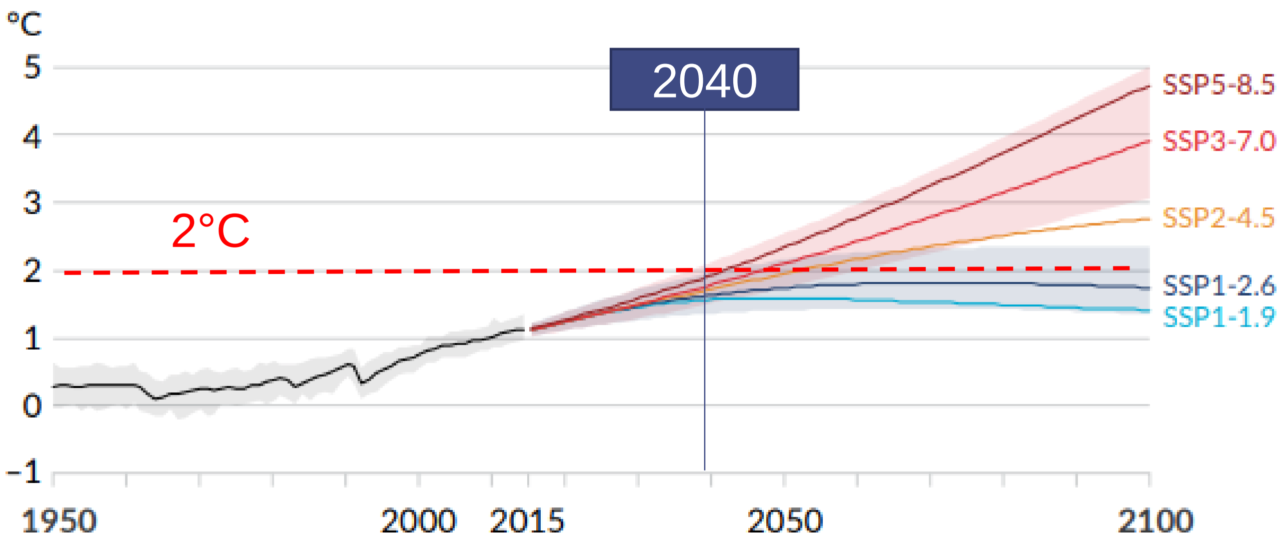
Valoriser le CO_2 par réduction en carburants et intermédiaires chimiques

Quels enjeux et quelles technologies ?

Alban CHAPPAZ and Isabelle ROUGEAUX

The energy transition and CO_2 mitigation

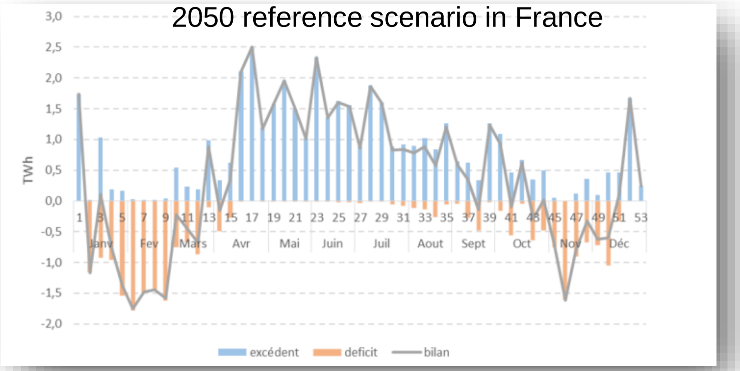
Increase of the greenhouse gases (GHG) concentration in the atmosphere → **increase of mean surface temperature**



IPCC, 2021: *Climate Change 2021: The Physical Science Basis*.

Global warming is likely to reach 2°C before 2040 if no changes are made

- **Energy transition**: fossil fuels → **renewable sources**
- **CO_2 capture** and storage (**CCS**) or utilization (**CCU**)



Etude portant sur l'hydrogène et la méthanation, E&E Consultant, Solagro, 2014

Intermittent nature of renewable energies

Targets

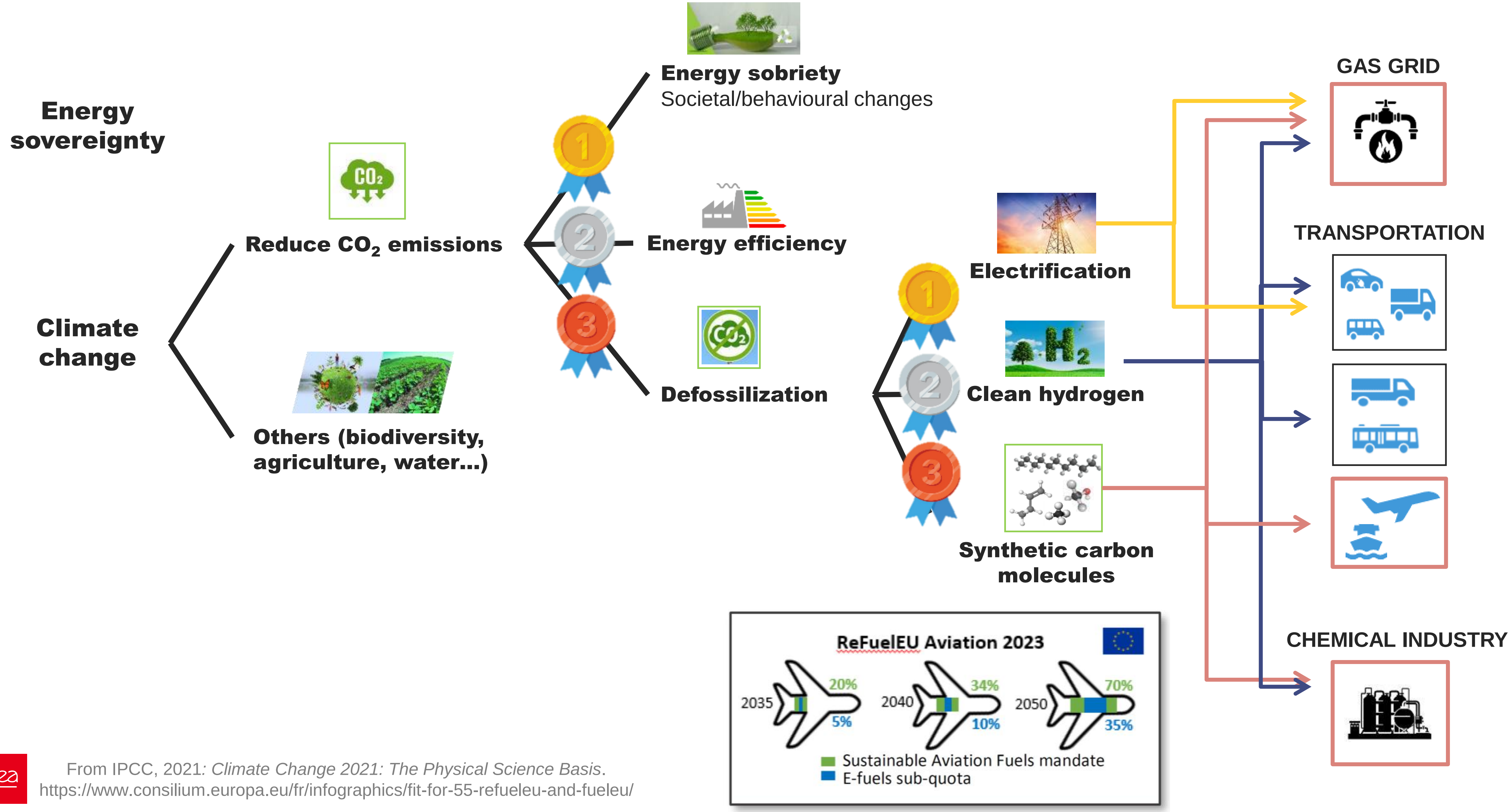
reduce by 50% the global greenhouse gas emissions over the next ten years

IPCC, 2021: *Climate Change 2021: The Physical Science Basis*.

Need to install decarbonized electric sources

Need to store the excess electricity into other forms of energy

Prioritization of solutions for climate change



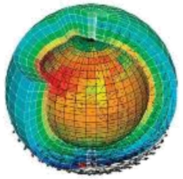
From IPCC, 2021: *Climate Change 2021: The Physical Science Basis*.
https://www.consilium.europa.eu/fr/infographics/fit-for-55-refueleu-and-fueleu/

From linear towards circular carbon economy

A Carbon Circular Economy is based on:

a collection of technologies able to convert CO_2 and its derivatives into useful products, from low-carbon energies (incl. nuclear and renewables), to achieve carbon neutrality with a positive environmental and societal impact.

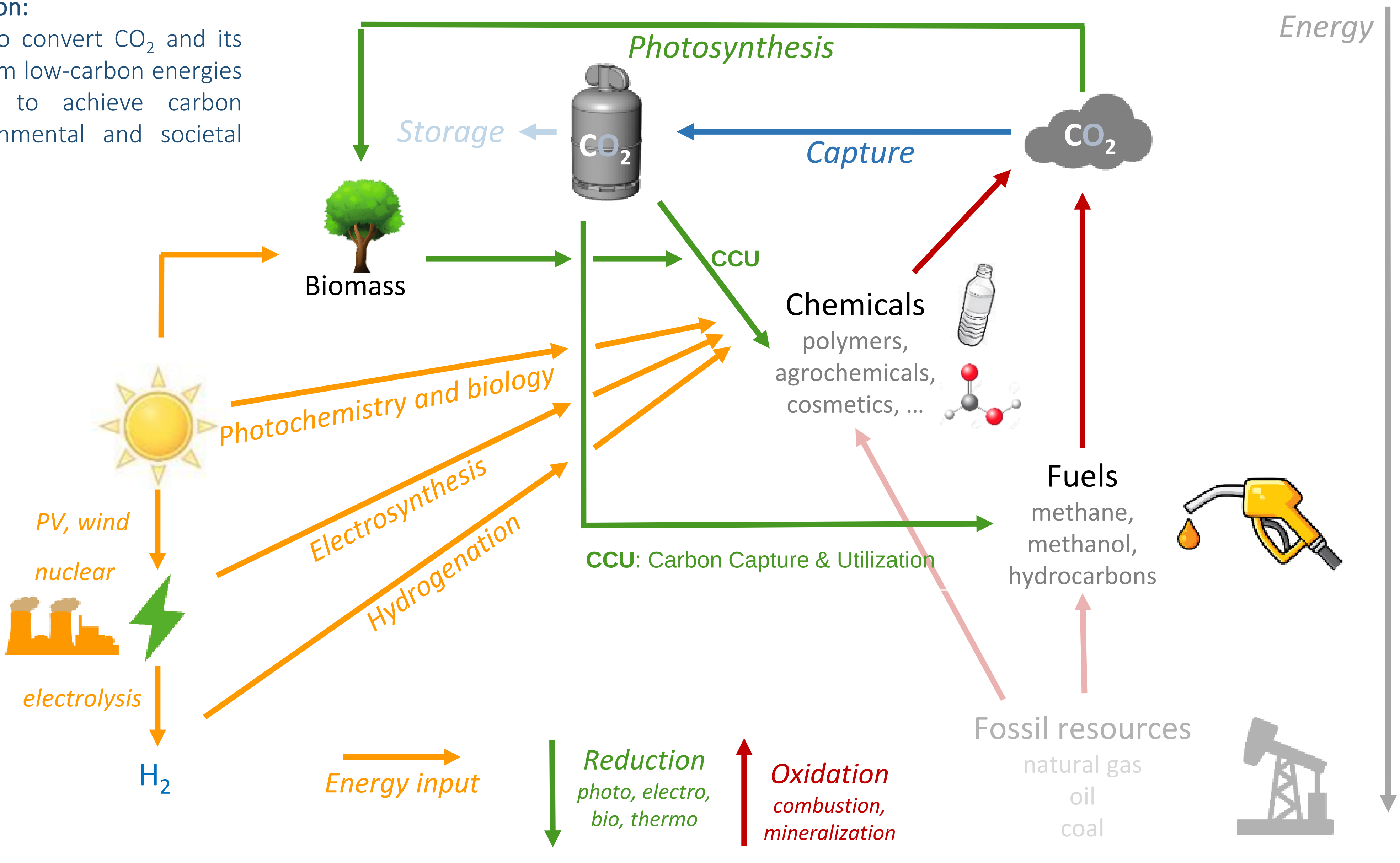
Cross-cutting challenges



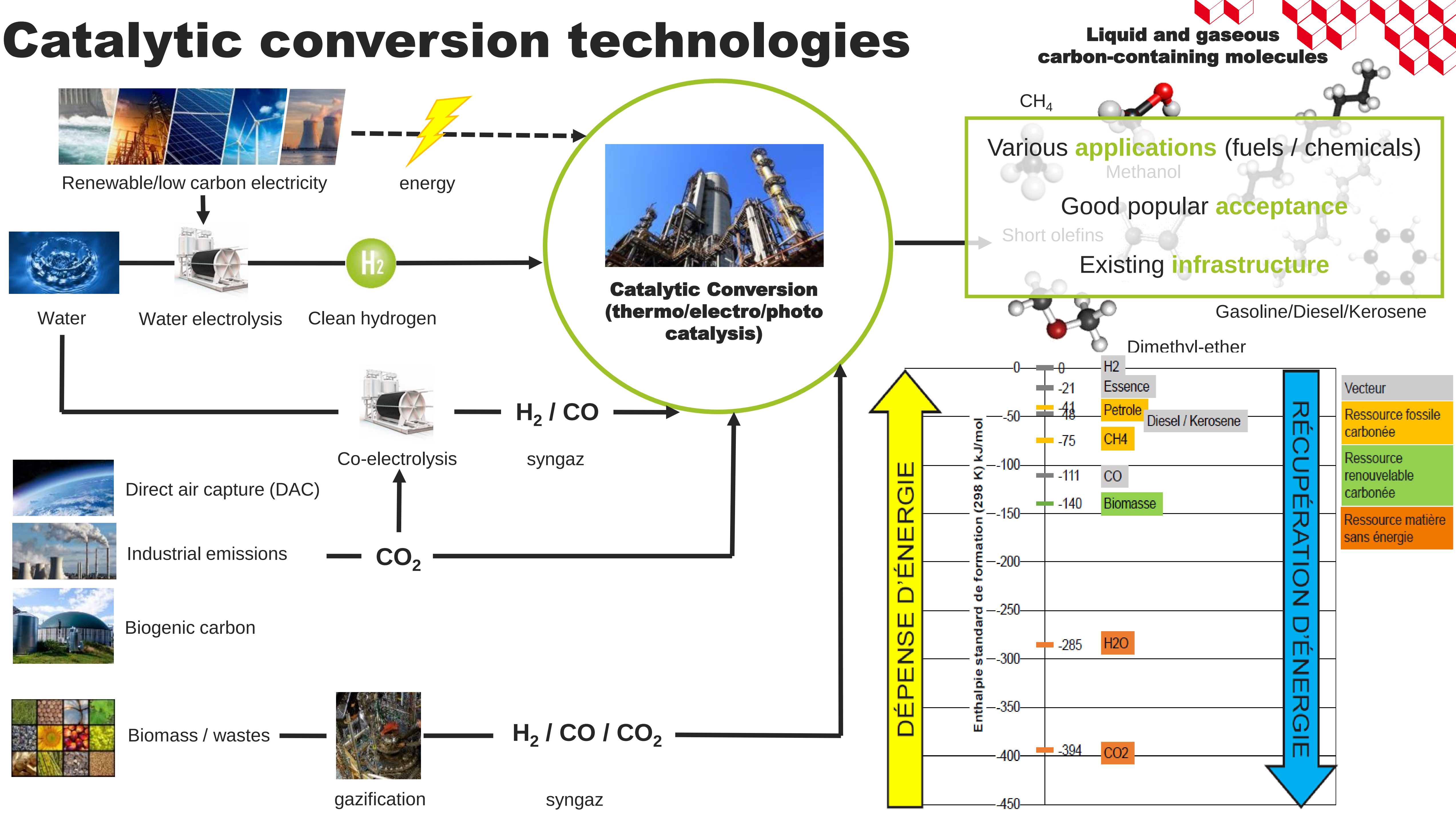
Impact analysis of soils and climate

Multicriterai Life Cycle Analyses

Sustainability of resources



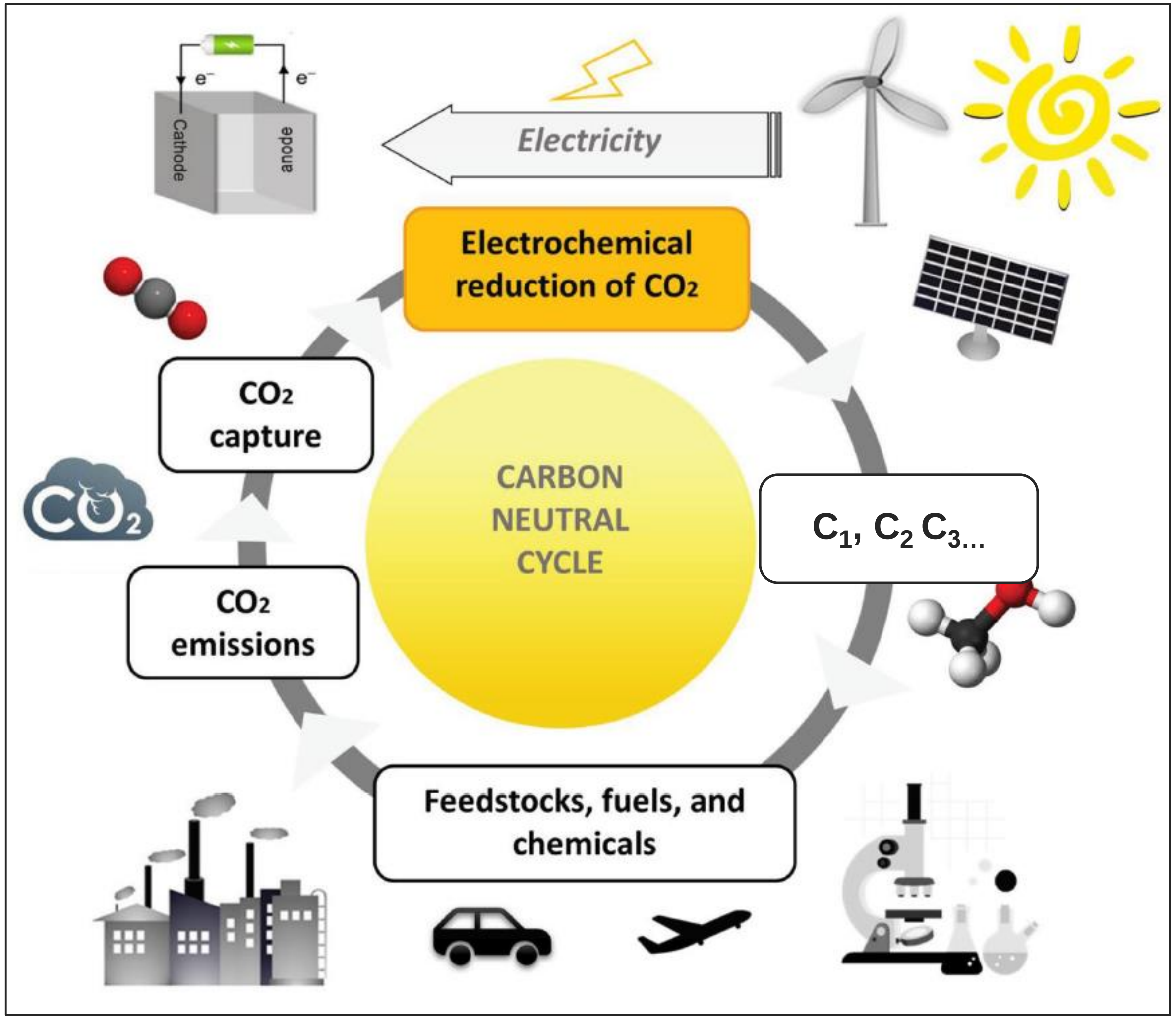
Catalytic conversion technologies



1. Electro-catalytic reduction

OVERVIEW ON ELECTROCHEMICAL CO_2 REDUCTION REACTION (CO2RR)

- Novel research field towards :
  - A CO_2-neutral global economy / Circular Carbon Economy
  - Combating fast accelerating and disastrous climate changes
  - New solutions to store renewable energy in value-added chemicals and fuels
- CO_2 capture : Industrial fumes or DAC (Direct Air Capture)
- Powering electrochemical cells with renewable energies



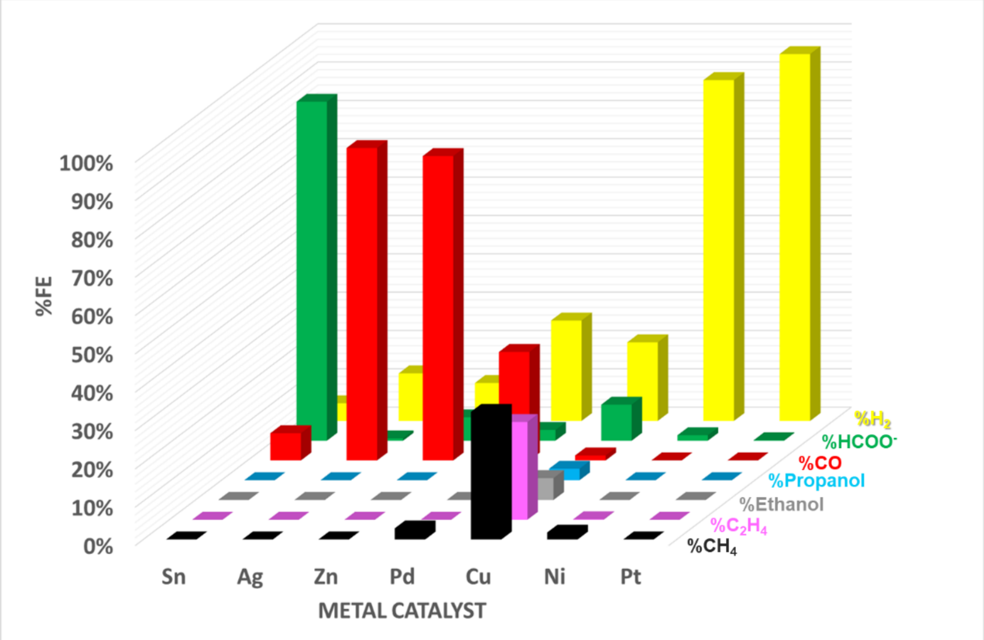
ChemNanoMat 2021, *7*, 1–10

ELECTROCHEMICAL REACTIONS

Cathode :
Several possible reactions :

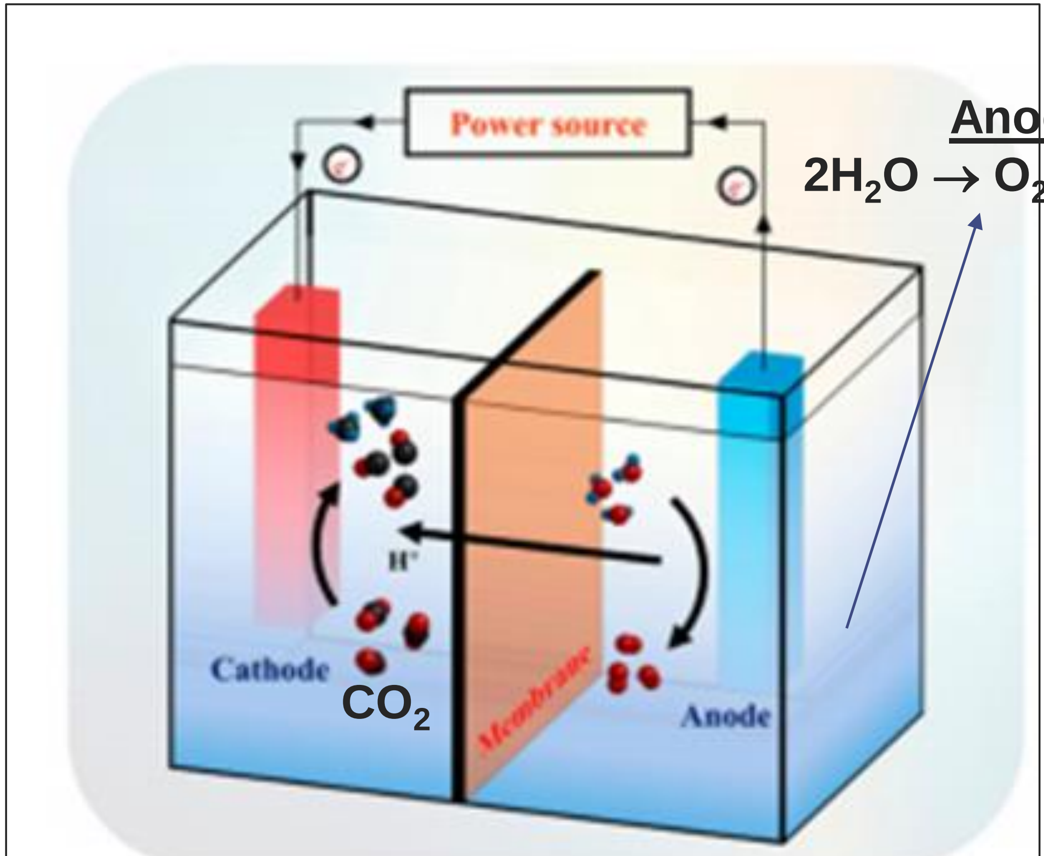
Half–Electrochemical Thermodynamic Reactions	Product	E° Redox
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	CO_2 anion radical	−1.90 V
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	Formic acid	−0.61 V
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	Carbon monoxide	−0.53 V
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	Formaldehyde	−0.48 V
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	Methanol	−0.38 V
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	Methane	−0.24 V
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	Ethylene	−0.41 V

$2H^+ + 2e^- \rightarrow H_2$: Parasitic Hydrogen Evolution Reaction (HER)



Chem. Rev.2019, 119, 7610−7672

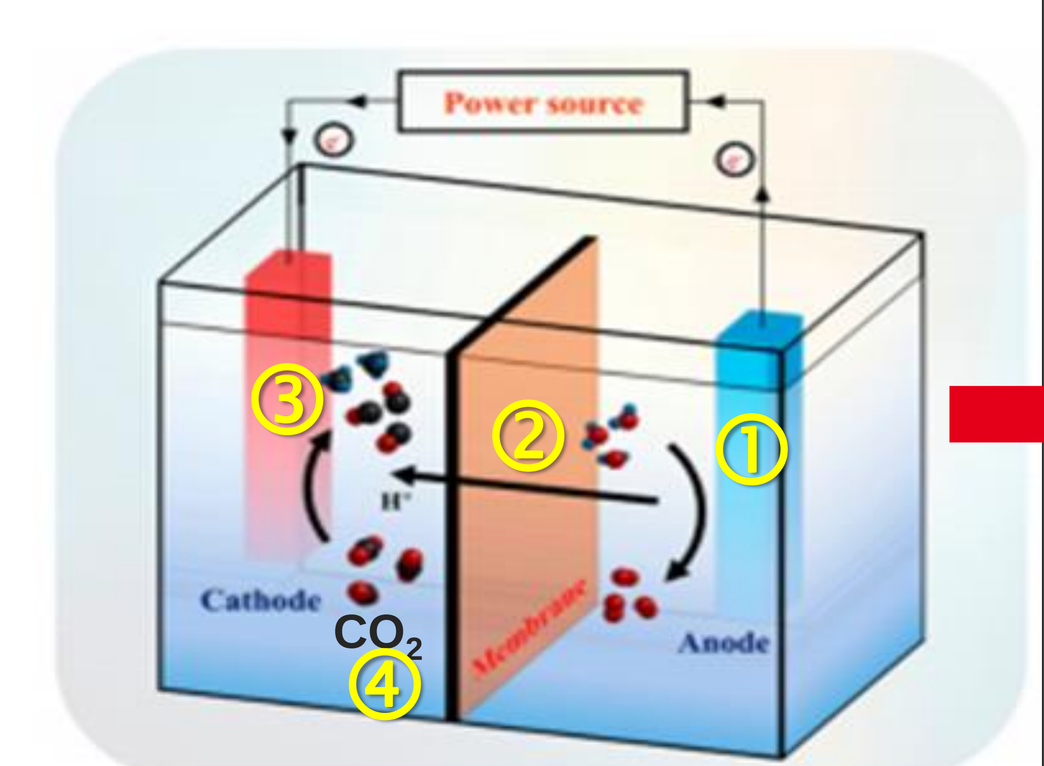
Anode :
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$



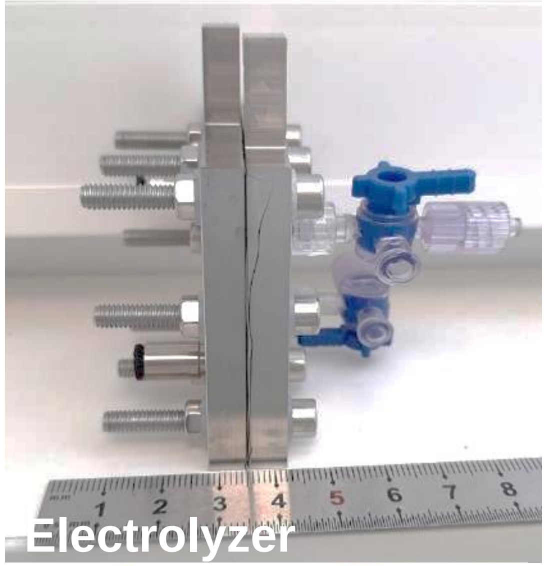
Catalysts 2020, 10, 98; doi:10.3390/catal10010098

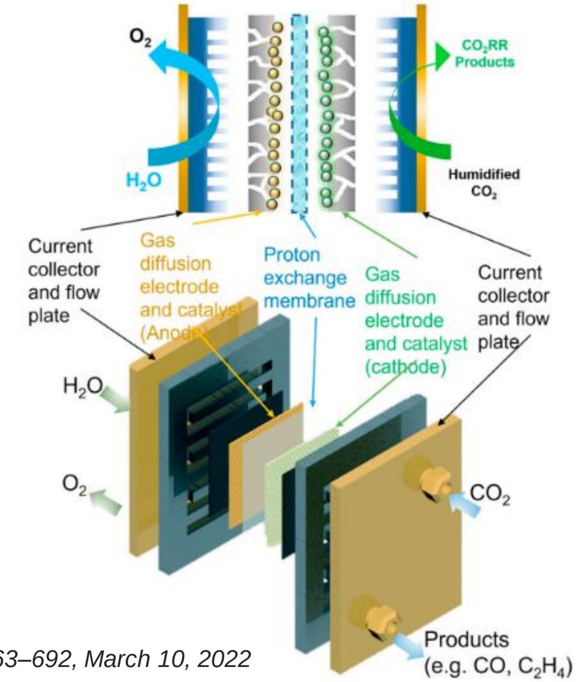
- **Mild reaction conditions (suitable with intermittent energy)**
- **Flexible and controllable process by different parameters (electrode materials, electrolytes and applied potentials)**

CO2RR INDUSTRIALIZATION



Catalysts 2020, 10, 98; doi:10.3390/catal10010098





Chem 8, 663–692, March 10, 2022

- Need to optimize :

① Anodic materials

② Membrane

③ Cathodic materials

④ CO_2 feeding

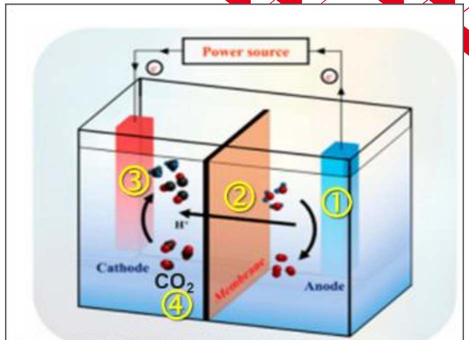
⇨ High Current density / High energy efficiency

⇨ High CO_2 conversion

⇨ Long term stability

⇨ Good selectivity

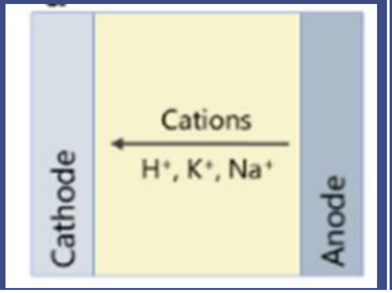
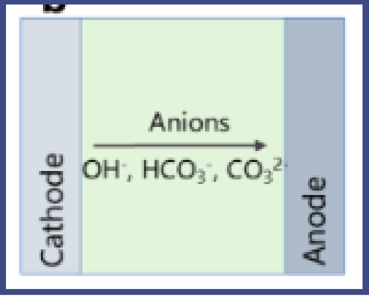
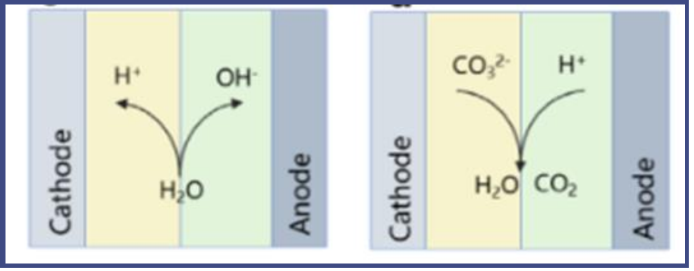
PARAMETERS TO OPTIMIZE FOR INDUSTRIALIZATION



Catalysts 2020, 10, 98; doi:10.3390/catal10010098

1 • Anodic catalysts : Expensive materials (Iridium, Platinum …)
 ⇨Need to be replaced by lower cost materials

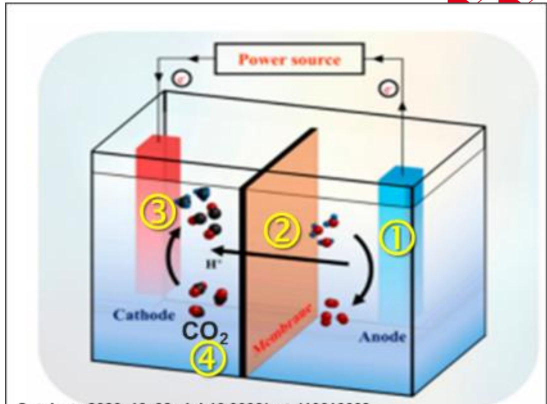
2 • Membrane : How to select the suitable polymer?

	Cationic 	Anionic 	Bi-Polar 
Performances (conductivity, current density)	☺	☹	☺
HER	☹	☺	☺
Stability	☺	☹	☺
Cost	☹	☺	☹ *Not currently marketed*

cea

https://doi.org/10.1016/j.cej.2022.140942

PARAMETERS TO OPTIMIZE FOR INDUSTRIALIZATION

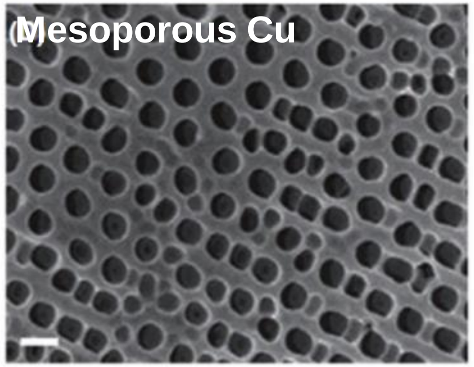


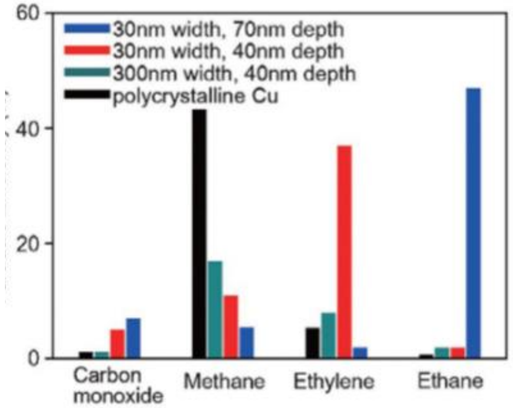
Catalysts 2020, 10, 98; doi:10.3390/catal10010098

③ • **Cathodic materials :**

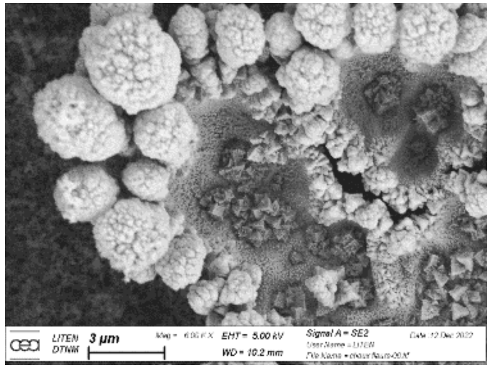
- **Catalysts** : Influence of the nature and the morphological structure of the catalyst on the product obtained, the rate of the reaction and the selectivity

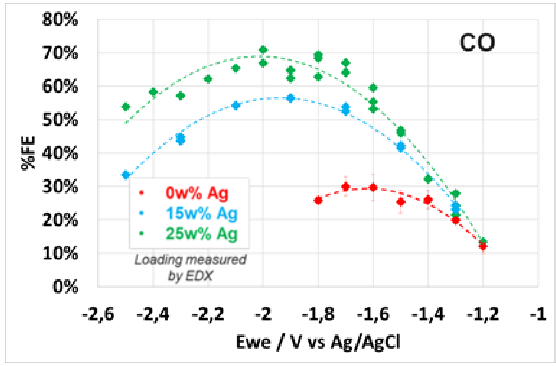
⇨ **Need specific synthesis way / no directly commercially available**



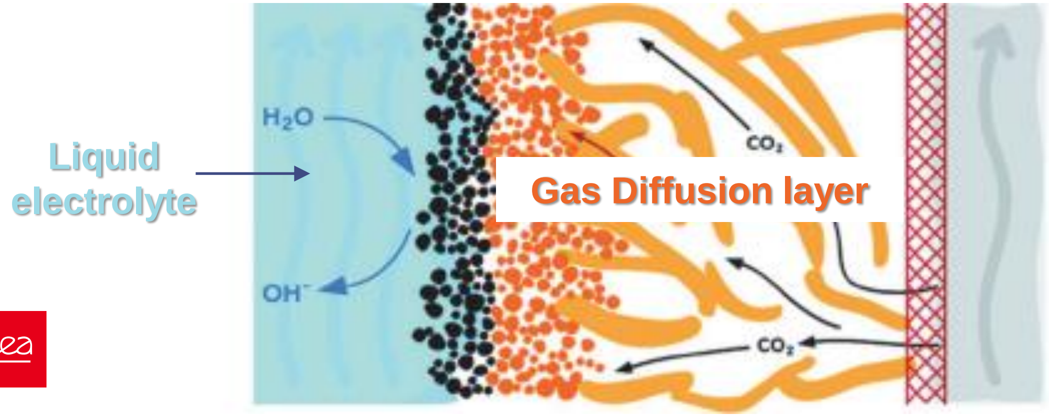


DOI: 10.1002/ese3.935





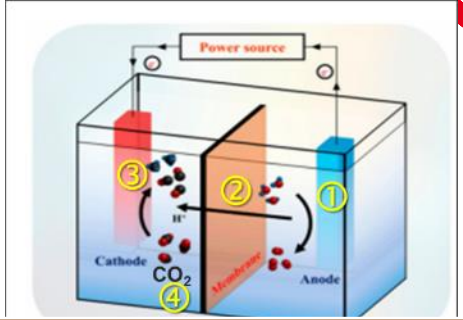
- **Catalyst support** : Key role to control the gas and water diffusion



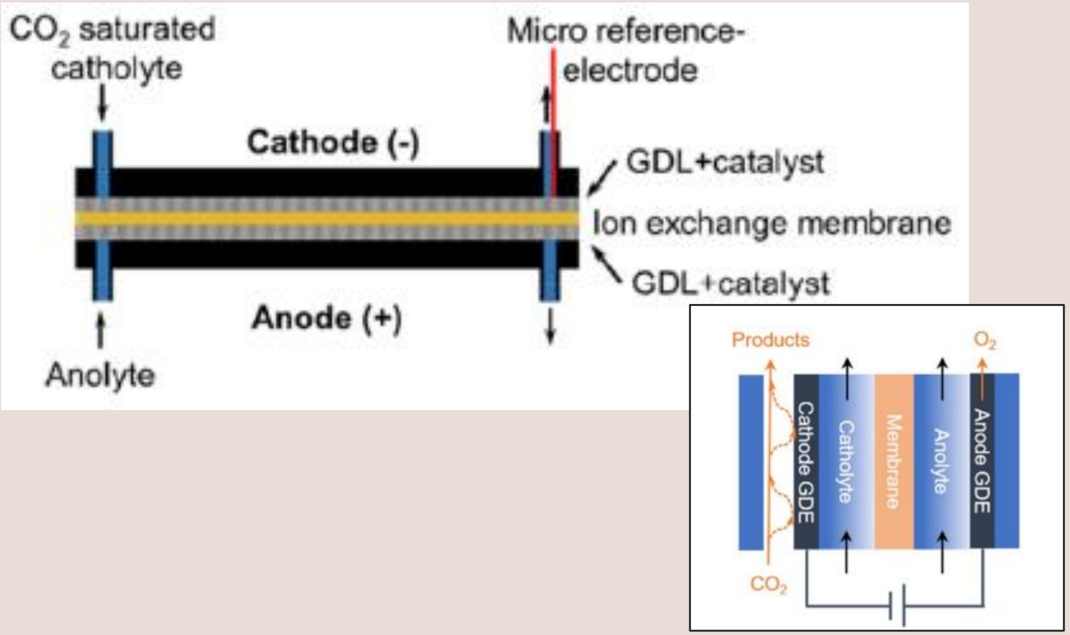
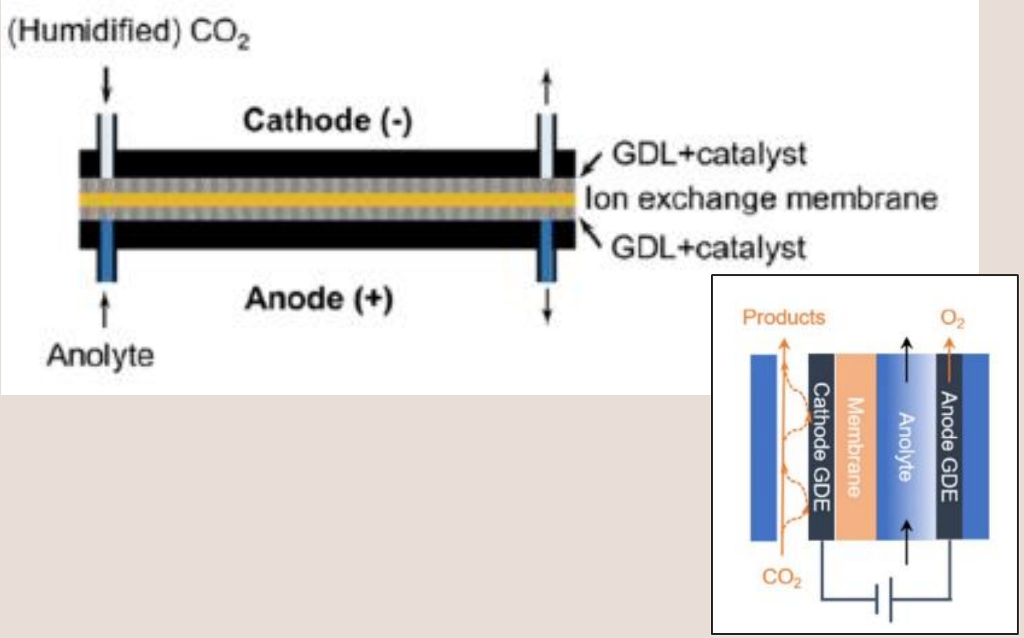
- Catalyst
- Carbon Powder
- Carbon Fiber

Acta Phys. -Chim. Sin. 2021, 37 (5), 2009021 (1 of 15)

PARAMETERS TO OPTIMIZE FOR INDUSTRIALIZATION

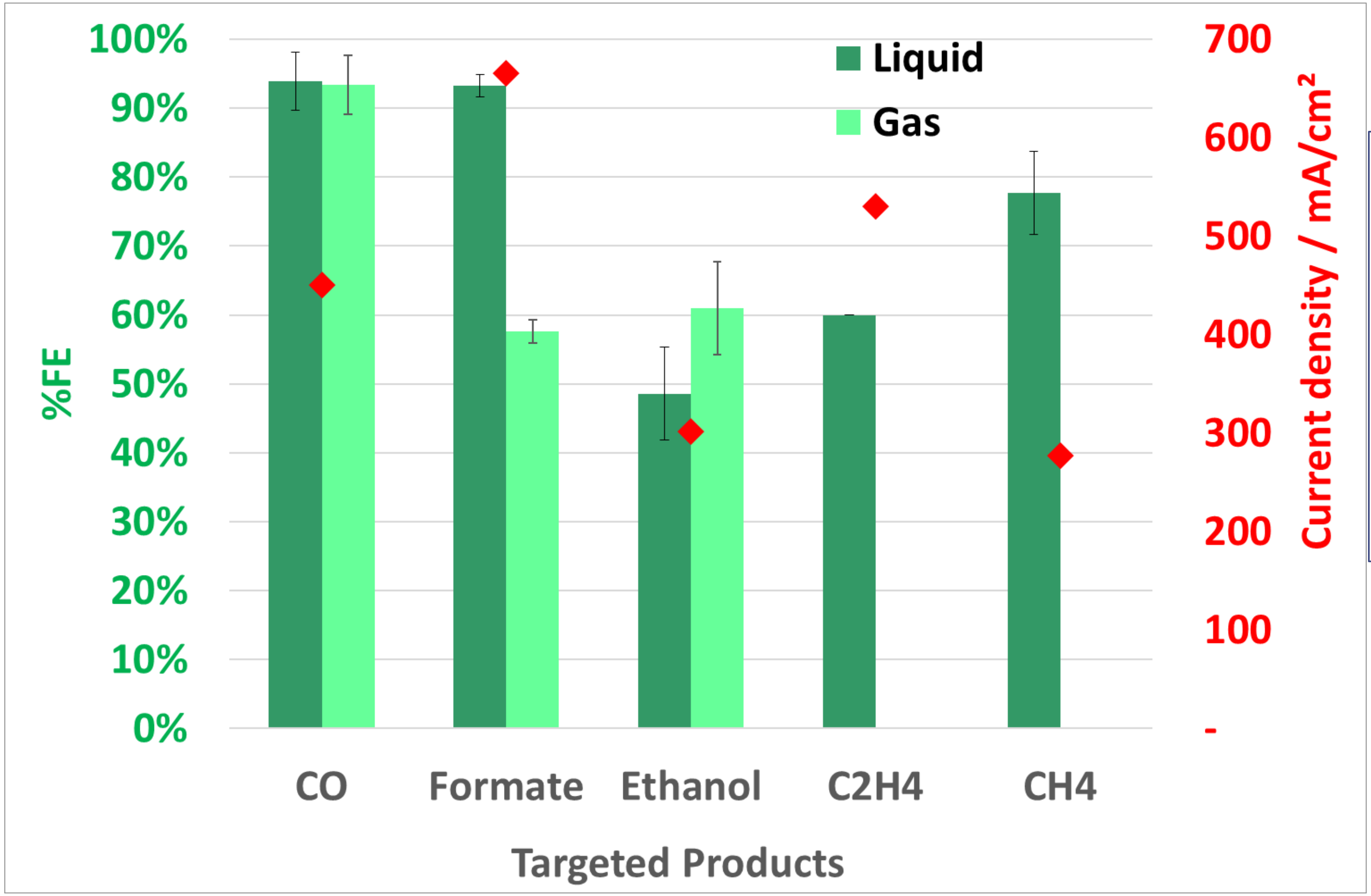


④ • CO_2 feeding : It depends on the design of electrolyzer

	Gaseous CO_2	CO_2 dissolved in liquid
		
Advantages	- No CO_2 capture step required - No electrolyte required - High concentration of CO_2 on the catalyst ⇨ High reaction rate (current) ⇨ Rapid diffusion through GDL	CO_2 capture + Electro-reduction in 1 single step
Drawbacks	Need to pressurize cathodic compartment	- CO_2 must be dissolved in electrolyte with high CO_2 capacity : ~~Aqueous solution~~, Ionic liquid (but expensive) - Reaction limited by the supply of CO_2 to the catalyst

Materials Reports: Energy 3 (2023) 100194
https://doi.org/10.1016/j.cogsc.2019.01.005
https://doi.org/10.1016/j.cej.2022.140942

RECENT ELECTROLYZER PERFORMANCES



- High current densities
- Good selectivity
- High %FE for C_1 (CO, Formate and CH_4)
- Limited performances for complex molecules (>C_2)

Materials Reports: Energy 3 (2023) 100177

CONCLUSIONS

- **CO2RR to high value-added chemicals ⇨ Promising technology to achieve sustainable carbon neutralization**
- **Interesting results for :**
  - C_1 : possibility to be further chemically converted to important chemicals (acids, alcohols, and olefins)
  - C_2 : directly synthesized with complex catalysts (Ethanol, Ethylene …)
- **But it seems difficult to obtain molecules beyond C_3**
- **No H_2 needed → Safety aspect**
- **Flexibility of the technology (compatibility with intermittent energy)**
- **Actual TRL : 4-5 *(>7 : industrialization)* → Many optimizations still required**
- **Emerging companies : OPUS-12, Dioxide Materials, DNV, CO2 CERT, Siemens and CarbonEnergy**

2. Thermocatalytic CO_2 reduction

Thermocatalytic conversion technologies

Renewable/low carbon electricity

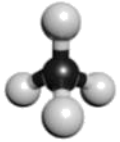
Water

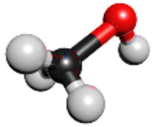
Water electrolysis

Clean hydrogen

Catalytic Conversion (thermocatalysis)

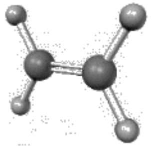
CH_4

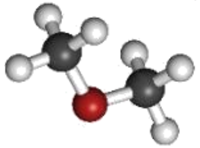




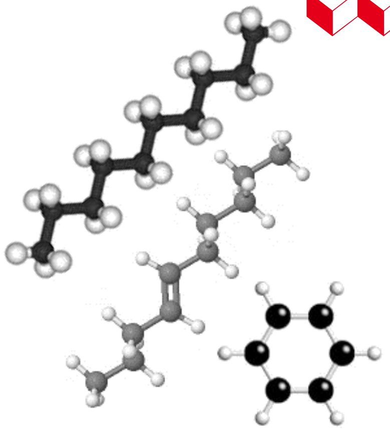
Methanol

Short olefins





Dimethyl-ether



Gasoline/Diesel/Kerosene

Liquid and gaseous carbon-containing molecules

Direct air capture (DAC)

Industrial emissions

Biogenic carbon

CO_2

Heterogeneous catalysis (solid catalyst/gas reageants)

Exothermic reactions (due to high H_2/CO_2 ratio)

Direct (one reactor) or **indirect** (two or more reactors)

Methanation (Sabatier) – TRL = 9

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

➔ **Thermodynamic control** (equilibrium X~95% at 350°C, 5 bar)

➔ **High kinetics** (Ni or Ru catalysts)

Methanol synth. – TRL = 8

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

➔ **Thermodynamic control** (equilibrium X~25% at 250°C, 50 bar)

➔ **Lower kinetics** (Cu or In catalysts)

Hydrocarbons synth. – TRL = 7 indirect / 3

$$CO_2 + 3H_2 \rightarrow \frac{1}{n}(-CH_2-)_n + 2H_2O$$

➔ Kinetic control (no equilibrium)

➔ **Limited selectivity** (syncrude) (Fe or Co catalysts)

High maturity : history of technologies

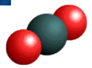

Coal


Natural gas


Biomass


Reforming/gazification
+ purif.

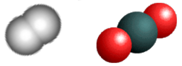

Water


CO_2

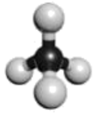

Co-electrolysis

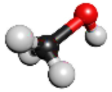
H_2 / CO
syngaz

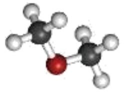
RWGS

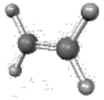

H_2 / CO_2


Catalytic Conversion (thermocatalysis)

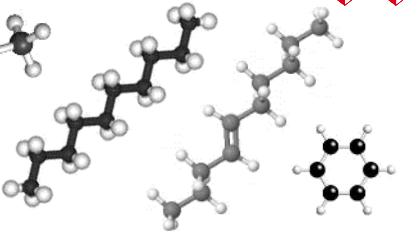

CH_4


Methanol


Dimethyl-ether


Short olefins

Liquid and gaseous carbon-containing molecules


Gasoline/Diesel/Kerosene

More than 100 years of …
Heterogeneous catalysts development
Reactors design **optimization**
Cost reduction / **Upscaling** and sizing to the available resource

Methanation 1902 (Sabatier)

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$


Paul Sabatier
Nobel Prize 1912

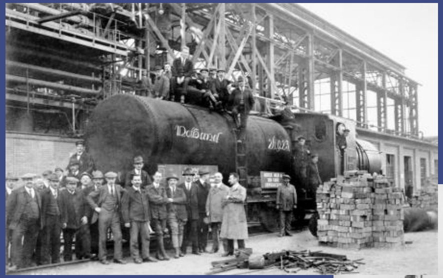
CO epuration in syngas for NH_3 prod.

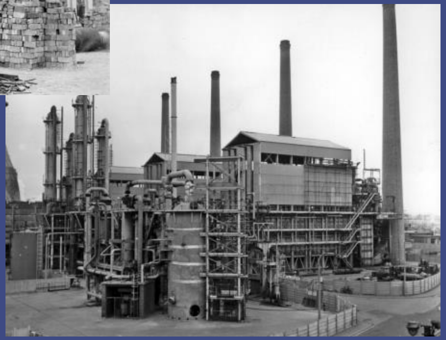
(1970 oil crisis) SNG from coal

(1980) CO_2 méthanation

Methanol synth. 1923 (Pier & Mittasch)

$$CO + 2H_2 \rightarrow CH_3OH$$

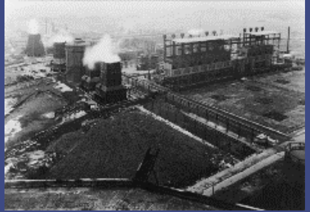

1st synthetic MeOH shipment
BASF, Leuna, 1923


1st « low » pressure MeOH Plant
ICI, 1966

(1990) Indirect CO_2 MeOH synthesis

Hydrocarbons synth. 1923 (Fischer & Tropsch)

$$CO + 2H_2 \rightarrow \frac{1}{n}(-CH_2-)_n + H_2O$$


1st Coal-to-Liquid Plant
Ruhrchemie, Oberhausen, 1936

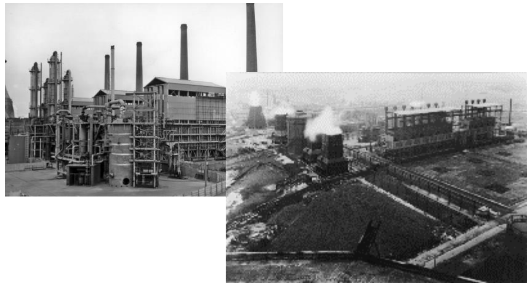
(1930) Coal-to-Liquid fuel (Germany)

(1945-1970) Coal-to-Liquid fuel (USA)

(1990) Coal-to-Liquid (South Africa & China)
+ Gas-to-Liquid (where Natural Gas available)

(2000) Biomass-to-Liquid / (2010) Power-to-Liquid

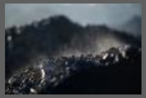
But still R&D to be done



…Yesterday

Tomorrow…

Feedstock available/storable in large quantity
(C + energy source)



Constant CO + H_2 inlet feed

Centralized ecosystem/infrastructures (pipes / harbours / networks)

Low costs (cheap fossil ressources)

KPI = mainly costs €

Feedstock limited (biomass) or diluted (CO_2 in air)
Need of decarbonized energy sources (intermittency)

CO_2 or variable syngas (CO + CO_2 + H_2) inlet feed

Decentralized usages / various sizes / multi-energy

Expensive electricity + CO_2 capture / H_2 production

KPI = CO_2 footprint + costs € / avoided CO_2

LCA - environmental footprint : impact on soil, water, biodiversity

Dynamic behaviour of the **process** / management of **Stop&Go**

New catalysts development / **water tolerant** catalysts

Modular and **scalable reactors** and units

Improve performances to have the best use of electricity

Multi-criteria analysis for process selection

Context of a process (example of methanation)

Constraints (Upstream)

Quantity (power scale)
Electrical Sources
(on/off grid, intermittency)
Heat availability

Water availability
Water quality (purification)

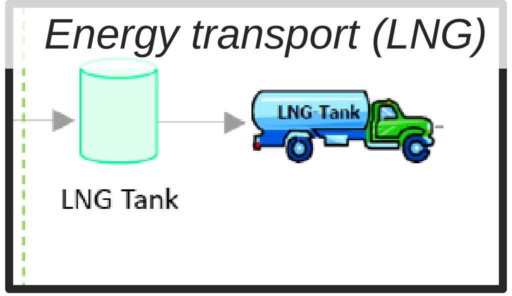
Quantity
Quality (Purification)
Stoichiometry

Land take
Regulation
Social-acceptance
Industrial landscape

Catalytic process

For each technologies :
Adaptability,
Flexibility
Scale
& process optimization/integration

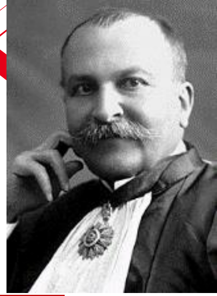
Applications (downstream)



Intrinsic methanation limitations

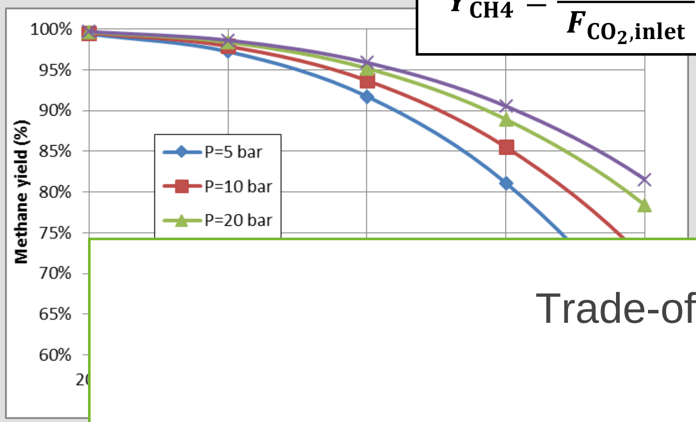
Sabatier reaction : $CO_2 + 4H_2 \Leftrightarrow 2H_2O + CH_4 \quad (\Delta_r H_{298} = -165 KJ/mol)$

Paul Sabatier
Nobel Prize 1912



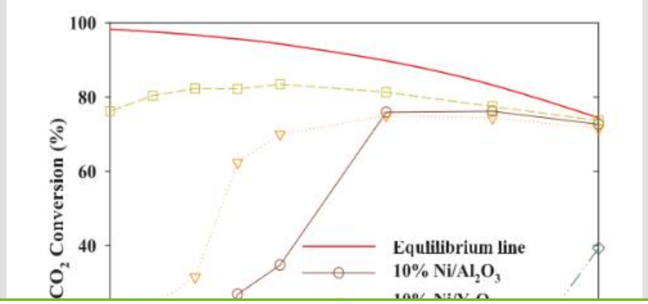
Thermodynamics

$$Y_{CH4} = \frac{F_{CH4,outlet}}{F_{CO_2,inlet}}$$



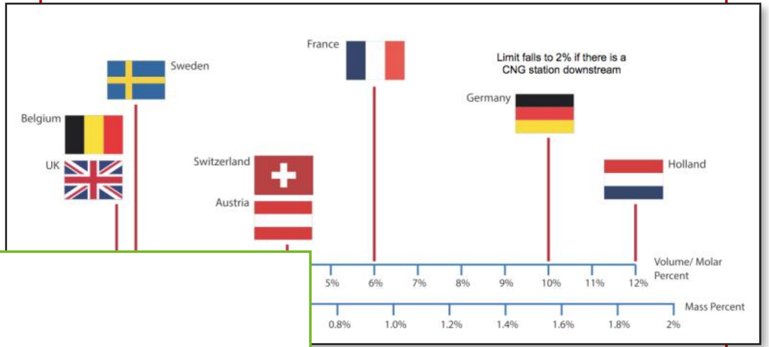
(H_2:CO_2 = 4:1)

Kinetics



J.Y. Ahn et al, Fuel 250 (2019) 277–284

Product specifications



grid H_2 tolerance
2 < 6 vol.% (now ~ 0 %),
5 vol.% CO < 2 vol.%

Trade-off between Thermodynamics and Kinetics
+ catalyst lifetime
+ costs
+ specs …

Exothermal → favored by **high P** and **low T**

Yield > 97% for **T<300°C**

Catalyzed by Ni active sites

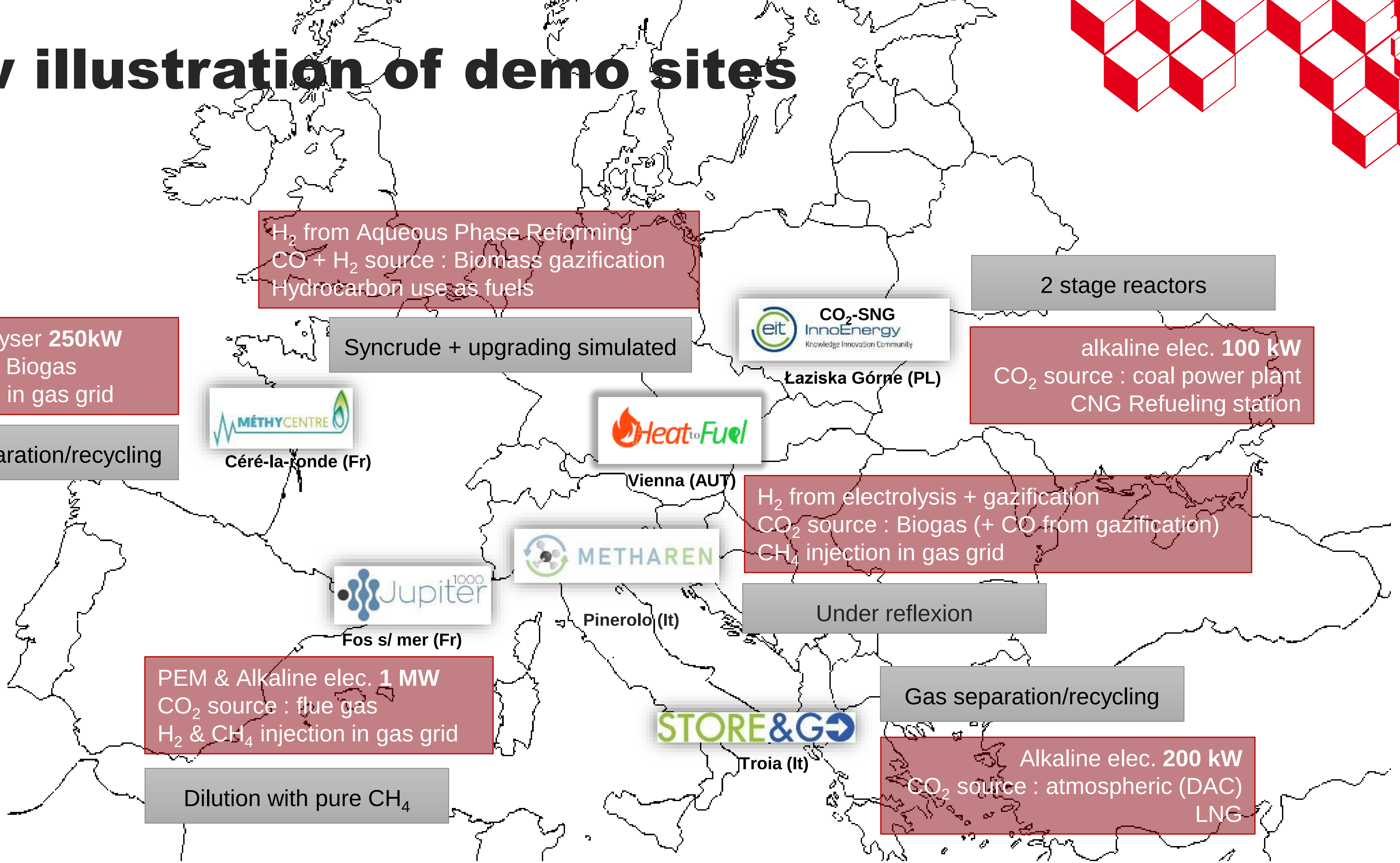
→ minimum activation temperature

T < 250°C

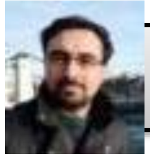
Active catalyst

Hard to reach in one reactor pass

Few illustration of demo sites

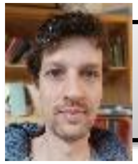


Any question ?



Parviz
HAJIYEV

Vincent
FAUCHEUX



Arthur
ROUSSEY

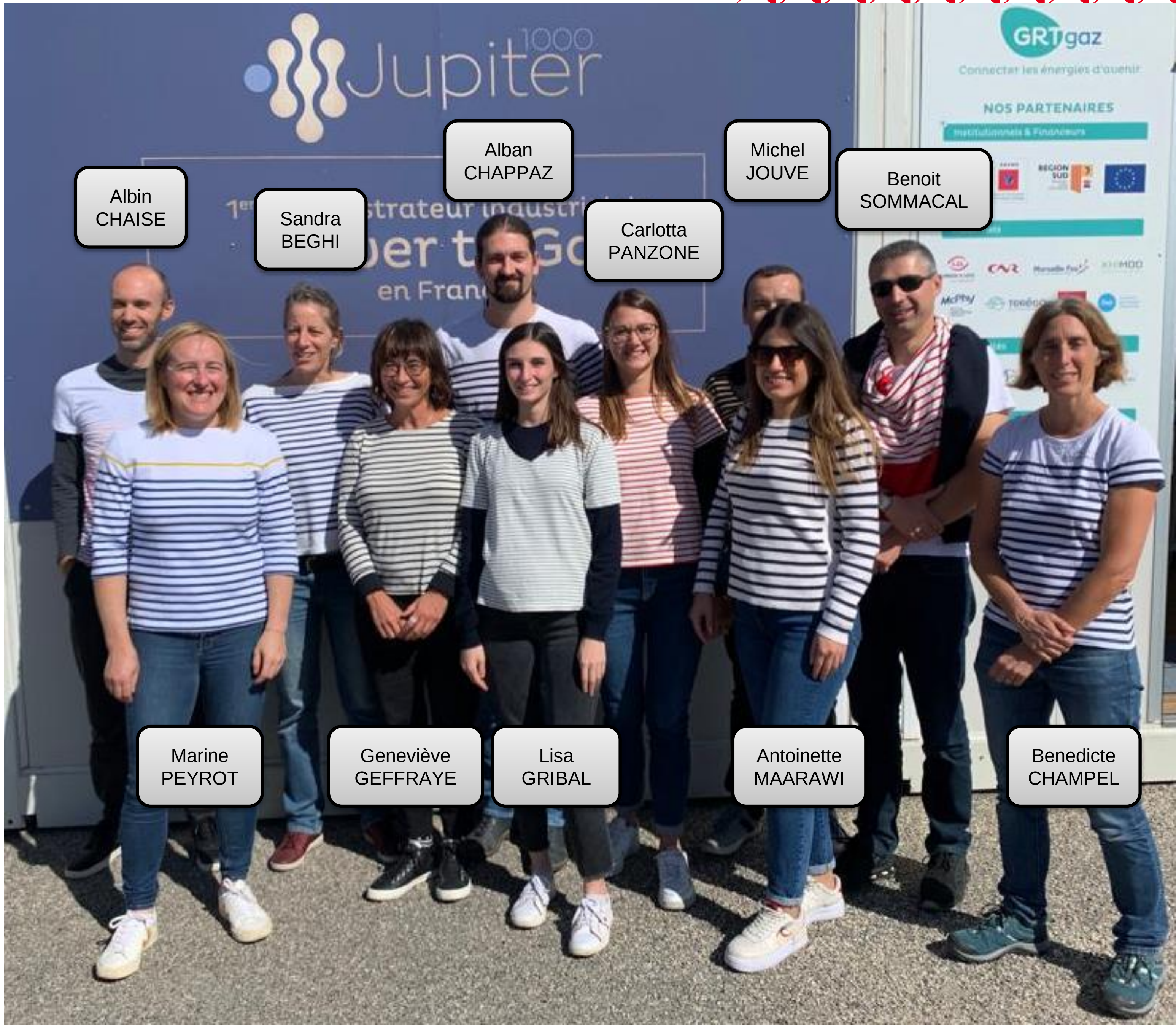
Isabelle
ROUGEAUX

Corentin
CHATELIER

Konstantin
TARASOV

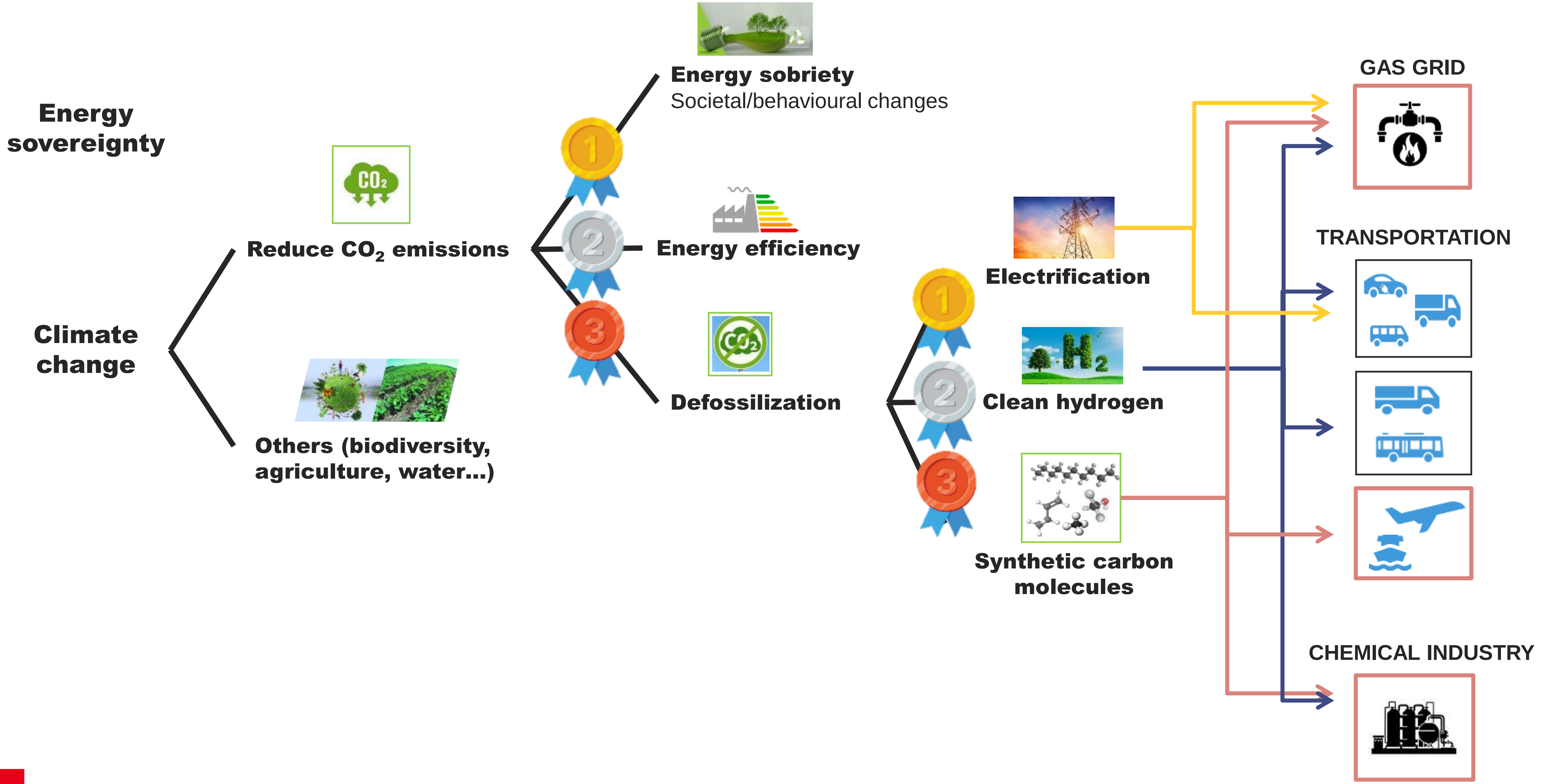
Elhassan
AMATERZ

ANDRÉ LUIZ
ALVARENGA MARINHO



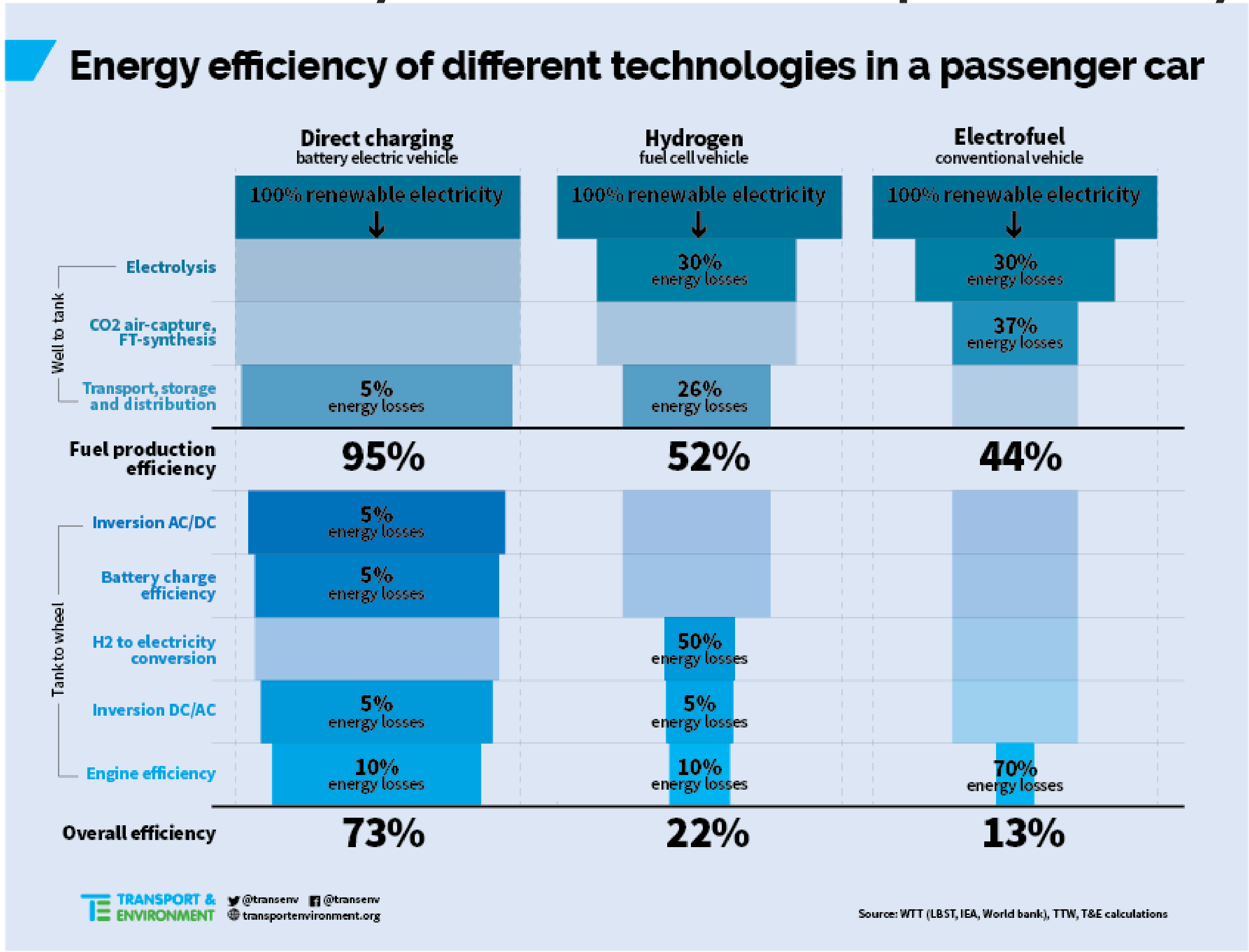
3. Energy efficiency Low duty vehicle case study

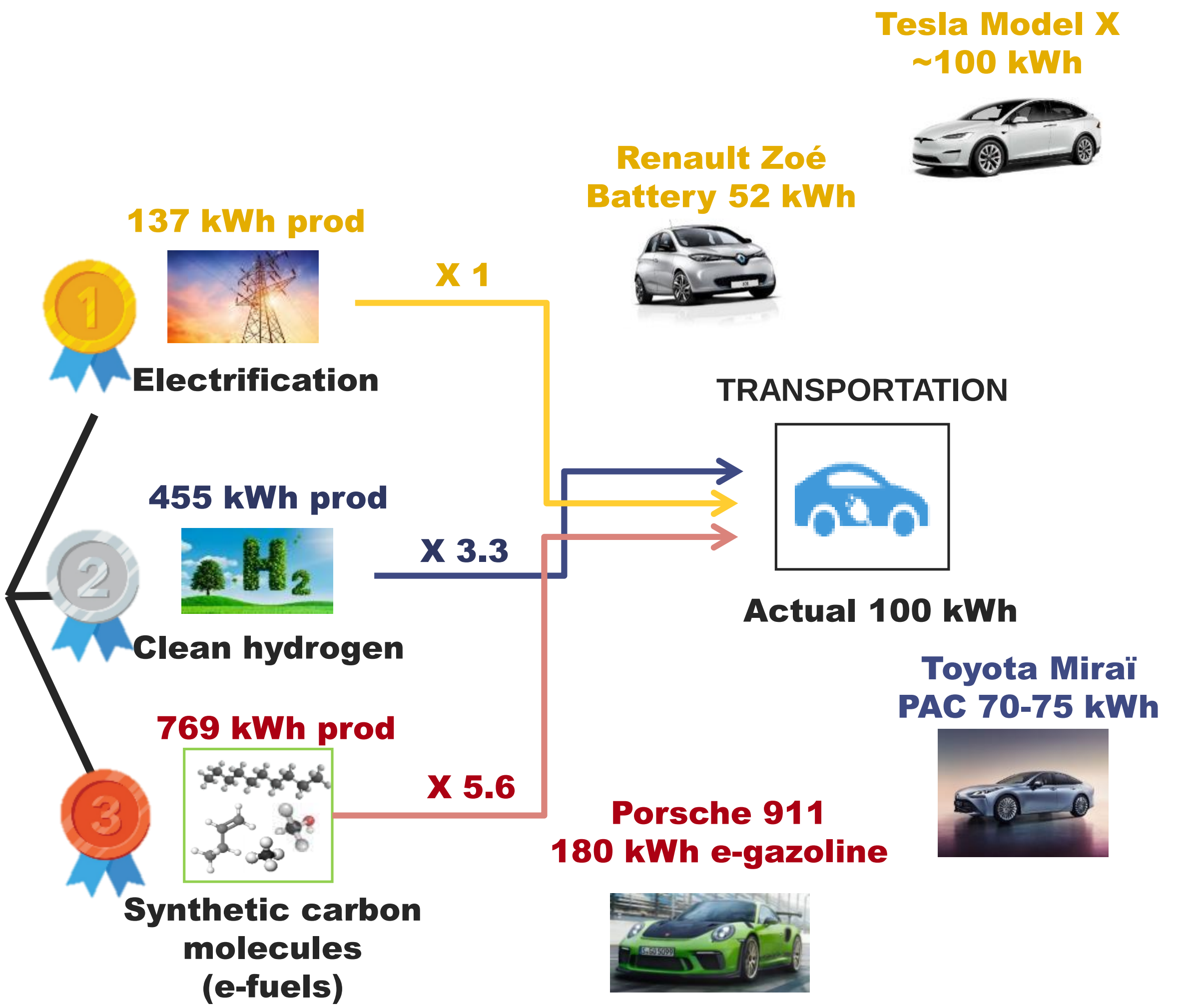
Prioritization of solutions for climate change



From IPCC, 2021: *Climate Change 2021: The Physical Science Basis*.

Efficiency of different pathways

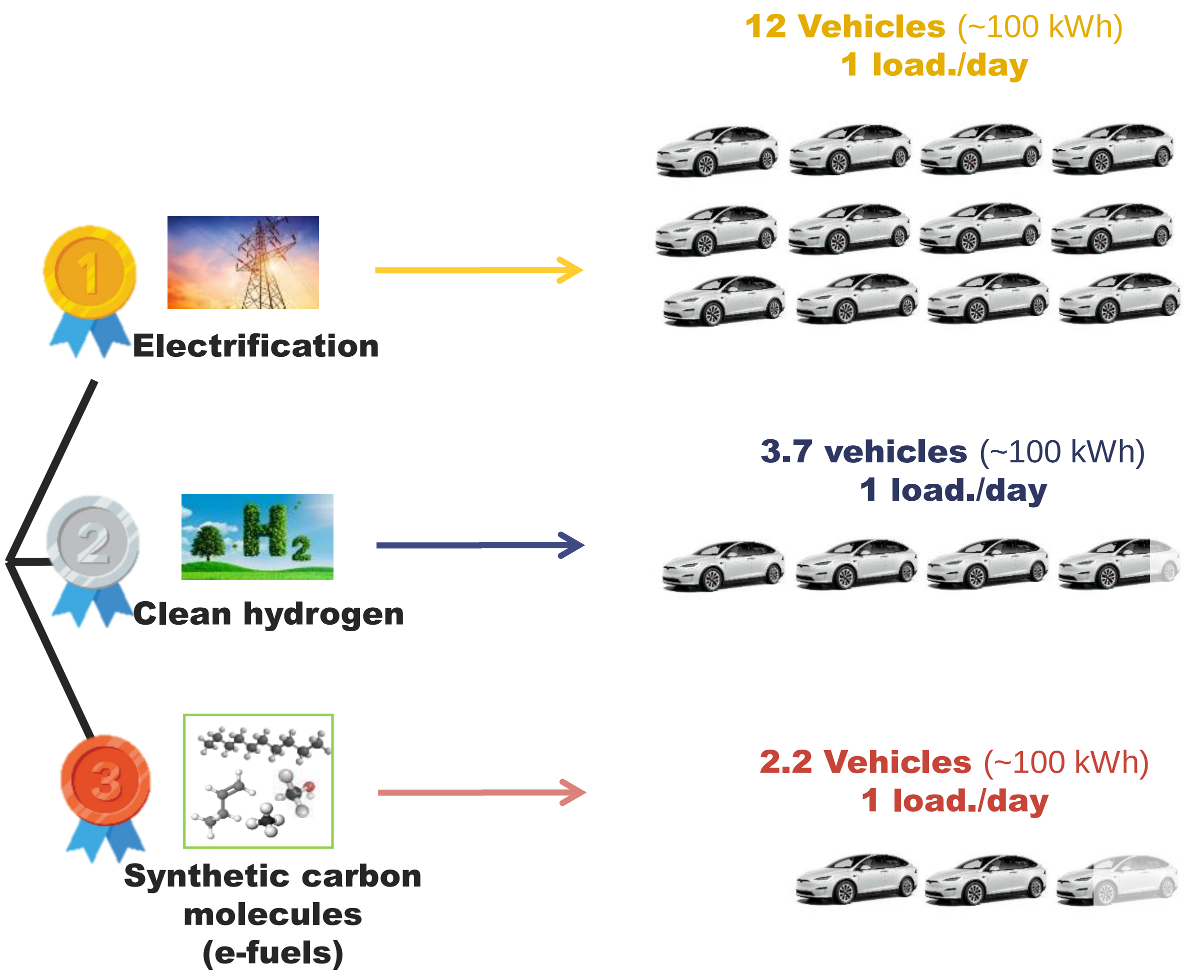




Carbon molecules will be needed in sectors where we don't have other choice ➔ **non-fossil sources of carbon molecules** Where **low carbon electricity** is **available**

Efficiency of different pathways

Grand Place extension, Grenoble
1730 m² PV panels → ~450 MWh annual production



Carbon molecules will be needed in sectors where we don't have other choice → **non-fossil sources of carbon molecules**

From IPCC, 2021*: Climate Change 2021: The Physical Science Basis*
Eberle U. et al., Angewangdte Chemie International Edition, 2009

Thank you

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liten.cea.fr