

# CO2 UTILISATION: KEY ELEMENT WITHIN THE ENERGY AND MATERIAL TRANSITION



**TNO** innovation  
for life

Goetheer, E.L.V. (Earl)

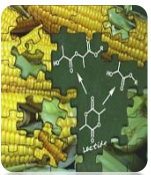
# CHEMICAL INDUSTRY AND ENERGY SECTOR IN TRANSITION

## Raw Materials

## Chemical Production

## End-product usage

## End of Life



Feedstock

1) Shift to renewable feedstock



Energy

2) Shift to renewable energy

Intermediaries and final products



3) Process and energy efficiency

Application 1

Application 2

Application 3

Waste

4) Circularity

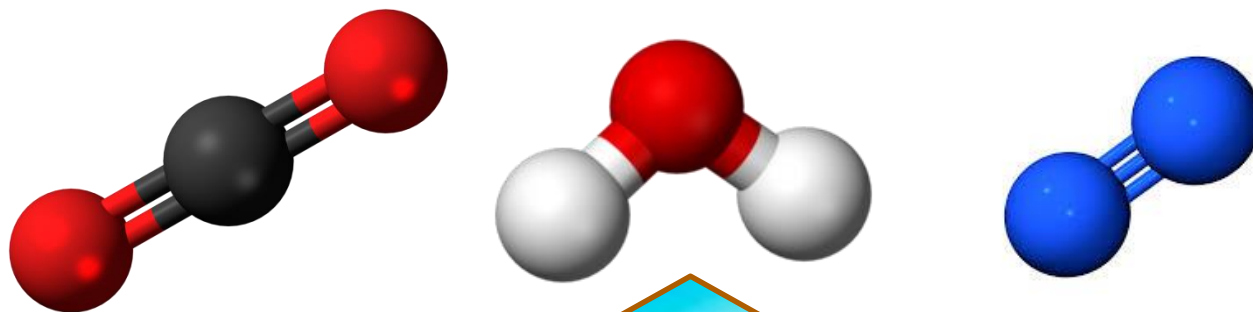


Decarbonisation

5) CCUS



# Grand challenge: Man On The Moon



Renewable production of fuels and (platform) chemicals from CO<sub>2</sub>, water and nitrogen based on photochemistry, electrochemistry, biotechnology



## Synthetic fuels



*hydrogen*    *carbonmonoxide*

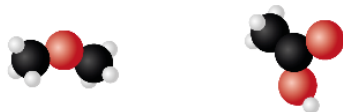


*ammonia*    *Fisher-Tropsch*

## Platform chemicals

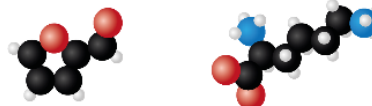


*alkanes*    *alcohols*

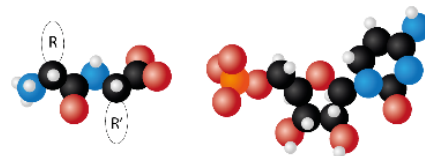


*ethers*    *carboxylic acids*

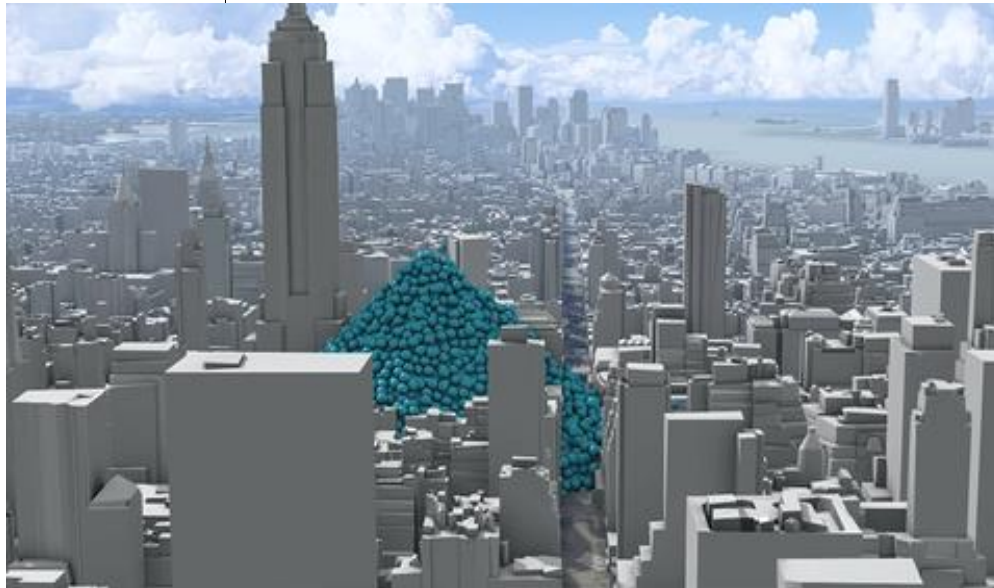
## Complex molecules



*carbohydrates*    *lipids*

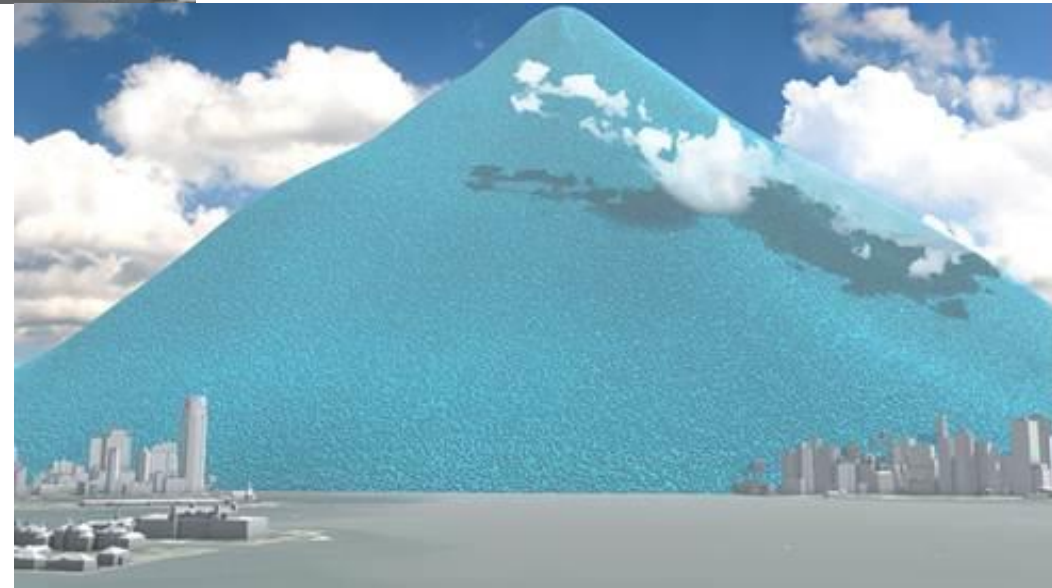


*proteins*    *nucleic acids*



single hour's emissions from  
New York City: 6,204 one-  
metric-ton spheres (one  
sphere is 33 feet across).

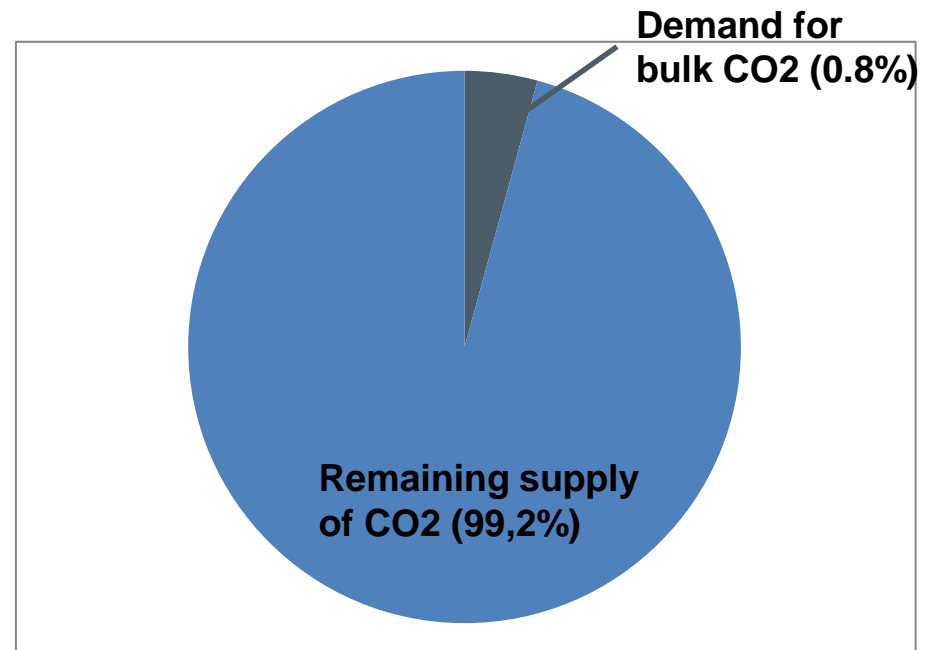
a year's carbon dioxide  
emissions from New York  
City: 54,349,650 one-  
metric-ton spheres



# THE GLOBAL CO2 MARKET

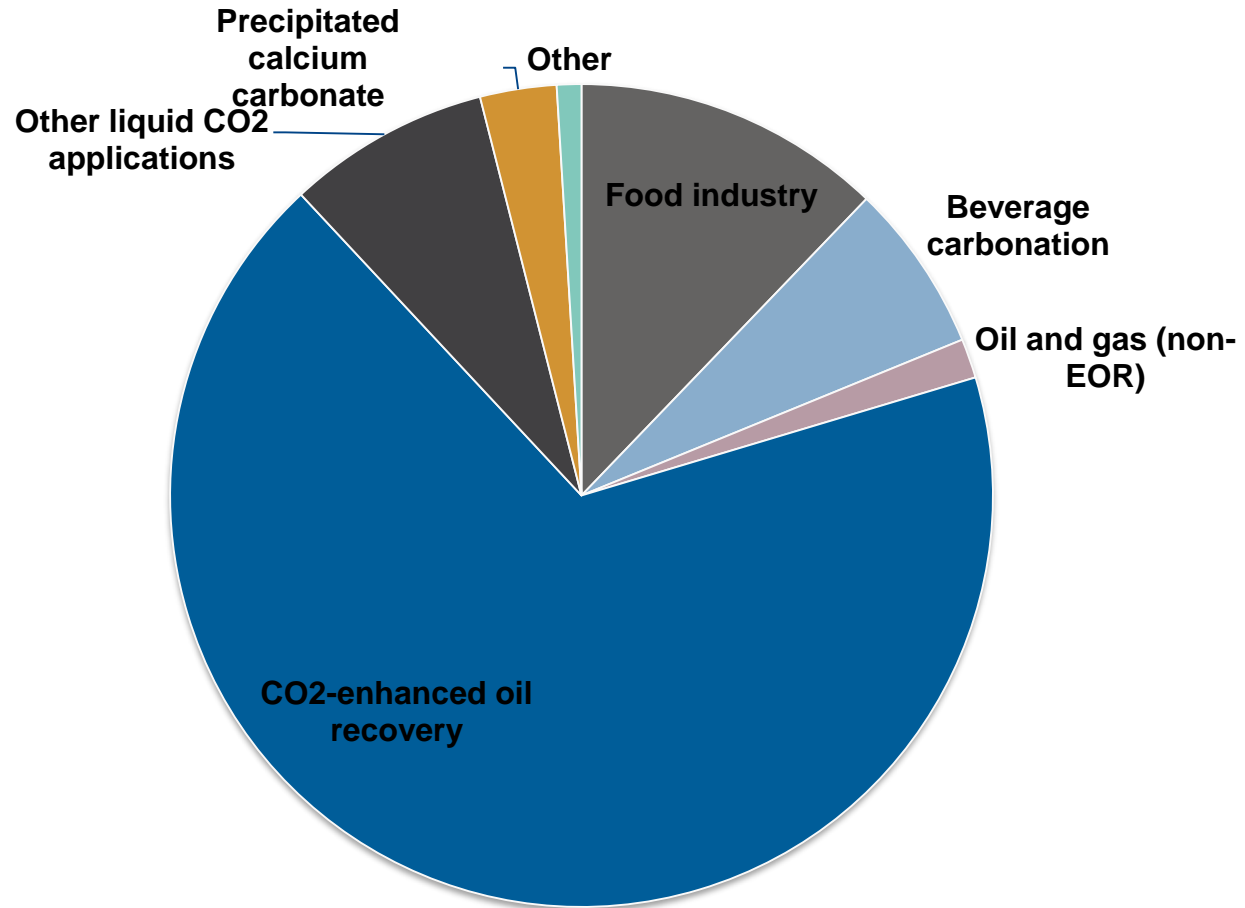
*There is a very large global surplus of CO2. CO2 available from lower cost sources is likely to supply the majority of near-term reuse demand growth.*

- ▶ **C**urrent global CO2 demand is estimated to be 80 Mtpa - 50Mtpa is used for EOR in North America.
- ▶ CO2 demand is expected to rise to 140 Mtpa by 2020.
- ▶ CO2 supply from large point sources is currently 18,000 Mtpa which includes:
  - ▶ 500 Mtpa from high concentration sources like Amonia & hydrogen production, gas processing **(low cost sources)**
  - ▶ An extra 2,000 Mtpa is available from low to medium cost sources



**Current Demand and Supply for Bulk CO2**

# EXISTING BULK CO<sub>2</sub> MARKET: 80 MTON



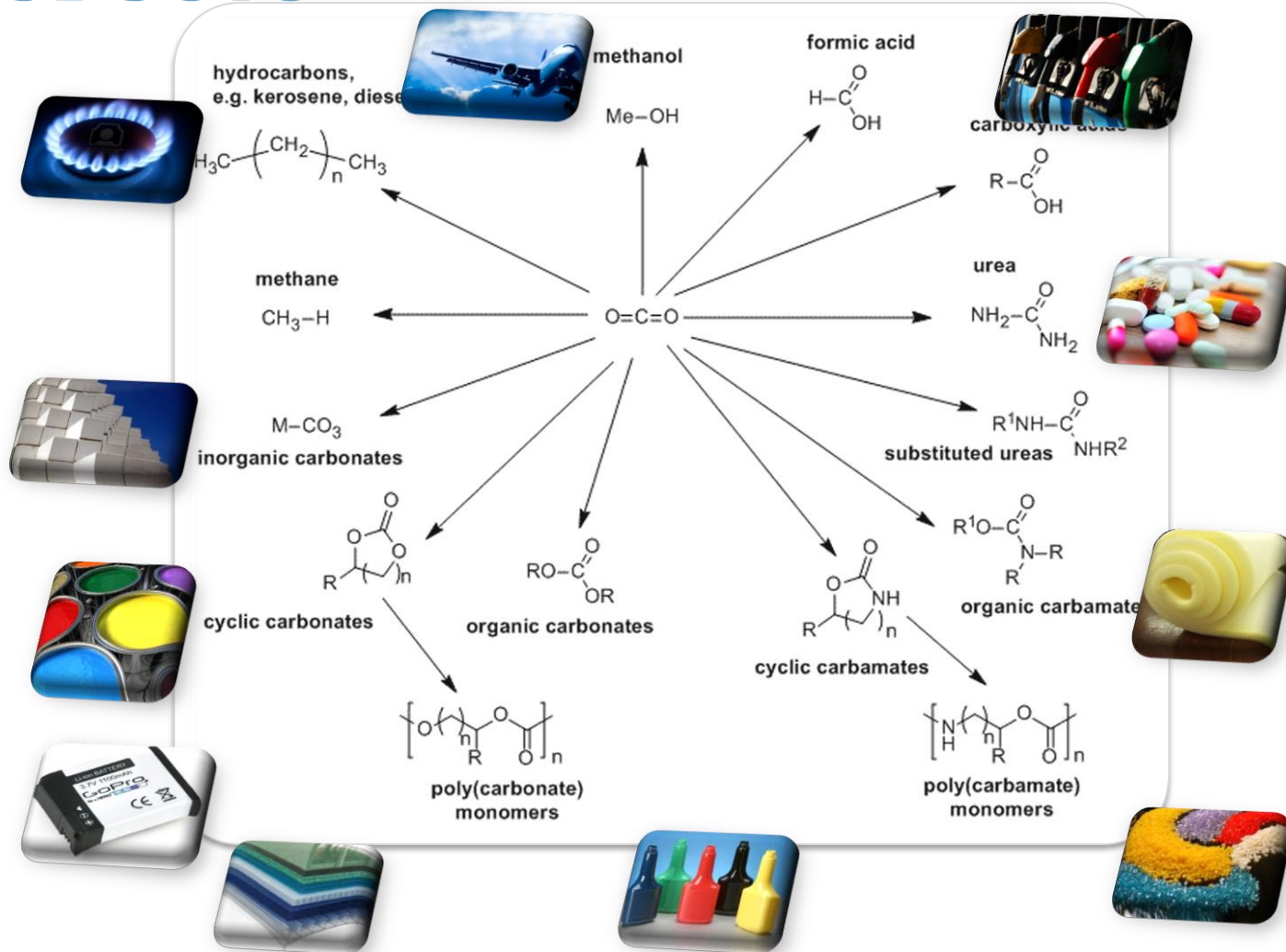


- › If we were to convert 50% of the worlds methanol capacity:  $\sim 33 \times 10^6$  ton to a  $\text{CO}_2$  basis, and if the  $\text{H}_2$  needed for such a process could be produced in a  $\text{CO}_2$ -free manner....

we would need in the order of 25 megaton of  $\text{CO}_2$ . This is 5 average 1000 MW powerplants

So, it would appear that utilization of  $\text{CO}_2$  for products is not going to make an impact in reducing atmospheric carbon....

# EXAMPLES OF CO<sub>2</sub> CONVERSION PRODUCTS





# INDUSTRIAL USES OF CO<sub>2</sub> BY POTENTIAL FUTURE DEMAND

EXISTING USES	Current non-captive CO <sub>2</sub> demand (Mtpa)	Future potential non-captive CO <sub>2</sub> demand (Mtpa)
Enhanced Oil Recovery (EOR)	50 < Demand < 300	30 < Demand < 300
Fertilizer – Urea (Captive Use)	5 < Demand < 30	5 < Demand < 30

NEW USES	Future potential non-captive CO <sub>2</sub> demand (Mtpa)
Enhanced Coal Bed Methane Recovery (ECBM)	Demand >300
Enhanced geothermal systems – CO <sub>2</sub> as a working fluid	5 < Demand < 30
Polymer processing	5 < Demand < 30
Algal Bio-fixation	>300
Mineralisation	
Calcium carbonate & magnesium carbonate & Sodium Bicarbonate	>300
CO <sub>2</sub> Concrete Curing	30 < Demand < 300
Bauxite Residue Treatment ('Red Mud')	5 < Demand < 30
Liquid Fuels	
Renewable Methanol	>300
Formic Acid	>300

# Conversion Technologies

**1. Catalytic Hydrogenation**

**2. Electrochemical**

**3. Polymerization**

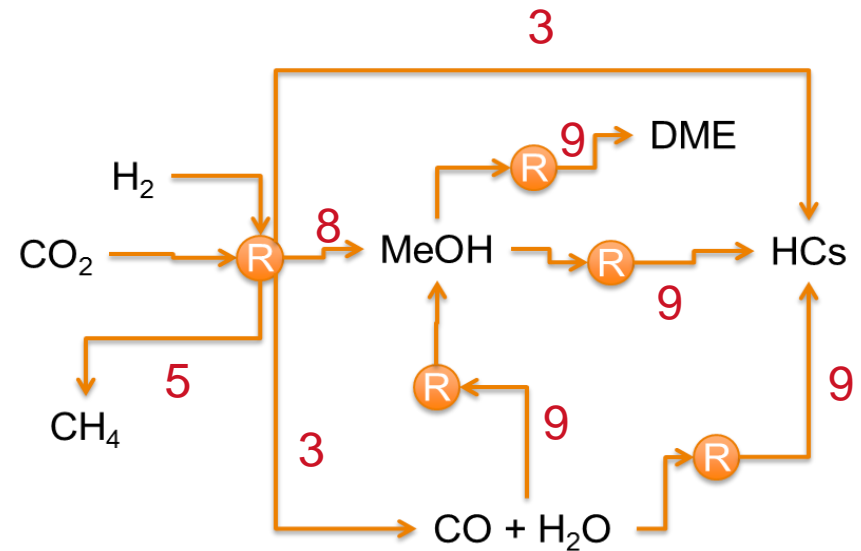
**4. Biochemical**

**5. Mineralisation (not discussed in this presentation)**

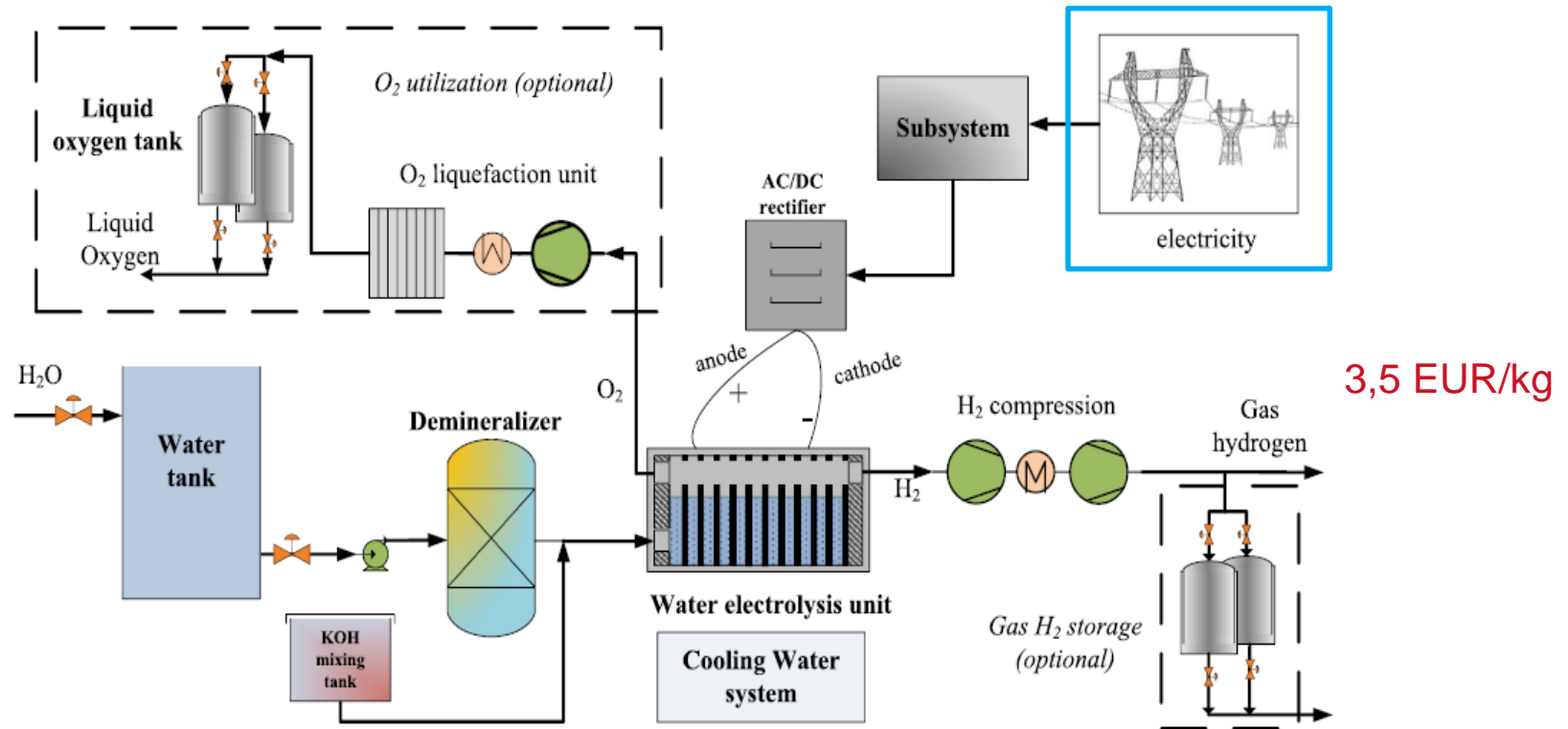
# **1. CATALYTIC HYDROGENATION**

# CO<sub>2</sub> utilization via catalytic hydrogenation

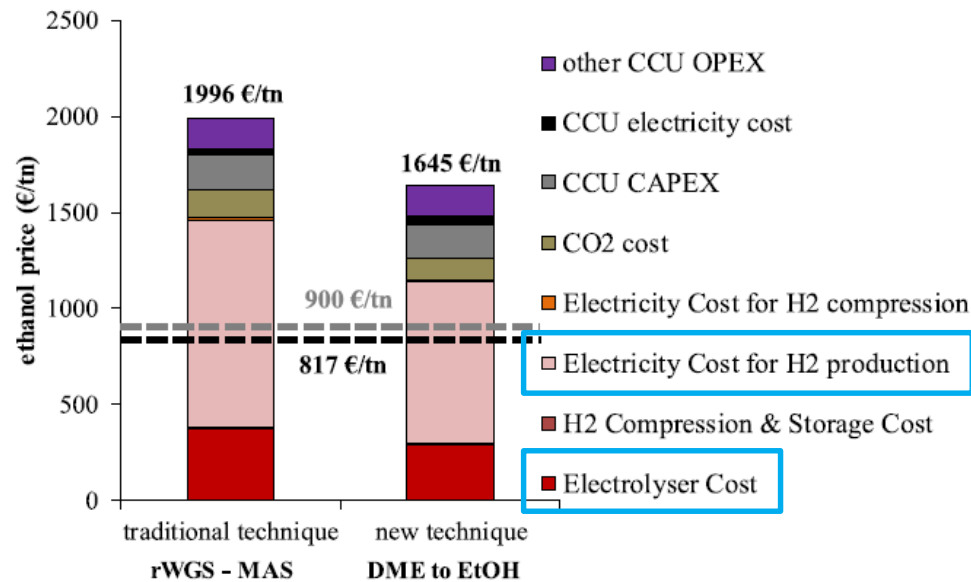
- Multiple pathways
- Methanol economy
- Intensive use of hydrogen
- TRL from 3 to 8



# Hydrogen via electrolysis



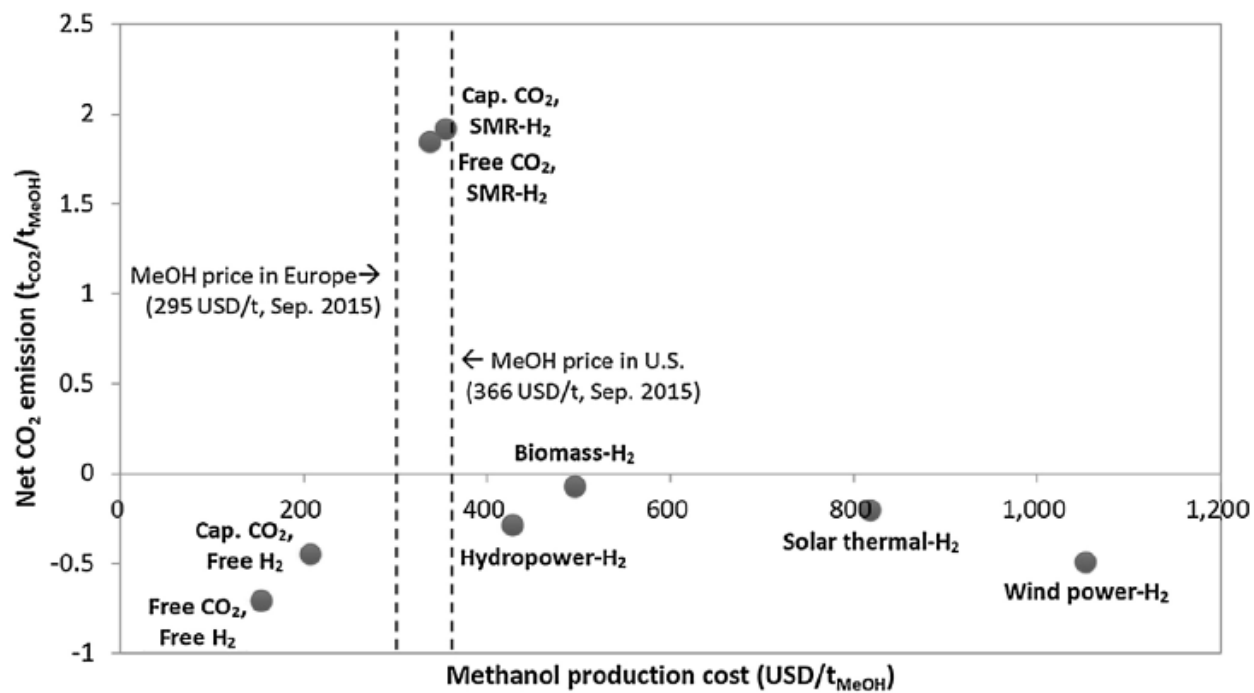
# Impact of hydrogen cost



**Fig. 11 – Ethanol production cost breakdown for the two CO<sub>2</sub>-to-Ethanol schemes (the black dash line represents the corn based bioethanol price and the grey dash line the cellulosic bioethanol price).**

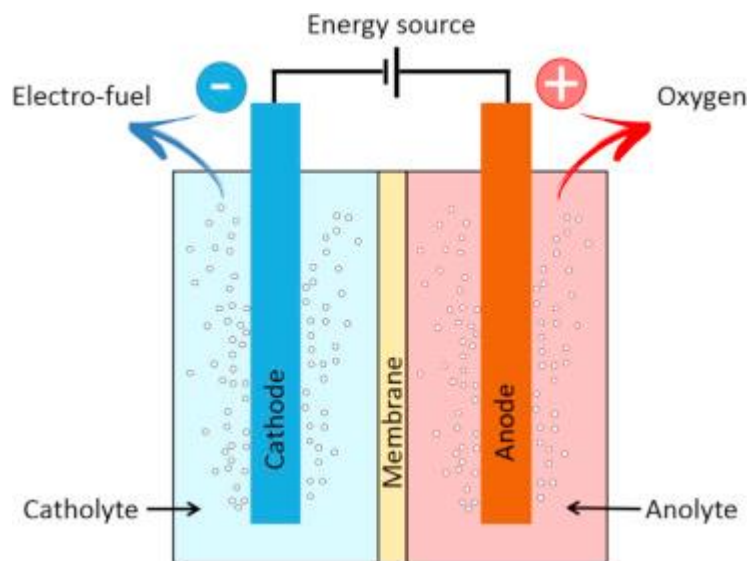


# Cost vs CO<sub>2</sub> footprint



## **2. ELECTROCHEMICAL**

# Electrochemical reduction



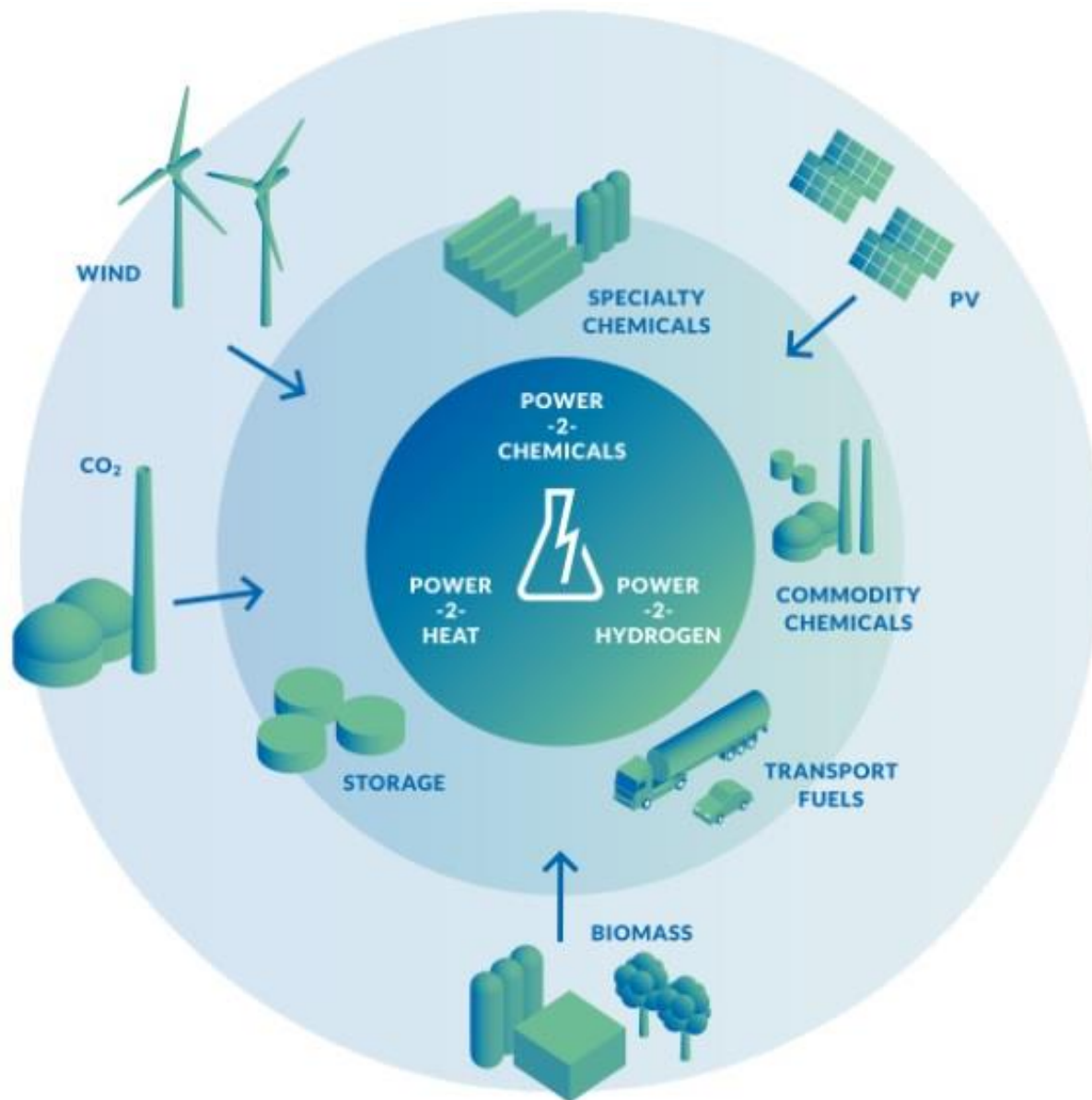
0.1–0.5 M NaHCO<sub>3</sub> or KHCO<sub>3</sub>

TRL 3

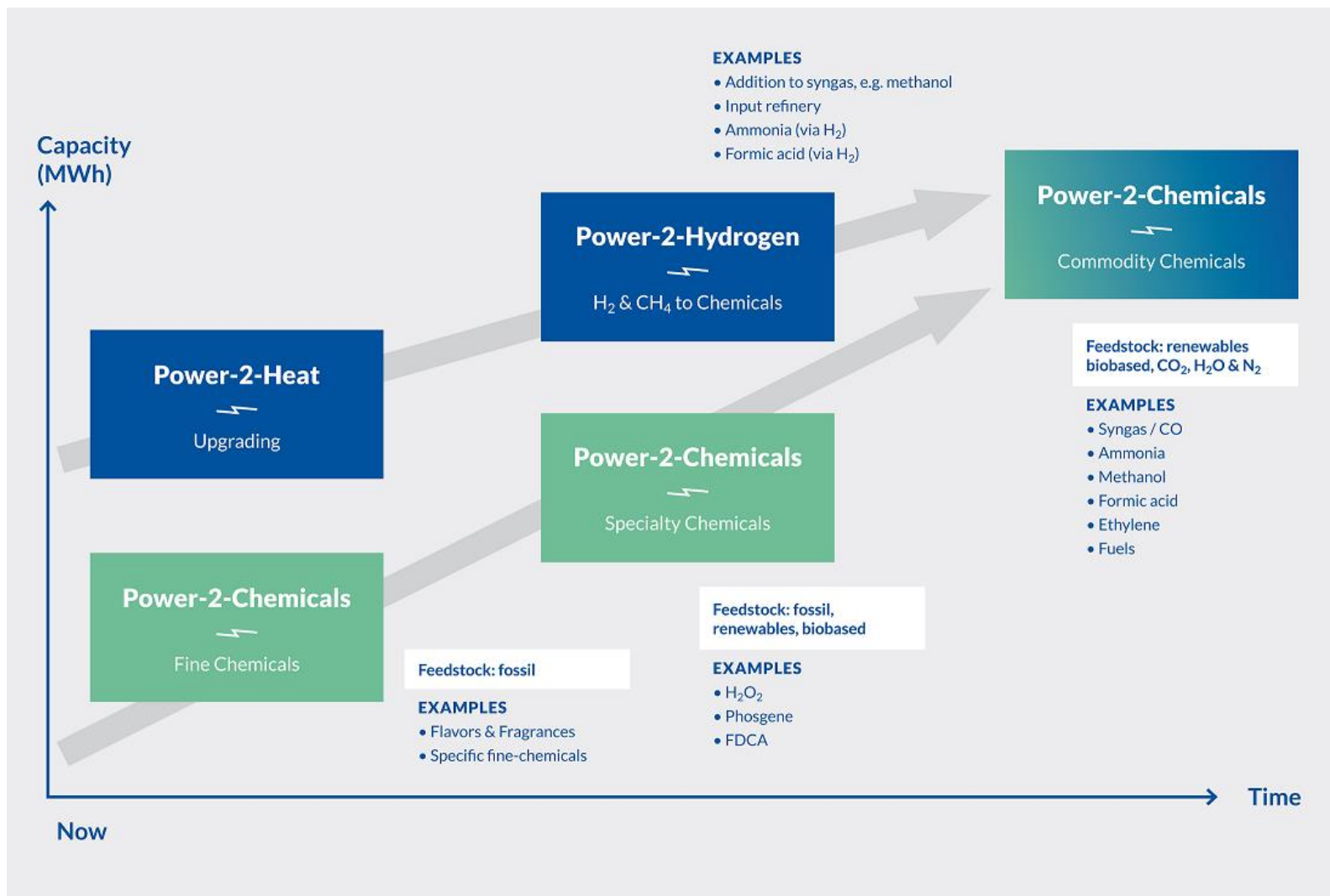
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.41
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{C} + 2\text{H}_2\text{O}$	-0.20
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24

# Electrochemical reduction

Product	# of electrons per product molecule	Market price	Electricity cost	Best known catalyst
Syngas	2	25–90	376	Au, Ag, Zn
Carbon monoxide	2	600	271	Au (95%), Ag (92%)
Formic acid	2	1200–1600 (90%)	163	Sn (80%)
Formaldehyde	4	3500	501	B-doped diamond (74%)
Methanol	6	350	705	Cu (<5%)
Methane	8	150–250	1880	Cu (55%)
Ethanol	12	700–1000	981	Cu (<5%)
Ethylene	12	950–1200	1611	Cu (<5%)
Propanol	18	1800	1128	Cu (<5%)



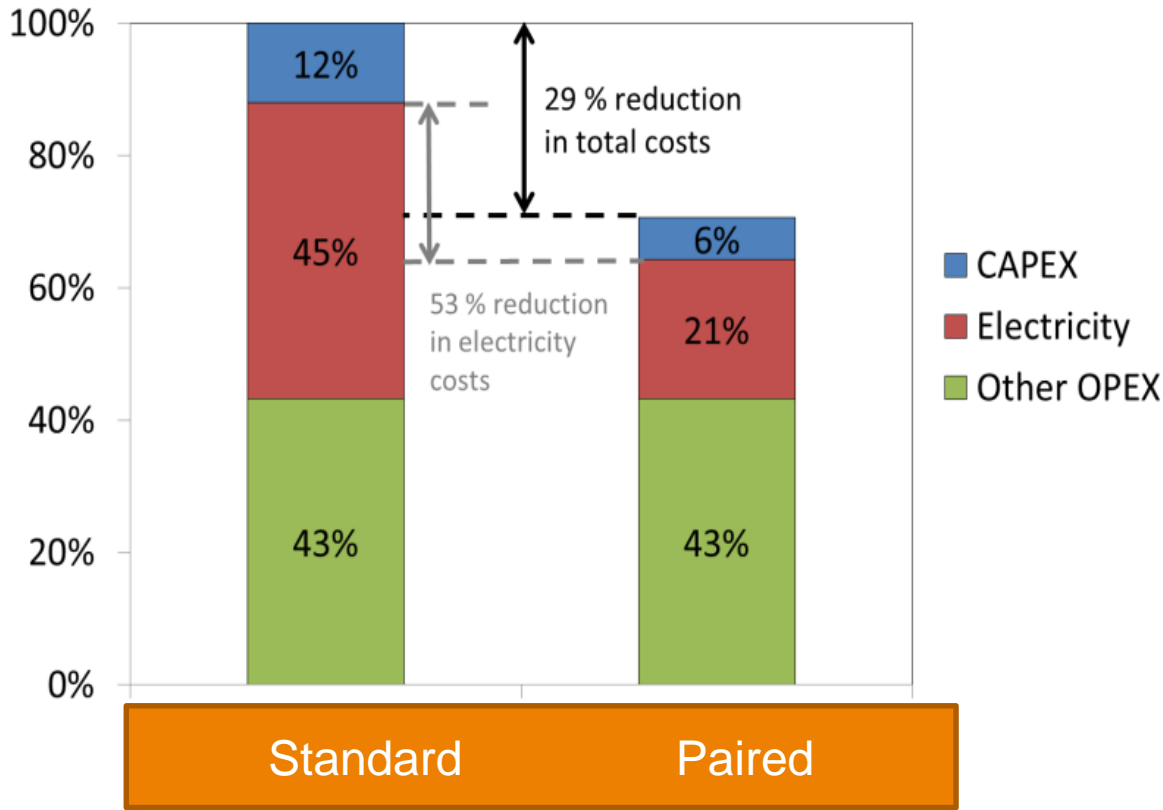
# THE VOLTACHEM ROADMAP





# FOCU

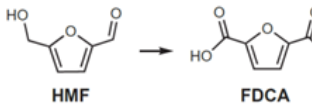
Develop  
product



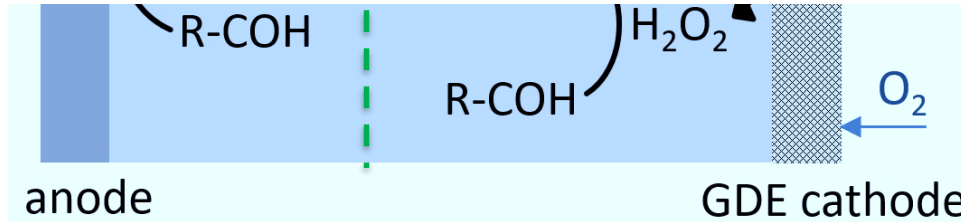
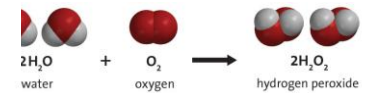
Formulation of

- CAPEX
- Electricity
- Other OPEX

## Showcase FDC



## Mediator H<sub>2</sub>O<sub>2</sub>



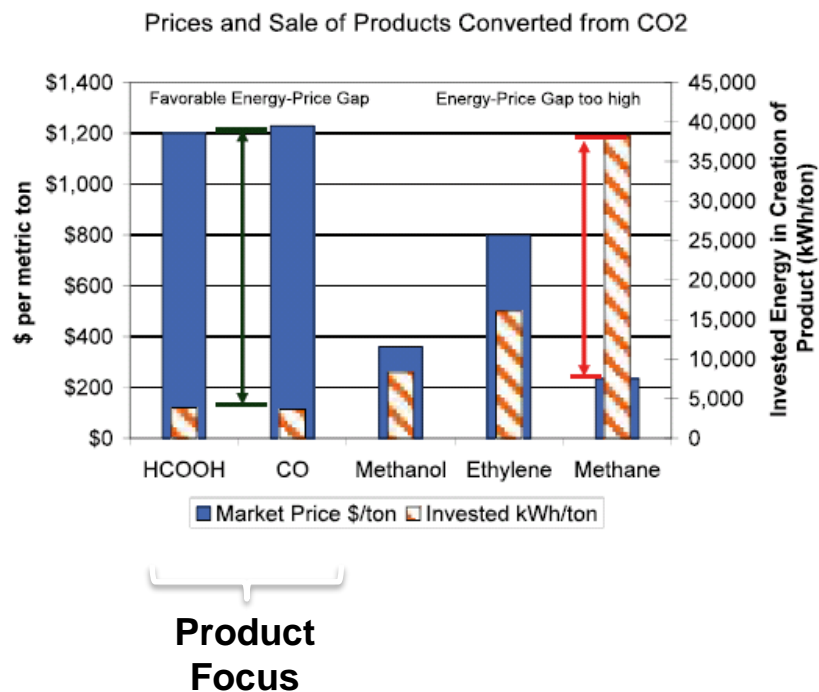
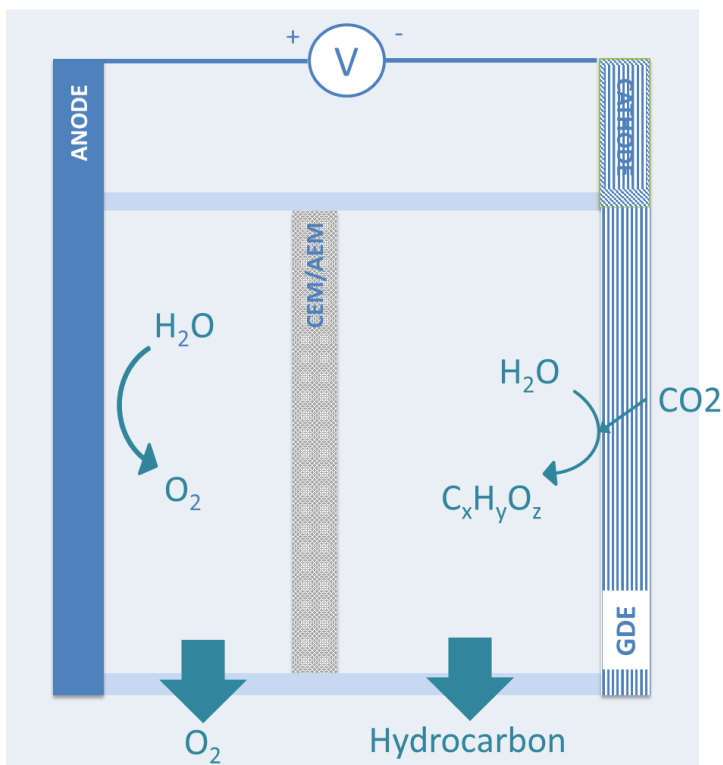
Businesscase  
Efficient conversion

Paired synthesis:  
2x production

Businesscase  
Local H<sub>2</sub>O<sub>2</sub> production

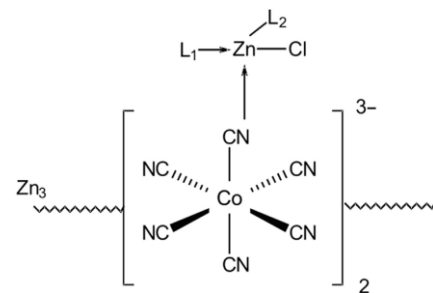
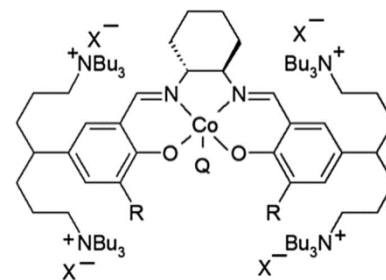
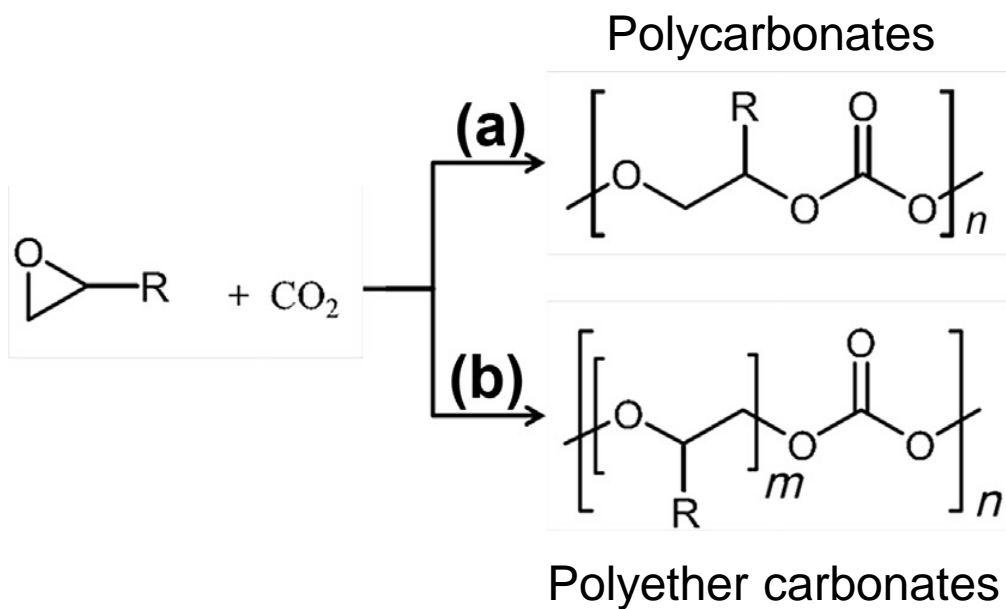
# FOCUS POWER-2-COMMODITIES

Developing a platform for local **electrochemical production of hydrocarbons from CO<sub>2</sub>** based on power-2-specialties know-how.

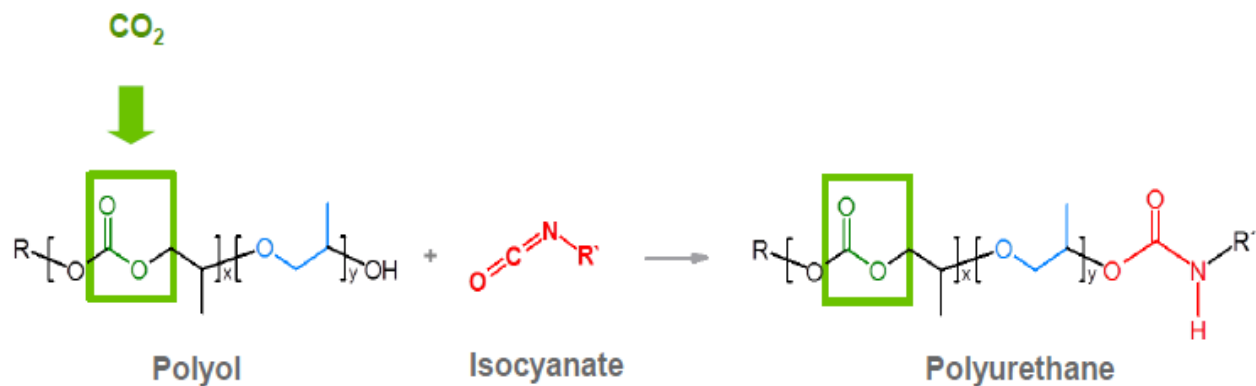
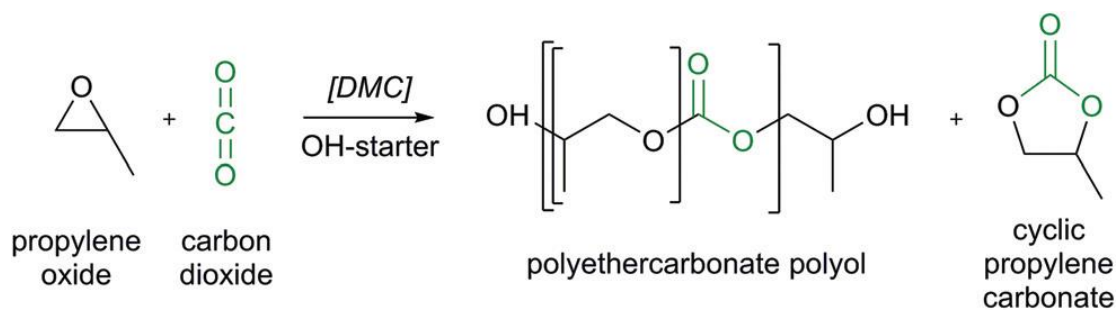


# 3. POLYMERIZATION

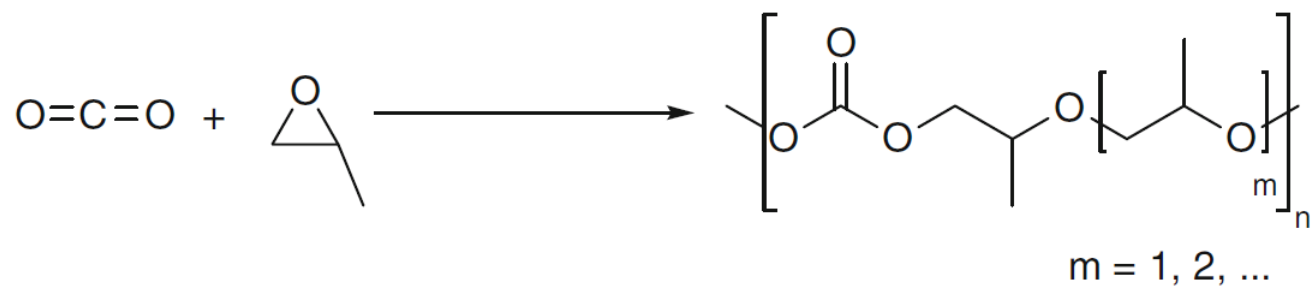
# CO<sub>2</sub>-based polymers



# CO<sub>2</sub>-based polymers



# Poly(propylene carbonate)

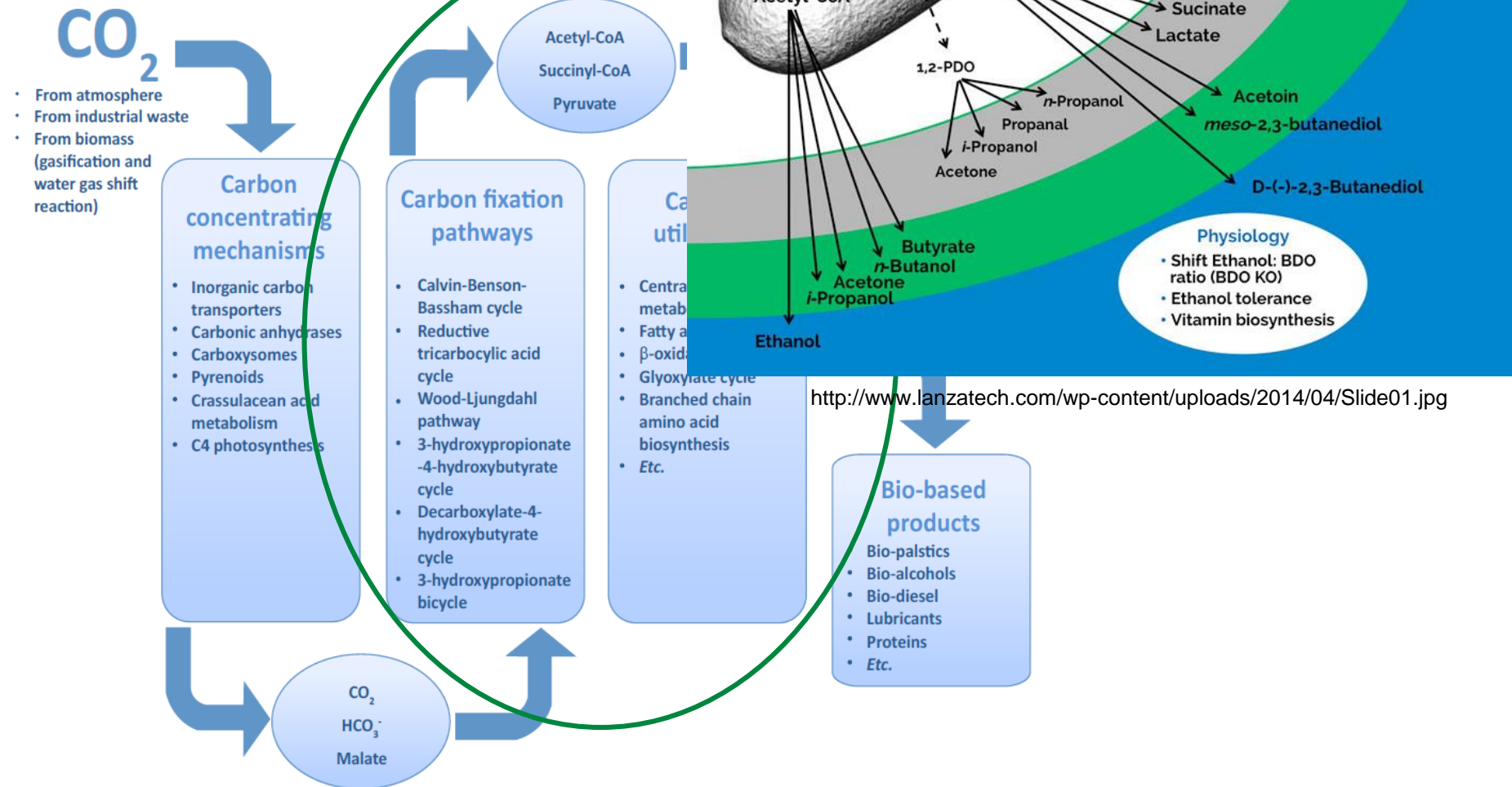


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## **4. BIOCHEMICAL**

# Biochemical conversion



Jajesniak, P. et al., 2014. Carbon Dioxide Capture and Utilization using Biological Systems : Opportunities and Challenges. Bioprocessing & Biotechniques, 4(3), p.15. Available at: <http://omicsonline.org/open-access/carbon-dioxide-capture-and-utilization-using-biological-systems-opportunities-and-challenges-2155-2224-1322155-1-2.pdf>

# Biochemical conversion

1. Provide CO<sub>2</sub> in a “proper” way;
2. Find/engineer a microorganism that uptakes CO<sub>2</sub> fast;
3. (One of) the end products in the microorganism metabolism is the desired product;
4. Harvest the desired product

# Biochemical conversion

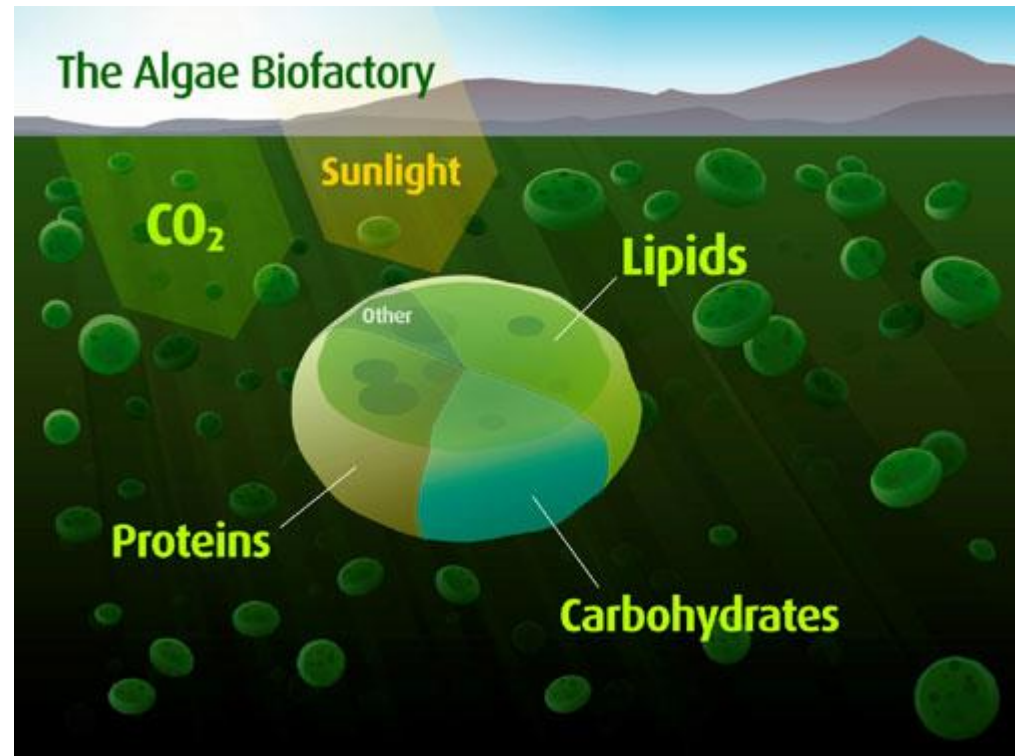
Lipids can be up to 80% of microalgae mass

Lipids can be used for biodiesel production (replacing soy oil)



TRL7

<http://www.biofuelstp.eu/algae-aquatic-biomass.html>



<http://making-biodiesel-books.com/wp-content/uploads/2012/02/algabiofactory.jpg>

# Cultivation technologies



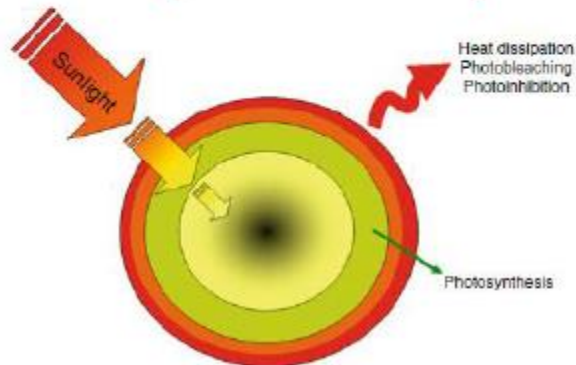


## Problem 1: LIGHT USE



Low light penetration = Low productivity

### Photosynthetic efficiency



Up to 80% of light energy is converted  
into **HEAT** and **NOT GROWTH!**

## Problem 2: CO<sub>2</sub> CAPTURE & FEEDING



**Direct flue gas feeding is not scalable!**

**Pure CO<sub>2</sub> bubbling  
too expensive for large  
scale production systems!**

€0,20 – €0,50 per kg DW



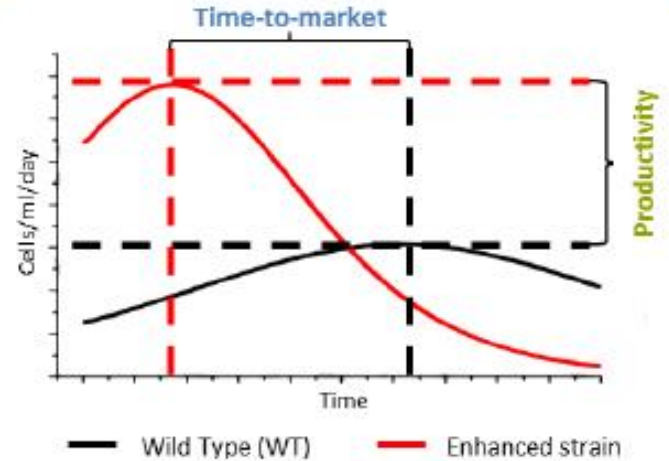




## Enhanced Algae-strains (Non-GMO)



Need a lot of CO<sub>2</sub> to grow fast!



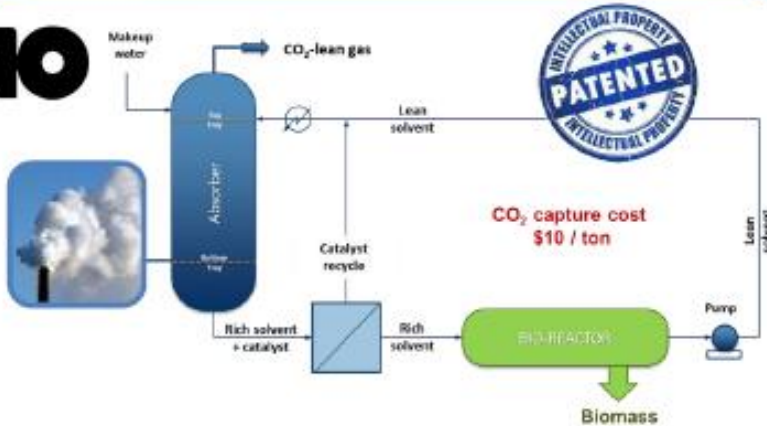
Existing algae farms:

- ✓ More than 2 x higher productivity
- ✓ Lower operational cost

New built algae farms:

- ✓ More than 3 x higher productivity
- ✓ Lower operational & capital cost

TNO



CO<sub>2</sub> capture cost \$10 / ton

Concentrated CO<sub>2</sub> feed w/ integrated capture

# THANK YOU FOR YOUR ATTENTION

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**TNO** innovation  
for life

**EARL.GOETHEER@TNO.NL**