CURRENT STATUS OF CCU TECHNOLOGIES & ROLE OF HYDROGEN

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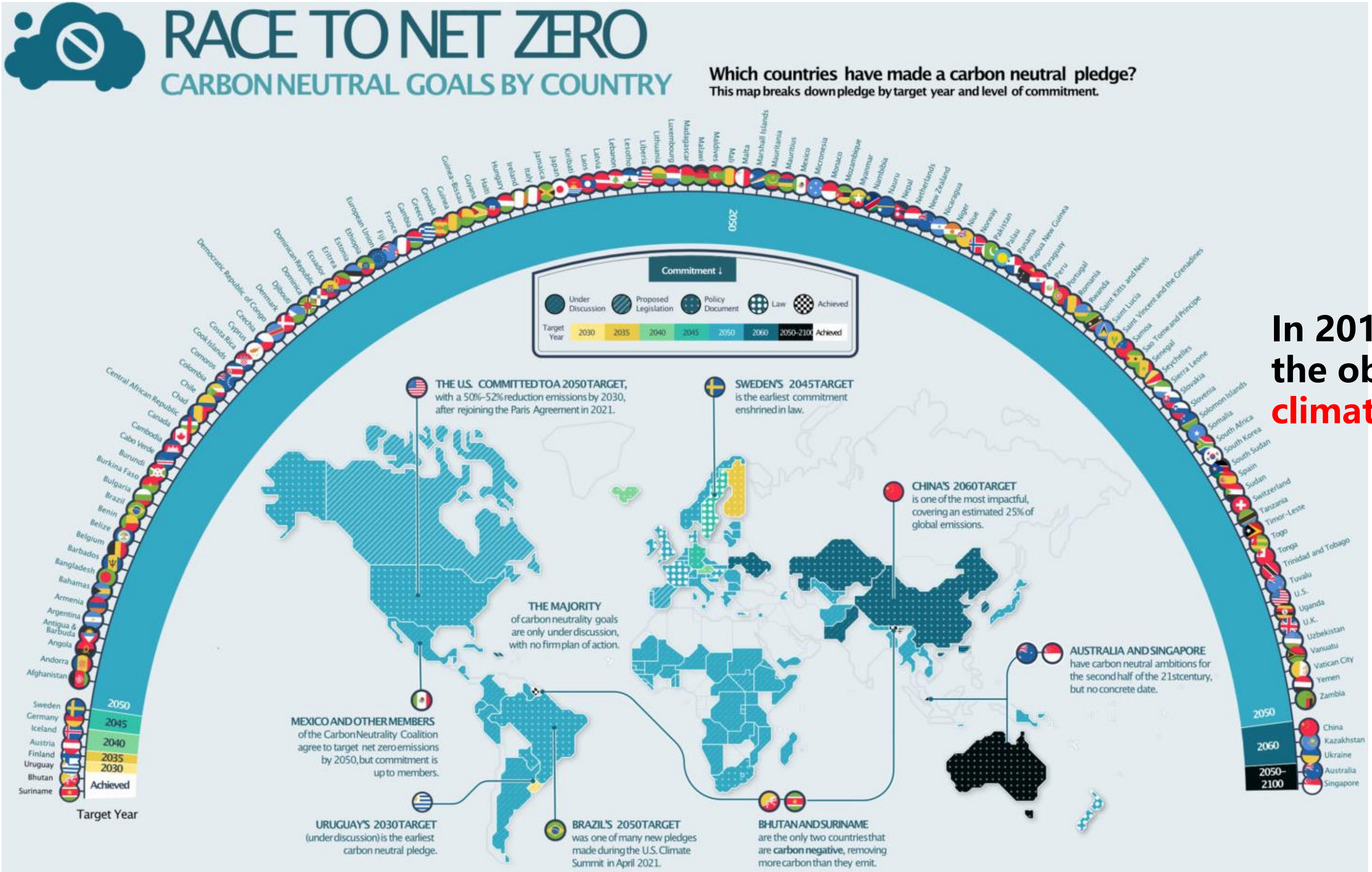
23/05/2022

OUTLINE

- The global challenges
- Possible solutions
- CO_2 conversion pathways
  - Electrochemical
  - Biological
- CO_2 to Fuel (Thermochemical)
- Technology comparison
- Global CCUS status

Carbon neutrality by 2050: the most urgent mission in the world



In 2019, EU leaders endorsed the objective of achieving a **climate-neutral EU by 2050.**

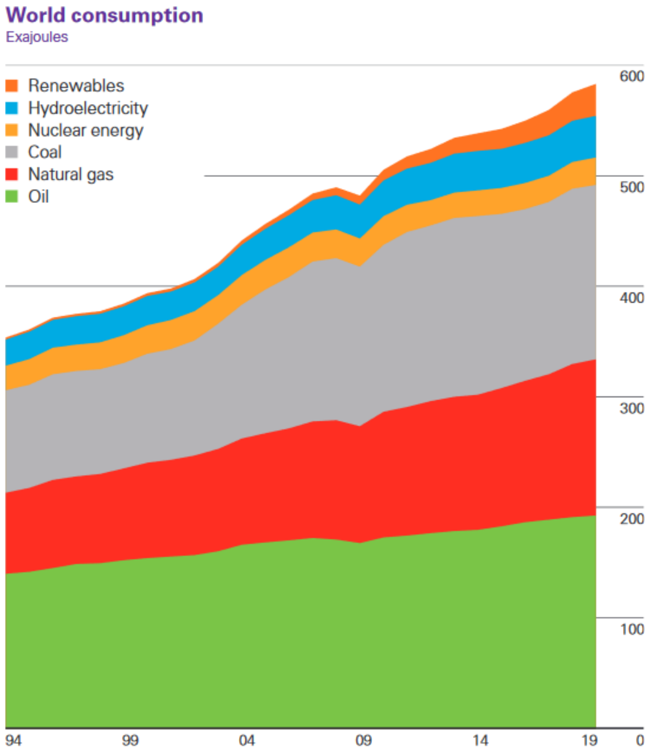
https://www.motive-power.com/npuc-resource/carbon-neutral-goals-by-country/

The energy ~~transition~~ revolution is on-going but it won't be easy…

2 objectives in contradiction:

- Limit GHG emissions
- Meet the worldwide increasing energy demand!

Meeting the increasing demand is already a challenge in itself!



5%
6.5%
4.3%
27%
24.2%
33%

BP Statistical Review of World Energy 2020.

CHEMICAL ENGINEERING

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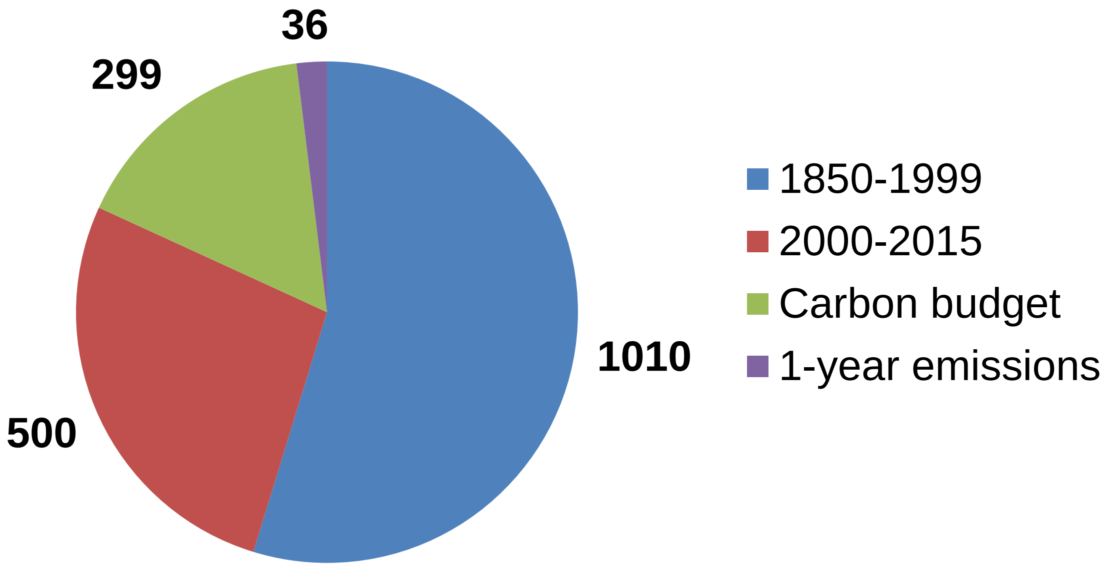
CO_2 Budget

Budget by 2050 for having 80% chances to stay below 2 °C



Note: Values in Gt CO_2 eq

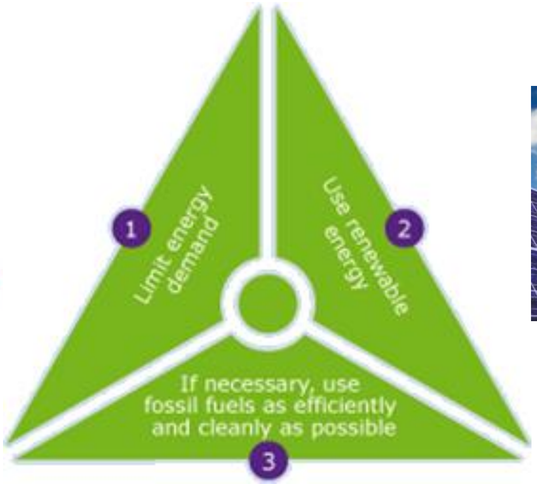
IPCC, SR15 (2018).

Reaching climate neutrality won’t be easy…

- Belgium CO_2 emissions ~ 100 Mt/a
- This corresponds to ~ 8.6 t/hab.a
  - => Everyday, each of us puts 24 kg CO_2 into the environment !!

- Source: Our world in data
  - Related reference: https://doi.org/10.5194/essd-12-3269-2020
  - https://ourworldindata.org/co2/country/belgium
  - https://ourworldindata.org/co2-emissions

Possible answers: Trias Energetica



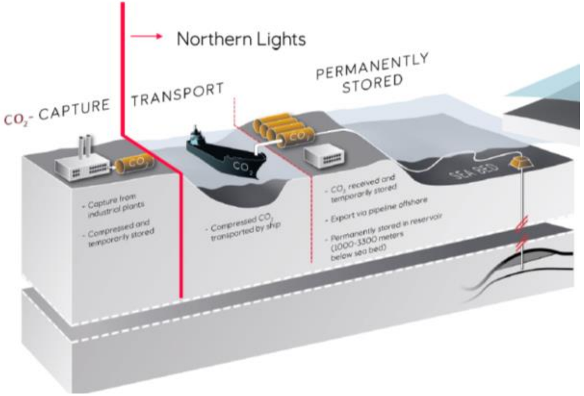
Lysen E., The Trias Energica, Eurosun Conference, Freiburg, 1996

CO_2 capture

- It's a question of fluid separation!
  - Sources usually contain CO_2, N_2, H_2O, H_2, CH_4, O_2 …
  - CO_2 concentration varies between 0.04% and almost 100%
  - Mature (exist for >50 years) & flexible, but costly!

And then, what with the CO_2: waste or feedstock?

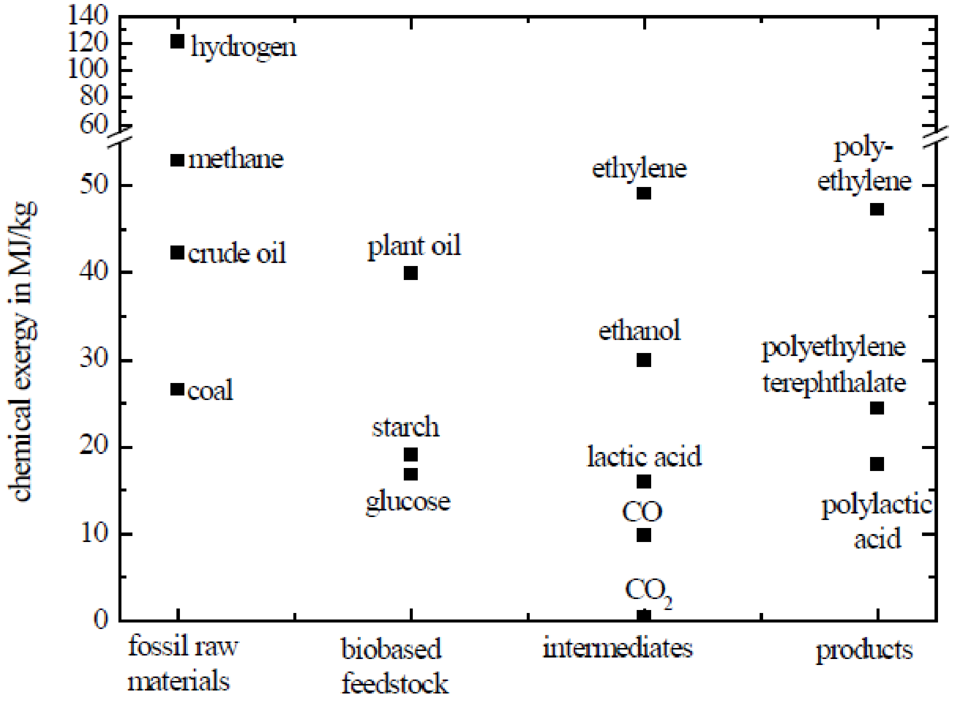
- CCS (excluding EOR) is a cost only technology!
  - Requires infrastructure off-site (pipelines, ships, storage sites determined by geology)
  - Basically permanent landfilling
  - Any better idea?



- We'll need CO_2 as a source for carbon!
  - Our society is based on carbon
  - If we ban fossils, we can get carbon only from
    - Biomass
    - CO_2

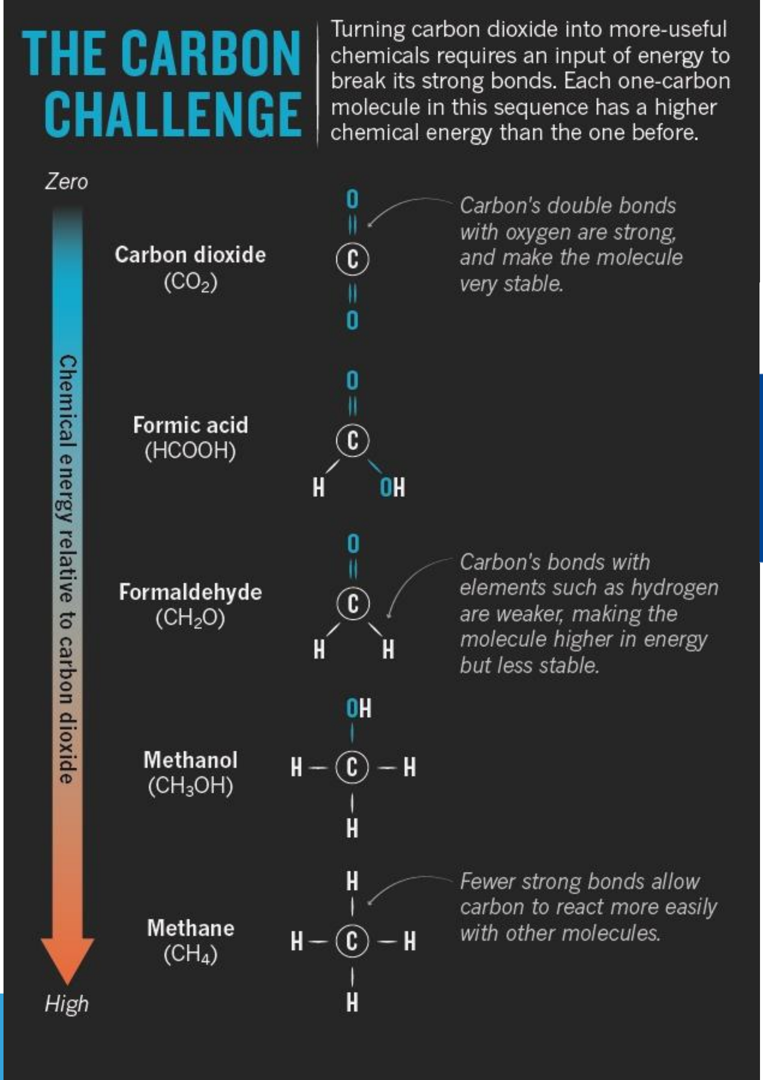
Main CO_2 re-use pathways

- Direct use, no transformation
- Biological transformation
- Chemical transformation
  - To lower energy state
    - Carbonatation
  - To higher energy state



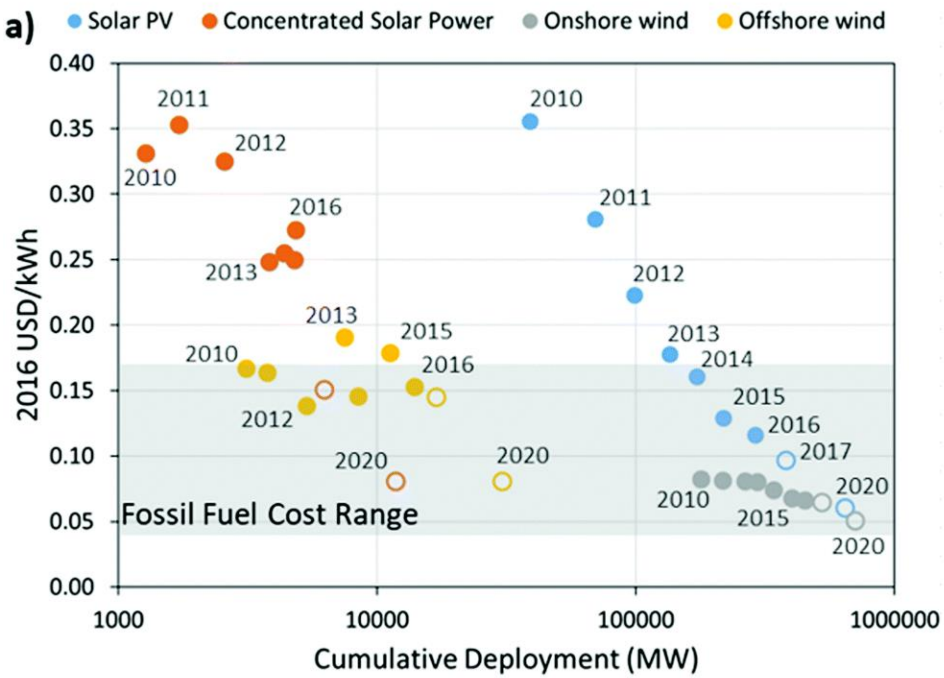
=> At large scale, need to make sure that energy comes from renewables!

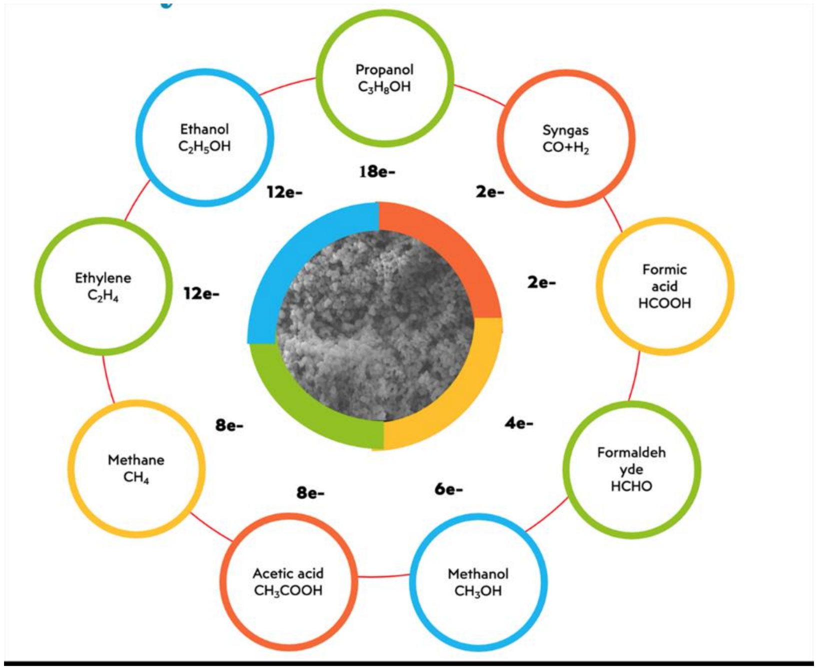
Frenzel et al, 2014. Doi:10.3390/polym6020327



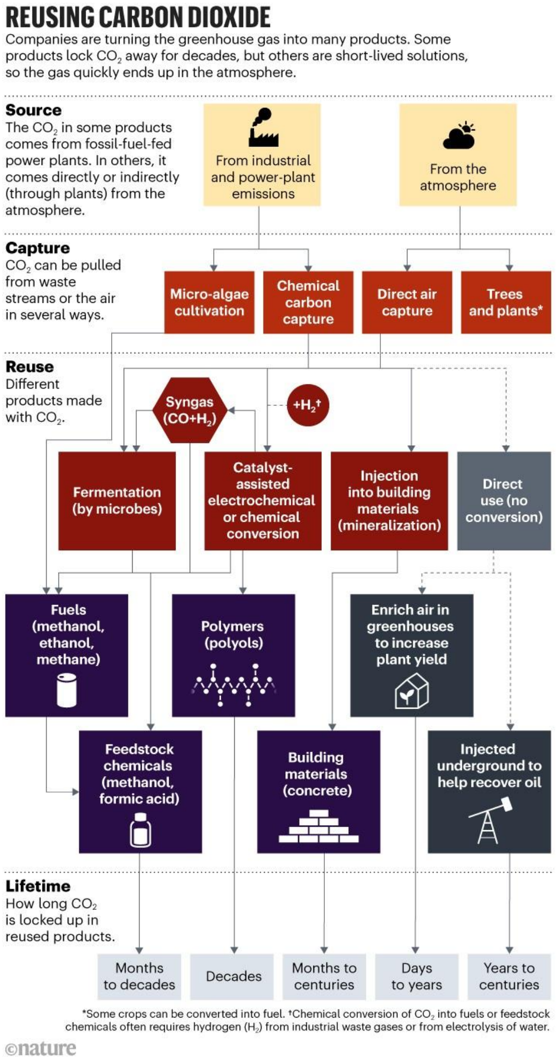
Lim, 2015. How to make the most of Carbon dioxide. Nature, 526, 628–630

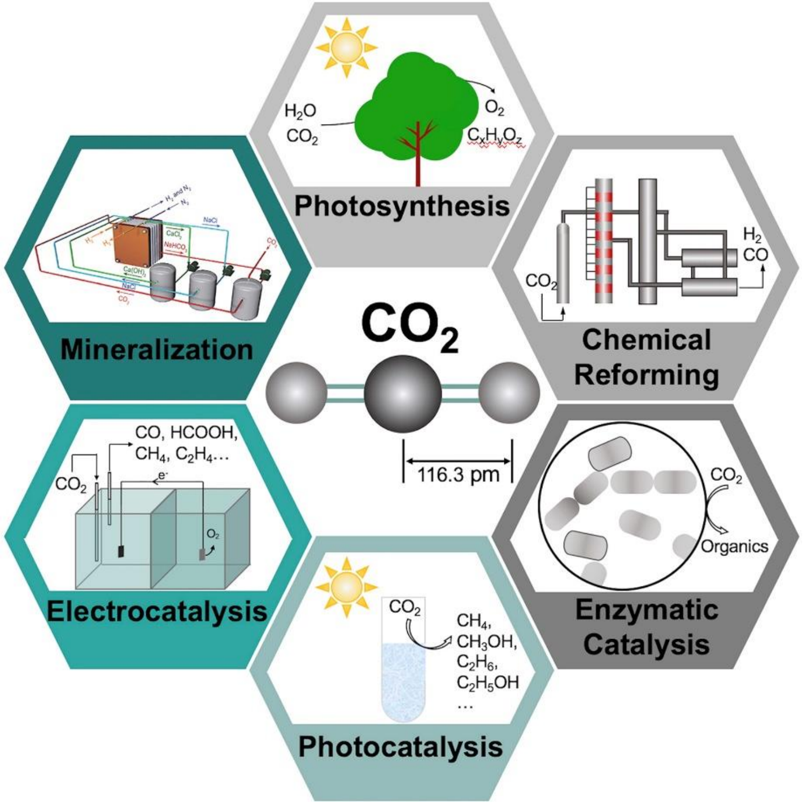
LEVELIZED COST OF SOLAR AND WIND DERIVED POWER VERSUS DEPLOYED CAPACITY





Grim et al., 2020. Transforming the carbon economy: challenges and opportunities in the convergence of low-cost electricity and reductive CO_2 utilization. Energy & Environmental Science, 13(2), pp.472-494.

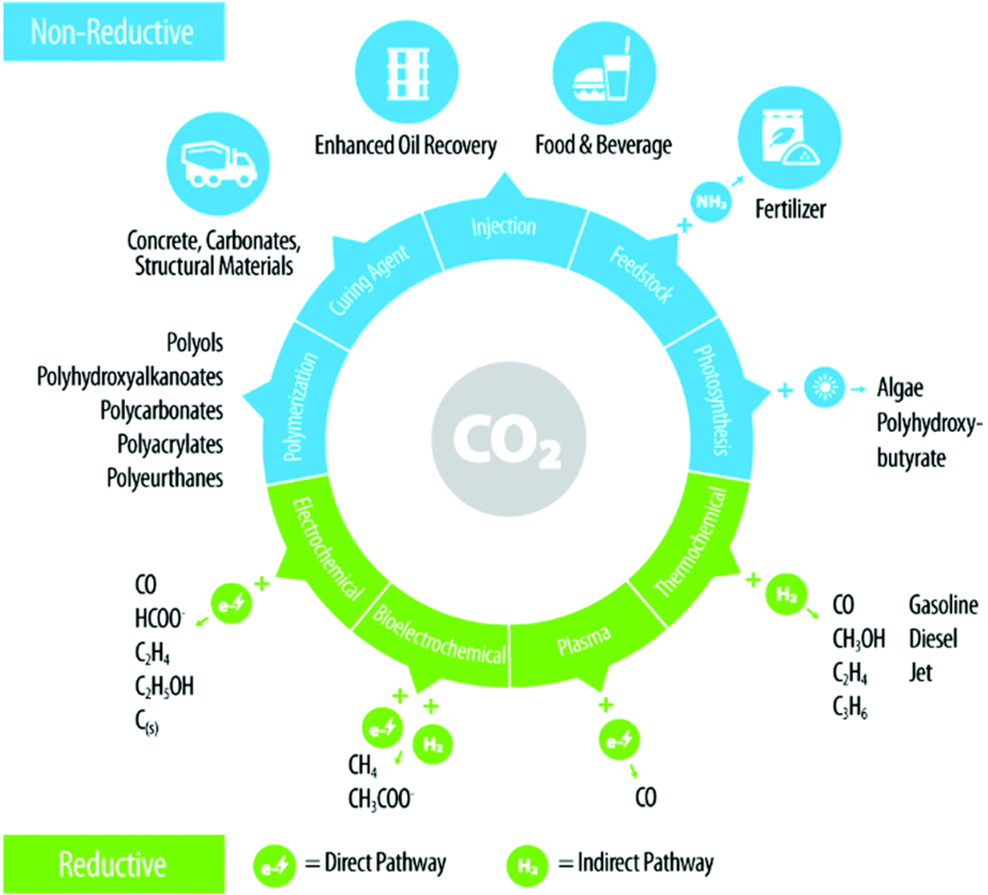




Wang et al., 2018. *Joule*, 2(12), pp.2551-2582

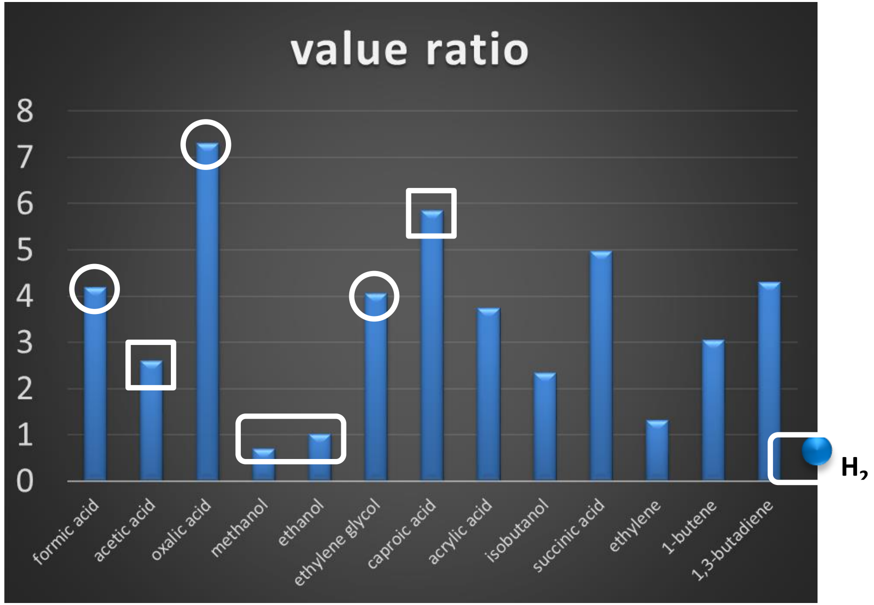
Peplow, M., 2022. *Nature*, *603*(7903), pp.780-783.

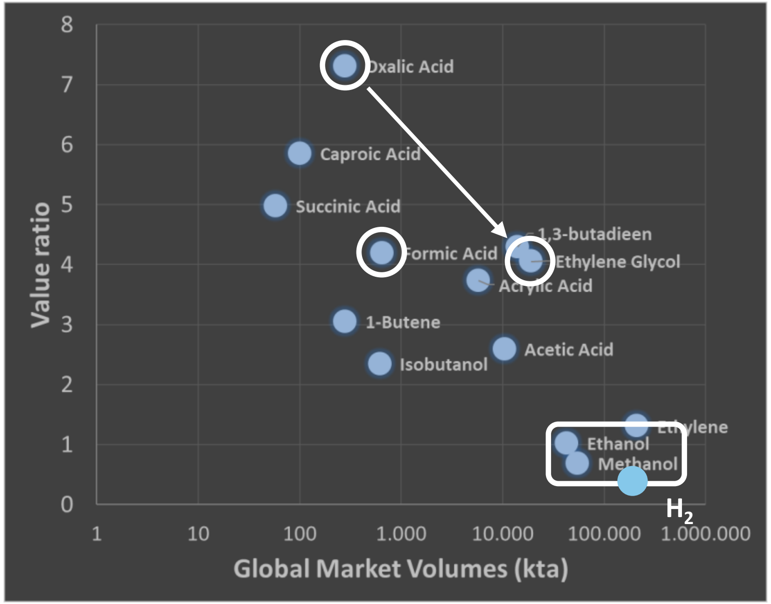
REDUCTIVE AND NON-REDUCTIVE PATHWAYS FOR CO_2 CONVERSION



Grim et al., 2020. Transforming the carbon economy: challenges and opportunities in the convergence of low-cost electricity and reductive CO_2 utilization. Energy & Environmental Science, 13(2), pp.472-494.

VALUE-DRIVEN CO_2 CONVERSION



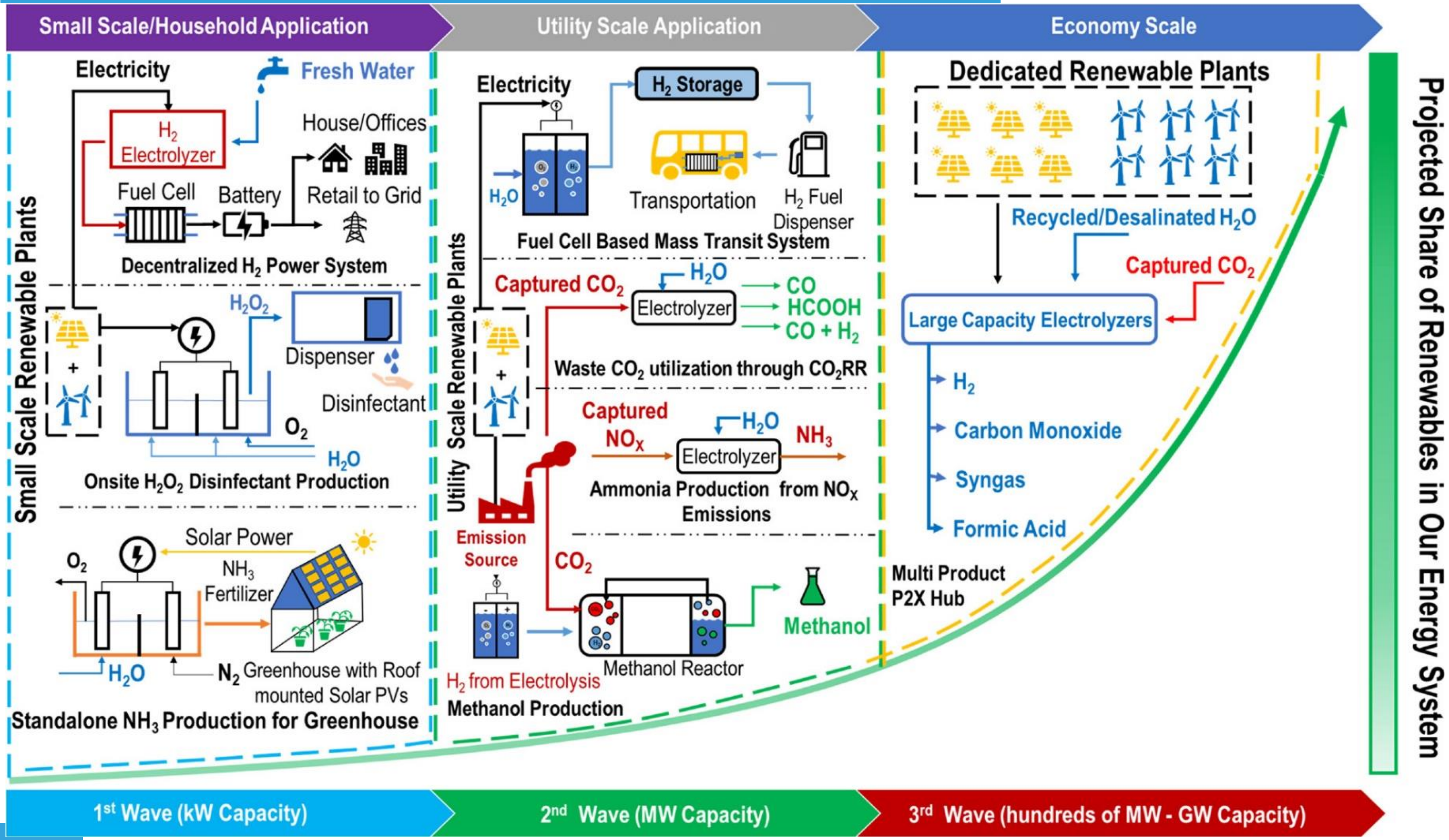


Profit potential relates to:

$$\text{Value Ratio} = \frac{\text{Market price}}{\text{Unavoidable cost}}$$

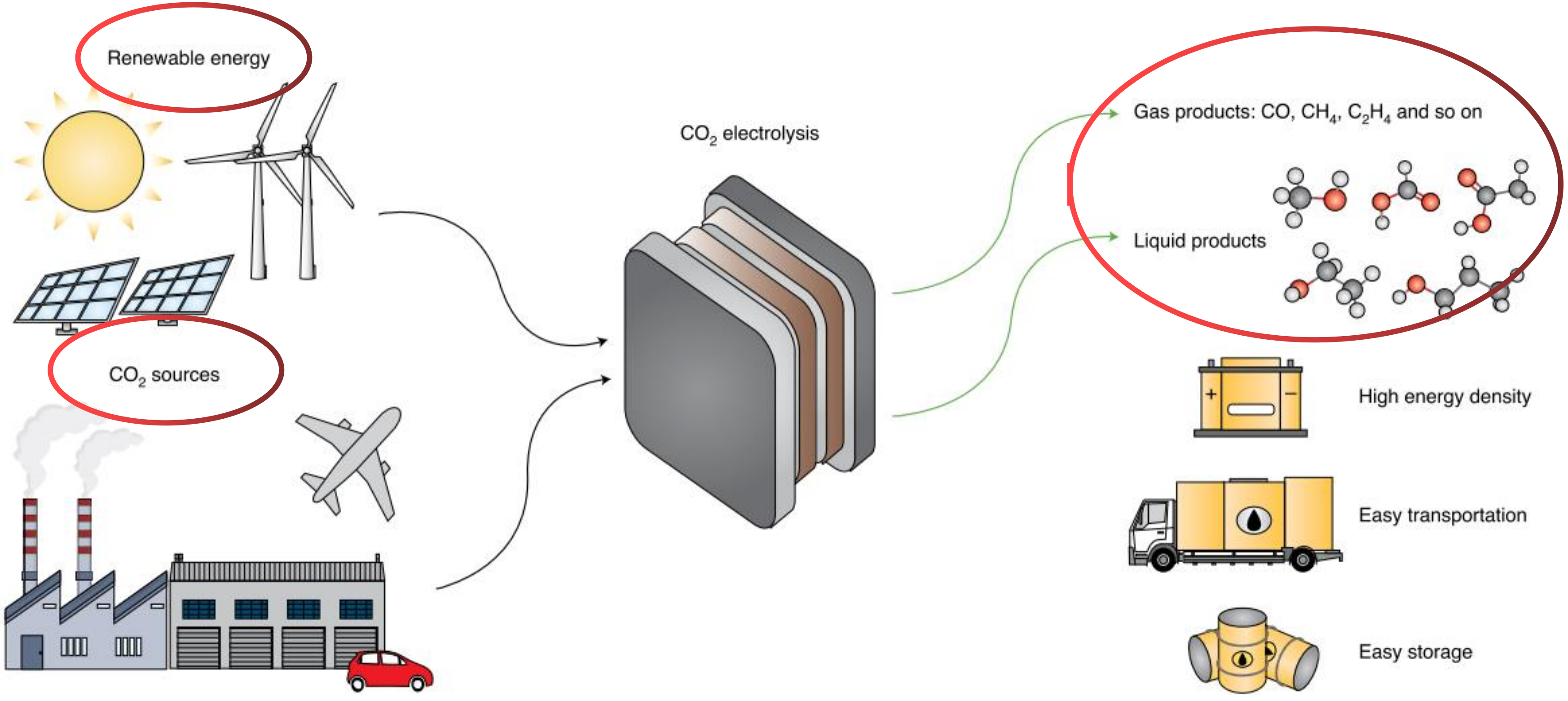
- **Formic acid:** small market, but H_2 carrier and ‘liquid syngas’
- **Oxalic acid:** small market, but high value/volume derivatives
- **Fuels:** legislation, incentives / large market

POWER2X DEPLOYMENT ROADMAP



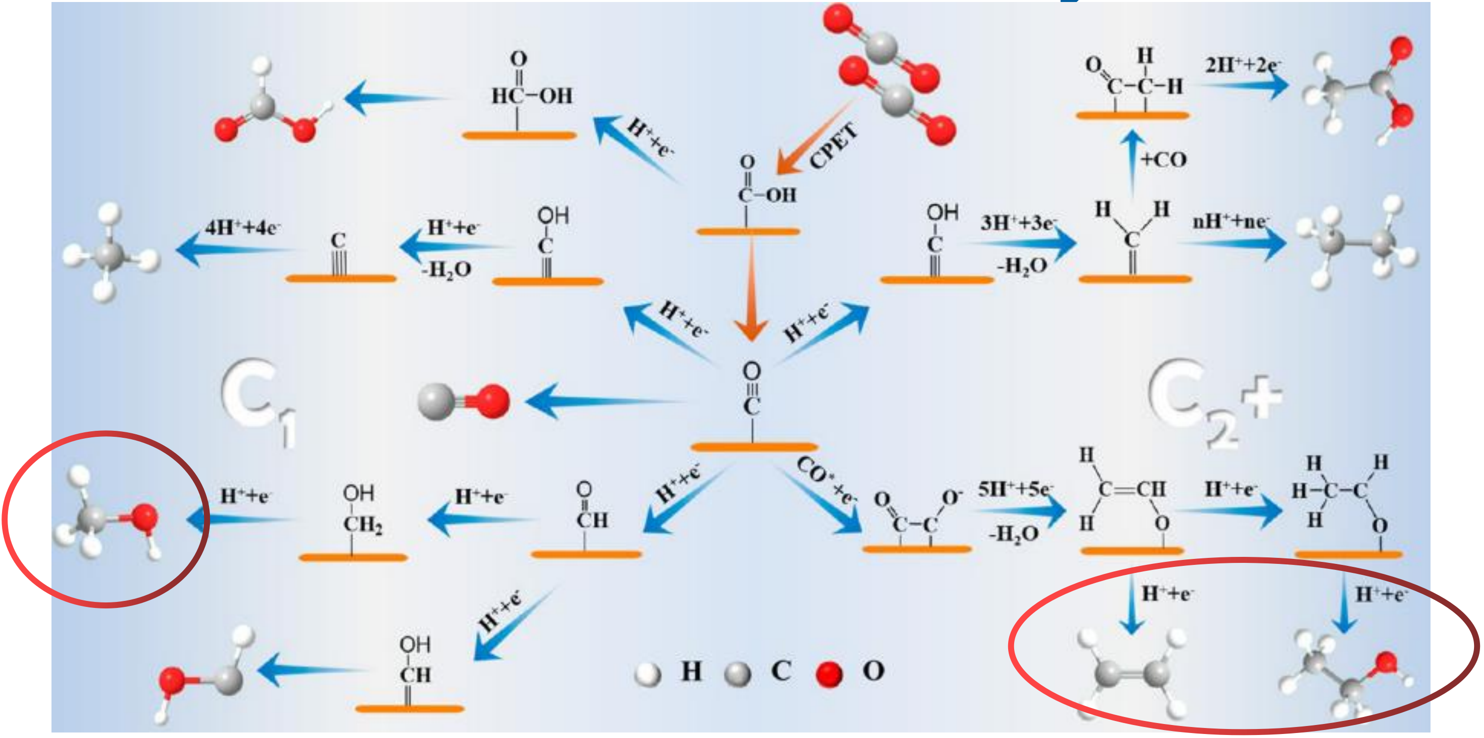
Daiyan et al., 2020. Opportunities and Challenges for Renewable Power-to-X. ACS Energy Letters, 5(12), 3843-3847.

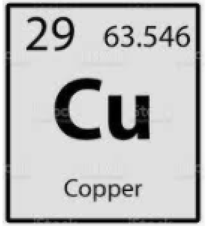
Electrochemical CO_2 reduction reaction

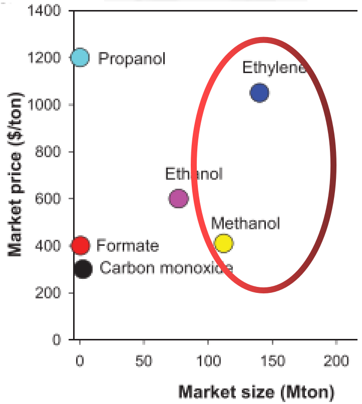


Haotian Wang* et al. Nature Catalysis | VOL 4 | NOVEMBER 2021 | 943–951

Copper-based catalysts, high selectivity for valuable fuels and chemicals, ethylene and alcohols





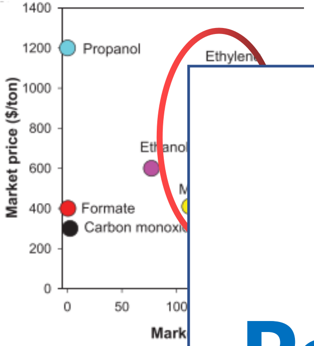


Edward H. Sargent* et al. Adv. Mater. 2019, 31, 1807166

The binding energy of Cu to the intermediate is neither strong nor weak.

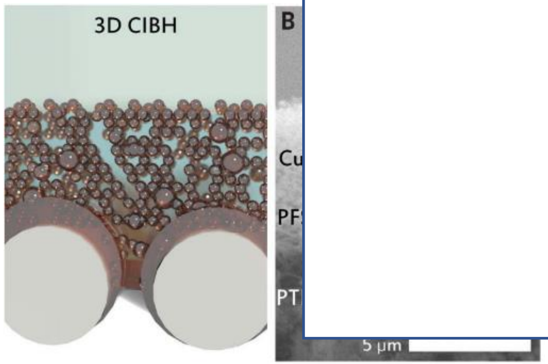
Wenxing Chen* et al. ACS Energy Lett. 2021, 6, 3992–4022

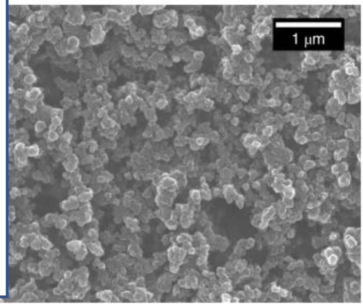
What it takes for industrialization?



Target performance metrics:

Poor stability mostly less than 50 h!





World record of current density

Current density of 1.3 A cm^{-2}

But FE of 45%, Cell voltage ~ 4.5 V

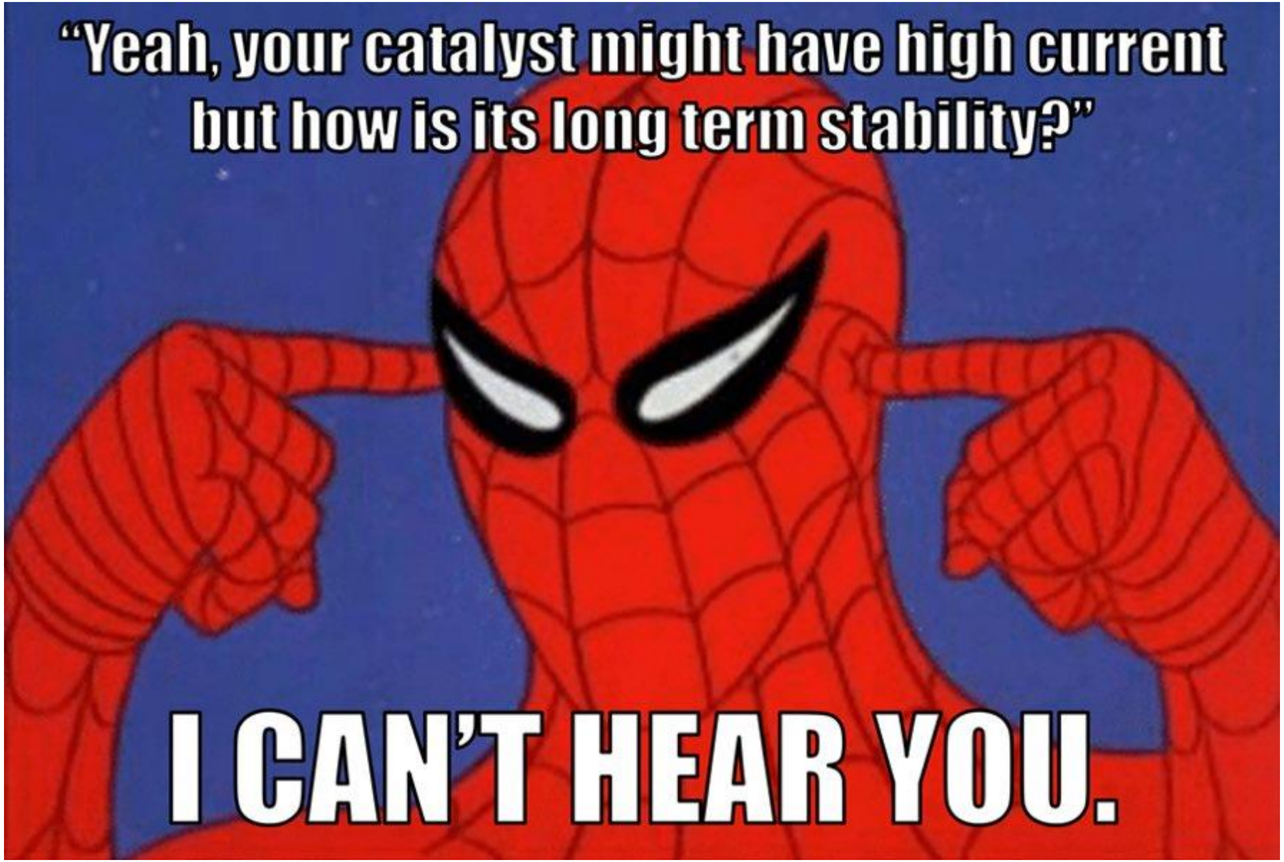
World record of FE

FE of 87%, Current density of ~32 mA cm^{-2}, Cell voltage of 2.02 V

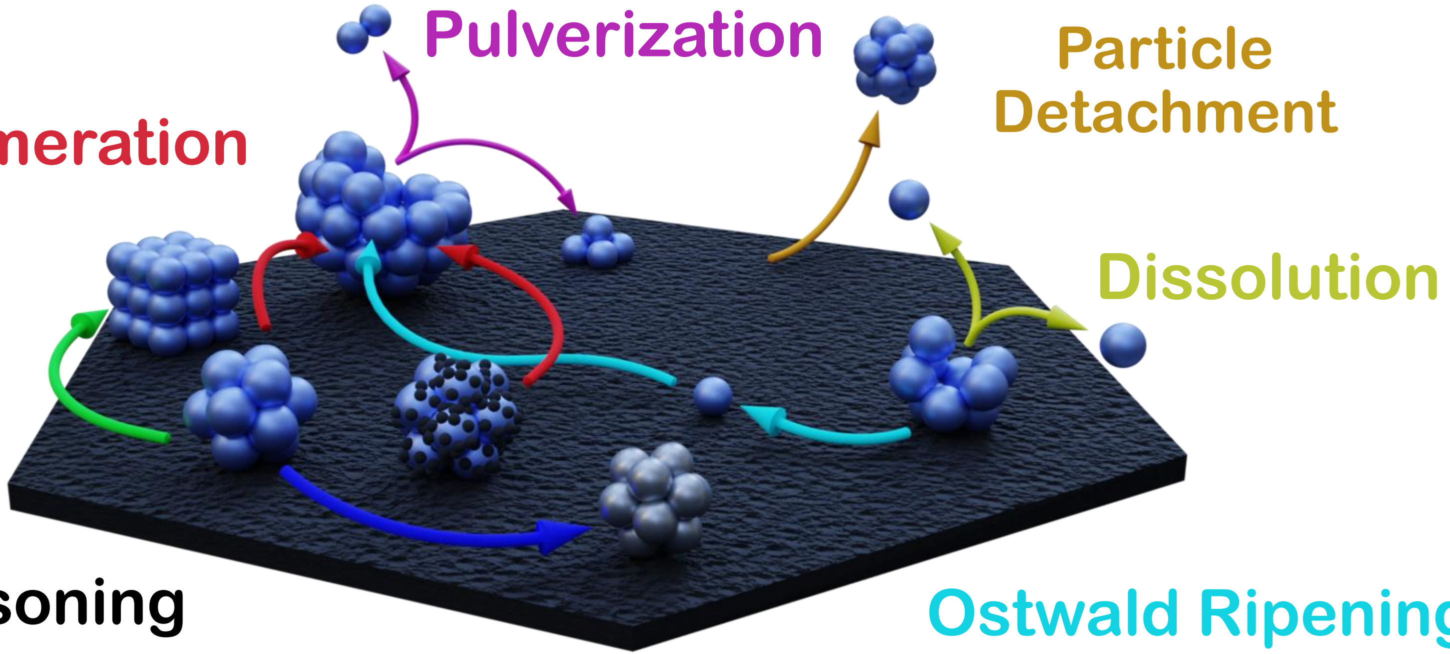
García de Arquer et al., Science 367, 661–666 (2020)

Andrew A. Gewirth* et al. Nature Catalysis| VOL 4 | JANUARY 2021 | 20–27

CURRENT DENSITY VS STABILITY



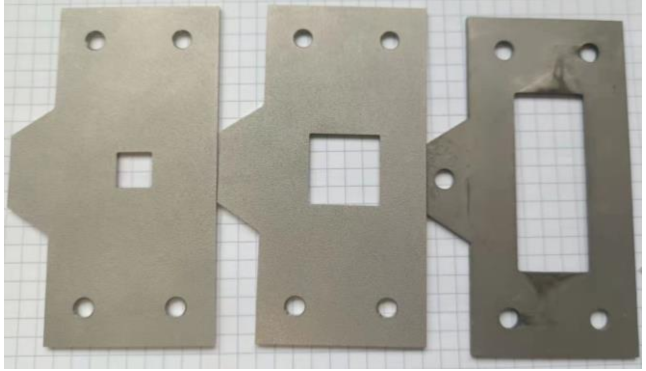
Degradation Mechanisms



SnO_2 Reduction

ELCAT
Applied Electrochemistry & Catalysis
University of Antwerp

Van Dale et al., 2021. Sn-Based Electrocatalyst Stability. ACS Energy Letters, 6, 4317-4327.

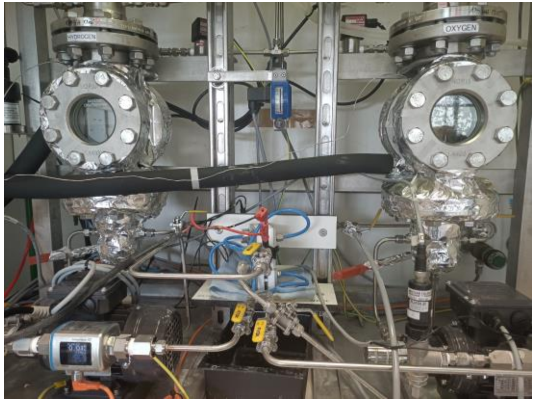


From lab scale:

1 cm^2, 4 cm^2, 10 cm^2

To Pilot scale:

20 cm^2 up to 600 cm^2

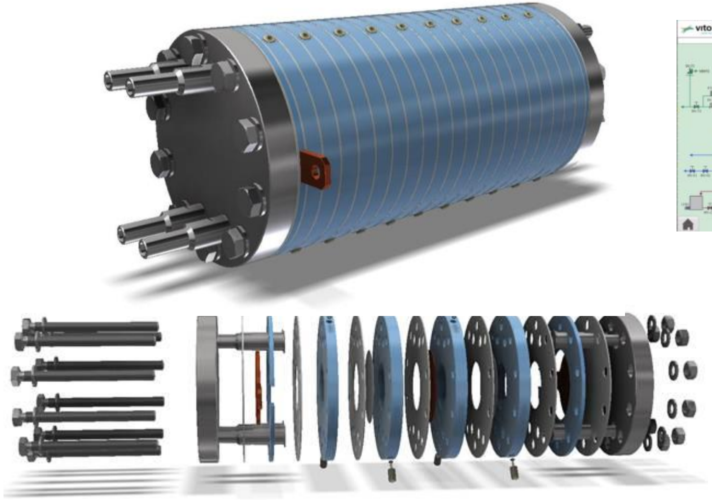


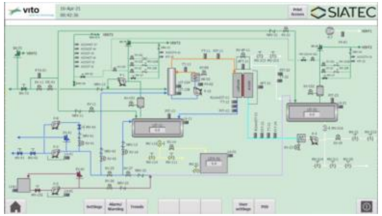
Booster: 20V 20A

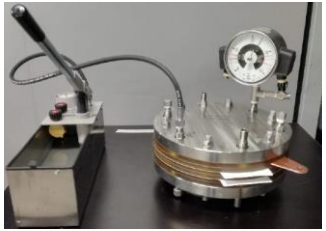
High pressure reactor: 20

CO2 ELECTROLYZERS

- H2020 **LOTER.2M** and ETF **PROCURA** projects TRL 6 - 5 kW pilot in progress today
- **ECO2FUEL** Green Deal project: 50 kW electrolyzer in 2023
- Towards renewable fuels – ranges (e.g. methanol, C_1-$C_{4,}$ …), also gasses: H_2, CO, …
  - 50 kW (5000 h/y): 20 t methanol/y (100 % select., 50 % η^{energy})

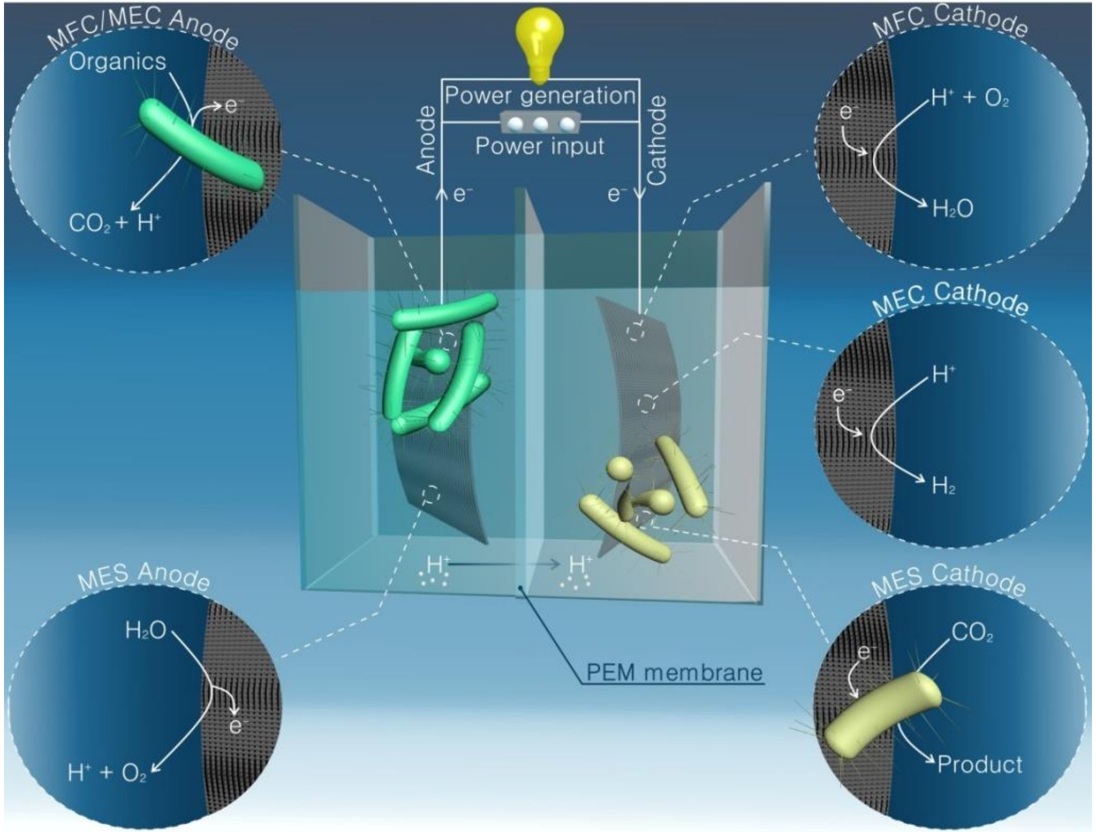






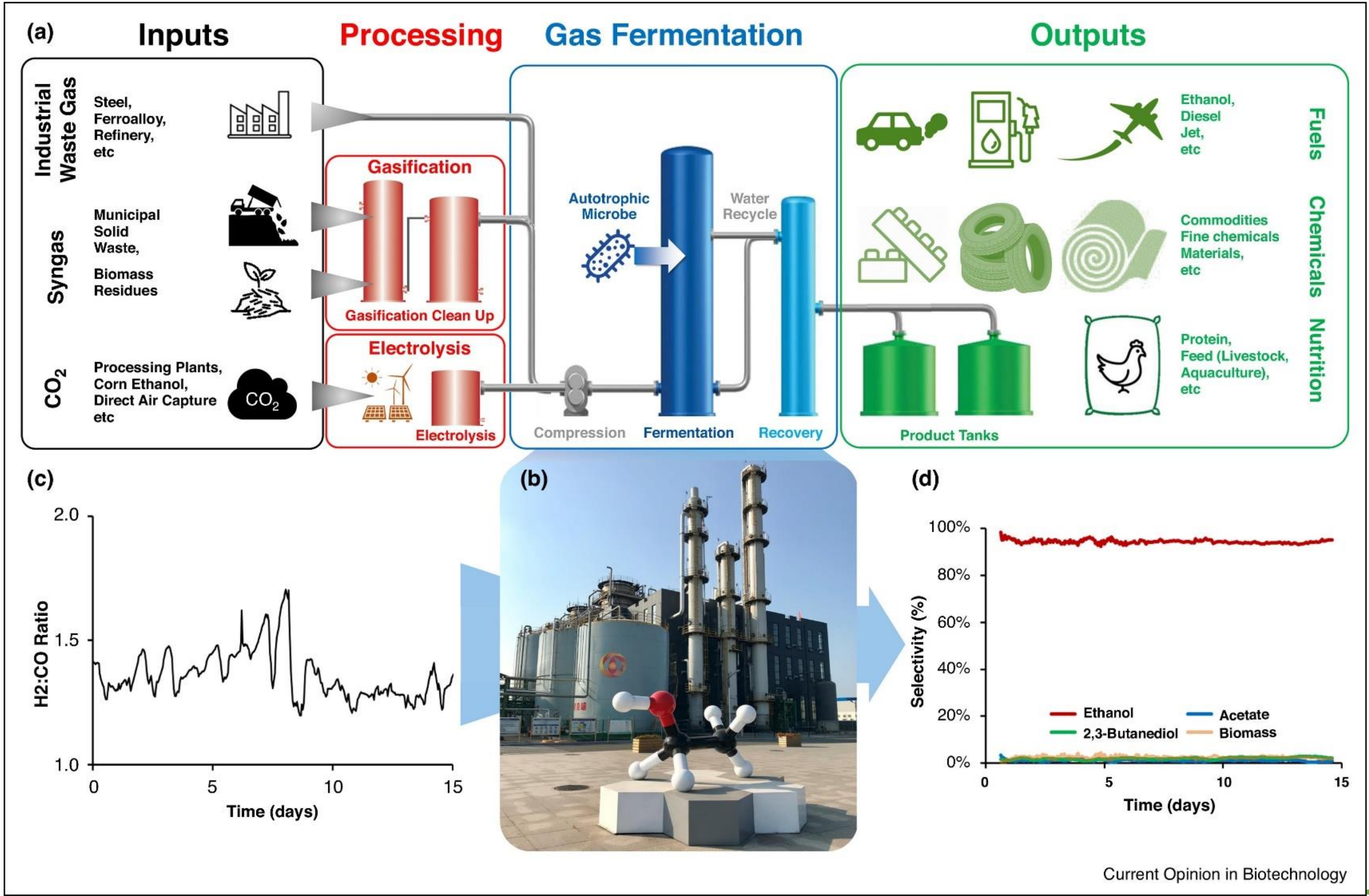
DEMONSTRATOR CONSTRUCTION

BES FOR BIOLOGICAL AND ENZYMATIC CONVERSIONS



Katuri et al. 2018, Adv. Mat. 30 (1707072), 1-18

L A N Z A T E C H



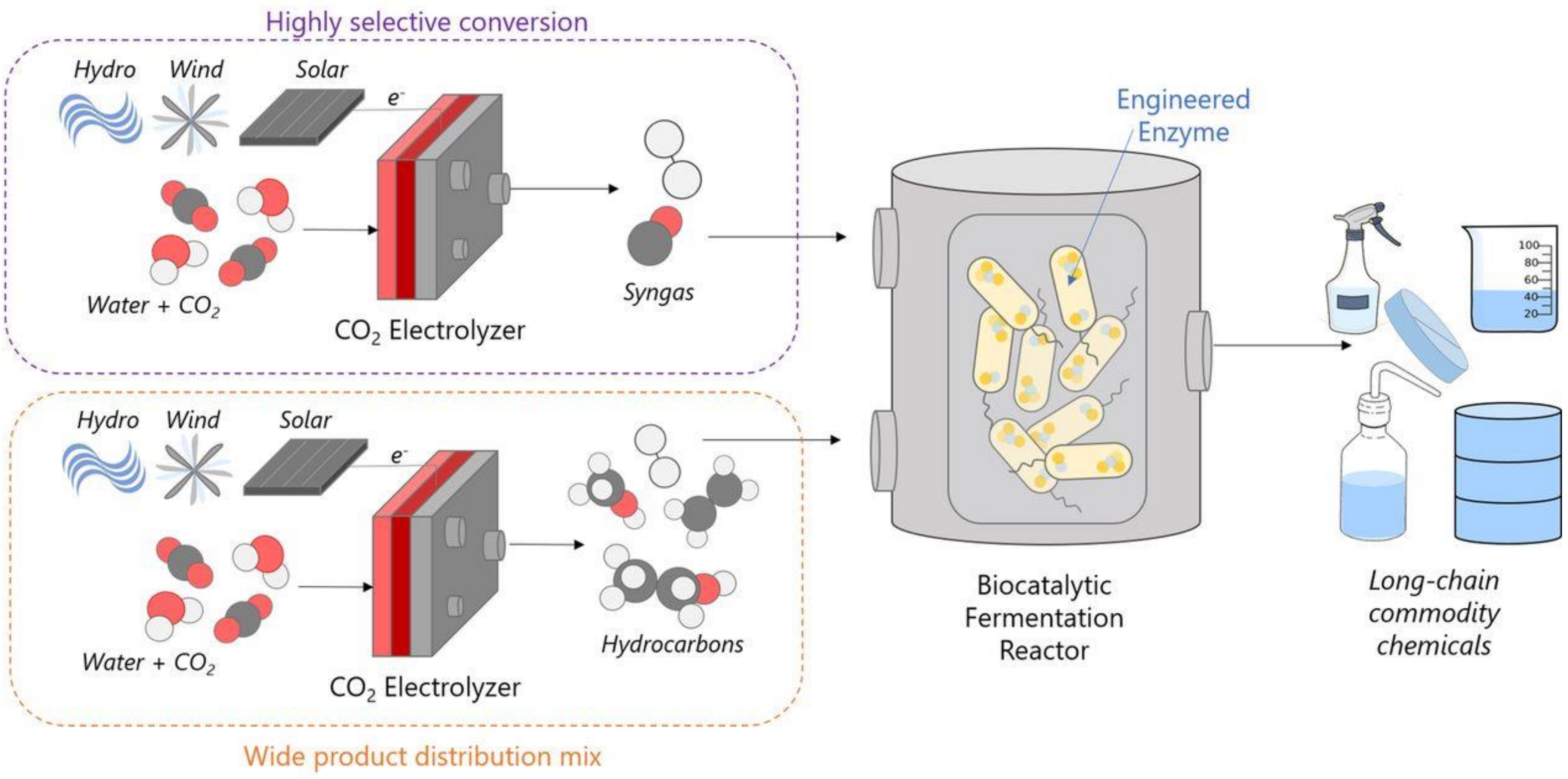
Köpke, M. and Simpson, S.D., 2020. Pollution to products: Recycling of “above ground” carbon by gas fermentation. Current Opinion in Biotechnology, 65, 180-189.

BIOCHEMICALS AND BIOFUELS OBTAINED FROM CO2 IN MES

Product	Highest production rate (g/(L·d))	Main carbon sources	pH	T (°C)	Potentiostatic control (V *vs.* SHE)	Galvanostatic control (mA/cm²)	Cathode	Reference
Acetate	77	$NaHCO_3$	5.2	35	-1.10	n.a	3D-reticulated vitreous carbon	Jourdin et al. (2016)
Butyrate	5.70	CO_2:N_2 30:70 %	5.8	32	-0.85	-5 to -12	Carbon felt	Jourdin et al. (2019)
Caproate	2.41	Ethanol, CO_2 and $NaHCO_3$	7.0	30	n.a.	-1.0	Carbon felt	Jiang et al. (2020)
Butanol	0.06	CO_2	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
Ethanol	0.18	CO_2	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
	0.05	CO_2	5.4	25	-0.80	n.a.	Granular graphite	Blasco-Gómez et al. (2019)
Isopropanol	0.06	CO_2:N_2 10:90%	5.0	30	n.a.	-0.5	Carbon felt	Arends et al. (2017)
Methane	12.5^b	$NaHCO_3$	7	30	n.a.	-1.0 to -3.5	Graphite felt	Geppert et al. (2019)

Dessi et al., 2021. Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO2 emissions. Biotechnology Advances, 46, p.107675.

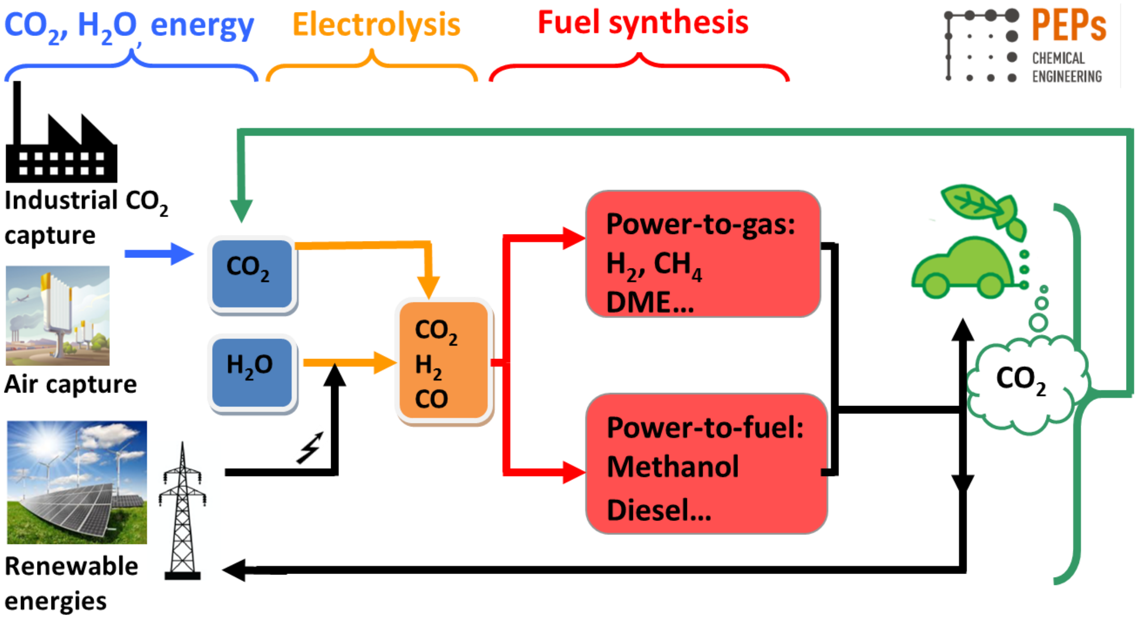
COMBINING ELECTROCONVERSION WITH BIOCONVERSIONS



De Luna et al., 2019. What would it take for renewably powered electrosynthesis to displace petrochemical processes? Science, 364(6438).

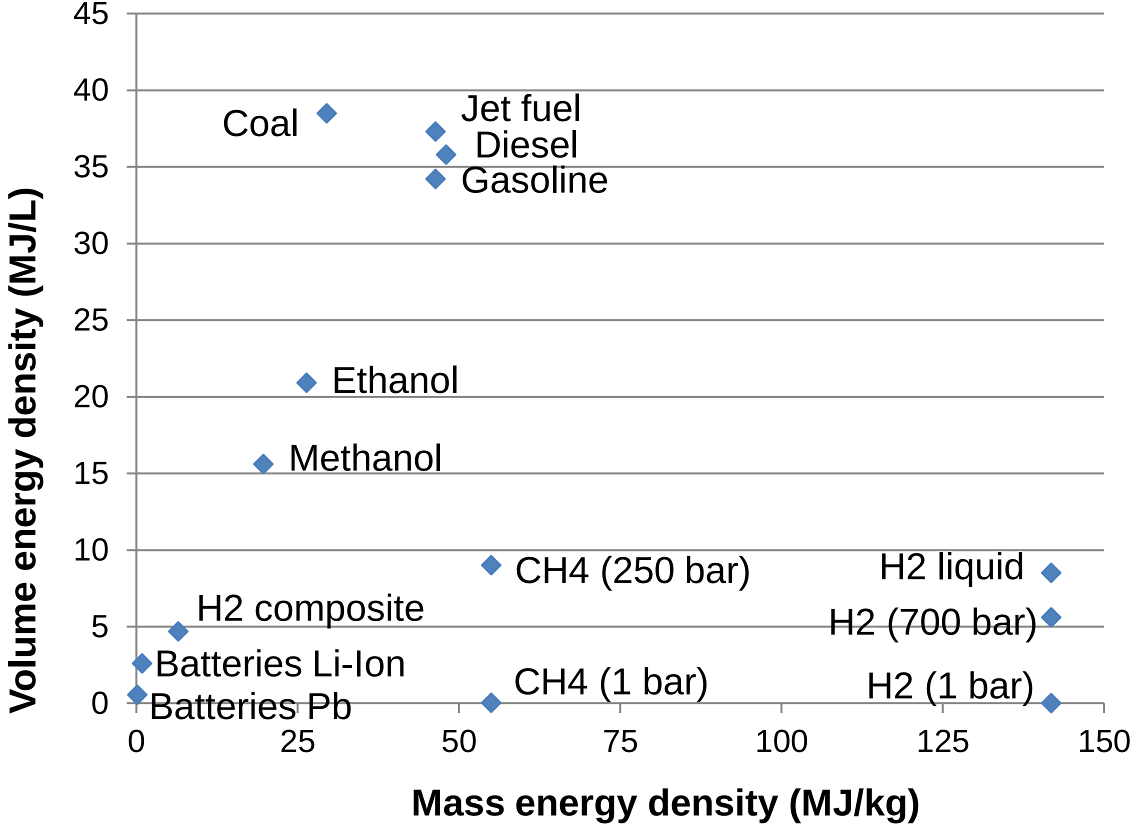
Thermochemical CO_2 conversion: power-to-fuel

- Idea: store renewable energy in the C-C and C-H bonds



=> Sustainability is possible with carbonated fuels!

Decisive advantage: a fantastic volume energy density!

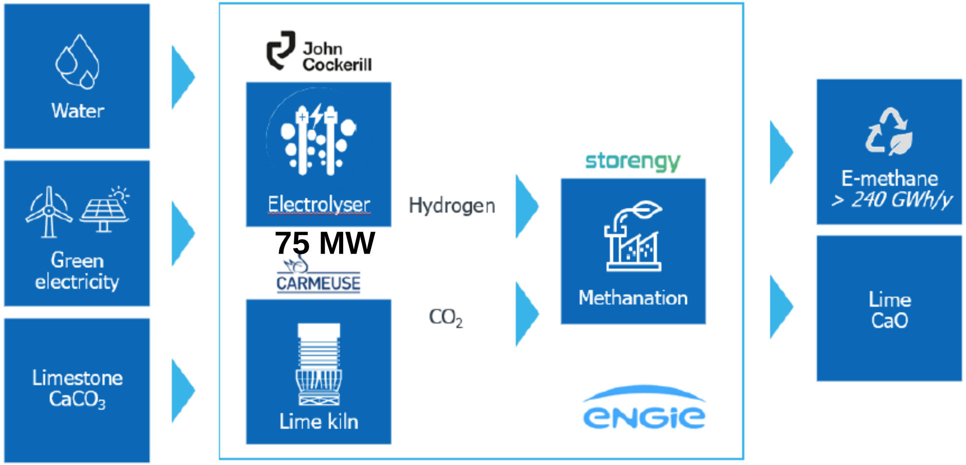


Energy storage

- Quick calculations
  - How many cars tanking at the same time are needed to develop a power of 3 GW_{th} (i.e. a nuclear plant)?
    - 1 L/s gasoline transfer
    - Gasoline ~ 35 MJ/L
    - => 1 car = 35 MW_{th}
    - 3 GW_{th} ~ 85 cars

CO_2 to fuels

- Methane
  - $CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$
  - Sabatier reaction, $\Delta H° = -165$ kJ/mol
- Commercial uses:
  - Great Plain synfuel plant
  - Methanation in ammonia synthesis
  - Producing fuel on Mars
    - $CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$
    - CH_4 used as fuel, H_2O electrolyzed for (re)generating H_2 and O_2
  - Jupiter1000 in Marseille (Fos-sur-mer), Audi e-gas plant (54% efficiency)…
- CH_4 is a greenhouse gas!
  - Lock-in effect of infrastructures…

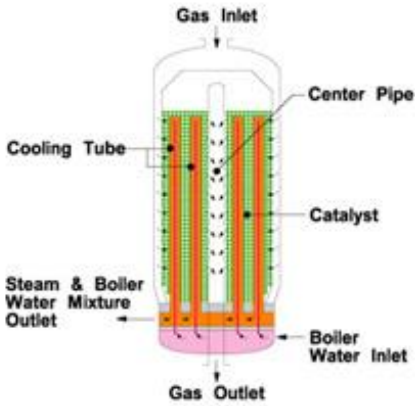


https://www.sciencedirect.com/science/article/pii/S1364032117311346#s0110
https://en.wikipedia.org/wiki/Sabatier_reaction

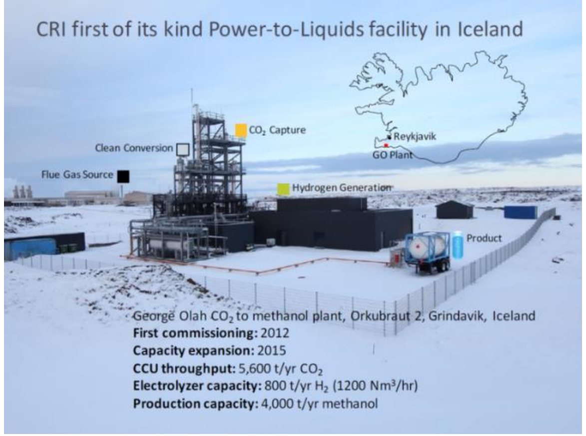
CO_2 to fuels

- Methanol
  - $CO + 2\ H_2 \rightarrow CH_3OH \quad (\Delta H_{300K} = -\ 90.8\ kJ/mol)$
  - $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O\ (\Delta H_{300K} = -\ 49.2\ kJ/mol)$

Haldor Topsoe, > 10 000 t/d



3,000 t/d methanol plant at Oman Methanol Company L.L.C., TOYO Engineering



12 t/d renewable methanol - CRI

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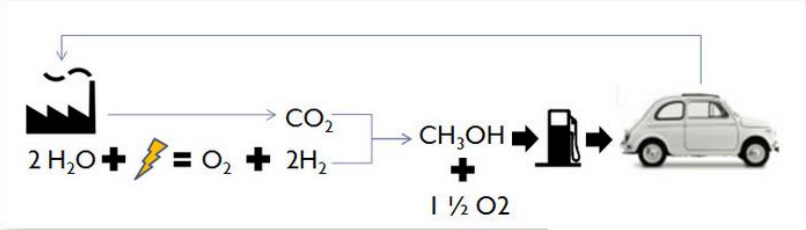
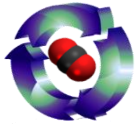
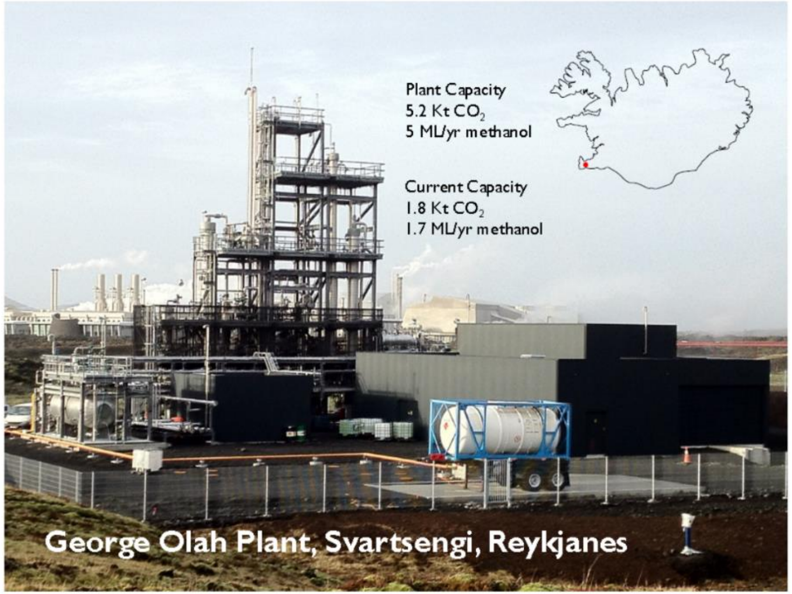
Power to Liquid : methanolisation





Source : http://www.carbonrecycling.is/
last access 16th March 2015



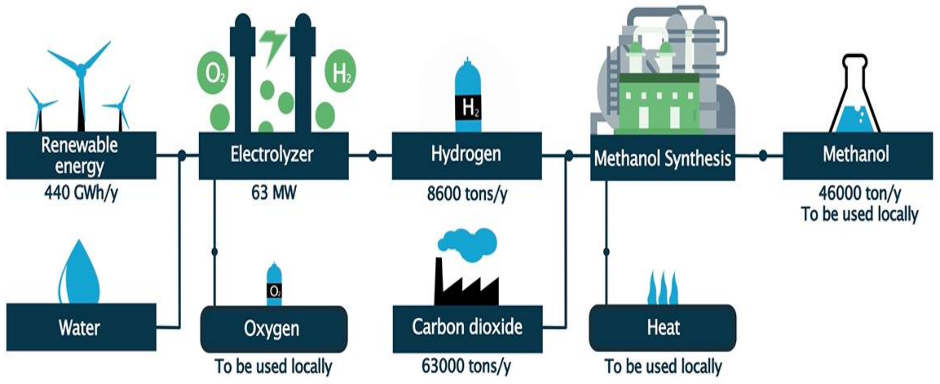
- *Methanolisation of carbon dioxide coming from geothermal power plant with renewable hydrogen (geothermy)*
- *Operational since 2011*

Recent announcements …

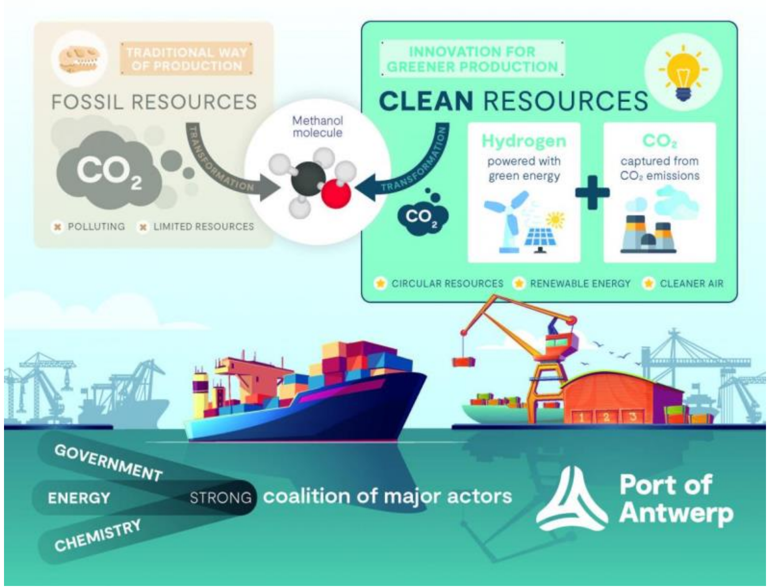
The North-C-Methanol project

NORTH C METHANOL

https://northccuhub.eu/



Became North-C-Hydrogen in 2022 due to non-selection of the project for European funding

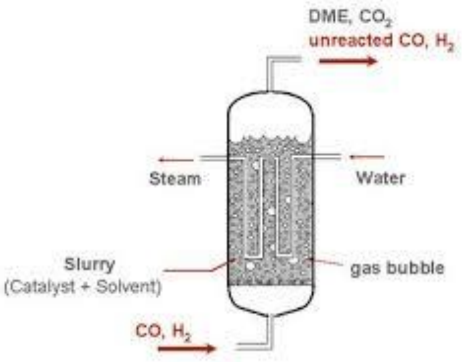


8000 ton/y, operation start: due in 2023

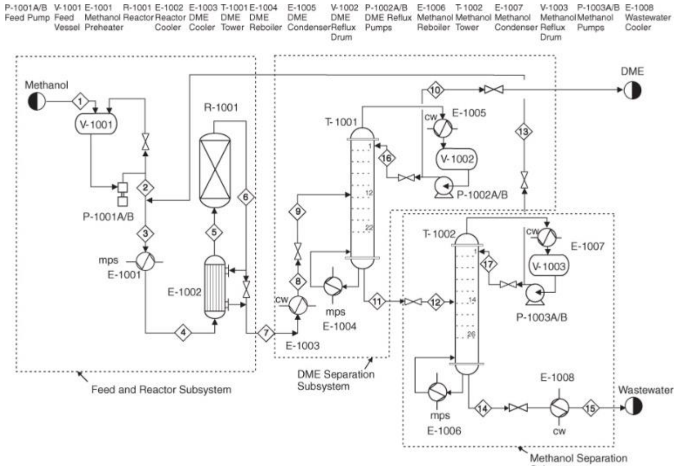
https://powertomethanolantwerp.com/

CO_2 to fuels

- DME (CH_3-O-CH_3)
  - $2\ CH_3OH \rightarrow CH_3\text{-}O\text{-}CH_3 + H_2O$ ($\Delta H° = -23.4$ kJ/mol)
  - Similar to diesel fuel, but stored under pressure
  - Can be made from methanol, or directly CO_2



Yagi et al., 2010. DOI: 10.2202/1542-6580.2267



Turton et al., Prentice Hall, 2012

CHEMICAL ENGINEERING

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CO_2 to fuels

- Syngas
  - Reverse water-gas shift
    - $CO_2 + H_2 \rightarrow CO + H_2O$
      $\Delta H° = +\ 40.9$ kJ/mol
  - Dry Reforming
    - $CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2$
      $\Delta H° = +\ 247.3$ kJ/mol
  - Co-electrolysis:
    - $H_2O \rightarrow H_2 + 0.5\ O_2$ E°= 0.41 V vs.NHE
    - CO_2 -> $CO + 0.5\ O_2$ E°= 0.53 V vs.NHE

NETL, WGSR

Wikipedia, SOEC

CO_2 to fuels: gas-to-liquids (Fischer-Tropsch)

Gasoline:

- $8\ CO + 17\ H_2 \rightarrow C_8H_{18} + 8\ H_2O$

  $\Delta H_{298K} = -1276$ kJ/mol

Jet fuel

- $11\ CO + 23\ H_2 \rightarrow C_{11}H_{24} + 11\ H_2O$

  $\Delta H_{298K} = -1721$ kJ/mol

Global reaction from CO

$n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$

Global reaction from CO_2

$n\ CO_2 + (3n+1)\ H_2 \rightarrow C_nH_{2n+2} + 2n\ H_2O$

Difference is the RWGS: $CO_2 + H_2 \leftrightarrow CO + H_2O$

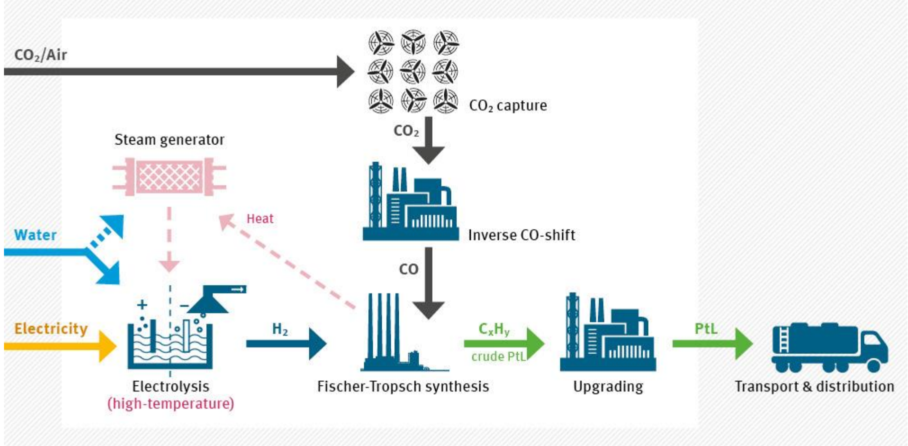
Rasmussen, 2019. Implementation of Fischer-Tropsch Jet Fuel Production in the Danish Energy System

CO_2 to fuels

- Fischer-Tropsch fuels
  - Similar to gasoline, complex mixture
  - Sunfire: 58 m^3/a, Efficiency ~70%

Figure 3

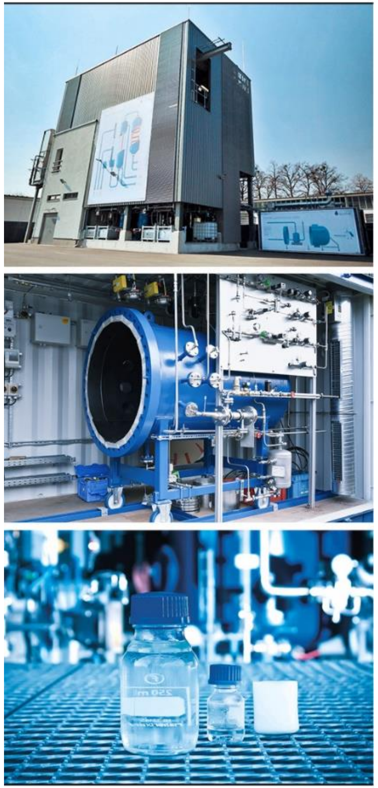
PtL production via Fischer-Tropsch pathway (high-temperature electrolysis optional)



Source: LBST

Figure 5

Sunfire PtL demonstration plant (top) using high-temperature electrolysis (middle) for the production of Fischer-Tropsch crude (bottom)



Sources: *top:* sunfire GmbH Dresden/CleantechMedia; sunfire GmbH Dresden/renedeutscher.de

Recent announcement

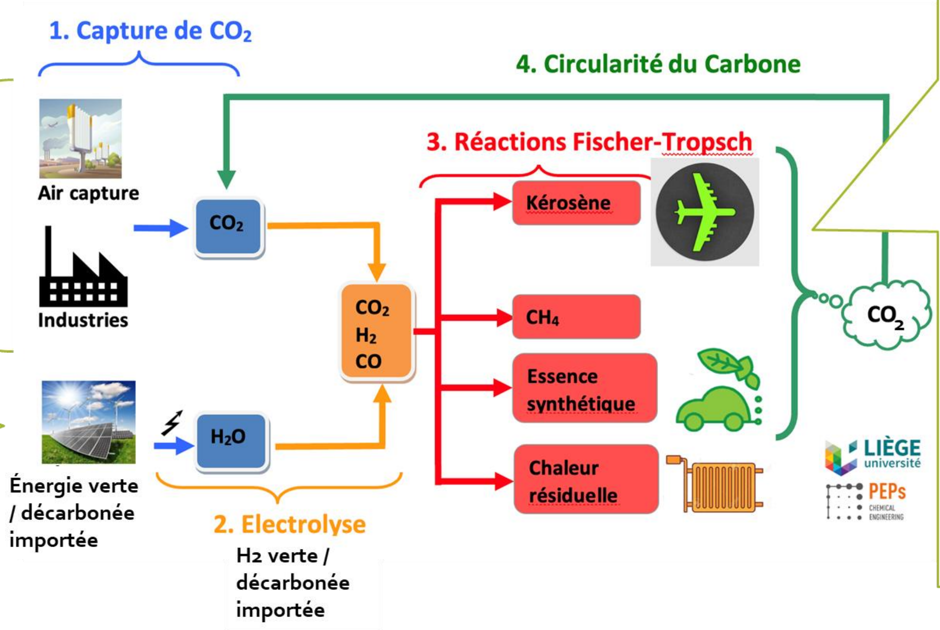
- Carbon neutral kerosene

Recent announcement

Capture de CO_2 + électrolyse + synthèse Fischer-Tropsch

1Mt CO2/an

0.15Mt H2/an (i.e. ~1GW en continu = 1 tranche nucléaire en base load

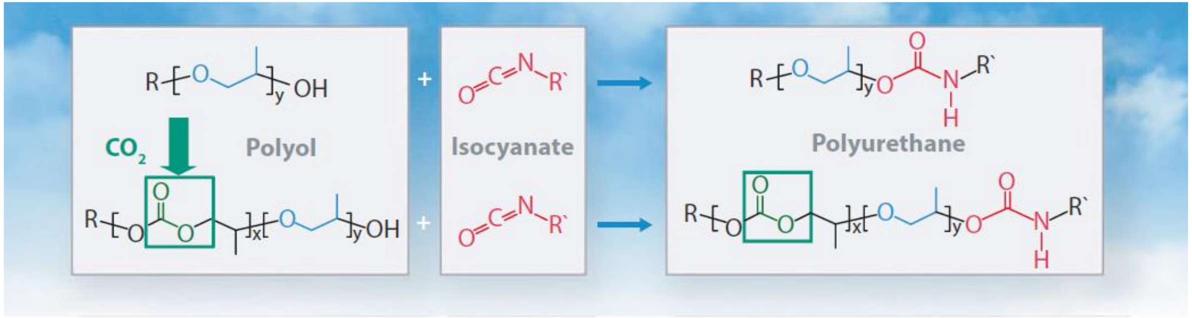


250.000 m³/an (~40% conso Liege Airport

Autres produits

- 117kt d'essence ;
- 16,5 kt autres (méthane, éthane…) ;
- chaleur : 1.282 GWh i.e. ~1,5x capacité actuelle du réseau de chaleur existant à Herstal (~800GWh/an)

DREAM PRODUCTION



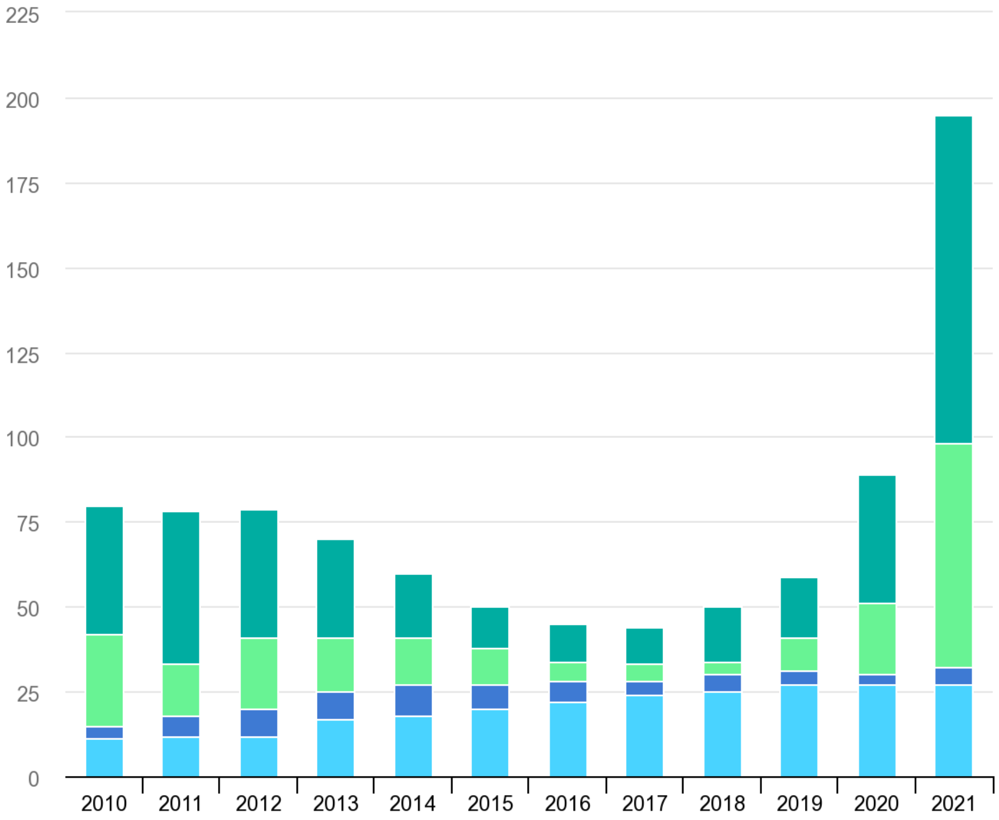
https://www.plasteurope.com/news/detail.asp?id=234342 vito

PHOTANOL

Photanol

https://www.agro-chemistry.com/news/photanol-to-build-demo-plant-on-akzonobel-site-delfzijl/

GLOBAL PIPELINE OF COMMERCIAL CCUS FACILITIES OPERATING & IN DEVELOPMENT



IEA, *Global pipeline of commercial CCUS facilities operating and in development, 2010-2021*, IEA, Paris
https://www.iea.org/data-and-statistics/charts/global-pipeline-of-commercial-ccus-facilities-operating-and-in-development-2010-2021

TOP TECHNICAL BARRIERS AND AREAS FOR FUTURE RESEARCH ACROSS CO2R PATHWAYS

	DIRECT			FLEXIBLE	INDIRECT	
	Electrochemical		Bioelectrochemical (MES)	Plasma	Bioelectrochemical (Fermentation)	Thermochemical
	C_1 (TRL: 4–6)	C_{2+} (TRL: 1–3)	TRL: 1–3	(TRL: 1-3)	TRL: 4-7	TRL: 5-8
Major Technical Challenges	• Scale up reactor / supporting systems • Increase long-term system stability	• Improve energy efficiency; reduce cell overpotential • Increase selectivity to individual C_{2+} products • Increase single-pass CO_2 conversion	• Develop fundamental understanding of electron transfer mechanism(s) • Raise CO_2 reduction rates • Increase product titers and cell toxicity limits • Increase CO_2 solubility / current density	• Decouple energy efficiency / conversion correlation • Raise yield to C_{2+} products • Develop commercially viable reactor design	• Increase solubility of gaseous reactants • Reduce separation costs • Increase product titers and cell toxicity limits	• Process intensification and scale-down • Develop multi-functional water and CO_2 tolerant catalysts • Improve product selectivity
Research Needs	• Transition to gas-phase, membrane electrode assemblies • Standardize testing protocols • Develop accelerated degradation testing methods • Test possible anodic chemistries to replace OER • Optimize reaction conditions (electrolyte, pH, mass transport) • Develop of new catalytic materials and membranes		• Expanded testing of mixed and pure cultures • Develop bio-compatible gas diffusion electrodes • Genetic engineering	• Develop specialized packed-bed catalysts for plasma conditions • Electronics development • Scalable reactor design	• Raise product titers • Improve reactant delivery / mixing • Develop low-cost *in-situ* separations	• Rapid screening of active materials • Improve catalyst performance through promoter additives • Intelligent systems integration and reactor design
Advantages	• Commercially deployed for C_1 species • Tunable distribution of over 20+ products • 100% theoretical conversion of CO_2 • High theoretical energy conversion efficiency • Access to high-value, high-volume intermediates & products		• Can form C-C bonds at ~100% selectivity • Specialized chemistry accessible through genetic modifications • ~98.6 % theoretical conversion of CO_2 • High theoretical energy conversion efficiency	• Adaptable to transient usage; quick to reach steady-state • Feedstock flexible • 100% theoretical conversion of CO_2	• Can form C-C bonds at ~100% selectivity • High TRL, deployed commercially • ~98.6 % theoretical conversion of CO_2	• Direct access to high volume fuels and chemicals markets • Highest TRL; deployed commercially at large-scale • Long history of R&D investments; existing infrastructure
Limitations	• Low selectivity to C_{2+} products • Reported products limited in carbon number ≤ 4 • Low TRL to C_{2+} products • Rapid deactivation and limited testing on long-term stability		• Low productivity • Limited number of direct C_1-C_3 products • Poorly understood reaction mechanisms	• Low TRL • High power demand • Low selectivity to C_{2+} products	• Poor mass transfer • Limited number of direct C_1-C_3 products • Large system footprint • Lower theoretical energy conversion efficiency	• Challenged economics at small-scale • Limitations in CO_2 equilibrium conversion • Lower theoretical energy conversion efficiency

PROPOSED TIMELINE OF CO_2 UTILIZATION METHODS

5 to 10 years		10 to 50 years		70+ years	
Electrocatalysis	Photocatalysis	Biohybrid	Nanoporous Confinement	Chain Insertion	Molecular Machines
• Flexible electricity source • Closest to scale and commercial application • Dependent on the cost of electricity	• Direct solar to fuel conversion • Portable • No CO_2 solubility issues • Efficiencies and activities are still low	• Coupling of enzymes to inorganic water splitting • Microbial synthesis • Complicated molecule synthesis • Stability is still an issue	• Catalysis of hydrocarbons achieved in zeolites and MOFs • High temperatures and pressures required	• Metal catalysts for polymerization through chain insertion. • Currently highly adopted by industry • Have yet to be demonstrated with CO_2	• Artificial enzymes with dynamic components • Potential for tandem catalysis with high selectivity • Has yet to be demonstrated

Bushuyev et al., 2018. What should we make with CO_2 and how can we make it? Joule, 2(5), pp.825-832.

CONCLUDING WORDS

- Multiple valorization routes are possible via CCU (several pathways) with different challenges associated to each pathways. Power to X route is a promising one allowing integration with renewable energy.
- The multiple pathways are at different level of TRL.
- There is a cost associated to each pathway and it varies according to different variables.
- **Thermochemical and bioelectrochemical** routes offer the most technically feasible near-term opportunities for CCU, representing immediately deployable pathways to high-value and relatively high-volume products → face inherent challenges with respect to lower equilibrium conversion (thermochemical) and a limited C1–C3 product distribution (biochemical), potentially hindering their long-term viability
- **Direct electrochemical pathway** show long-term promise and can theoretically overcome these limitations, yet currently face numerous technical barriers preventing near-term market adoption

State of technologies CCUS

- Cost of CO_2 capture and re-use
  - CCU routes are more expensive than fossil under both near- (2020s) and long-term (2050s) assumptions. In the near-term, CCU commodities are at least twice the cost of their fossil counterparts. In the long-term, cost premiums can decrease significantly due to reductions in the cost of green hydrogen and CO_2 capture.
  - Economic competitiveness of CCU routes is reliant on a 'cost of emission', estimated in the long-term between USD 120-225/tCO2.
- Structural impact on CO_2 prices due to European Green Deal

IEAGHG, 2021-03 CO2 Utilisation Reality Check: Hydrogenation Pathways. https://www.ieaghg.org/publications/technical-reports/reports-list/9-technical-reports/1052-2021-03-co2-utilisation-reality-check-hydrogenation-pathways
https://ember-climate.org/data/carbon-price-viewer/

State of technologies CCUS

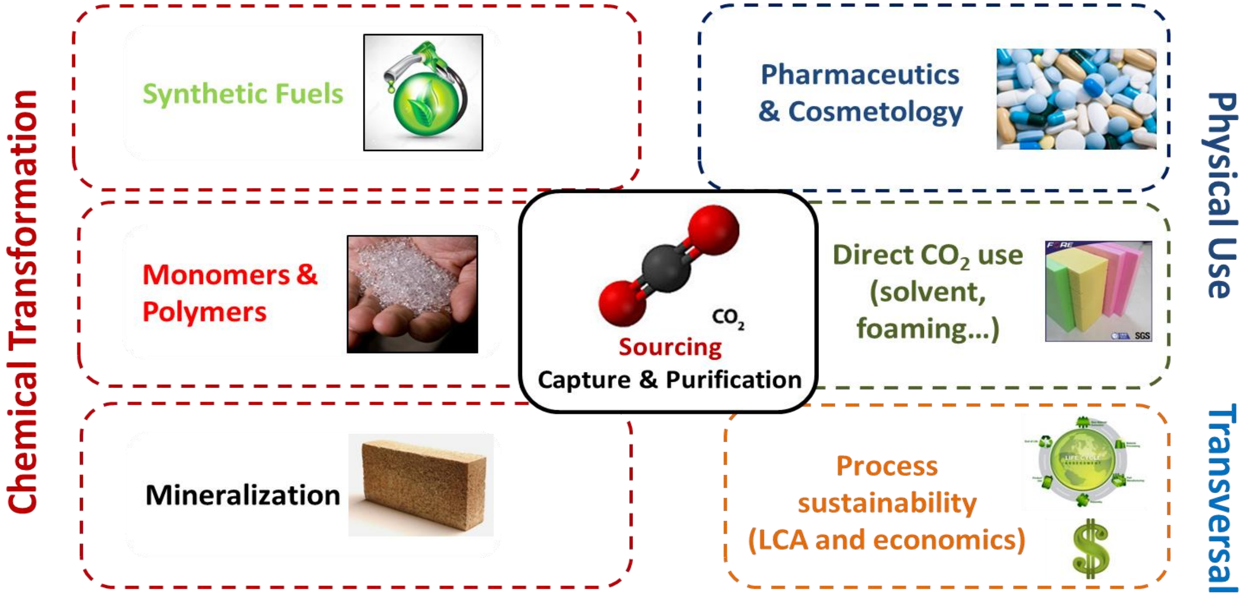
- Avoiding > 1 GtCO_2 requires very high levels of market penetration
  - For methanol: if methanol captures the entirety of the current market and then expands into the heavy-duty trucks market plus the plastics markets
  - For middle distillate hydrocarbons: only if they capture the entirety of today's aviation fuels and heavy-duty trucks market.
  - For formic acid: even if the CCU product were to penetrate the entire formic acid market, the abatement currently achievable is limited to approximately 2 MtCO_2.

- CCU pathways must be designed carefully to ensure lower life cycle emissions than the alternative pathways.

IEAGHG, 2021-03 CO2 Utilisation Reality Check: Hydrogenation Pathways. https://www.ieaghg.org/publications/technical-reports/reports-list/9-technical-reports/1052-2021-03-co2-utilisation-reality-check-hydrogenation-pathways

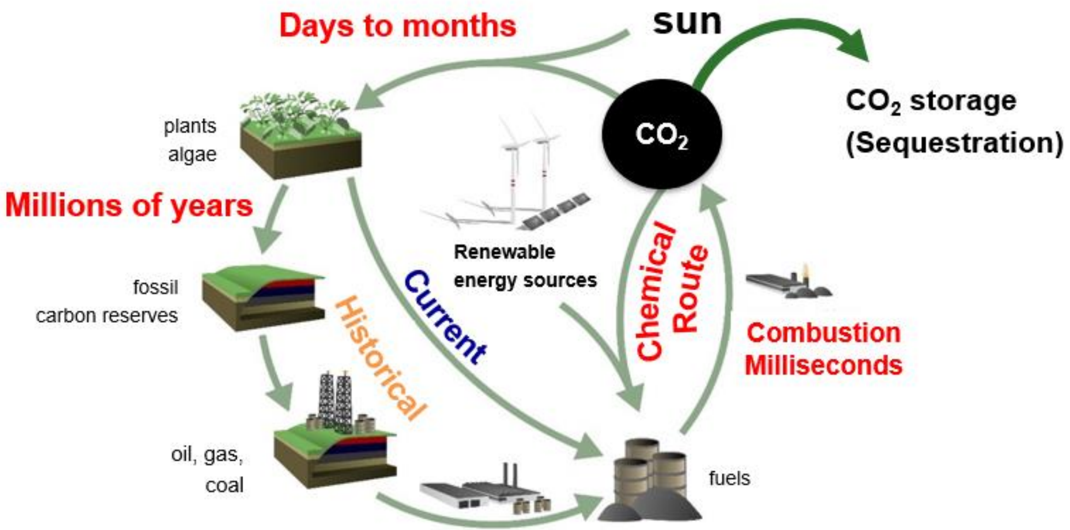
ULiège: FRITCO$_2$T platform

Federation of Researchers in Innovative Technologies for CO_2 Transformation



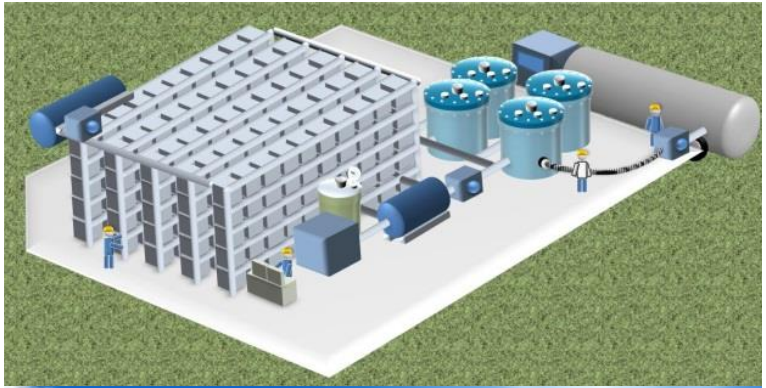
Perspective

- We live in a carbon-based society, with very good reasons for that !
- A CO_2 neutral future is in sight with passionating (and huge) challenges for engineers!
- This will require a large penetration of hydrogen as an (intermediate) energy carrier



Martens et al., (2017) The Chemical Route to a CO_2-neutral world, *ChemSusChem*
Saeys (2015), De chemische weg naar een CO_2-neutrale wereld, Standpunt KVAB

Thank you for your attention



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