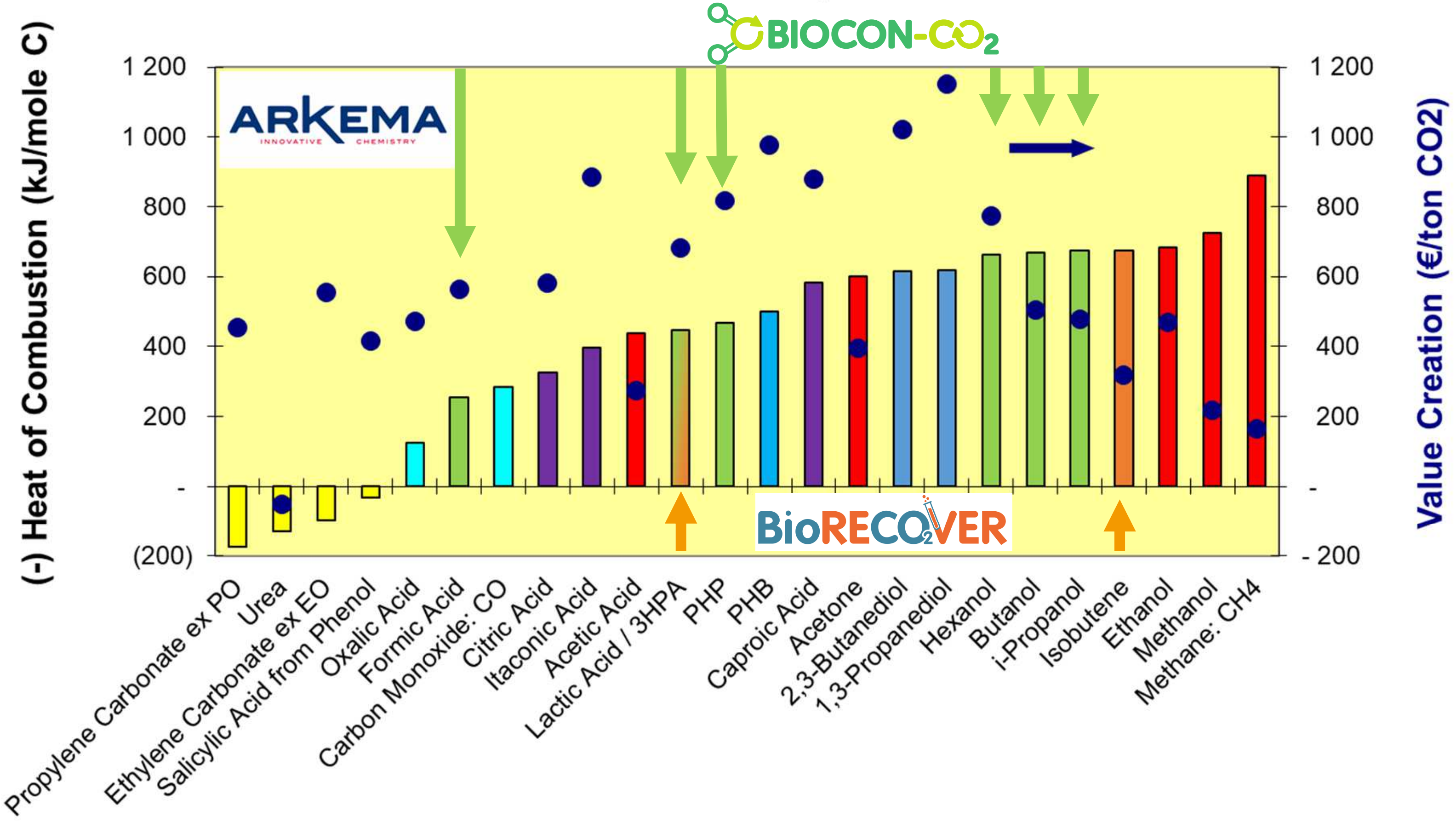
[1] *Number of accident or event per million worked hour*

TARGET PRODUCT SELECTION: VALUE CREATION AND ENERGY CONSUMPTION



Heat of Combustion as image of energy consumed to produce the molecule and Value created per CO2 consumed

HEAT MANAGEMENT

- ***Determination of the adiabatic temperature rise***

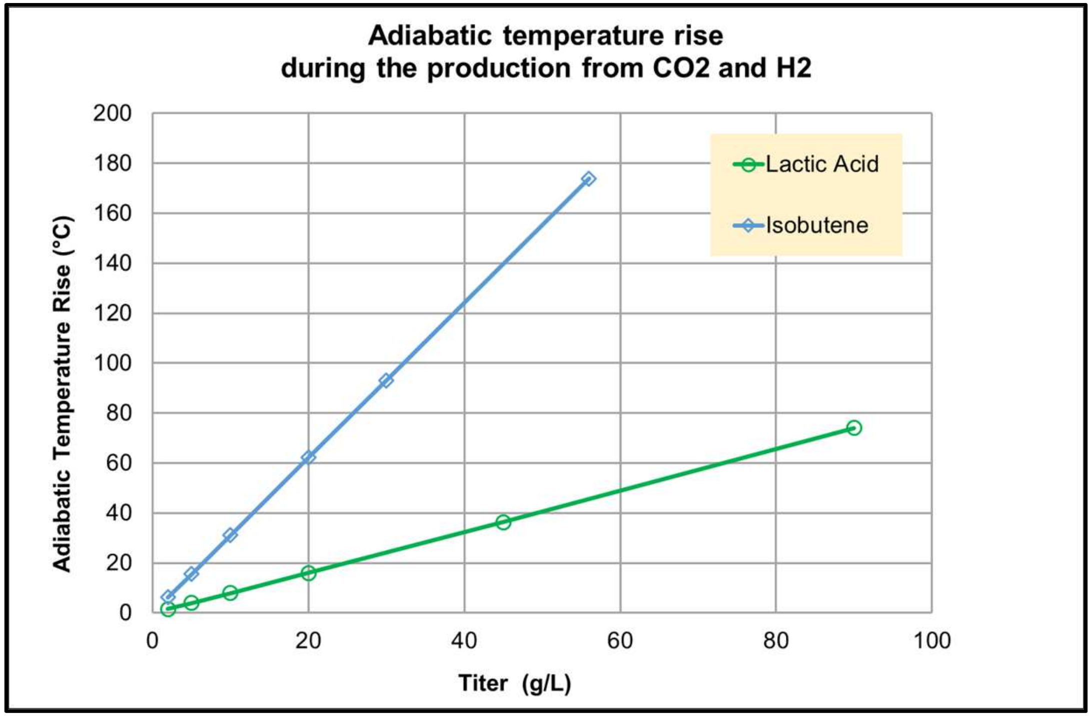
- $\Delta_r \mathrm{H}° \left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right] = \sum \Delta_{\mathrm{f}} \mathrm{H}°_{\mathrm{products}} - \sum \Delta_{\mathrm{f}} \mathrm{H}°_{\mathrm{reagents}}$

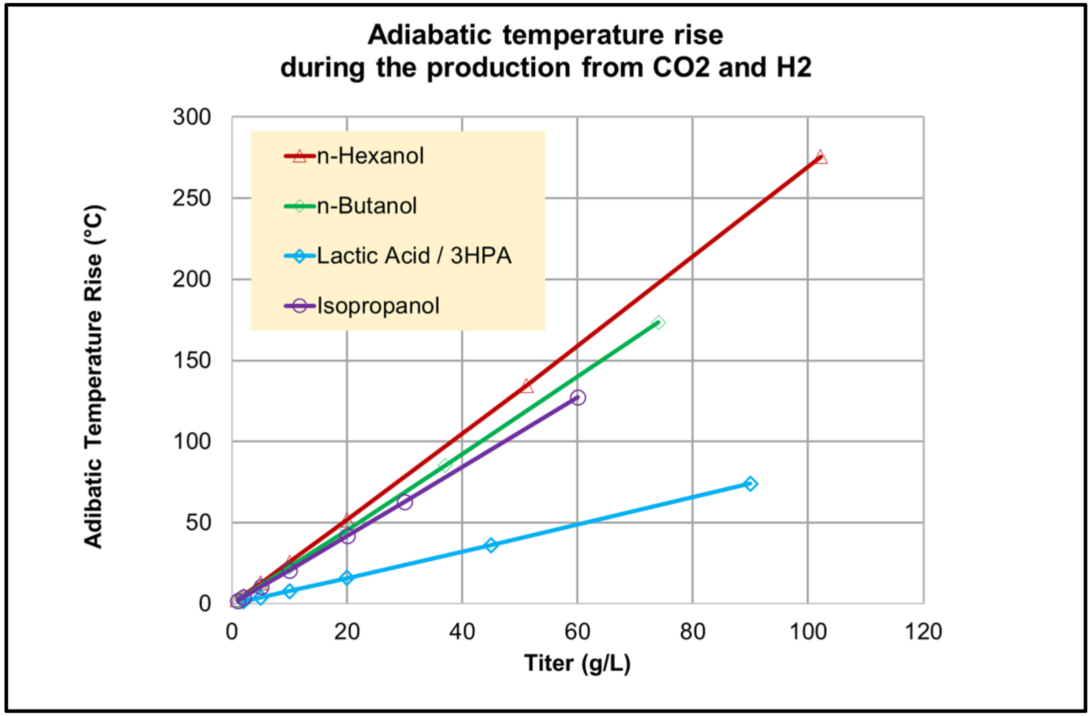
- $\Delta \mathrm{T}_{\mathrm{liquid\ product}} = \dfrac{-\Delta_r \mathrm{H}° \left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right] * \mathrm{product\ titer} \left[\frac{\mathrm{mol}}{\mathrm{L}}\right]}{\mathrm{product\ titer} \left[\frac{\mathrm{kg}}{\mathrm{L}}\right] * \left(\frac{c_{\mathrm{p,mol,product}}}{M_{\mathrm{product}}}\right) + \left(1 - \mathrm{product\ titer} \left[\frac{\mathrm{kg}}{\mathrm{L}}\right]\right) * c_{\mathrm{p,mass,water}}}$

- $\Delta \mathrm{T}_{\mathrm{isobutene}} = \dfrac{-\Delta_r \mathrm{H}° \left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right] * \mathrm{product\ titer} \left[\frac{\mathrm{mol}}{\mathrm{L}}\right]}{c_{\mathrm{p,vol,water}}}$

- ***Example: CO_2 to n-Butanol***
  - **Hypothesis: (no metabolic leakage)**
  - **$4\ CO_2 + 12\ H_2 \rightarrow C_4H_9OH + 7\ H_2O$**
  - **Heat of reaction calculated from enthalpy of formation → exothermic**

HEAT MANAGEMENT





- **Probably impossible to reach more than 10-20 g/L without external cooling**
- **Low Titers = High Capital Cost**
- **100 kt/year of lactic acid = energy loss of 93 900 MWh/year = equivalent of the energy consumed by more than 14 000 Europeans in their households.**

PROCESS SOLUTIONS

Option 1: Internal heat exchanger.

- High heat exchange area
- Occupy a lot of volume in a pressurized vessel ➔ cost

Option 2: External heat exchanger, on a liquid loop

- Same heat exchange area, but at reduced pressure
- Recirculation loop ➔ Pumps needed and large volume to circulate at low titer.
- Impurities can accumulate

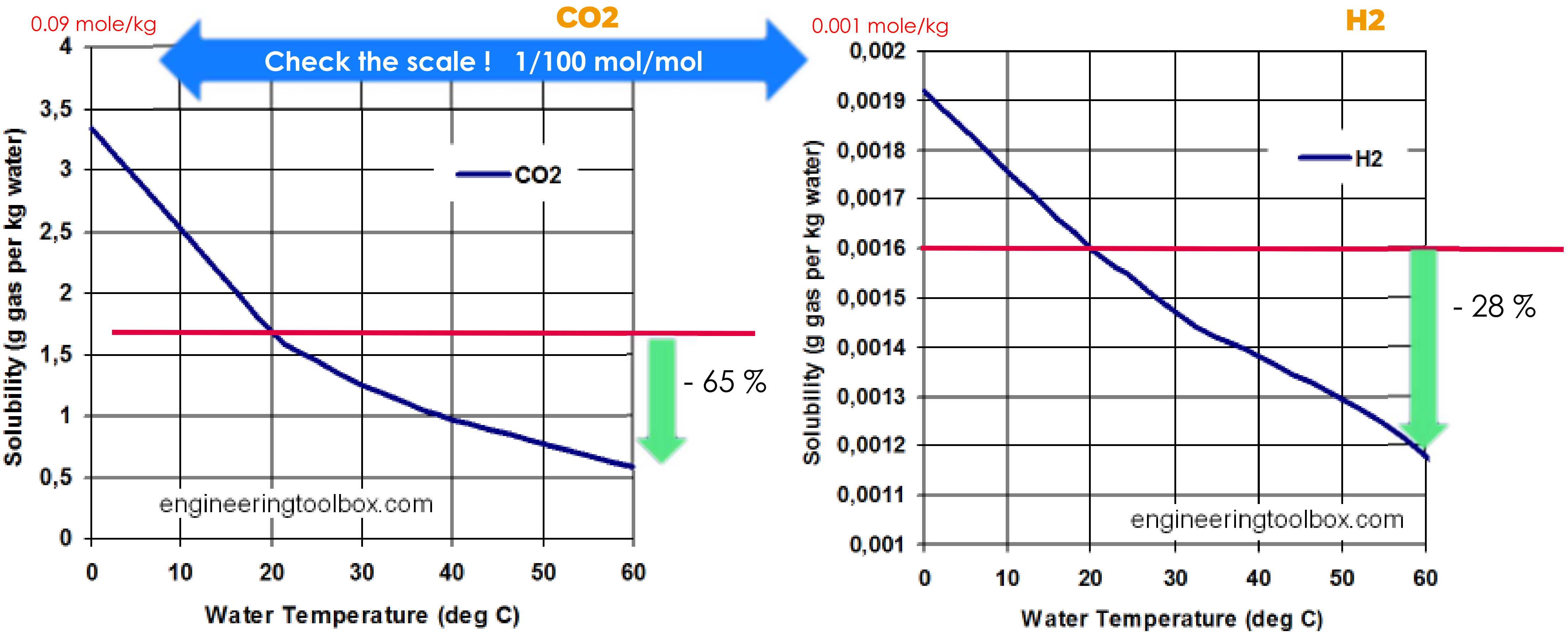
Option 3: Continuous feed of fresh water, in line with adiabatic temperature rise to keep reactor temperature constant.

- Titer might be limited ➔ High extraction cost

Option 4: Don't use hydrogen... Or any other good idea.

GAS SOLUBILITY IN WATER VS TEMPERATURE (solubility decreases with temperature)

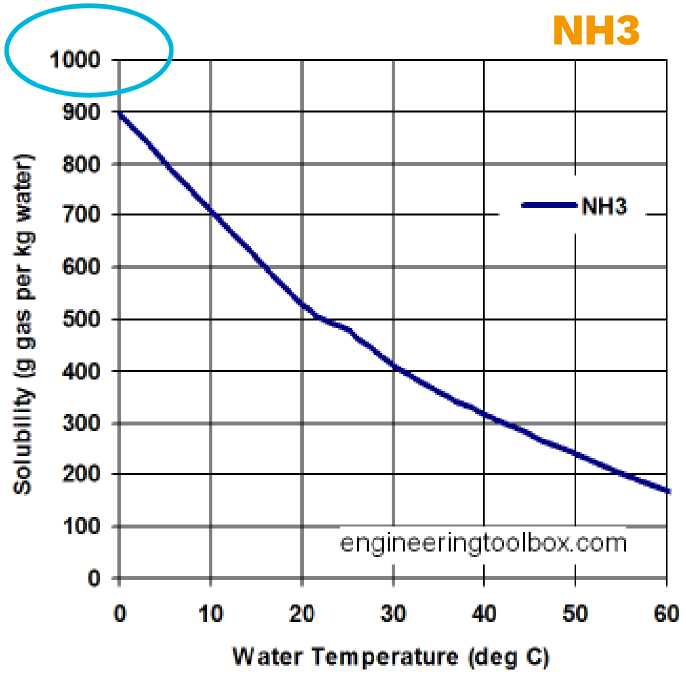
(source: Engineeringtoolbox.com)

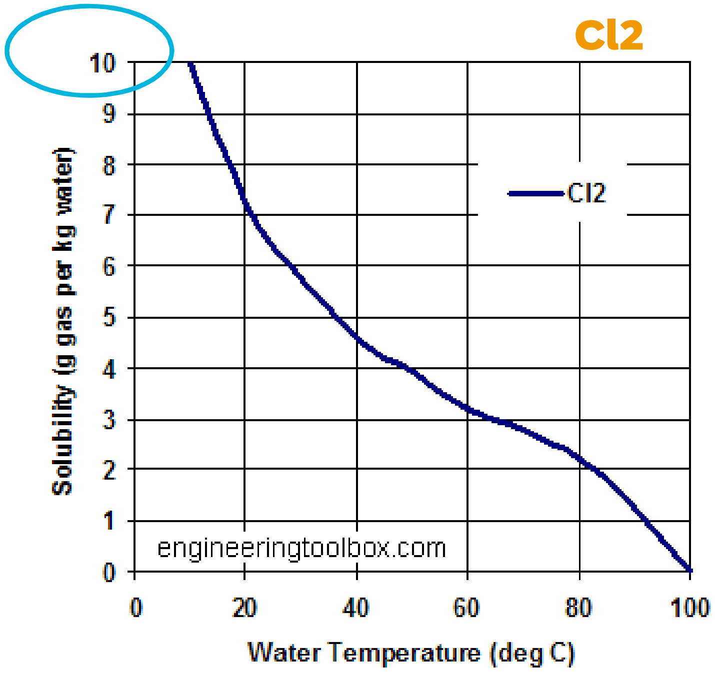


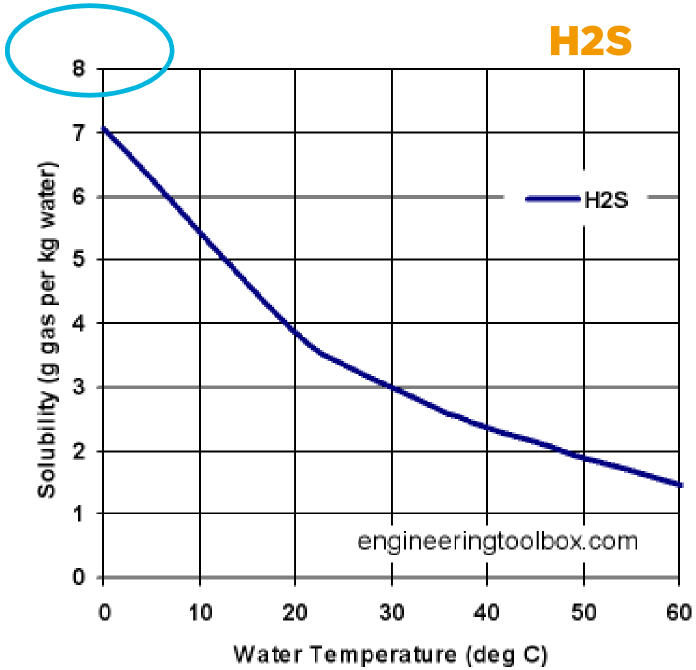
→ **Decreased solubility to be compensated by an increased pressure**

IMPACT OF GAS IMPURITIES

Impurities have a higher solubility and can accumulate in a liquid loop







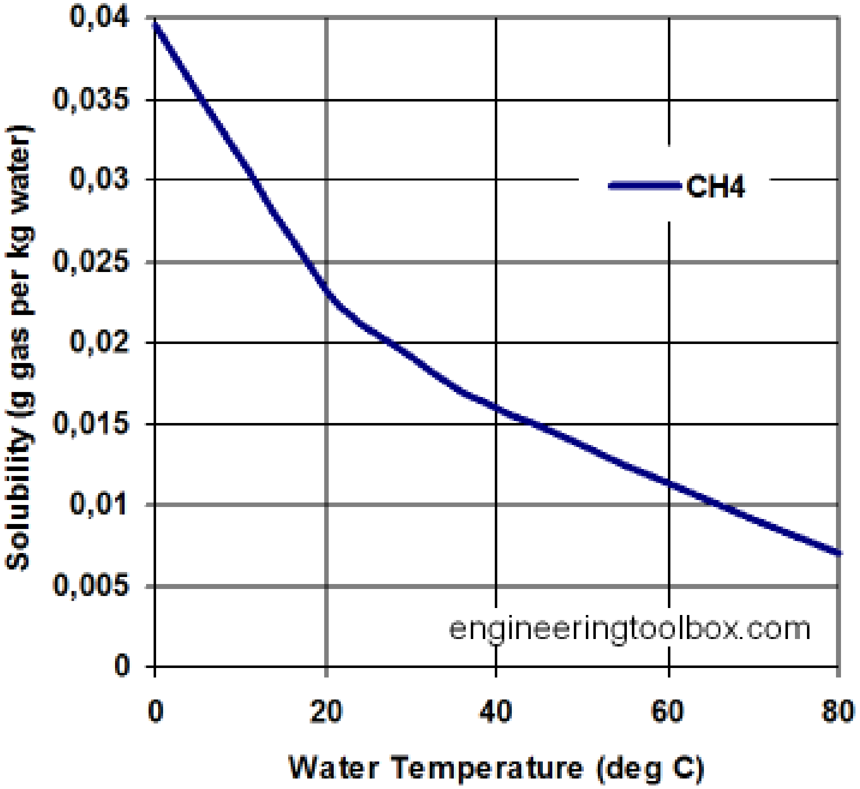
- **To be checked for any other impurities**
- **Significant solubilities of some impurities that could accumulate**

ALTERNATIVE CARBON SOURCES – Gas solubilities similar to H_2

(H_2 at 0°C: 0.001 mol/kg, CO_2 at 0°C: 0.09 mol/kg)

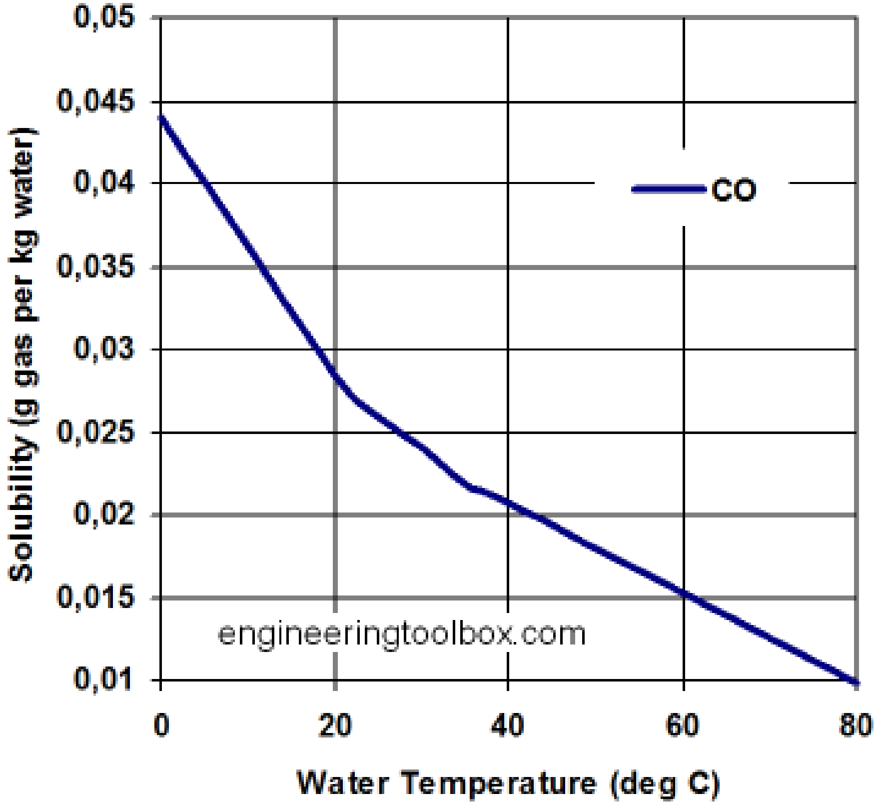
0.0025 mole/kg

CH4



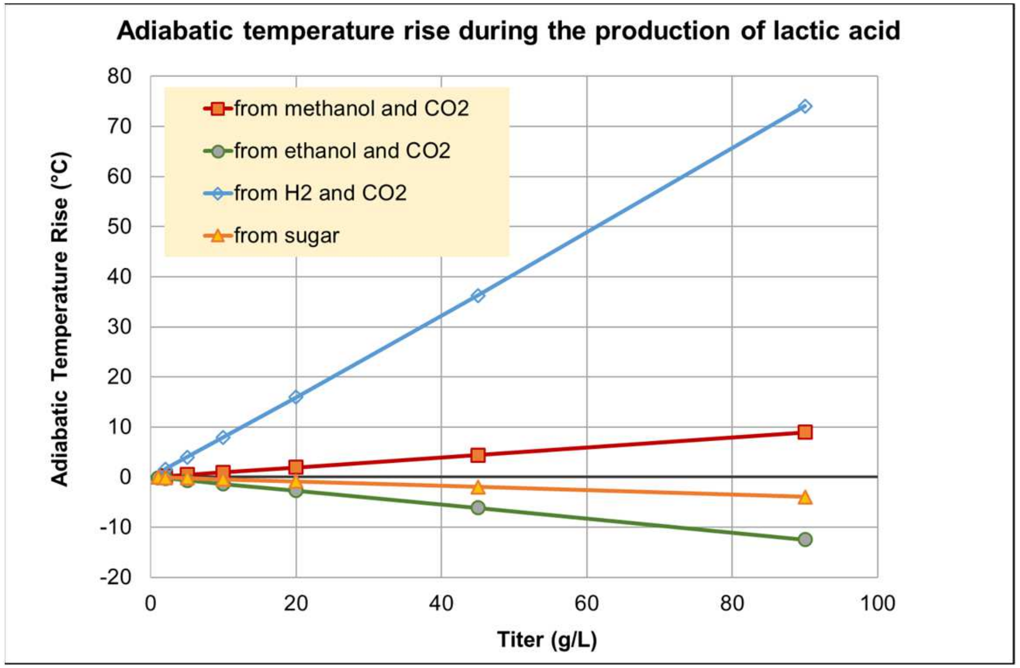
0.0018 mole/kg

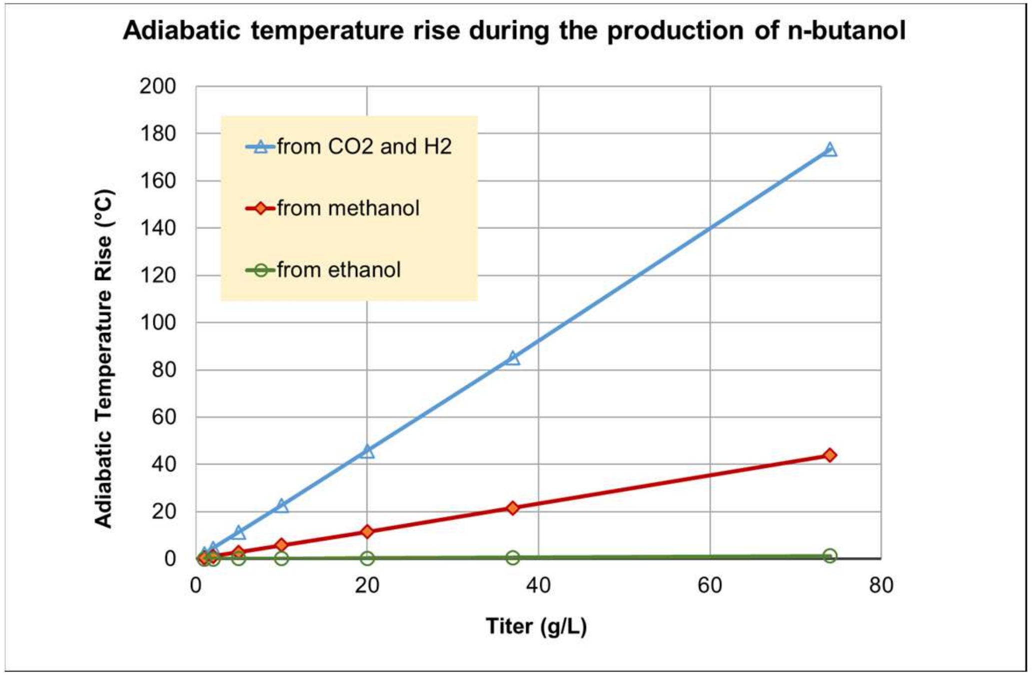
CO



ADIABATIC TEMPERATURE RISE:

H_2 makes the process difficult, other reducing agents to be considered


Adiabatic temperature rise during the production of lactic acid


Adiabatic temperature rise during the production of n-butanol

	Reaction	$\Delta_r H°$ (kJ/mol)
From H_2 and CO_2	$3\ CO_2 + 6\ H_2 \rightarrow C_3H_6O_3 + 3\ H_2O$	-298
From methanol and CO_2	$2\ CH_4O + CO_2 \rightarrow C_3H_6O_3 + H_2O$	-36
From ethanol and CO_2	$C_2H_6O + CO_2 \rightarrow C_3H_6O_3$	50
From sugar	$C_6H_{12}O_6 \rightarrow 2\ C_3H_6O_3$	32

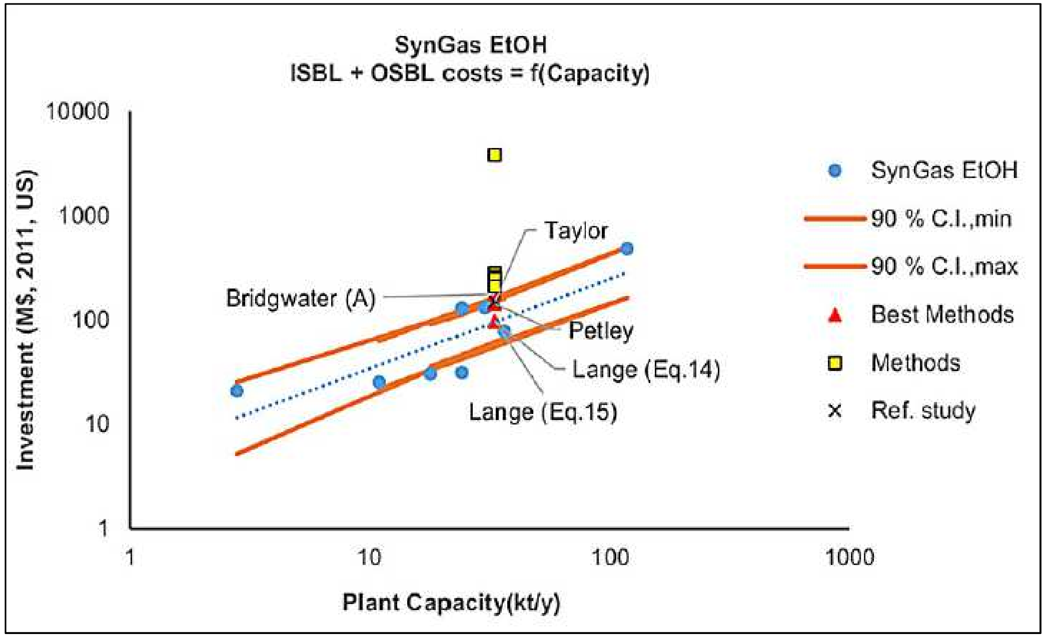
	Reaction	$\Delta_r H°$ (kJ/mol)
From H_2 and CO_2	$4\ CO_2 + 12\ H_2 \rightarrow 1\ C_4H_9OH + 7\ H_2O$	-701
From methanol and CO_2	$4\ CH_4O \rightarrow 1\ C_4H_9OH + 3\ H_2O$	-177
From ethanol and CO_2	$2C_2H_6O \rightarrow 1\ C_4H_9OH + 1\ H_2O$	-5

- **Challenging to have high titer, from CO_2/H_2 and good heat management. Methanol as alternative**

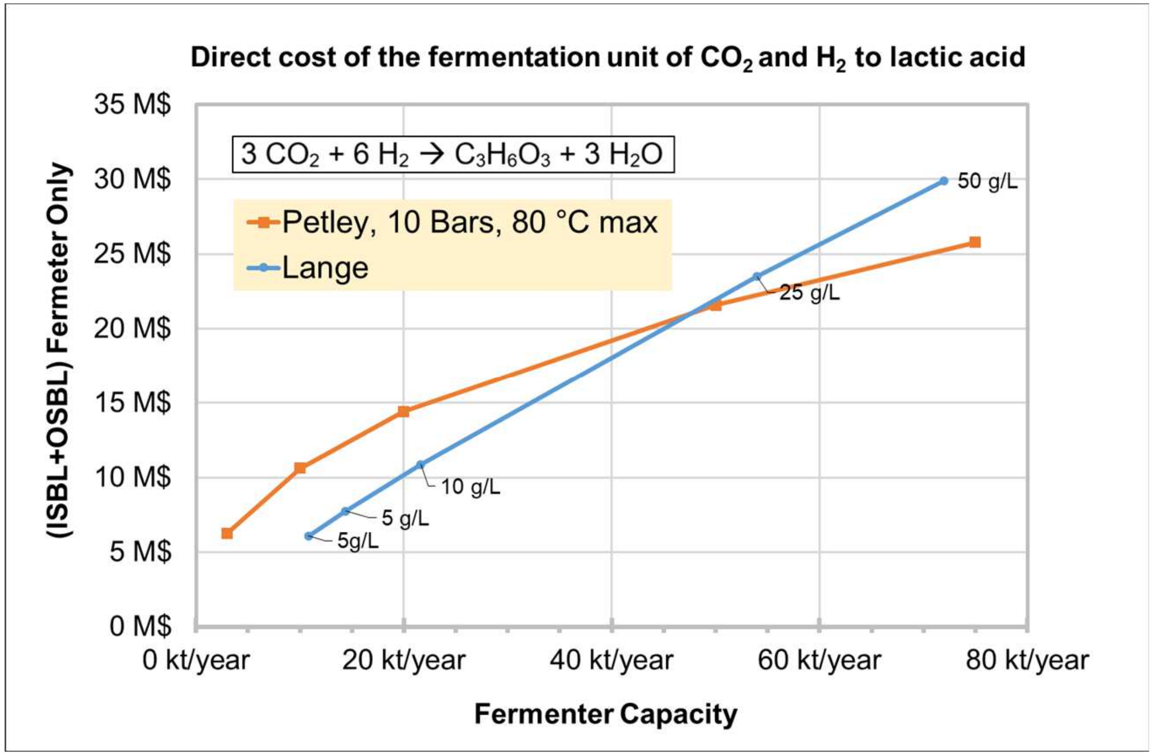
CAPITAL COST ESTIMATES

2 methods: Petley and Lange, Cost evaluation for the fermenter

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



Early-Stage Capital Cost Estimation of Biorefinery Processes: A Comparative Study of Heuristic Techniques, M Tsagkari, JL Couturier, A Kokossis and JL Dubois, **ChemSusChem 2016, 9, 2284 – 2297**

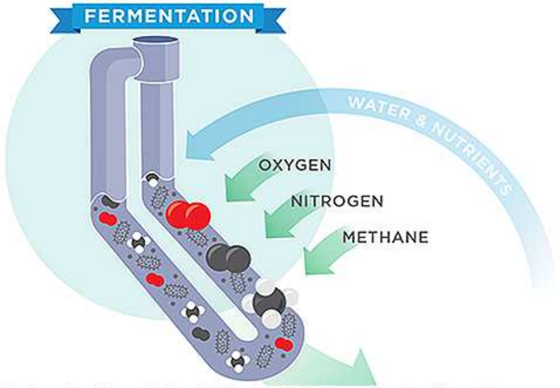


Other main equipments: Compressor, Filtration, Separation, water treatment, off gases treatment,…

INDUSTRIAL SCALE GAS FERMENTORS: 4 DIFFERENT TECHNOLOGIES

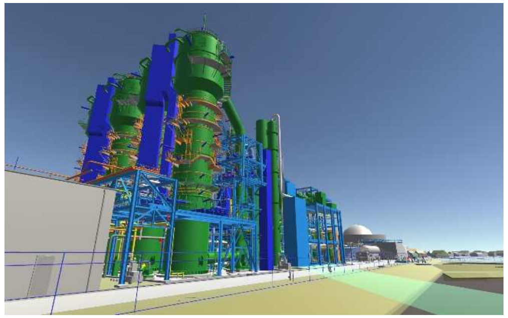
INEOS Gas (CO/H_2) fermenter (Idled)
Ethanol

Calysta Gas (CH_4) fermenter
Proteins



Calysta FeedKind Protein Manufacturing Process

Lanzatech/Shougang Gas ($CO/H_2/CO_2$) Fermenter
Ethanol



Lanzatech/Arcelor Mittal (under construction)
Ethanol

Unibio Gas (CH_4) Fermenter
Proteins

INDUSTRIAL SCALE GAS FERMENTATION PROCESSES: 3 – 6000 $/T PRODUCT

	Ineos Bio	Calysta	Lanzatech	Unibio	Coskata
Location	USA	China	Belgium	Russia	USA
Product	Ethanol & Electricity	Proteins	Ethanol	Proteins	Ethanol
Feedstock	Biomass to Syngas	Methane	CO	Methane	CO
Capacity product	24 kt/y 8 MW	20 kt/y	63 kt/y	6 kt/y	118 t/y (pilot/demo)
CAPEX	130 M$ (2011)	80 M$ (2020)	180 M$ (2020)	35 M$ (2016)	25 M$ (2008)
Technology	Stirred tank / Bubble column	Loop reactor	Jet Loop reactor	U-loop	

HEAT MANAGEMENT

- Challenges in heat management: a lot of heat is produced at low temperature.

- What to do with the heat produced?
  - Use for downstream/upstream process steps?
  - Use in district heating?
  - Use in green houses?

- Challenges for the process:
  - Higher temperatures would be preferable: better value for the heat.
  - May require extremophiles, enzymatic process
  - But gas solubility is decreasing at higher temperature…
  - And microorganisms survival might be compromised.

- Heat losses have to be seen in light of the production capacity
  - Not detectable at lab scale
  - May represent the energy consumption of several 10 000 European citizens at 100 000 tons/year.

THANK YOU FOR YOUR ATTENTION

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