Capture, stockage, ré-utilisation du CO_2

Grégoire LEONARD

18/10/2021

CHEMICAL ENGINEERING

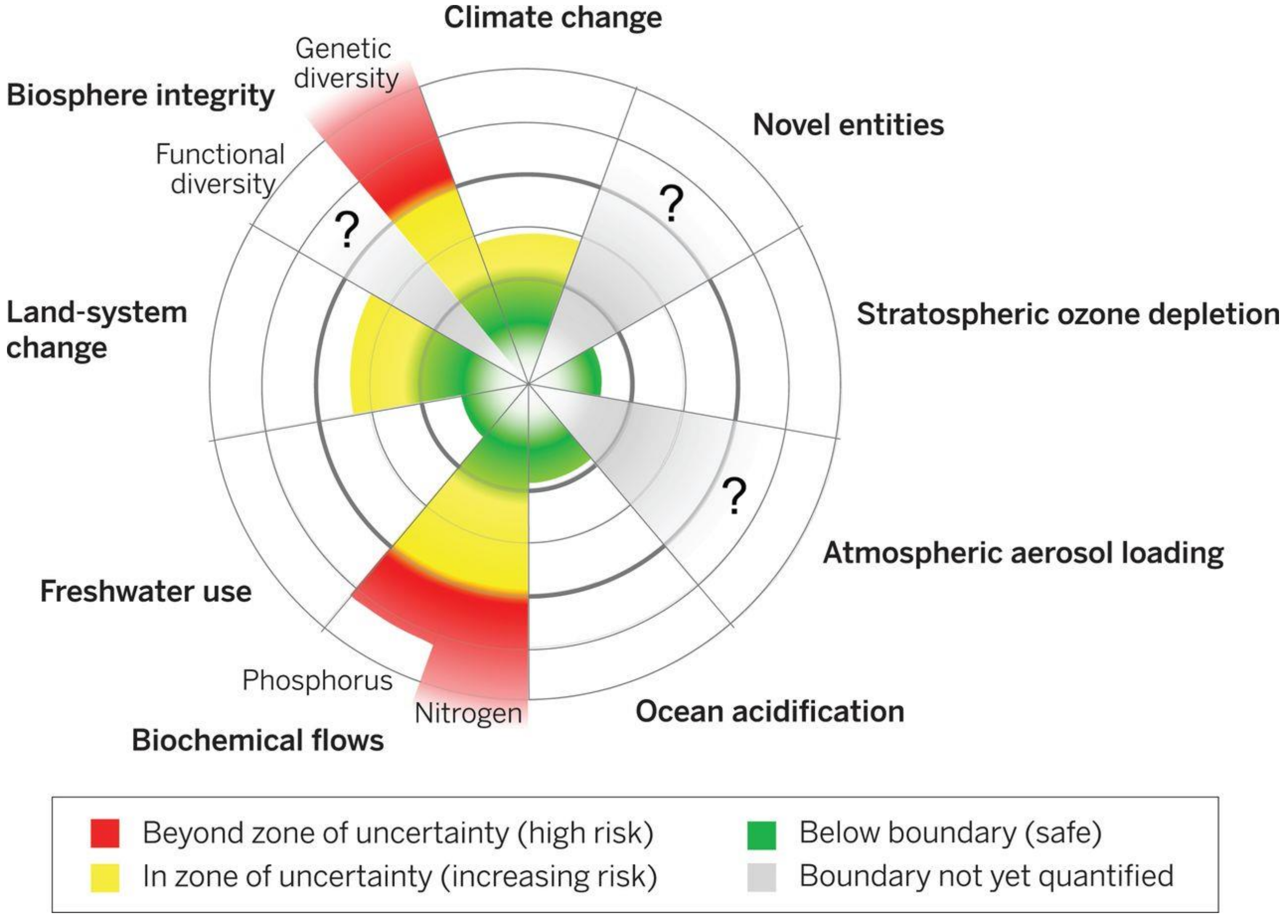
LIÈGE université

Outline

1. Context
2. Carbon Capture
3. Storage
4. Re-use
5. Perspectives & conclusions

Sustainable development

- How to keep a safe ecosystem?



Steffen W. *et al.* (2015), *Science 347* (6223), 1259855.

The energy transition has started…

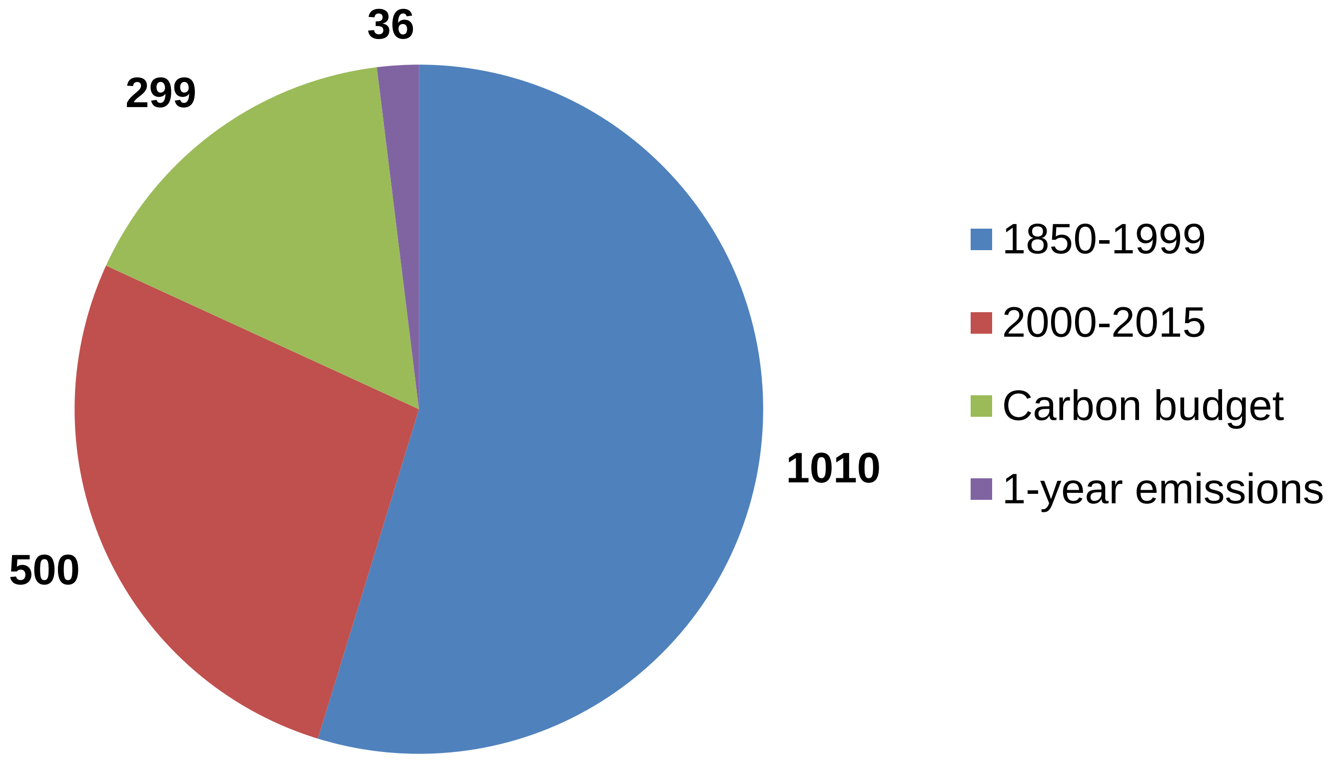
But it has to address 2 objectives in contradiction:

- Limit GHG emissions (BE ~120 Mtpa, world ~ 36 Gtpa)
- + meet the increasing energy demand!

www.carbontracker.org

CO_2 Budget

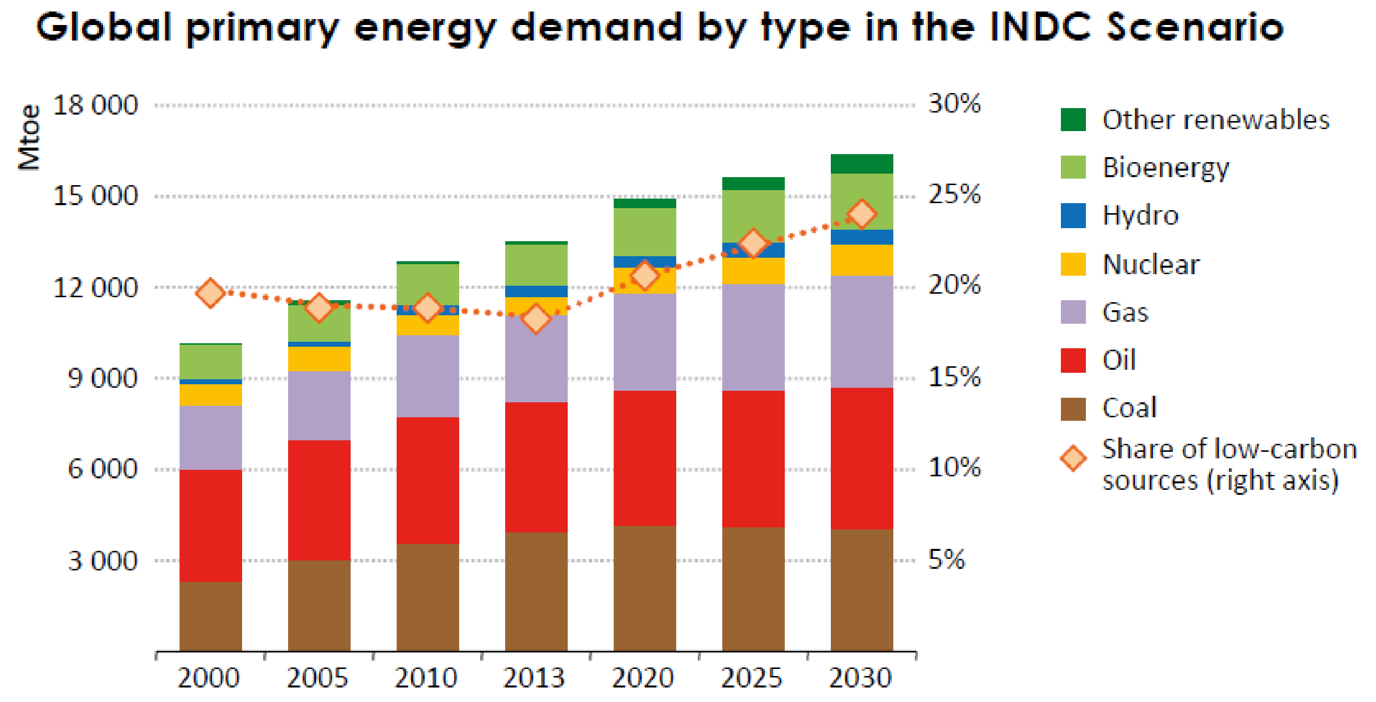
Budget by 2050 for having 80% chances to stay below 2°C



Note: Values in Gt CO_2 eq

https://informationisbeautiful.net/visualizations/how-many-gigatons-of-co2/

Meeting the increasing demand is already a challenge in itself!

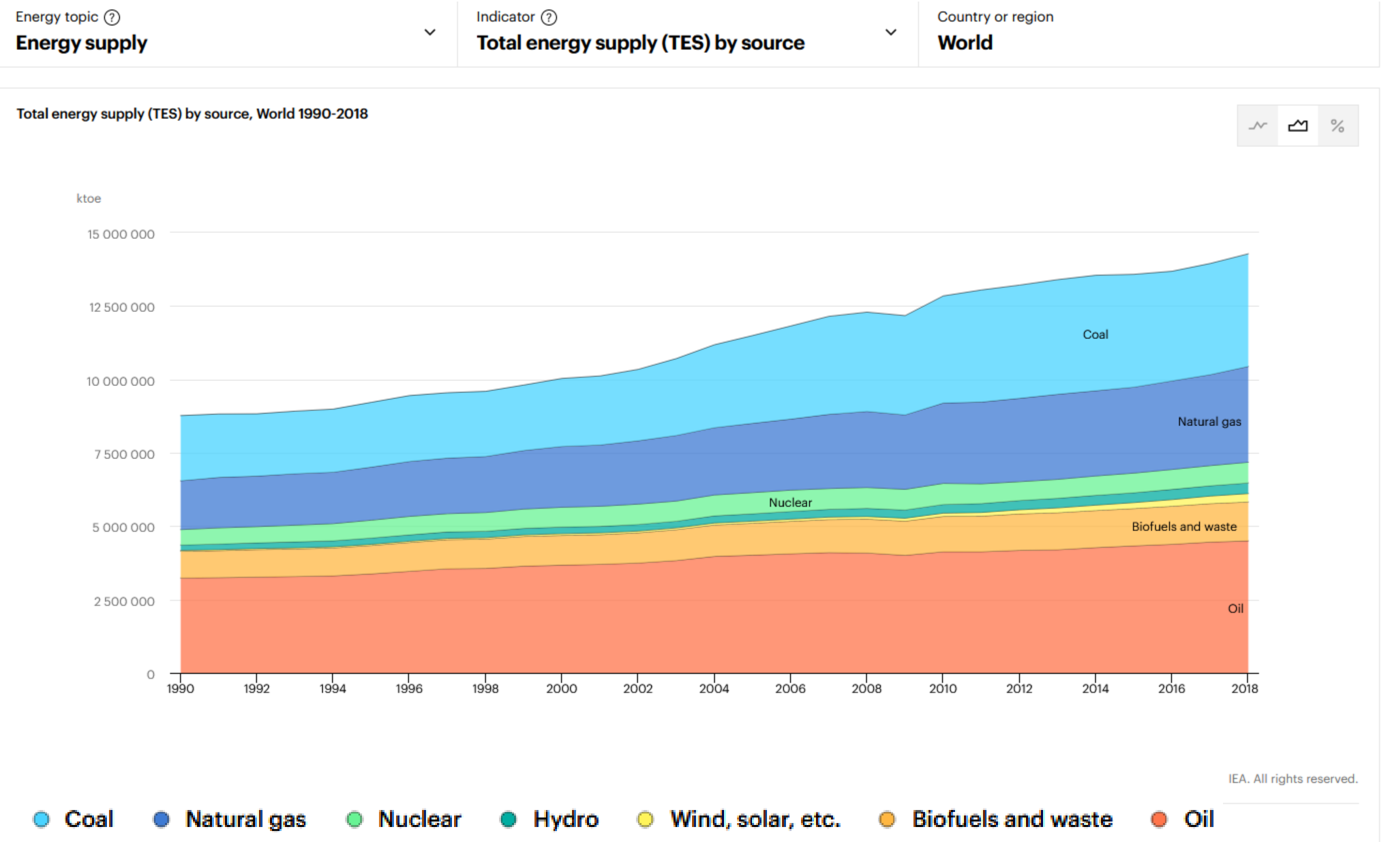


Note: "Other renewables" includes wind, solar (photovoltaic and concentrating solar power), geothermal, and marine.

IEA 2015, WEO special report, Energy & Climate Change

Meeting the increasing demand is already a challenge in itself!

- And most of the energy is still fossil…



Energy topic ⓘ
Energy supply

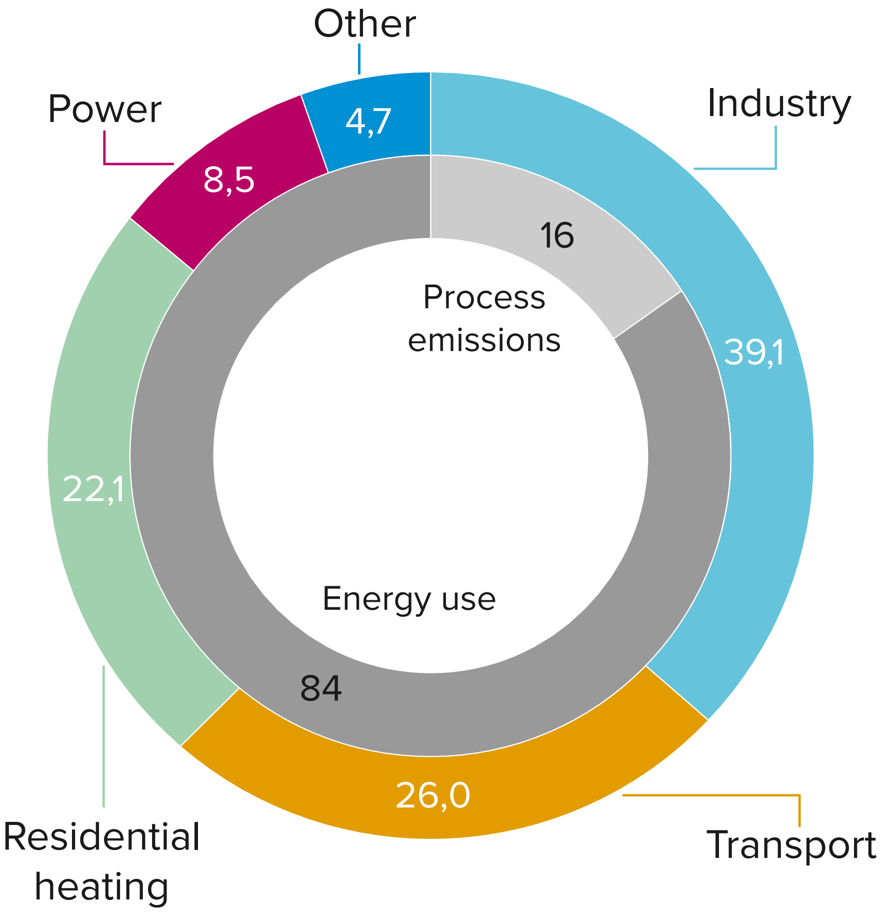
Indicator ⓘ
Total energy supply (TES) by source

Country or region
World

Total energy supply (TES) by source, World 1990-2018

IEA 2021, https://www.iea.org/data-and-statistics?country=WORLD&fuel=Energy%20supply&indicator=TPESbySource

Carbon emissions in Belgium for almost 40% originate from industry, either through energy use or process emissions.

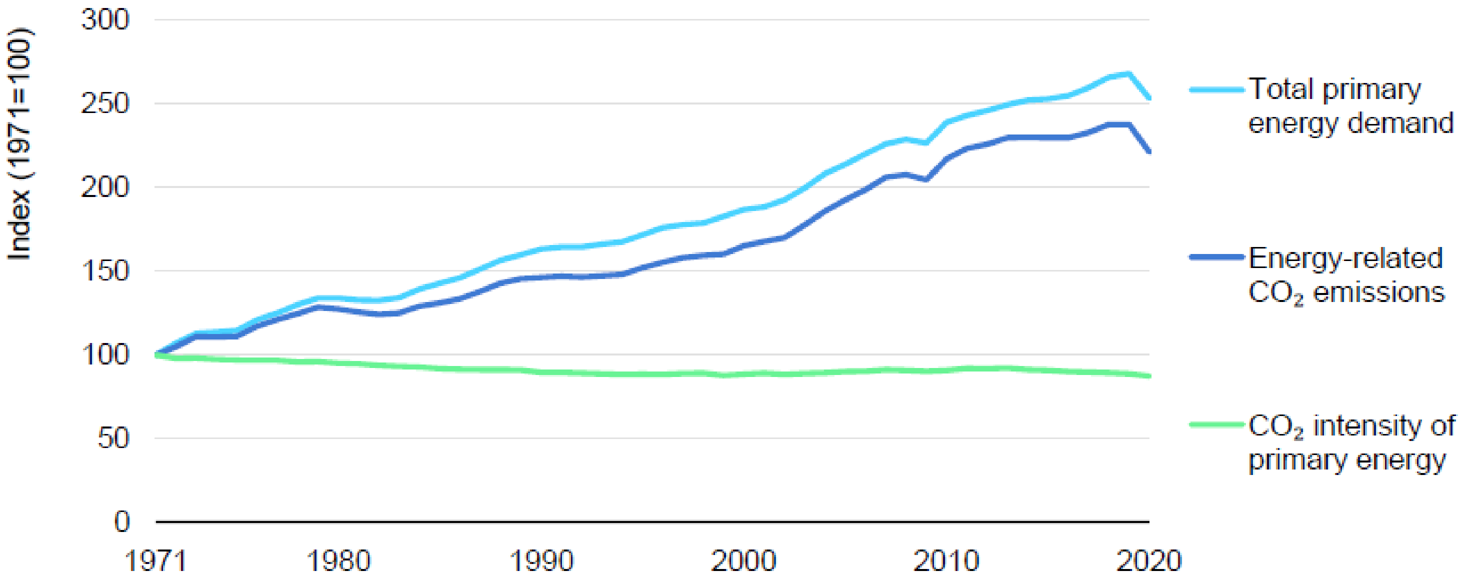


https://www.fluxys.com/en/energy-transition/hydrogen-carbon-infrastructure#double_solution

More recent update

- Impact of pandemics

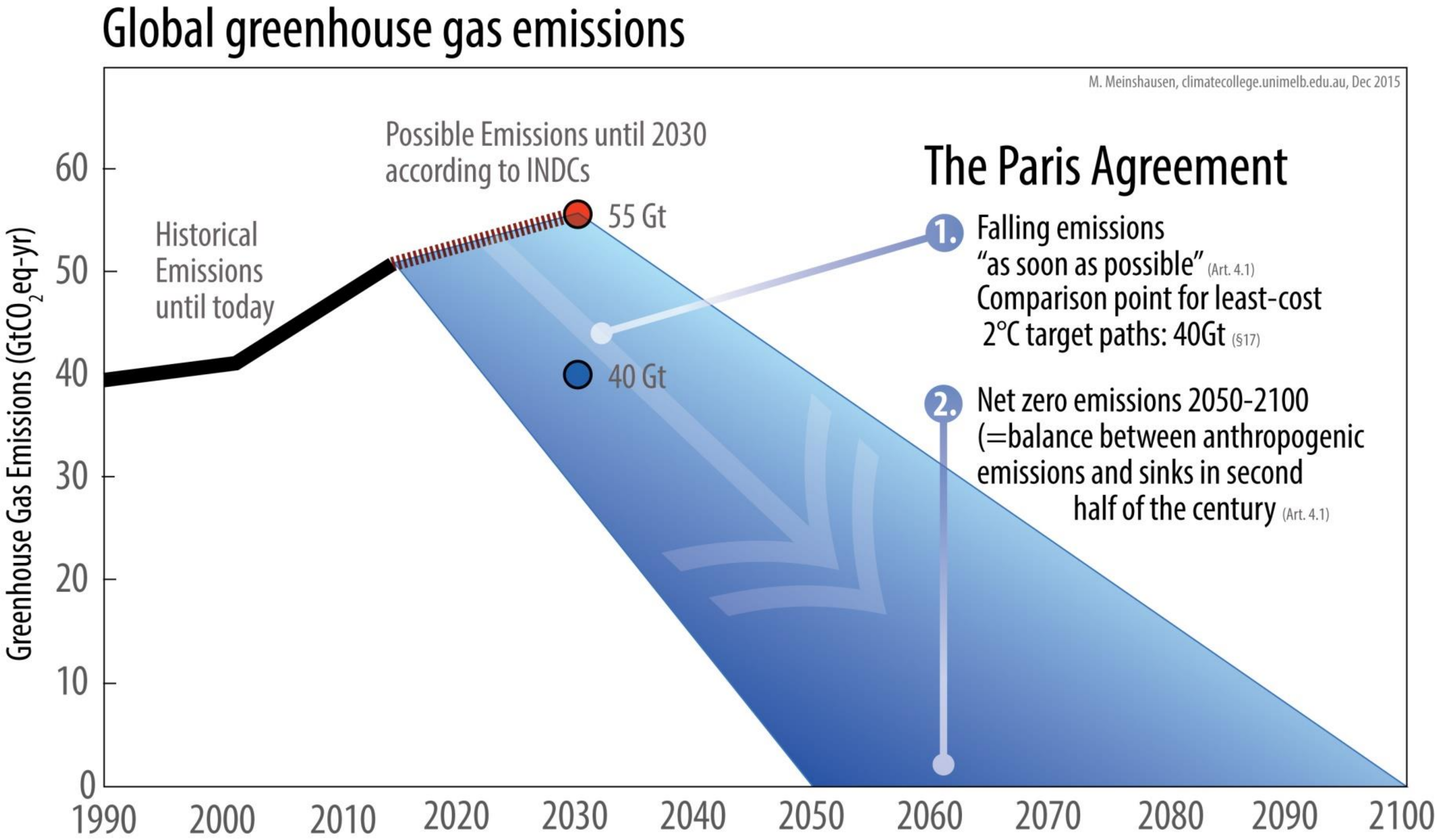
Figure 1.8 Global primary energy demand and energy-related CO_2 emissions, 1971-2020



IEA 2020. All rights reserved.

Energy-related CO_2 emissions generally have risen with energy demand since the 1970s; the Covid-19 is set to cause the largest decline in annual emissions over that period.

The COP […] notes that much greater emission reduction efforts will be required …



M. Meinshausen, Australian-German Climate & Energy College,
The University of Melbourne, climatecollege.unimelb.edu.au

At european level…

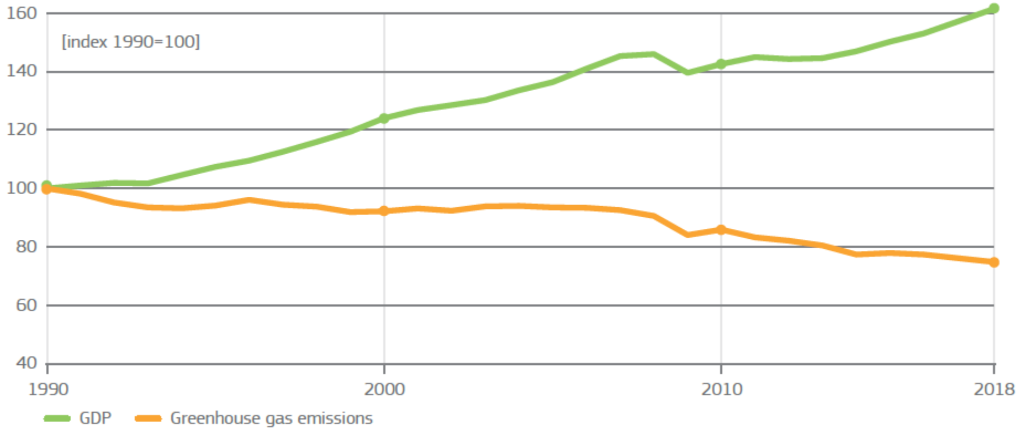
The green deal

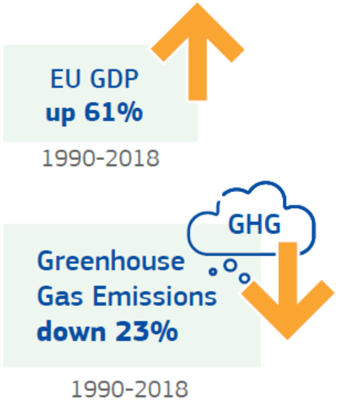
- Carbon neutrality by 2050
- - 55% CO_2 by 2030
- RED II: 32% Ren. En. 2030

The Economist

European achievements

Between 1990 and 2018, greenhouse gas emissions **decreased by 23%**, while the economy **grew by 61%.**

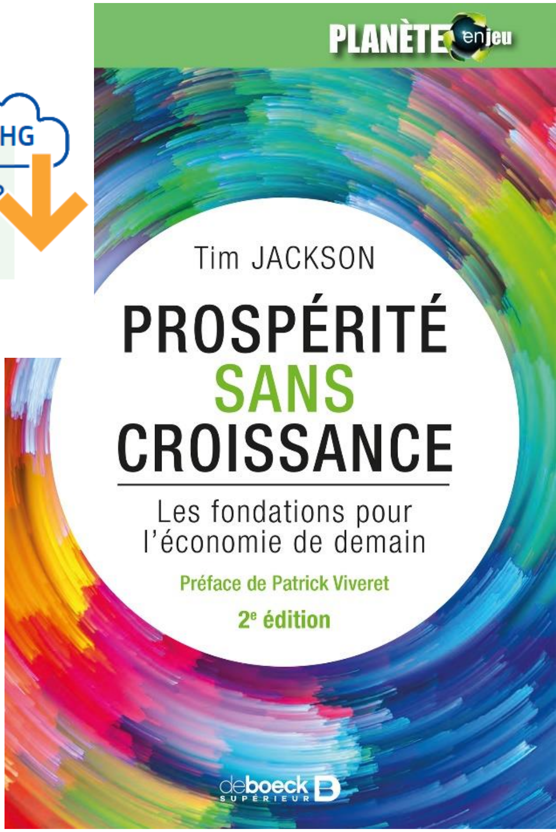



EU GDP
up 61%
1990-2018

Greenhouse
Gas Emissions
down 23%
1990-2018

Decoupling is a key topic! For more discussion, see Tim Jackson, prosperity without growth

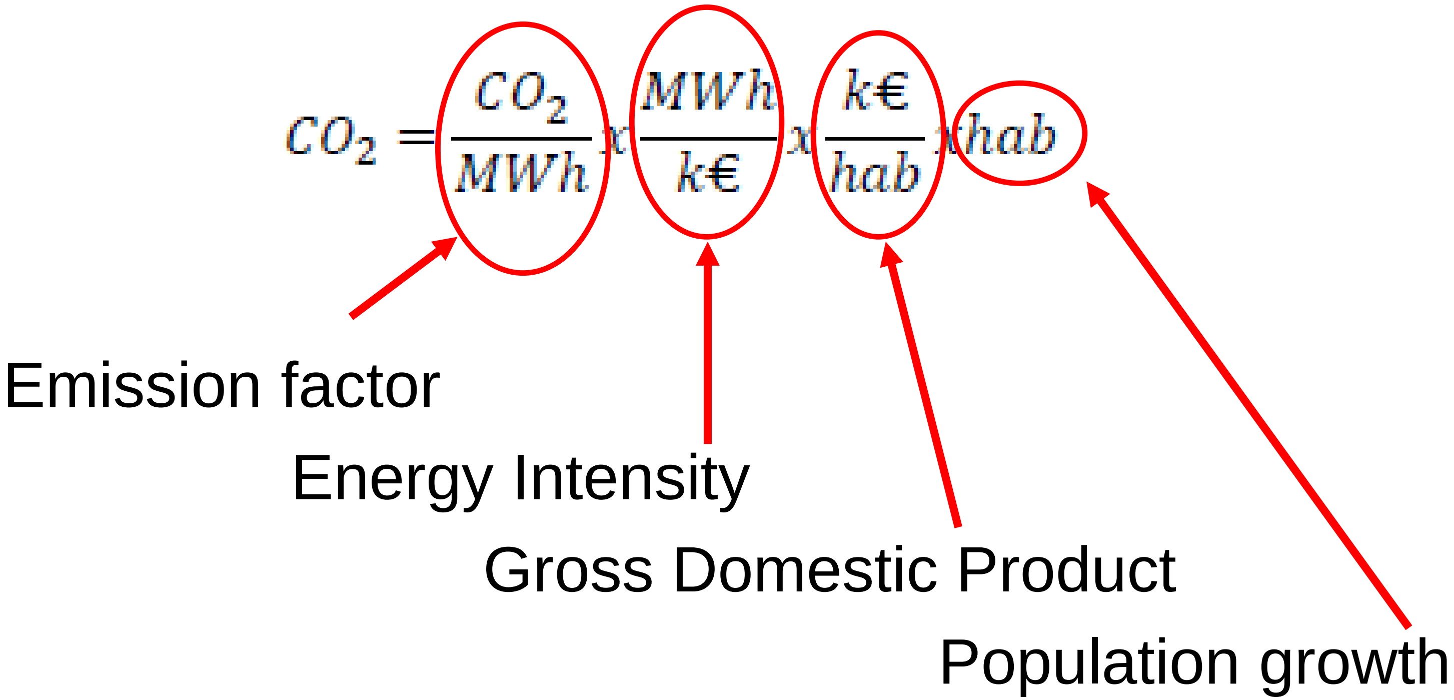
But… asymptotical behavior of energy intensity?



The EU's track record on climate action, EU Commission, 12/2019

This decoupling is a key challenge, not only for environment!

- Kaya’s equation relates many techno-economical variables



$$CO_2 = \frac{CO_2}{MWh} x \frac{MWh}{k€} x \frac{k€}{hab} x hab$$

Emission factor

Energy Intensity

Gross Domestic Product

Population growth

Fabi, 2019. Belgium Energy Outlook 2050. www.fabi.be

This decoupling is a key challenge, not only for environment!

- Strong link between economy and energy!

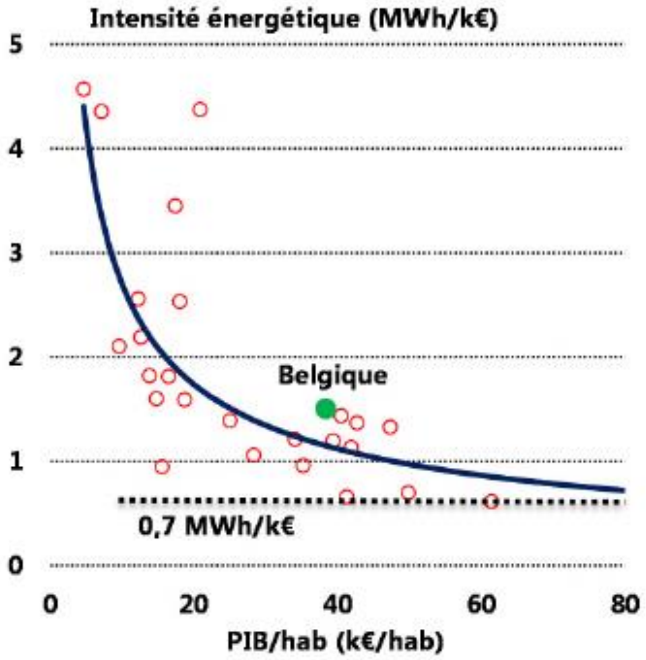


Figure 16 – Intensité énergétique en fonction du PIB/hab
Source des données : BP statistical review 2018 et World Bank

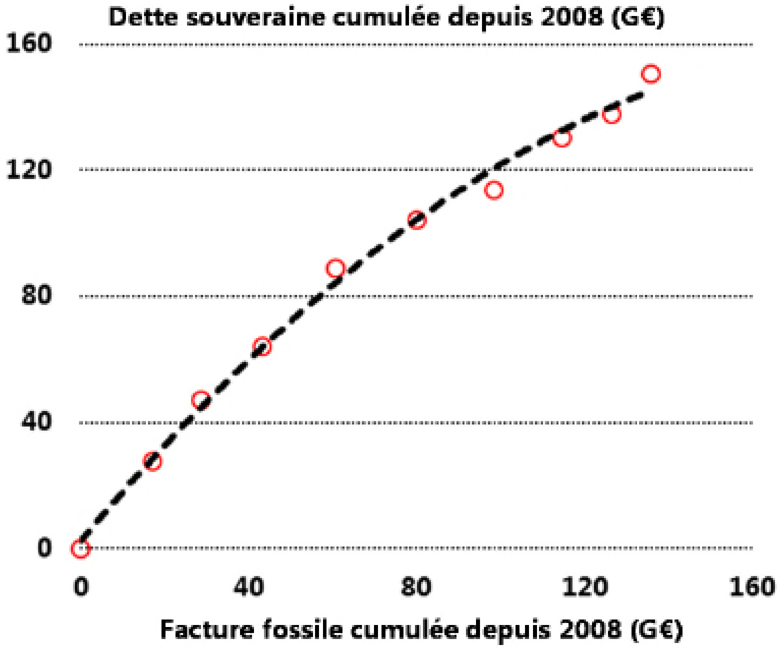
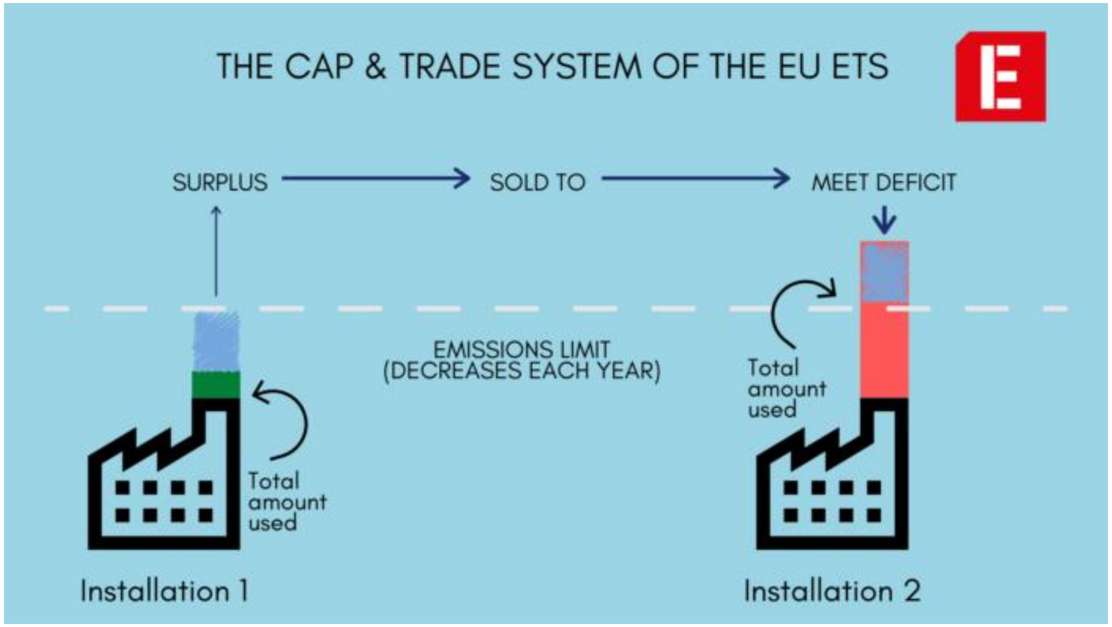


Figure 12 – Corrélation entre l'accroissement de la dette souveraine belge et sa facture fossile
Source des données : Eurostats et BP Statistical Review 2018

Fabi, 2019. Belgium Energy Outlook 2050. www.fabi.be

Possible answers: UE Example

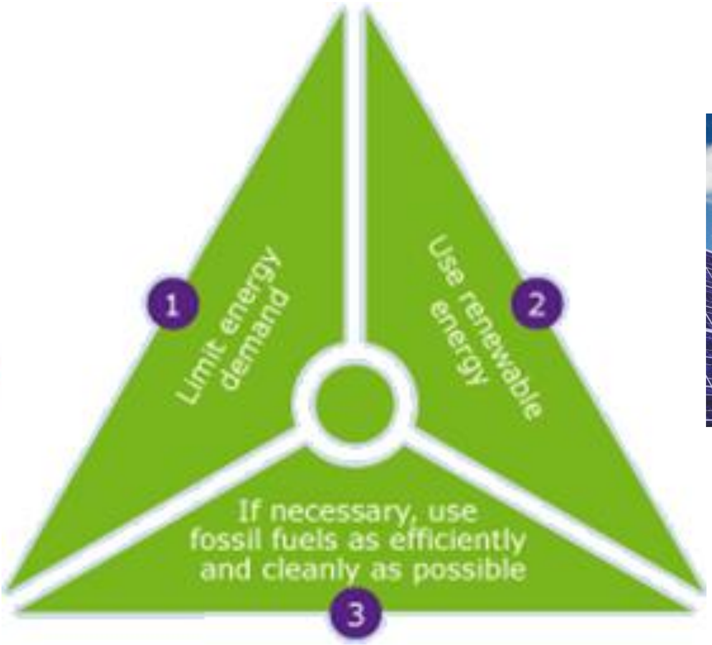
- The EU carbon market ETS



- Monitoring of emissions out of ETS (Effort sharing)
- Legislations with set objectives (energy efficiency, cars and truck emissions, minimal share of renewables…)
- Specific support for CCUS technologies

EU Climate action, 2021. https://ec.europa.eu/clima/policies/strategies/progress_en

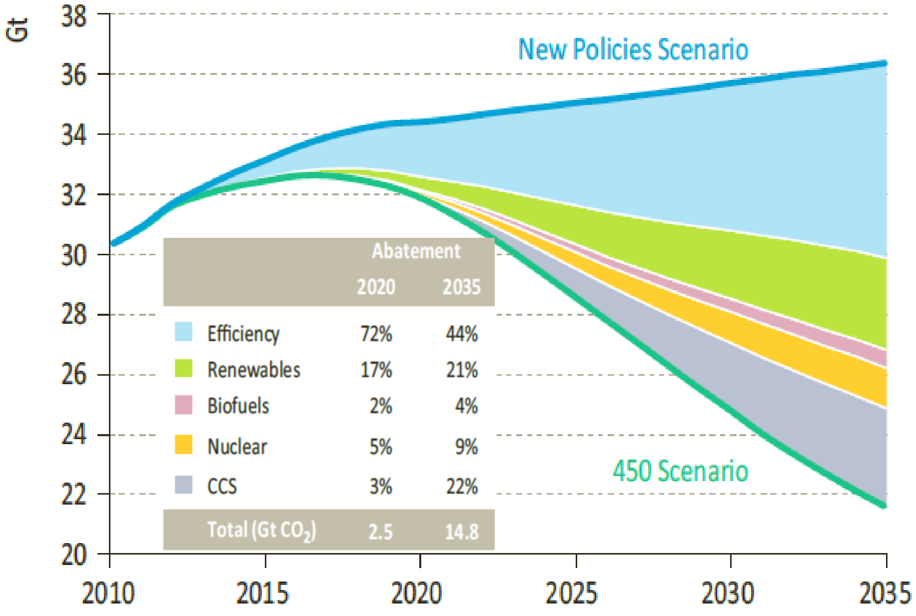
Possible answers: Trias Energetica



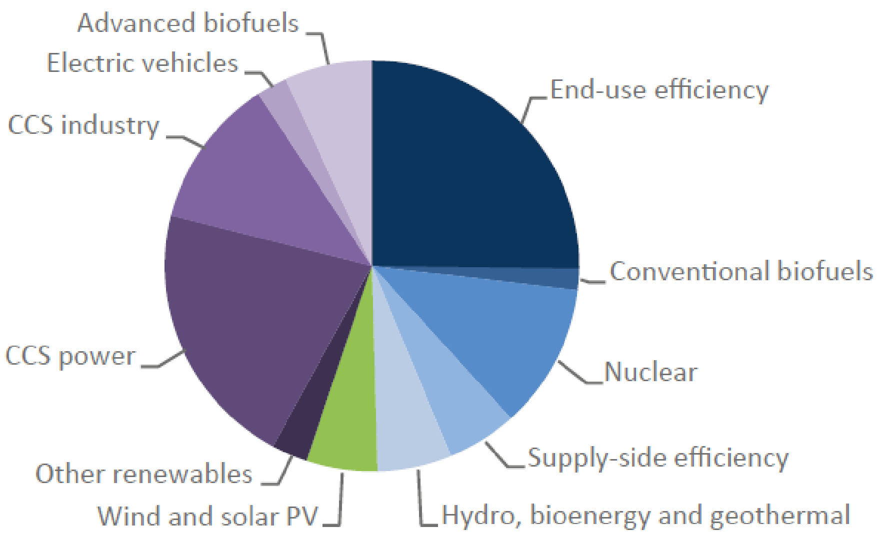
Lysen E., The Trias Energica, Eurosun Conference, Freiburg, 1996

CCUS forecasts

- CCUS = Carbon Capture, Utilization and Storage
  - Carbon capture and storage is mature & flexible technology, but cost only!
  - Re-use is at different maturity levels, depending on final product



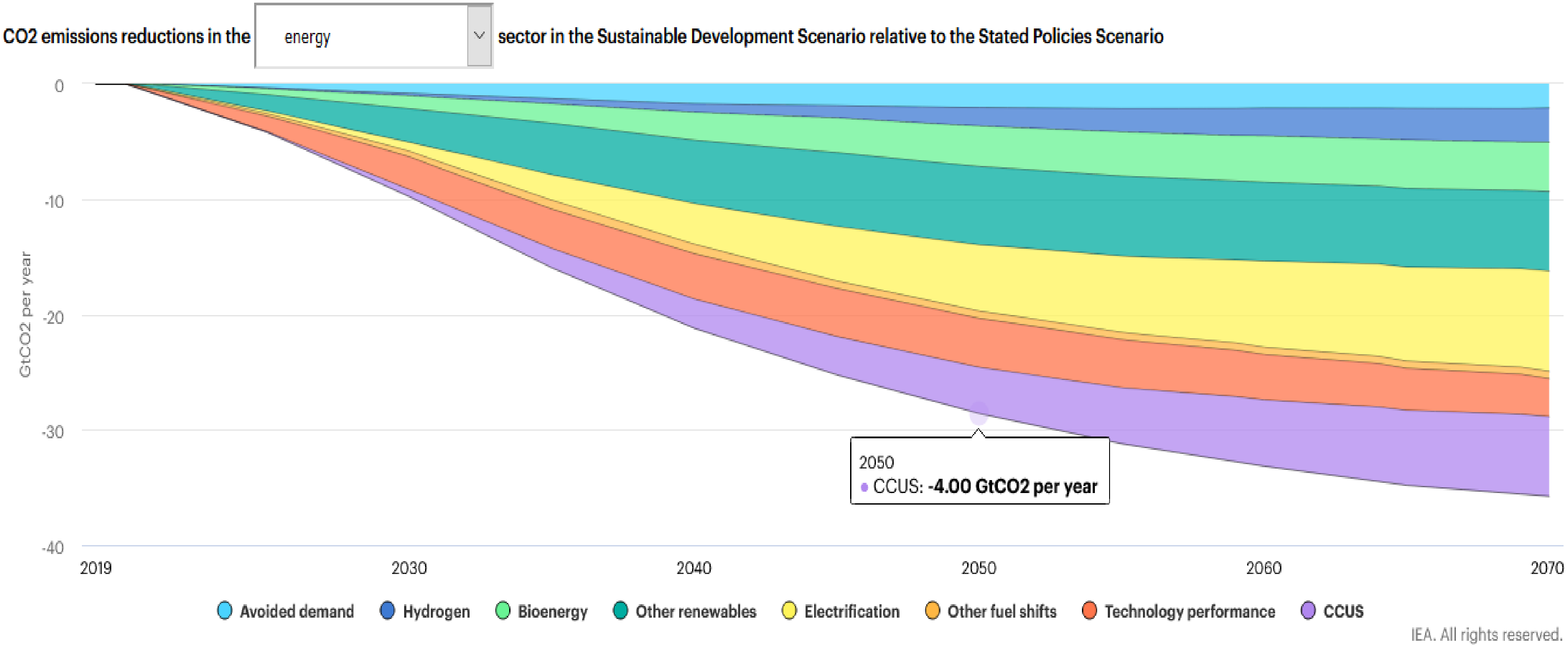
World CO_2 emissions abatement in the 450 Scenario (New Policies Scenario), IEA **2011**, WEO2011.



World CO_2 emissions abatement in the 450 Scenario (Bridge Scenario 2015-2040), IEA **2015**, WEO special report, Energy & Climate Change

CCUS forecasts

- CCUS = Carbon Capture, Utilization and Storage



CO2 emissions reductions in the energy sector in the Sustainable Development Scenario relative to the Stated Policies Scenario

2050
● CCUS: **-4.00 GtCO2 per year**

IEA. All rights reserved.

CHEMICAL ENGINEERING

IEA, 2020. https://www.iea.org/reports/energy-technology-perspectives-2020

LIÈGE université

CCUS forecasts

- What about Belgium?

- *« Le gaz, qui englobe à la fois les gaz de synthèse (renouvelables), le biogaz et du gaz naturel résiduel brûlé dans des unités thermiques équipées d'un système de capture et de stockage du carbone, représente un tiers (32 % à 33 %) du futur mix électrique. »*

- *« De manière générale, dans les deux scénarios [étudiés], la demande totale d'électricité augmente significativement d'ici 2050, en comparaison avec les niveaux actuels : la demande est jusqu'à trois fois supérieure à celle de 2018. »*

Source: Federal Planning Bureau, Fuel for the future, Working paper 4-20, October 2020

2. CO_2 Capture technologies & configurations

CHEMICAL ENGINEERING

LIÈGE université

CO_2 capture is basically a fluid separation process to be integrated into industry

Purity of sources varies between 0.04% and almost 100%

Usually mixture of CO_2, N_2, H_2O, H_2, CH_4, O_2 …

Not a new technology

- Exists for more than 50 years

India, 2006, Urea production,
2x450 tpd CO_2

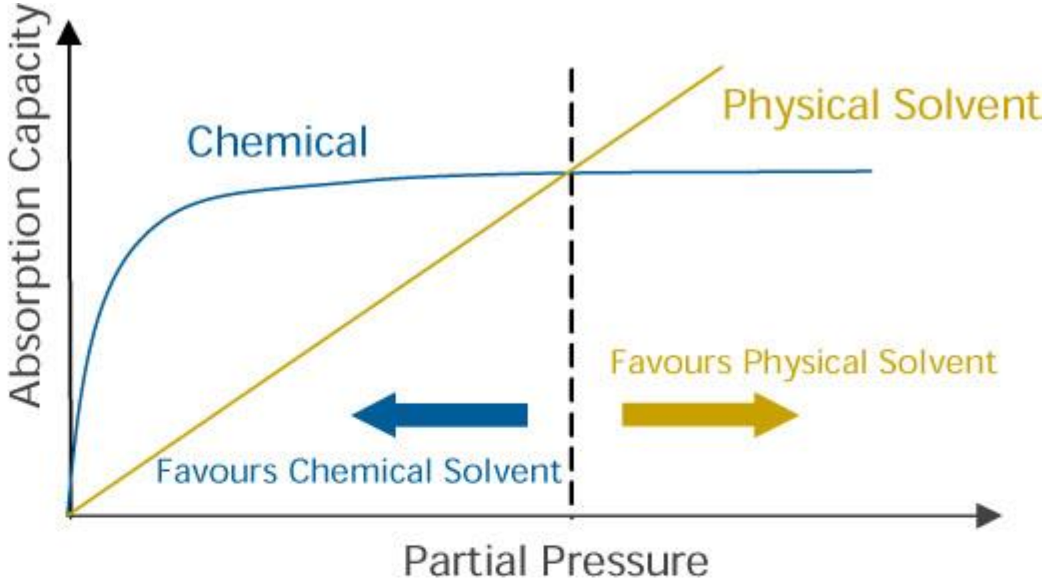
Natural gas sweetening with high CO_2 field:
1400 -2800 tpd CO_2

- ~ 250 Mtpa in 2016 (15% CCS, 50% Urea, 35% others)

Pictures: Mitchell R. (2008), MHI; Berchiche M. (2017).
Global CCS Institute (2017).

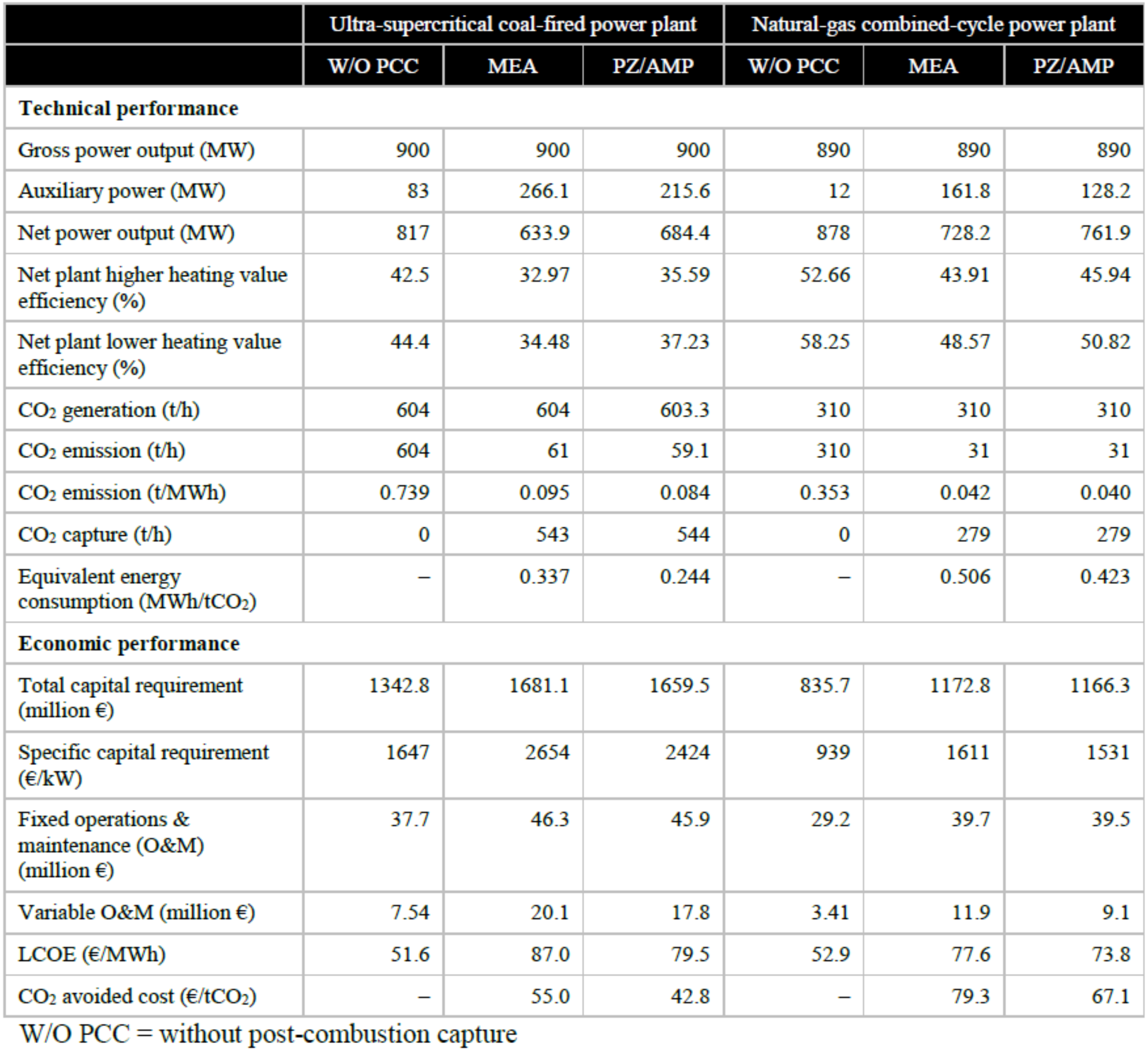
CO_2 separation technologies

- Avoid fluid mixtures
- Absorption
  - Physical
  - Chemical
- Adsorption
- Membranes
- Cryogenic separation
- Others…



Threshold value ~15 vol-% in flue gas,
or 4 bar of P_CO2

CO_2 capture benchmark



	Ultra-supercritical coal-fired power plant			Natural-gas combined-cycle power plant		
	W/O PCC	MEA	PZ/AMP	W/O PCC	MEA	PZ/AMP
Technical performance						
Gross power output (MW)	900	900	900	890	890	890
Auxiliary power (MW)	83	266.1	215.6	12	161.8	128.2
Net power output (MW)	817	633.9	684.4	878	728.2	761.9
Net plant higher heating value efficiency (%)	42.5	32.97	35.59	52.66	43.91	45.94
Net plant lower heating value efficiency (%)	44.4	34.48	37.23	58.25	48.57	50.82
CO_2 generation (t/h)	604	604	603.3	310	310	310
CO_2 emission (t/h)	604	61	59.1	310	31	31
CO_2 emission (t/MWh)	0.739	0.095	0.084	0.353	0.042	0.040
CO_2 capture (t/h)	0	543	544	0	279	279
Equivalent energy consumption (MWh/tCO_2)	–	0.337	0.244	–	0.506	0.423
Economic performance						
Total capital requirement (million €)	1342.8	1681.1	1659.5	835.7	1172.8	1166.3
Specific capital requirement (€/kW)	1647	2654	2424	939	1611	1531
Fixed operations & maintenance (O&M) (million €)	37.7	46.3	45.9	29.2	39.7	39.5
Variable O&M (million €)	7.54	20.1	17.8	3.41	11.9	9.1
LCOE (€/MWh)	51.6	87.0	79.5	52.9	77.6	73.8
CO_2 avoided cost (€/tCO_2)	–	55.0	42.8	–	79.3	67.1

W/O PCC = without post-combustion capture

CHEMICAL ENGINEERING

IEAGHG, 2019. Further assessment of emerging CO_2 capture technologies for the power sector and their potential to reduce costs

CO_2 capture technologies maturity

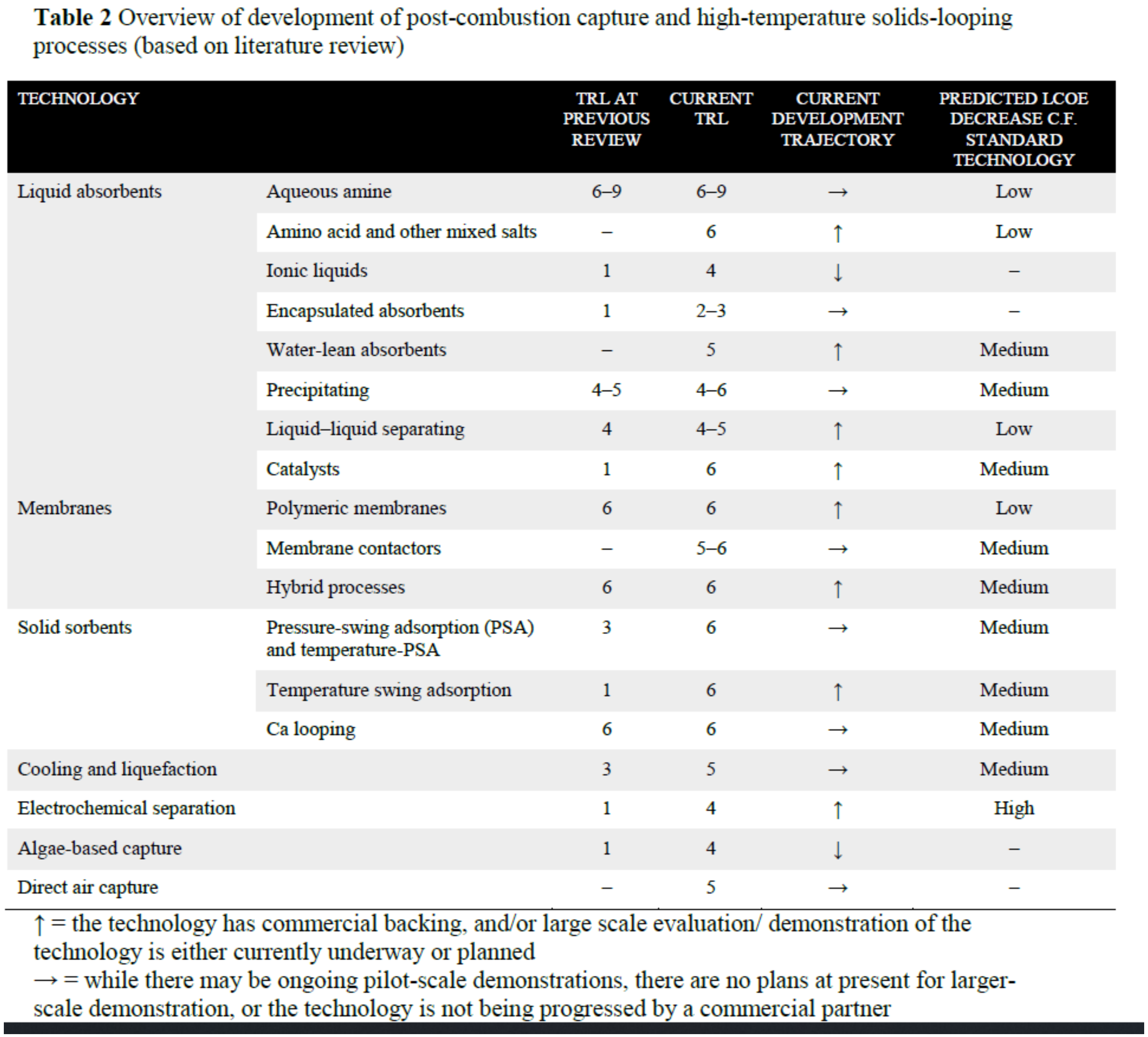


Table 2 Overview of development of post-combustion capture and high-temperature solids-looping processes (based on literature review)

TECHNOLOGY		TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Liquid absorbents	Aqueous amine	6–9	6–9	→	Low
	Amino acid and other mixed salts	–	6	↑	Low
	Ionic liquids	1	4	↓	–
	Encapsulated absorbents	1	2–3	→	–
	Water-lean absorbents	–	5	↑	Medium
	Precipitating	4–5	4–6	→	Medium
	Liquid–liquid separating	4	4–5	↑	Low
	Catalysts	1	6	↑	Medium
Membranes	Polymeric membranes	6	6	↑	Low
	Membrane contactors	–	5–6	→	Medium
	Hybrid processes	6	6	↑	Medium
Solid sorbents	Pressure-swing adsorption (PSA) and temperature-PSA	3	6	→	Medium
	Temperature swing adsorption	1	6	↑	Medium
	Ca looping	6	6	→	Medium
Cooling and liquefaction		3	5	→	Medium
Electrochemical separation		1	4	↑	High
Algae-based capture		1	4	↓	–
Direct air capture		–	5	→	–

↑ = the technology has commercial backing, and/or large scale evaluation/ demonstration of the technology is either currently underway or planned
→ = while there may be ongoing pilot-scale demonstrations, there are no plans at present for larger-scale demonstration, or the technology is not being progressed by a commercial partner

IEAGHG, 2019. Further assessment of emerging CO_2 capture technologies for the power sector and their potential to reduce costs

Pros and cons

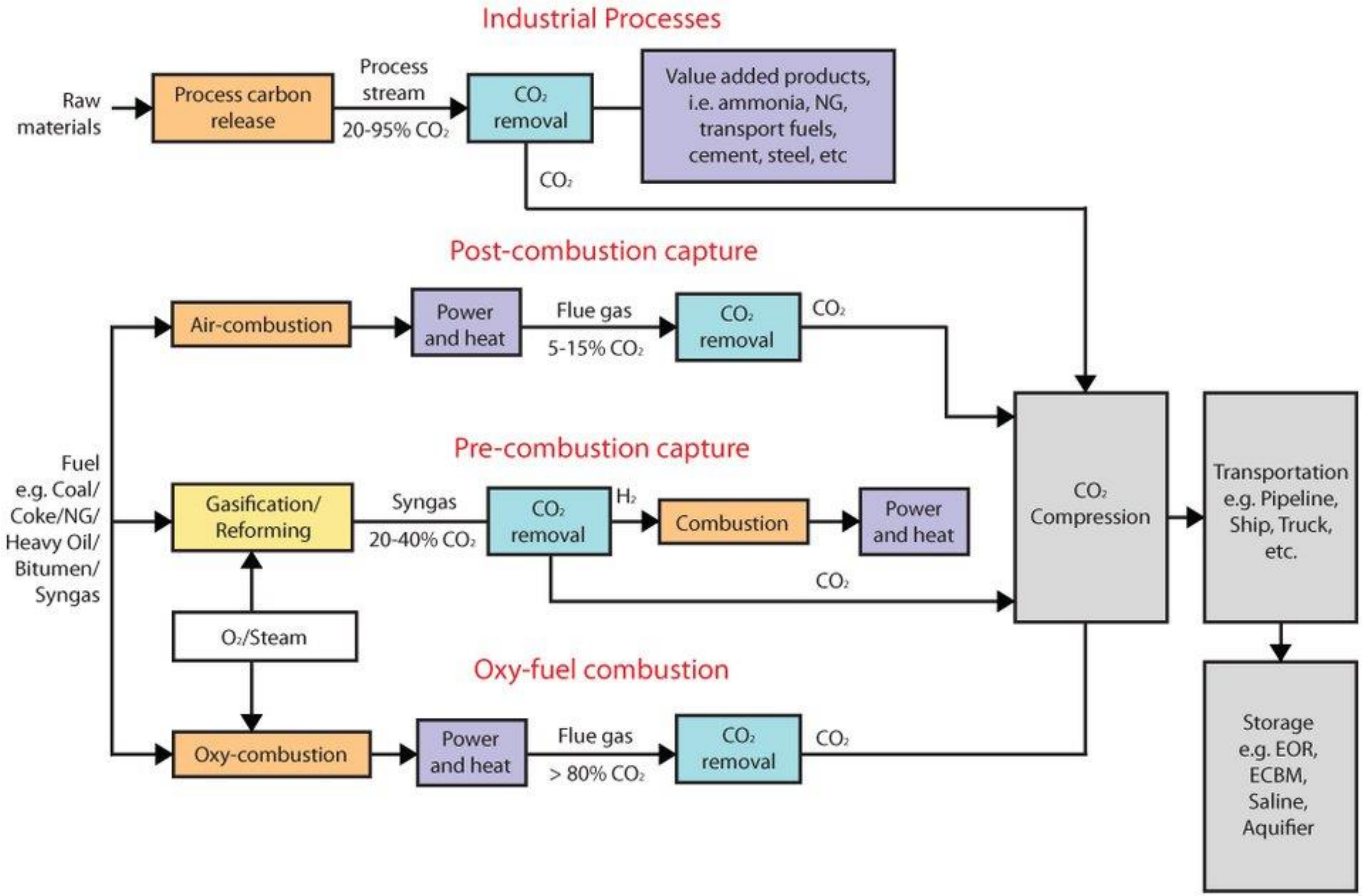
Pros:

- Rapidly scalable for different industries (end-of-pipe)
- Fast and flexible dynamics
- Retrofit possible on existing units

Cons:

- Large initial investissement
- Significant operating costs (efficiency drops by ~10-40%)
- Secondary emissions
- Technologies mature or close to maturity but not commercial yet

CO_2 capture configurations



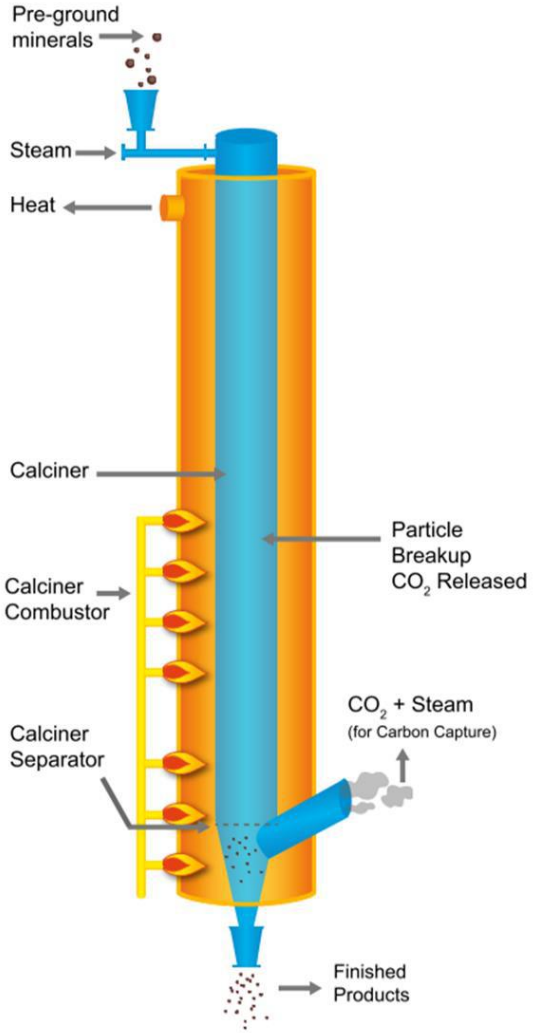
Industrial processes

1. **CO_2 not resulting from combustion**

- Cement plants
  - $CaCO_3 \rightarrow CaO + CO_2$
  - Potential gain: -60% CO_2
  - High temperature → 1000°C

  - Pilot plant close to Liège
  - End of construction: 2019
  - Investment: 21 M€

https://www.project-leilac.eu/videos

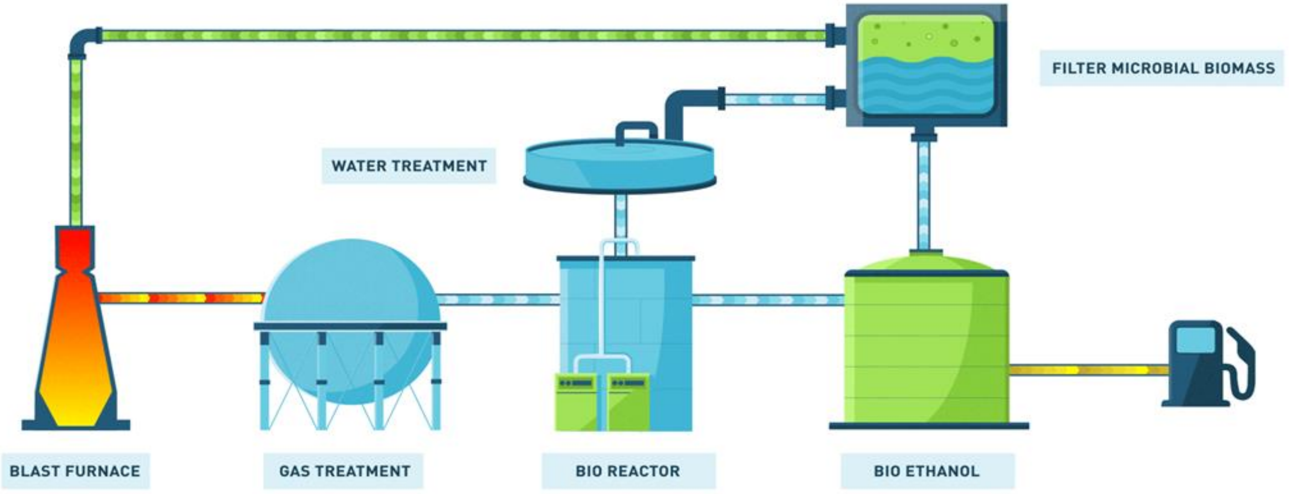


LEILAC public preFEED report, 2016

Industrial processes

1. **CO_2 not resulting from combustion**

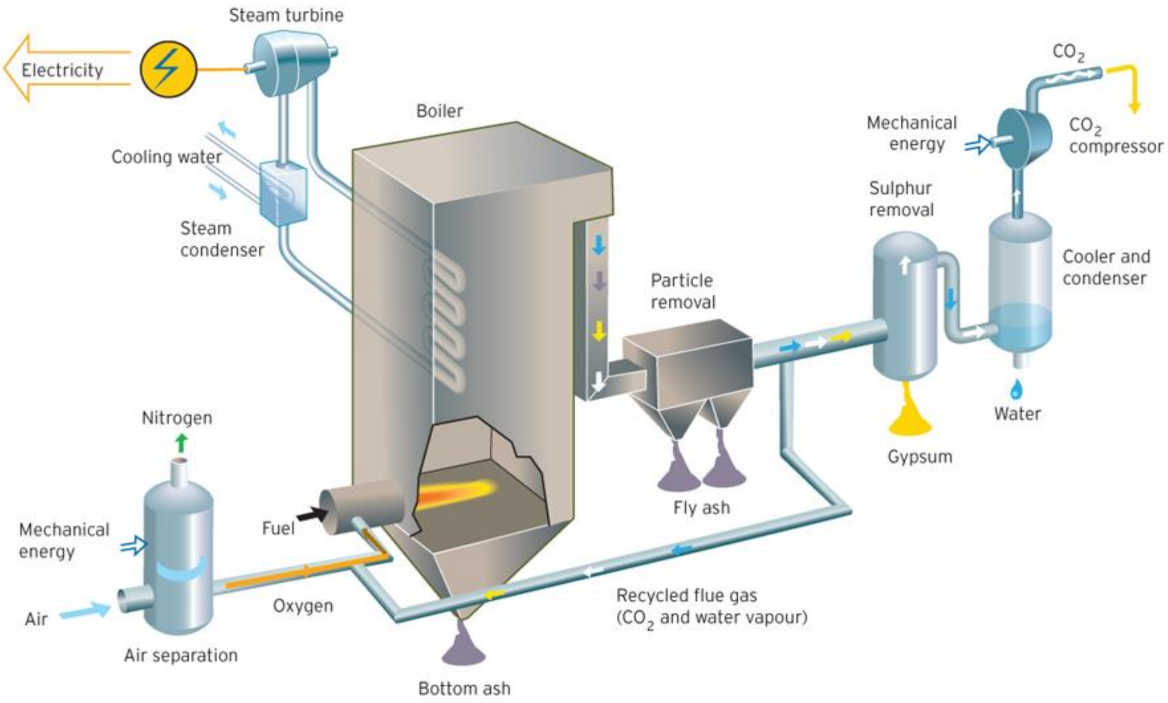
- Steel plants
  - Steelanol project: 87 M€, -70% CO2
  - Partners: Arcelor Mittal (Ghent plant), Lanzatech…
  - Investment in bioethanol production from CO_2 in flue gases
  - LanzaTech's technology recycles the waste gases and ferments them with a proprietary microbe to produce bioethanol



Steelanol project website

Oxyfuel combustion

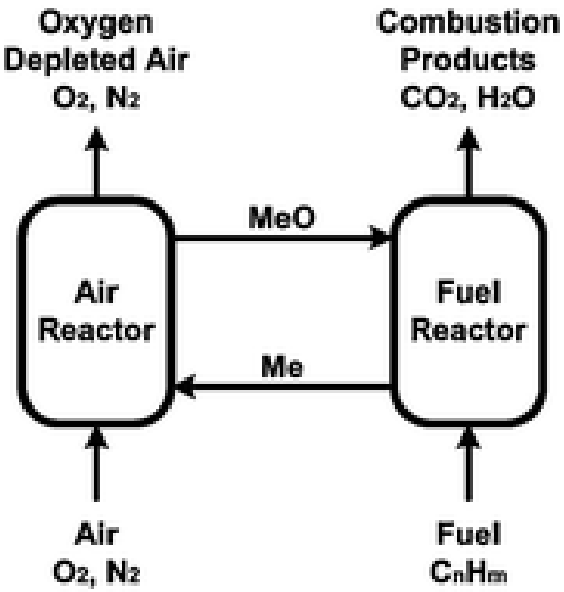
2. **Burn the fuel with pure oxygen**
    - Air separation needed
    - Waiting for large-scale projects

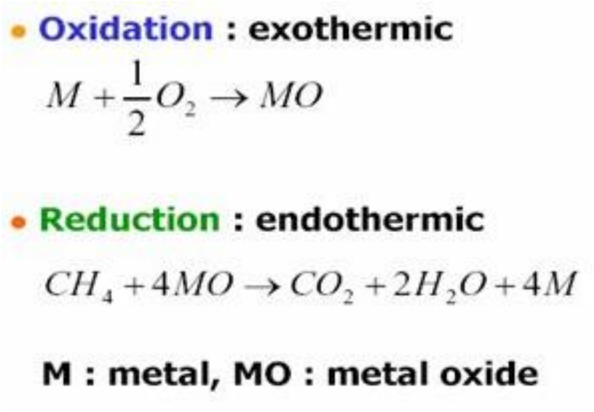


Chemical looping combustion

2. **Burn the fuel with pure oxygen**

- Special case: Chemical looping combustion
- Two reactors: air reactor, fuel reactor
- Metallic oxygen carrier flows in the loop





- **Oxidation : exothermic**

$$M + \frac{1}{2}O_2 \rightarrow MO$$

- **Reduction : endothermic**

$$CH_4 + 4MO \rightarrow CO_2 + 2H_2O + 4M$$

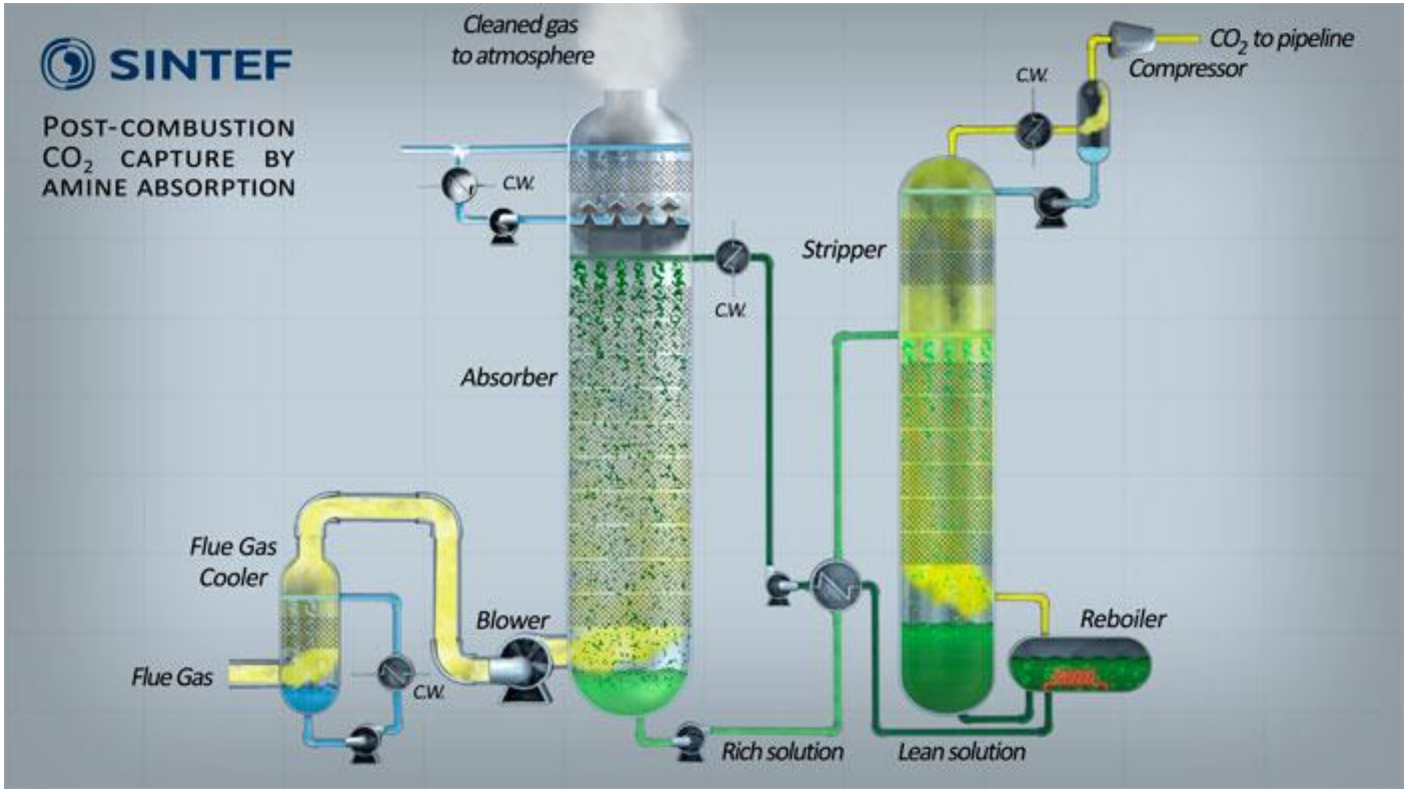
M : metal, MO : metal oxide

- In particular: Calcium looping well suited for cement industry

Post-combustion capture

3. Capture CO_2 from combustion gases

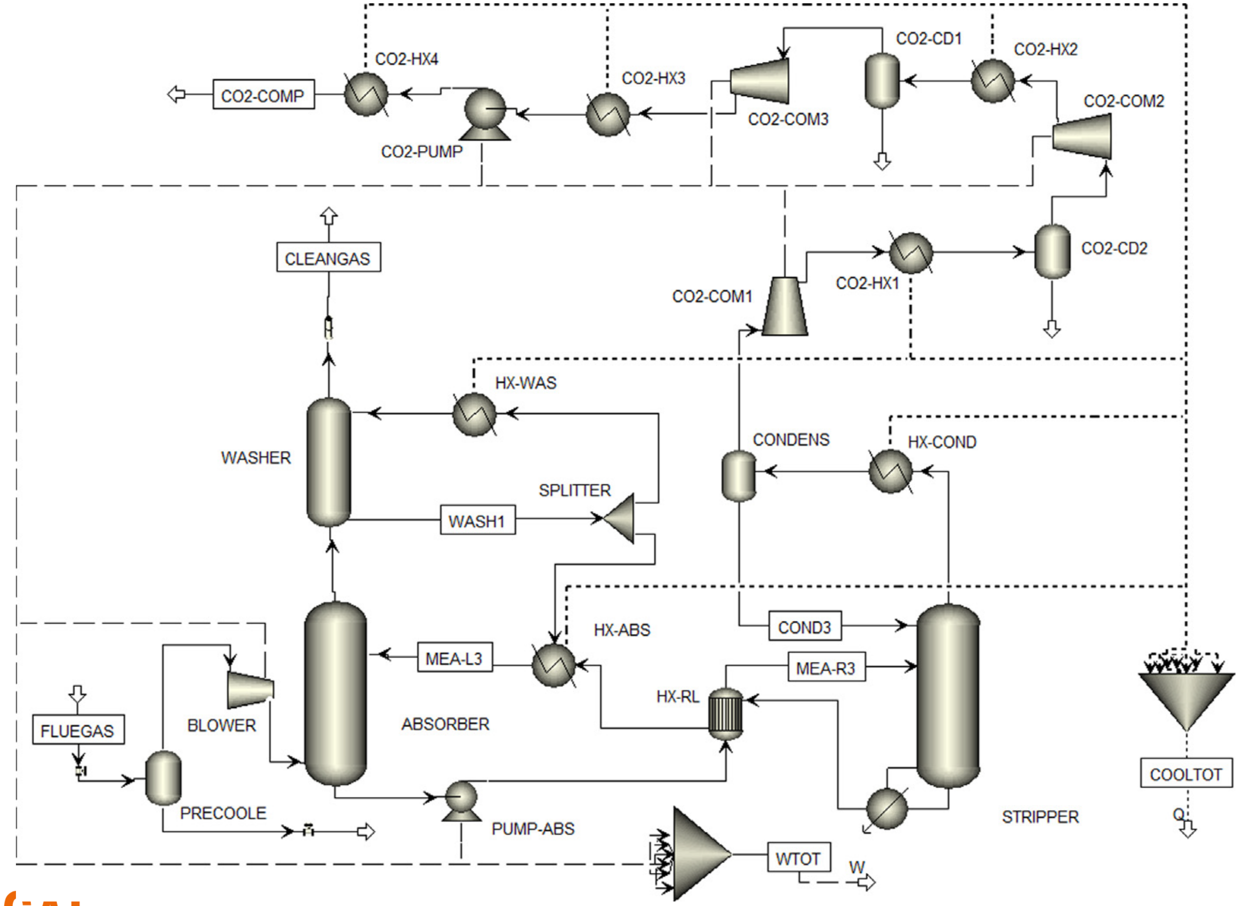
- Usually absorption-regeneration loop with chemical solvents



Post-combustion capture

3. **Capture CO_2 from combustion gases**

- Usually absorption-regeneration loop with chemical solvents

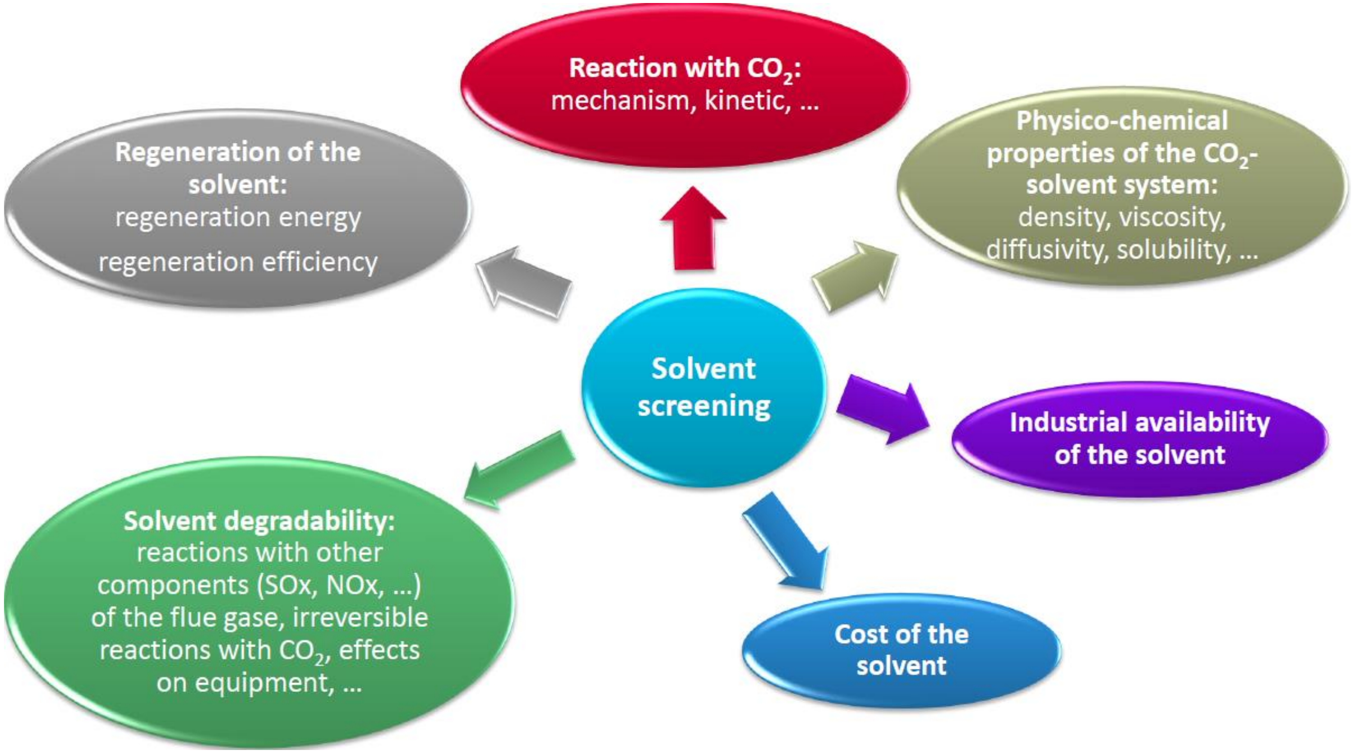


DOI: 10.1016/j.compchemeng.2015.05.003

Post-combustion capture

3. **Capture CO_2 from combustion gases**

- Characteristics of a chemical solvent



Solvent screening

Reaction with CO_2: mechanism, kinetic, …

Physico-chemical properties of the CO_2-solvent system: density, viscosity, diffusivity, solubility, …

Industrial availability of the solvent

Cost of the solvent

Solvent degradability: reactions with other components (SOx, NOx, …) of the flue gase, irreversible reactions with CO_2, effects on equipment, …

Regeneration of the solvent: regeneration energy

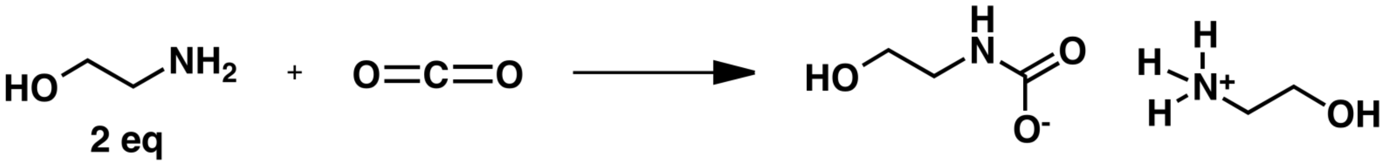
regeneration efficiency

Dubois, UMons, 2011

Post-combustion capture

3. **Capture CO_2 from combustion gases**

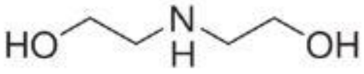
- Amines (1, 2ary) in water



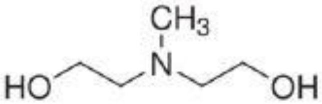
- Amine (3ary) in water $R_1R_2R_3N + CO_2 + H_2O \leftrightarrows R_1R_2R_3N^+H + HCO_3^-$

- Some examples

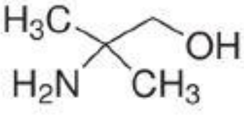
MEA



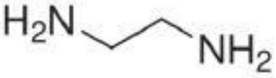
DEA



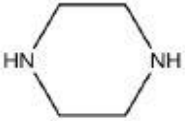
MDEA



AMP



EDA

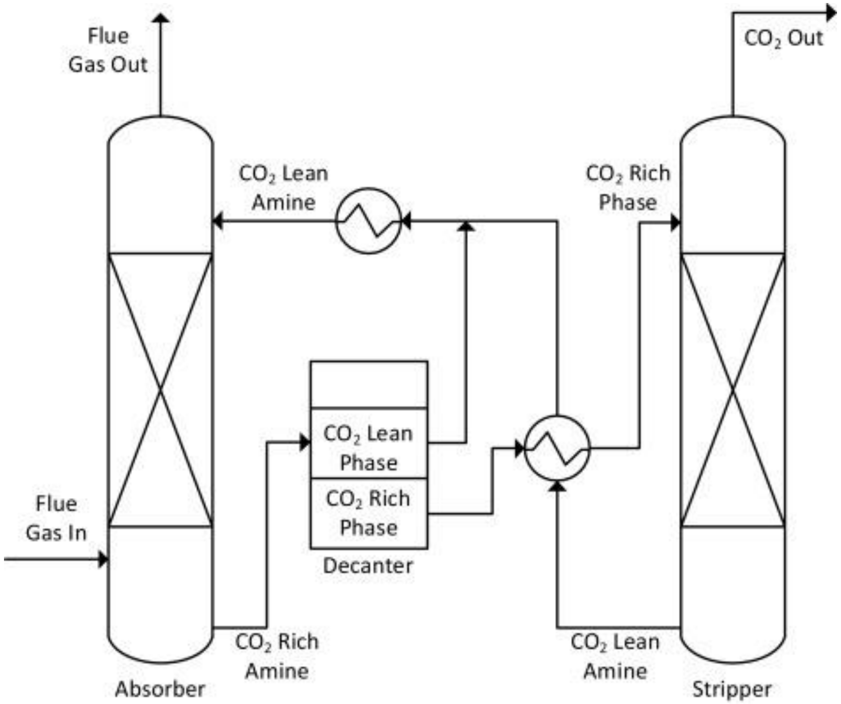


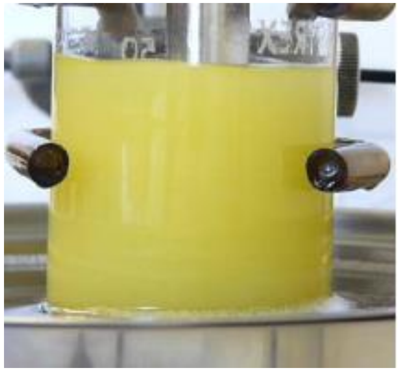
PZ

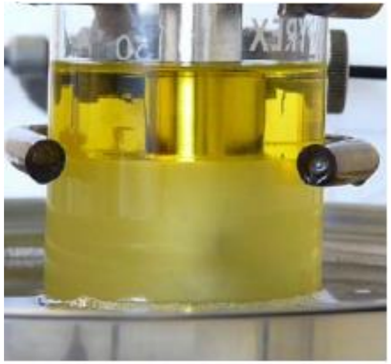
Post-combustion capture

3. **Capture CO_2 from combustion gases**

- Alternatives to amines
  - Chilled Ammonia, amino-acids, ionic liquids…
  - Demixing solvents => LLV and thermo models







Heldebrant et al., 2009; Raynal et al., IFP, 2011

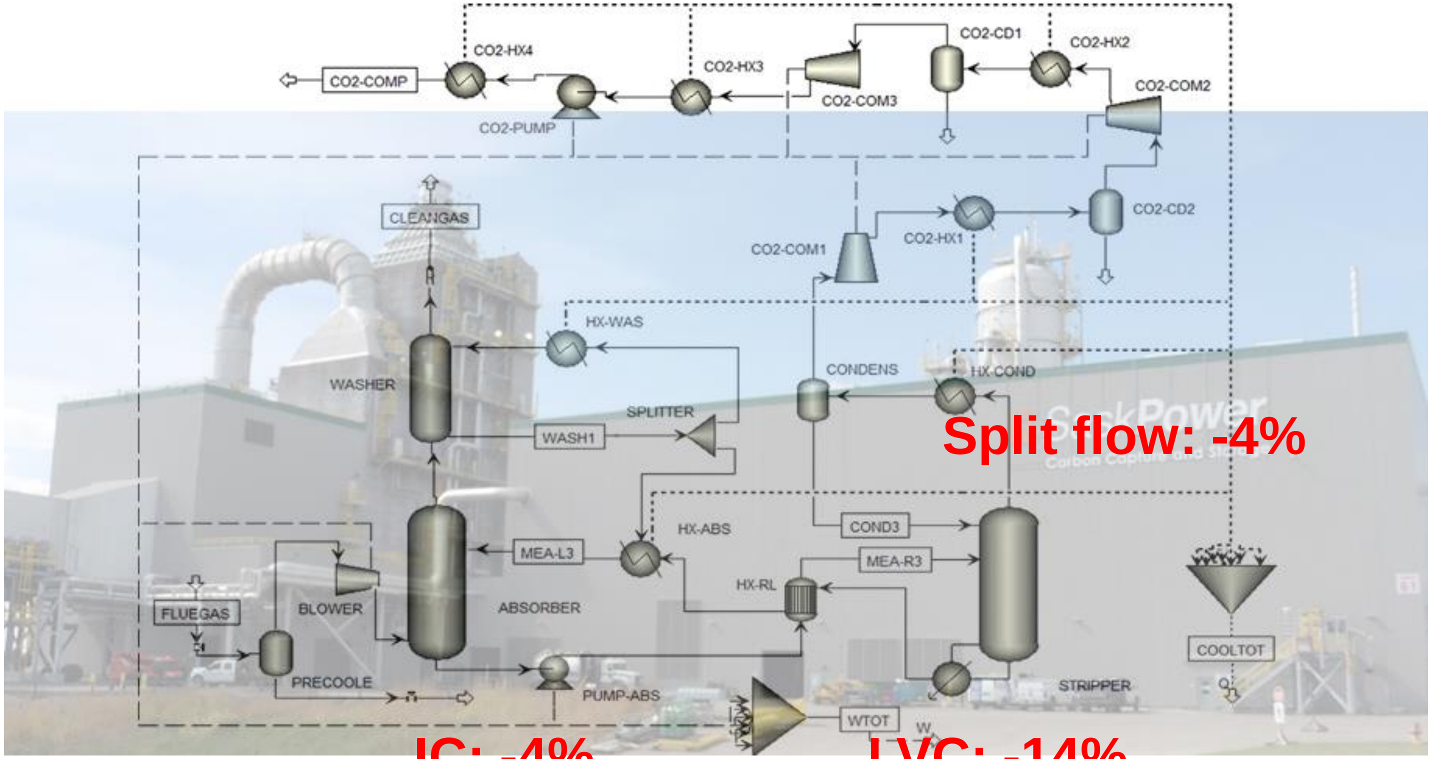
Post-combustion capture

- Commercial scale has been achieved
  - Boundary Dam, Saskatchewan (2014)
    - Coal power plant 160 MWe
    - 2700 tCO_2/day captured (~90% capture rate)

      => Flue gas: 180 Nm³/s ; Solvent: 550 L/s
  - Petra Nova, Texas (2017):
    - 4400 tCO_2/day, 1 milliard US$

Post-combustion capture

- Focus: research at ULiège
  - Modeling and energy optimization of systems



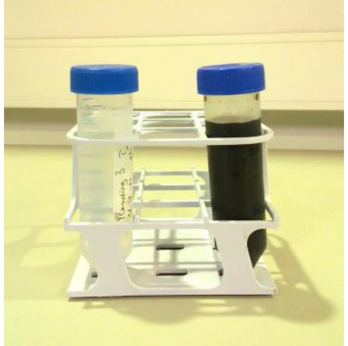
Split flow: -4%

IC: -4%

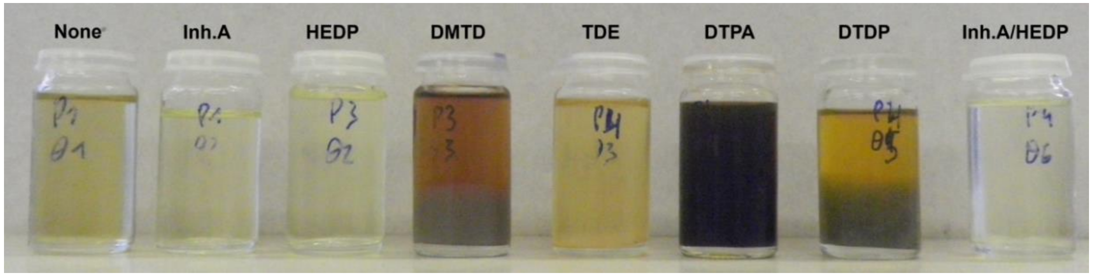
LVC: -14%

Léonard et al., 2014&2015. DOI:10.1021/ie5036572, DOI: 10.1016/j.compchemeng.2015.05.003

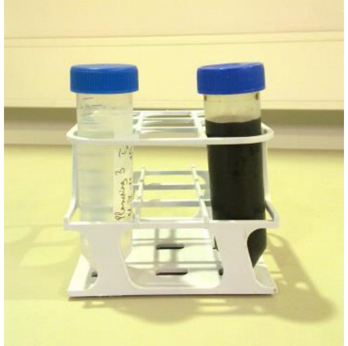
Post-combustion capture



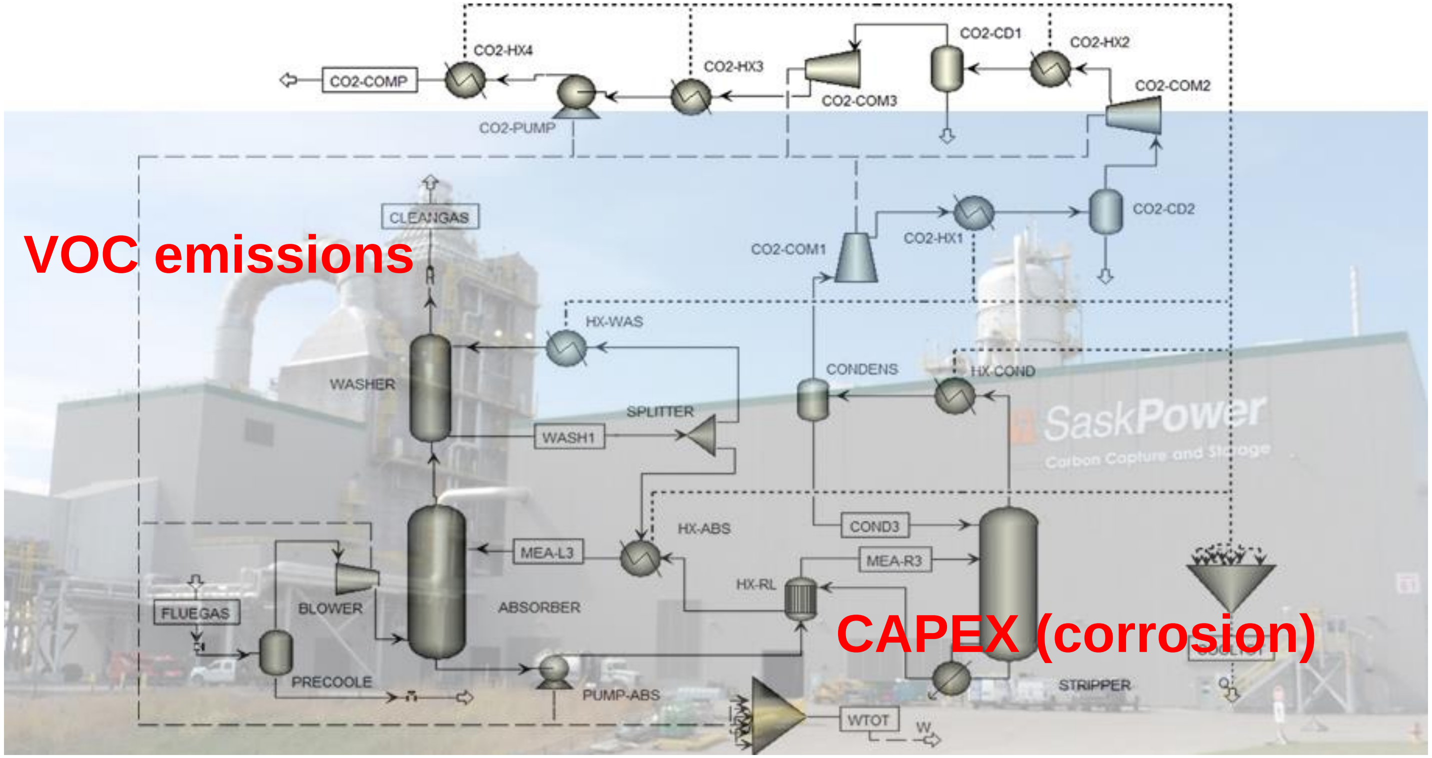
- Focus: research at ULiège
    - Stability of chemical solvents
    - Operational issues
        - Viscosity change, decrease of solvent properties…
        - Corrosivity of amine systems
        - Emissions of VOC
    - Different types of degradation
        - Oxidative
        - Thermal
        - SO_X, NO_X …



Post-combustion capture



- Focus: research at ULiège
  - Stability of chemical solvents



VOC emissions

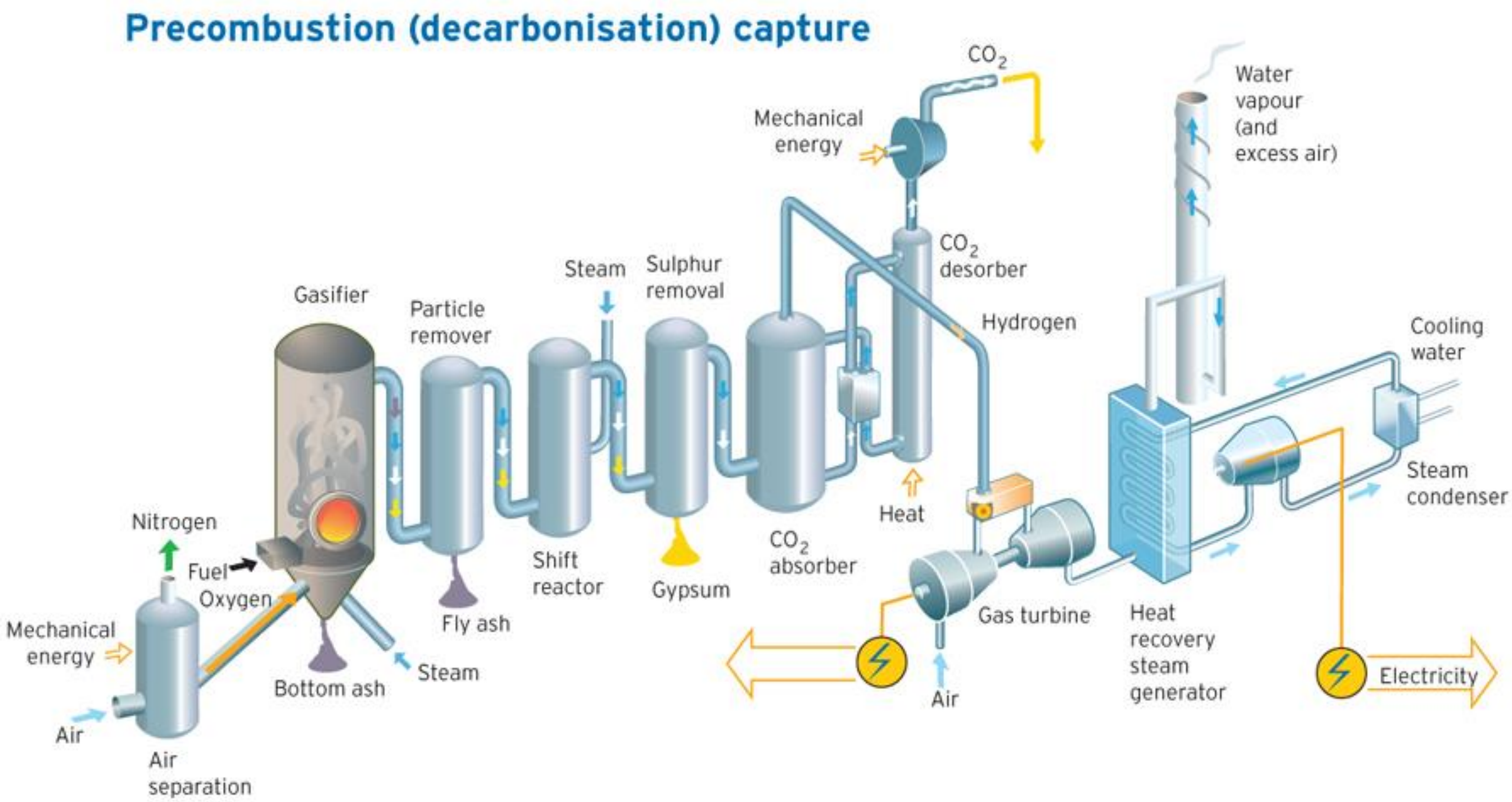
CAPEX (corrosion)

OPEX: viscosity, altered properties…

Léonard et al., 2014&2015. DOI:10.1021/ie5036572, DOI: 10.1016/j.compchemeng.2015.05.003

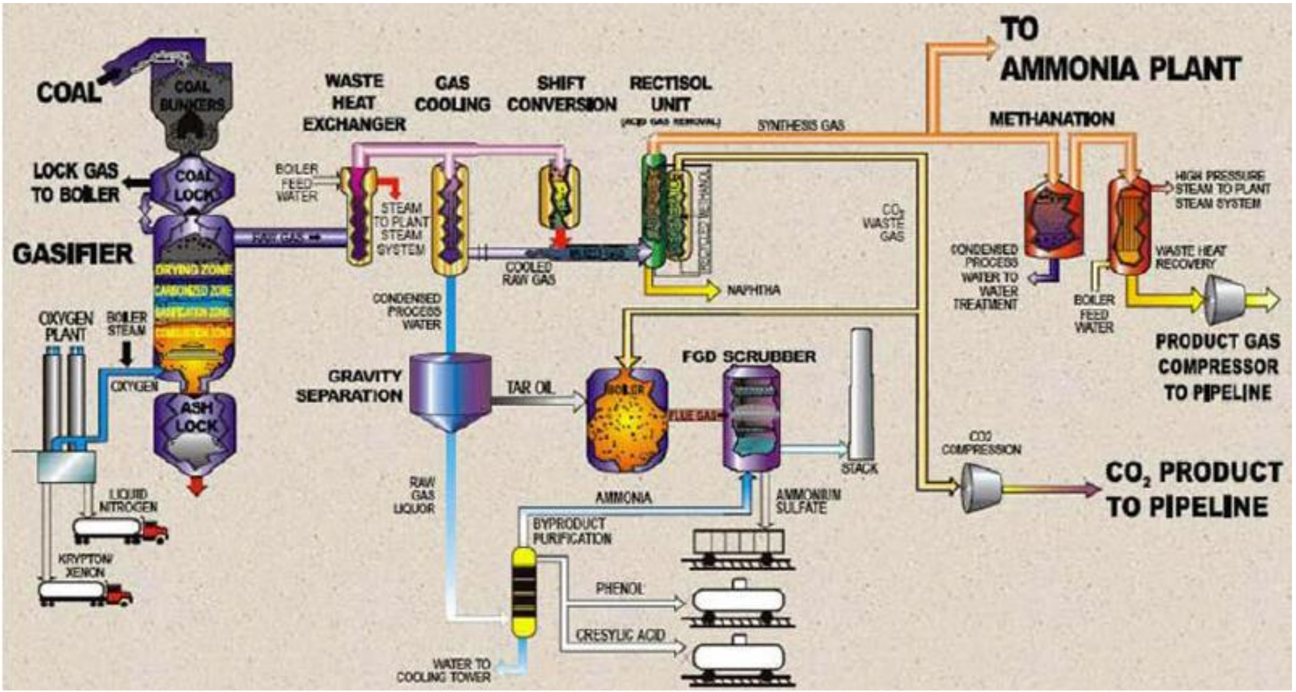
Pre-combustion capture

4. **Remove C from the solid fuel by gasification**



Pre-combustion capture

- Great Plains Synfuel Plant, North Dakota (US)
  - ❑ Gasification of 16 000 tpd of lignite
  - ❑ 8 200 tCO_2/day (~50% capture rate), 3 Mtpa since 2000

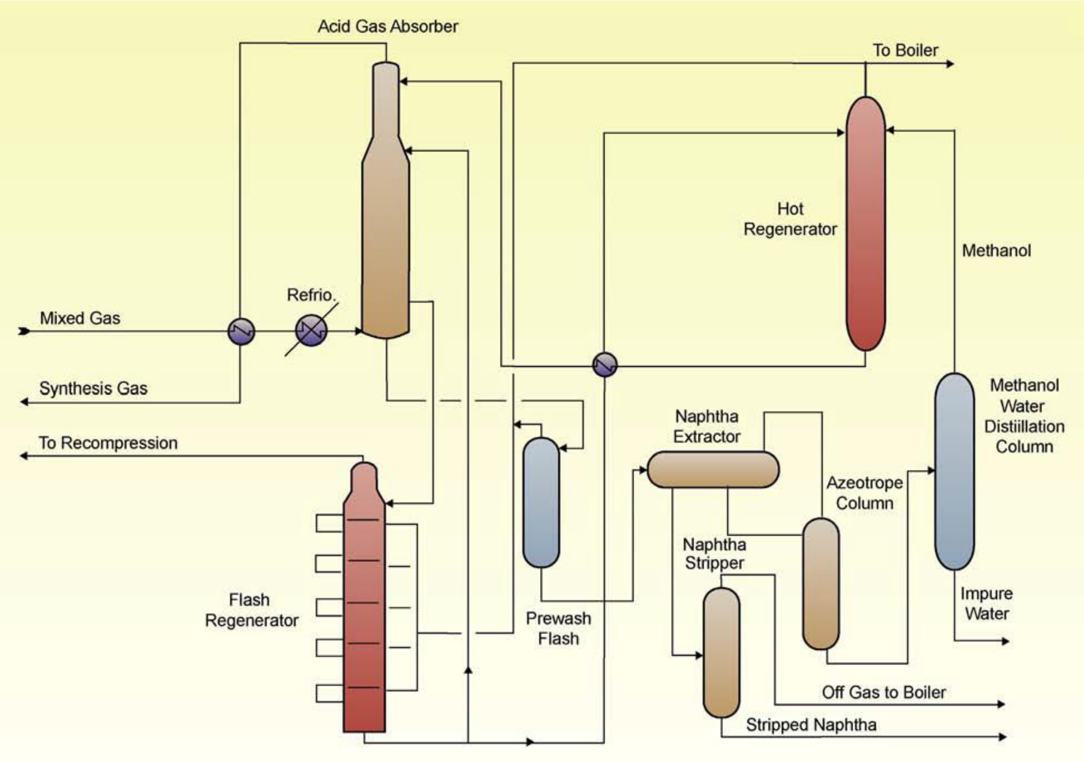


http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/great-plains

Pre-combustion capture

4. **Remove C from the solid fuel by gasification**

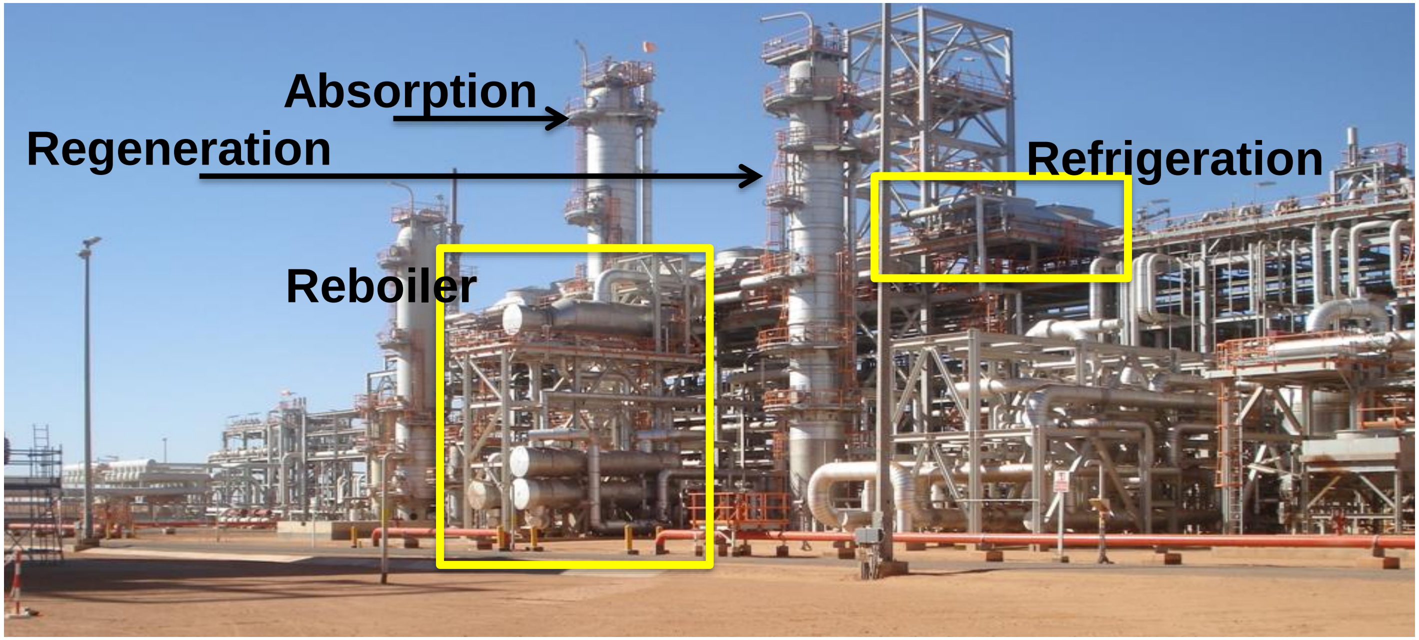
- GPSP Rectisol process: physical absorption in cold methanol
- Largest utility consumption and largest plant bottleneck



Practical experience gained at GSPS, US DOE report, 2006

Pre-combustion capture

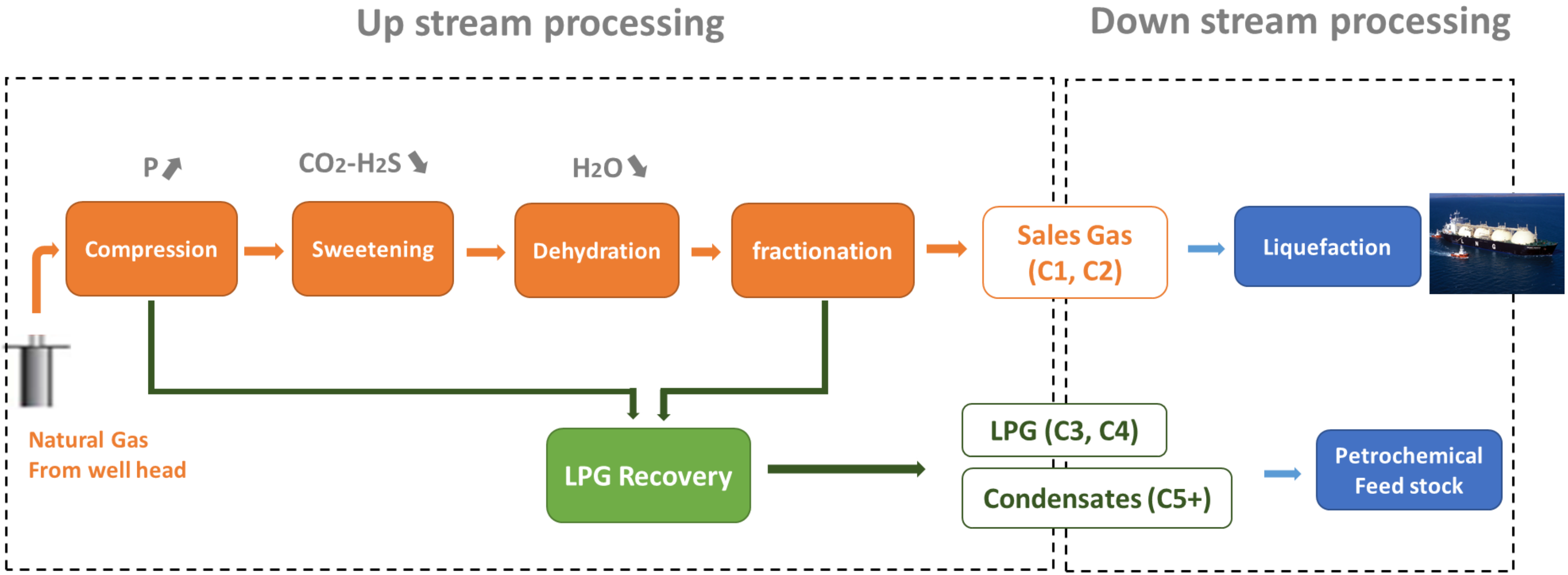
- Case study: natural gas sweetening
  - Conventional process: Absorption in liquid solvents



  - => PhD work (Berchiche M.): Multi-objective optimization and energy integration of CO_2 capture in natural gas sweetening

Pre-combustion capture

- Case study: natural gas sweetening
  - Conventional process: Absorption in liquid solvents



Up stream processing

Down stream processing

P ↗

CO_2-H_2S ↘

H_2O ↘

Compression → Sweetening → Dehydration → fractionation → Sales Gas (C1, C2) → Liquefaction

Natural Gas
From well head

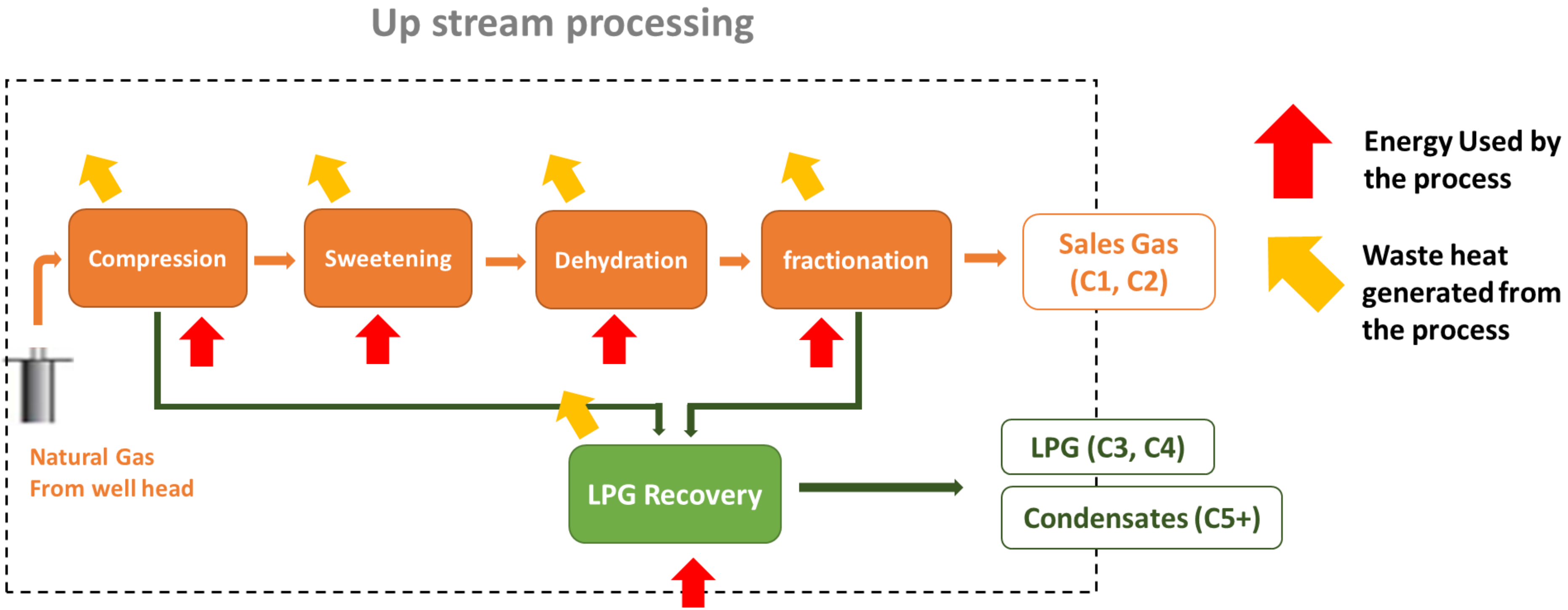
LPG Recovery → LPG (C3, C4)

Condensates (C5+) → Petrochemical Feed stock

Berchiche et al., 2020. CACE 48, 67-72
https://doi.org/10.1016/B978-0-12-823377-1.50012-4

Pre-combustion capture

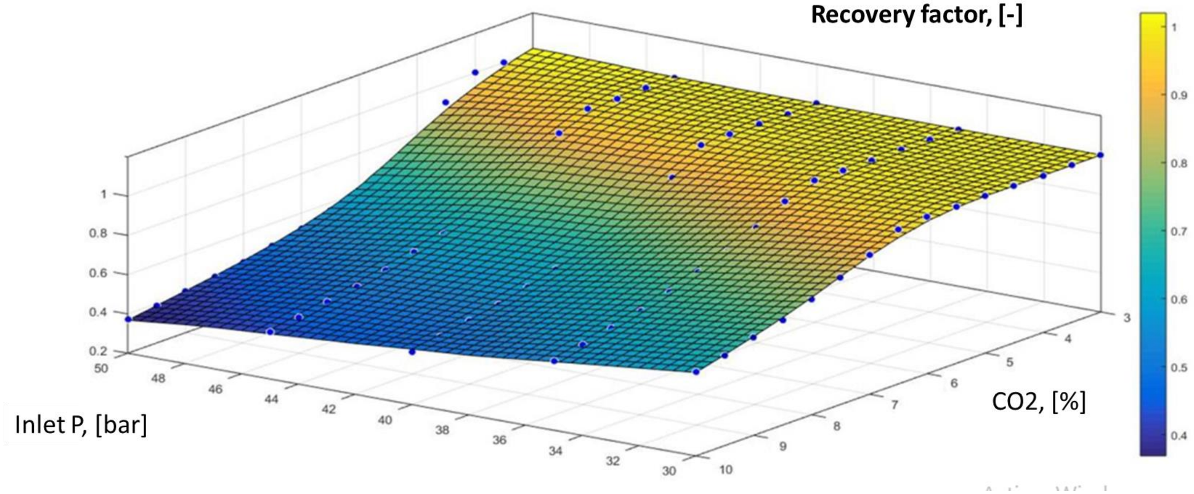
- Case study: natural gas sweetening
  - Conventional process: Absorption in liquid solvents



Berchiche et al., 2020. CACE 48, 67-72
https://doi.org/10.1016/B978-0-12-823377-1.50012-4

Pre-combustion capture

- Case study: natural gas sweetening
  - Conventional process: Absorption in liquid solvents

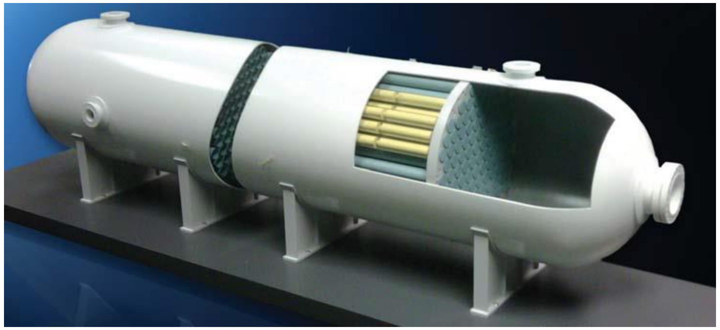


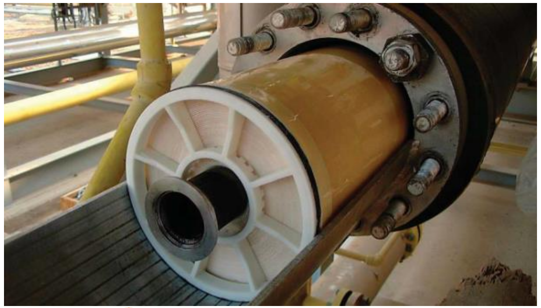
  - Direct use of waste heat into the process allows to recover an amount of 40 to 100% of thermal energy required by the process.
  - The use of ORC as a bottoming technology => energy output varying from 30 to 190% of the required pumping power with a reduction in cooling loads of the process ranging from 4 to 16%.

Berchiche et al., 2020. CACE 48, 67-72
https://doi.org/10.1016/B978-0-12-823377-1.50012-4

Pre-combustion capture

- Case study: natural gas sweetening
  - Usually physical and/or chemical solvents
  - Also membranes for off-shore platforms (still in development)
    - Space constraints
    - Pre-treatment: TSAdsorption for Hg, H_2O and heavy HC





UOP Separex^{TM} Membrane Systems, UOP LLC, 2011

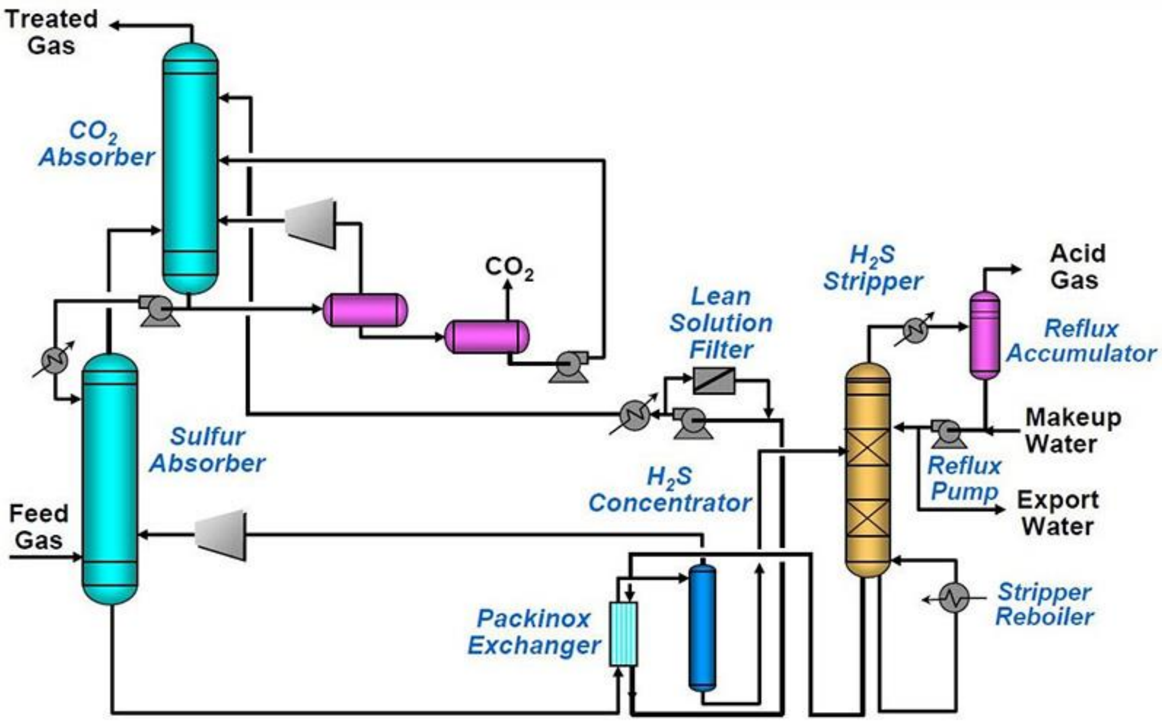
Pre-combustion capture

Not always a risk-free process!

- Kemper County (Mississippi): IGCC, 582 MWe
- 9500 tCO_2/day captured (~65% capture rate)
- Cost estimation: from 2.9 to 7.5 bn$ … then stop of the project

Pre-combustion capture

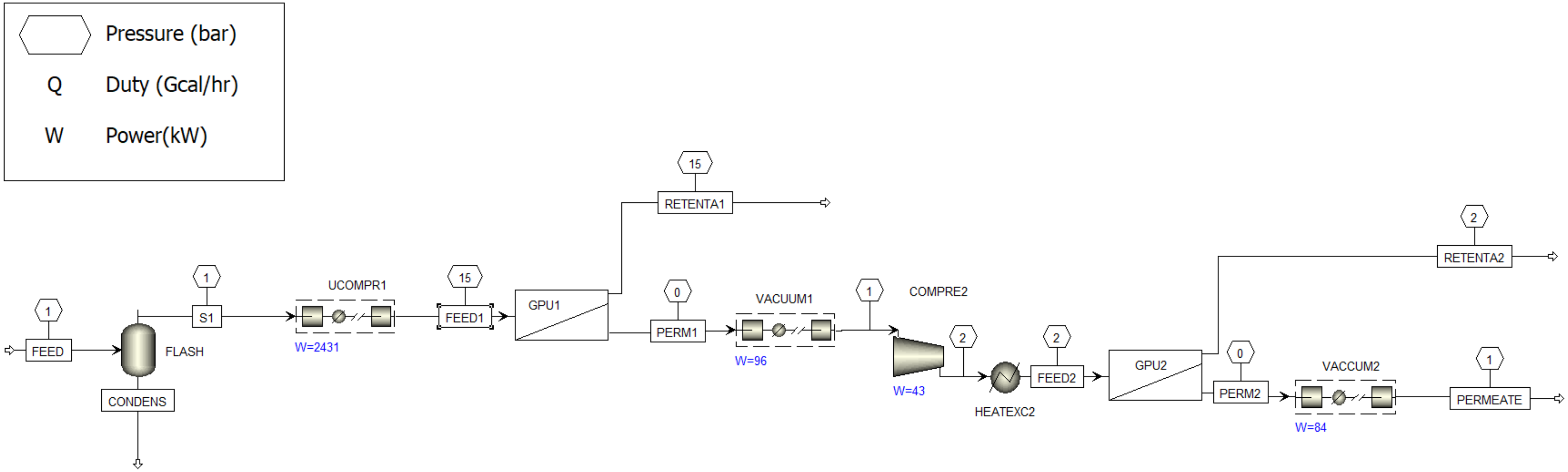
4. **Remove C from the solid fuel by gasification**
    - Kemper County: CO_2 separation using the Selexol process
    - Physical absorption in dimethylethers of polyethylene glycol



UOP Selexol^{TM} Technology for Acid Gas Removal, UOP LLC, 2009

Detailed process models

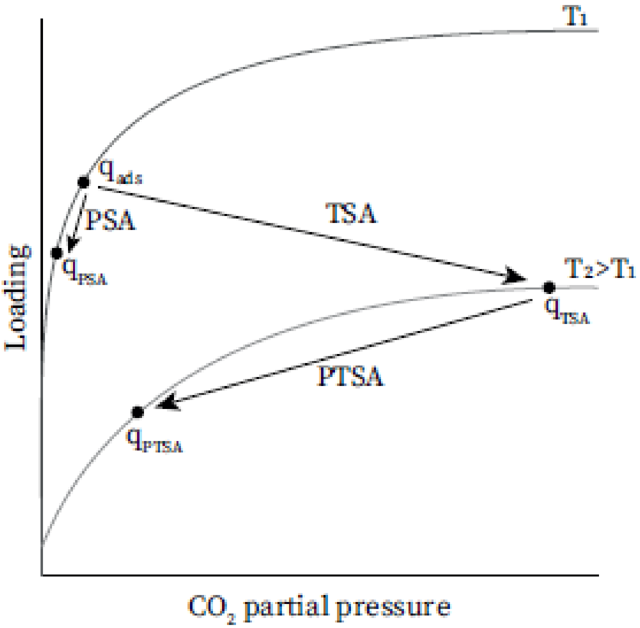
- Membrane plant with different configurations
  - Costs come mostly from a need for pressure driving force
  - With larger membrane area, more CO_2 is captured but its purity decreases
  - A lot of research is on-going to improve membranes properties

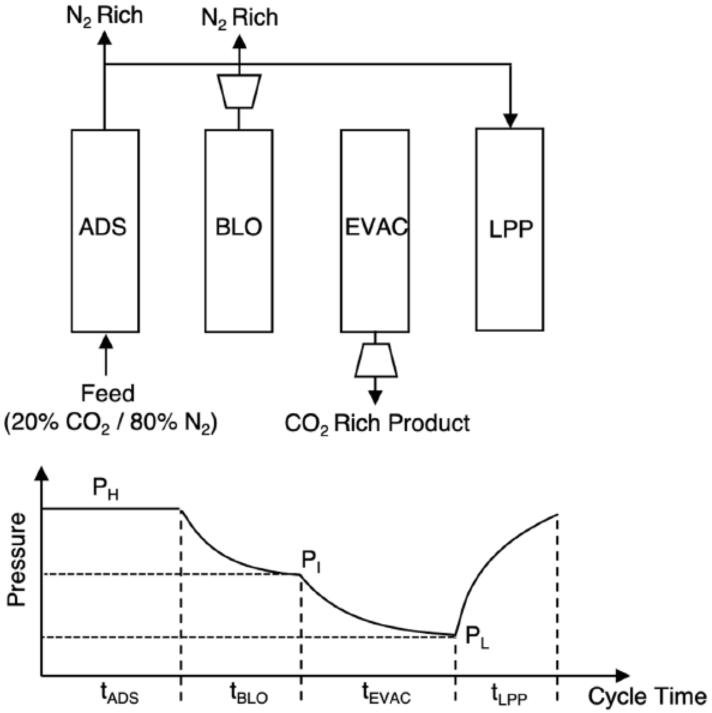


Bonanno R., Master's thesis

Detailed process models

- Adsorption plant with P/VSA
  - Technologies still under development, many sorbent candidates
  - Usually batch process with several beds in parallel
  - First-choice technology for Direct Air Capture



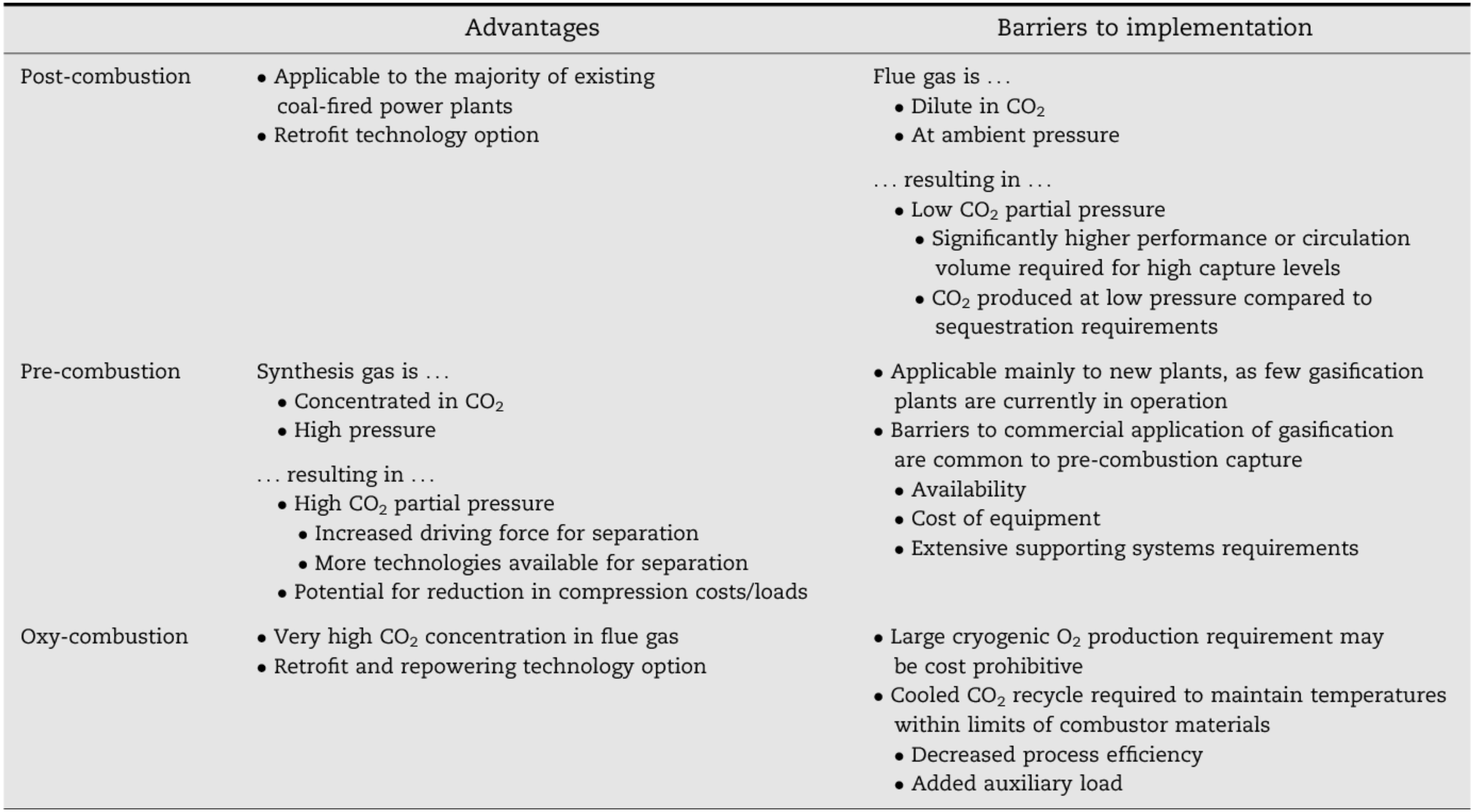


CHEMICAL ENGINEERING

https://doi.org/10.1016/j.seppur.2020.117832
Riva U., Master’s thesis

LIÈGE université

Comparison of some configurations…



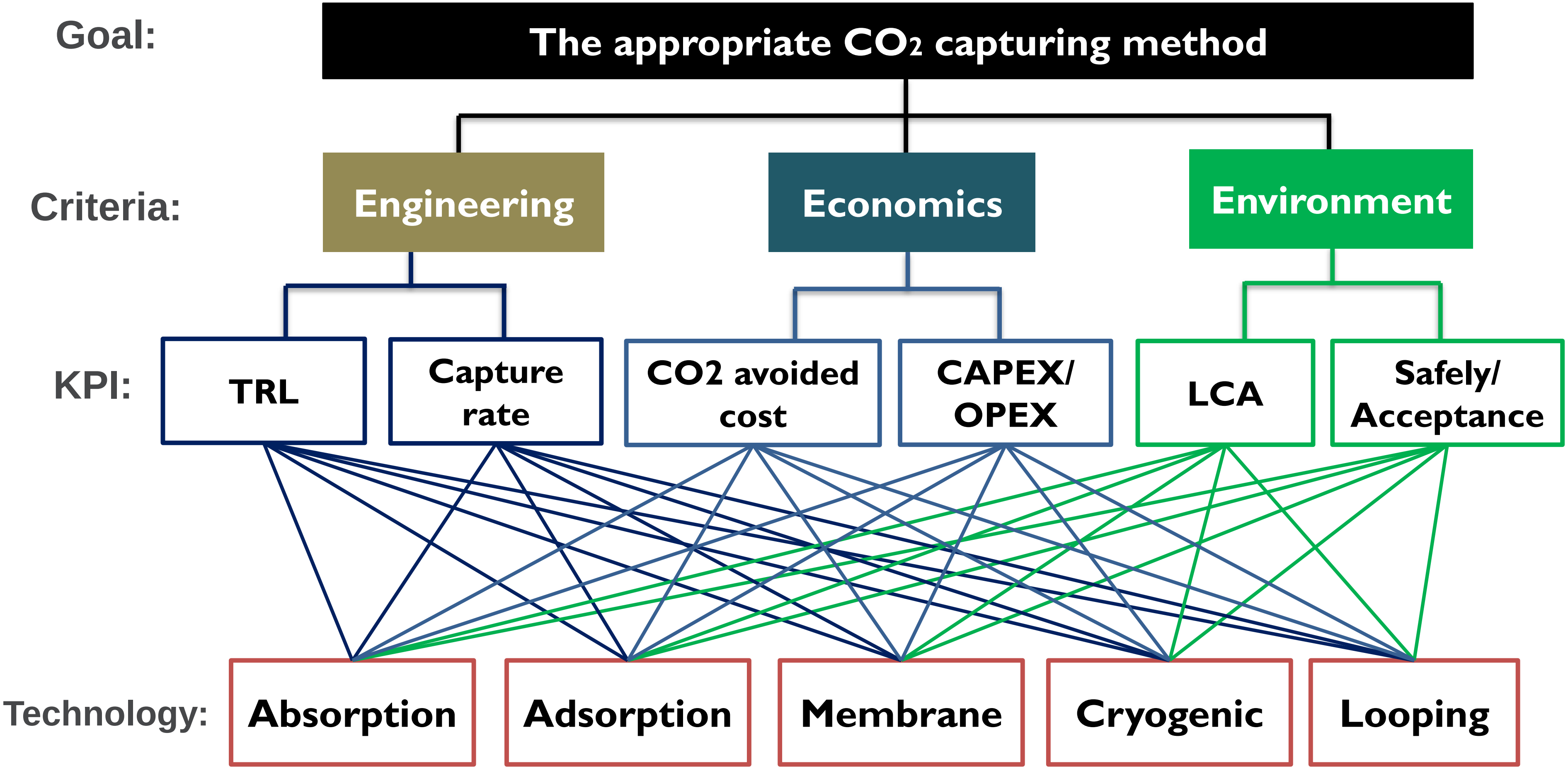
	Advantages	Barriers to implementation
Post-combustion	• Applicable to the majority of existing coal-fired power plants • Retrofit technology option	Flue gas is … • Dilute in CO_2 • At ambient pressure … resulting in … • Low CO_2 partial pressure • Significantly higher performance or circulation volume required for high capture levels • CO_2 produced at low pressure compared to sequestration requirements
Pre-combustion	Synthesis gas is … • Concentrated in CO_2 • High pressure … resulting in … • High CO_2 partial pressure • Increased driving force for separation • More technologies available for separation • Potential for reduction in compression costs/loads	• Applicable mainly to new plants, as few gasification plants are currently in operation • Barriers to commercial application of gasification are common to pre-combustion capture • Availability • Cost of equipment • Extensive supporting systems requirements
Oxy-combustion	• Very high CO_2 concentration in flue gas • Retrofit and repowering technology option	• Large cryogenic O_2 production requirement may be cost prohibitive • Cooled CO_2 recycle required to maintain temperatures within limits of combustor materials • Decreased process efficiency • Added auxiliary load

https://doi.org/10.1016/S1750-5836(07)00094-1

PROCURA ETF: Decision support tool

- We are convinced that CO_2 capture will play a role in future Belgian industrial systems
- But many technologies are available, and the right choice depends on many variables
  - Techno-economics and environmental footprint
  - Required purity of CO_2 ; presence of flue gas contaminants
  - …
- In the framework of the PROCURA project, we develop a decision support tool for helping local companies in their choice
  - Tool is currently at version 1.0, based on literature data
  - Next steps will refine the selection criteria, based on in-house process models (including TEA & LCA)
  - Tool will be demonstrated with Belgian case studies

PROCURA ETF: Decision support tool



Goal: The appropriate CO_2 capturing method

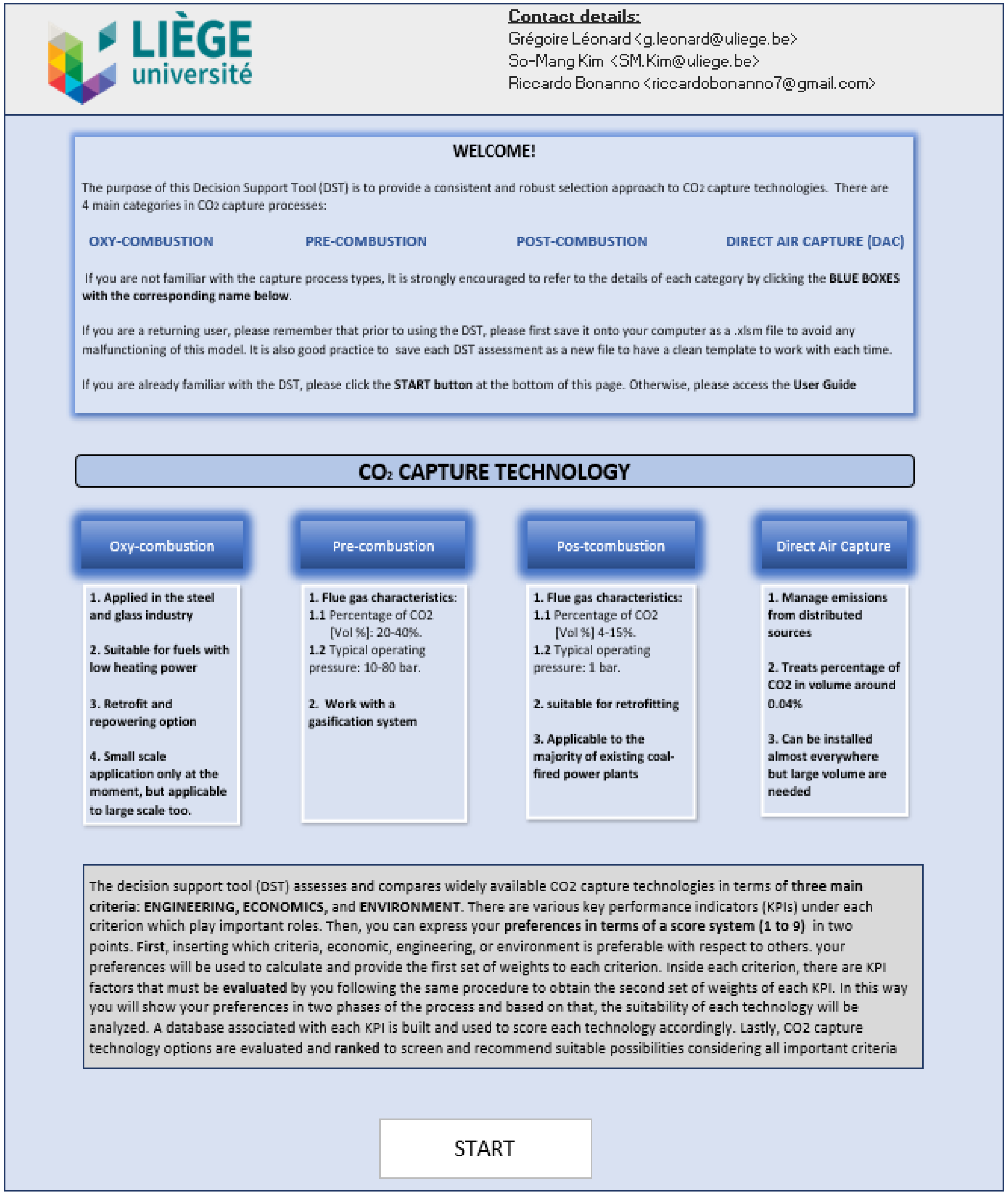
Criteria: Engineering, Economics, Environment

KPI:

- Engineering: TRL; Capture rate
- Economics: CO2 avoided cost; CAPEX/ OPEX
- Environment: LCA; Safely/ Acceptance

Technology: Absorption, Adsorption, Membrane, Cryogenic, Looping

Decision-support tool



Contact details:
Grégoire Léonard <g.leonard@uliege.be>
So-Mang Kim <SM.Kim@uliege.be>
Riccardo Bonanno <riccardobonanno7@gmail.com>

WELCOME!

The purpose of this Decision Support Tool (DST) is to provide a consistent and robust selection approach to CO_2 capture technologies. There are 4 main categories in CO_2 capture processes:

OXY-COMBUSTION PRE-COMBUSTION POST-COMBUSTION DIRECT AIR CAPTURE (DAC)

If you are not familiar with the capture process types, It is strongly encouraged to refer to the details of each category by clicking the **BLUE BOXES with the corresponding name below**.

If you are a returning user, please remember that prior to using the DST, please first save it onto your computer as a .xlsm file to avoid any malfunctioning of this model. It is also good practice to save each DST assessment as a new file to have a clean template to work with each time.

If you are already familiar with the DST, please click the **START button** at the bottom of this page. Otherwise, please access the **User Guide**

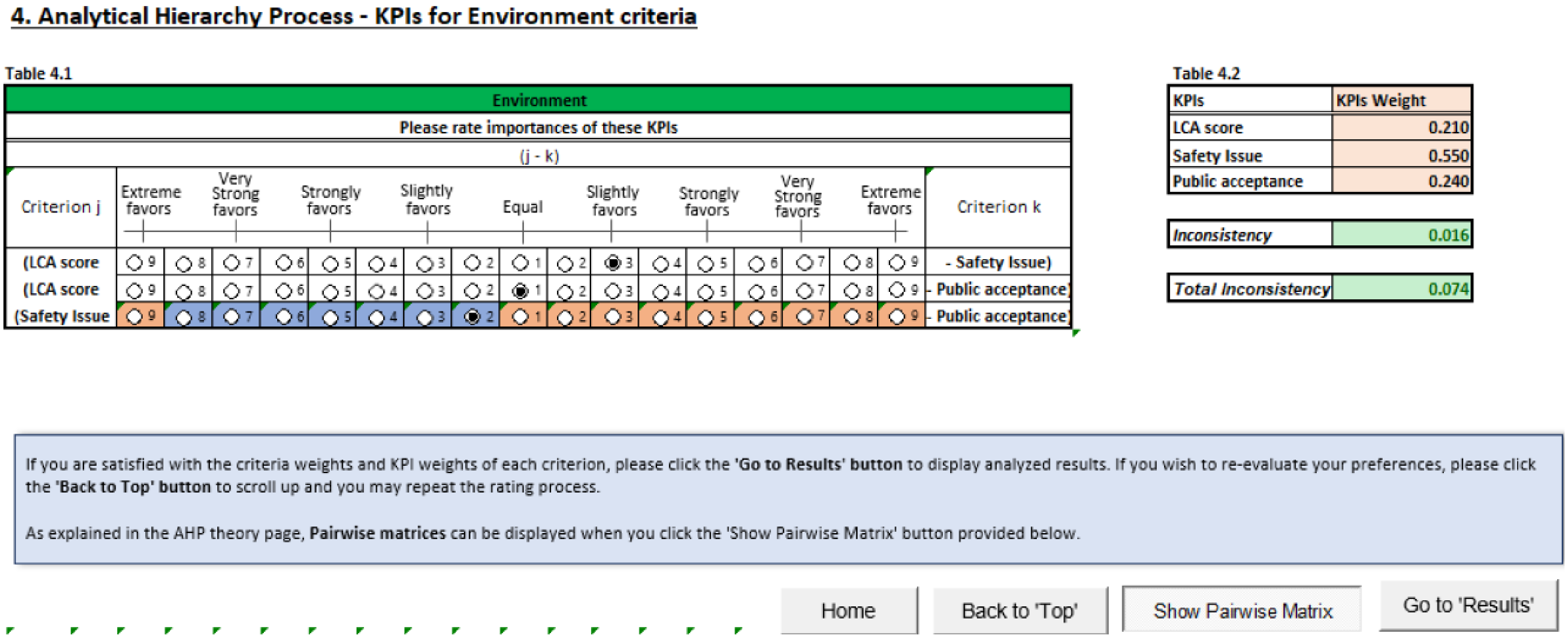
CO_2 CAPTURE TECHNOLOGY

Oxy-combustion	Pre-combustion	Pos-tcombustion	Direct Air Capture
1. Applied in the steel and glass industry **2. Suitable for fuels with low heating power** **3. Retrofit and repowering option** **4. Small scale application only at the moment, but applicable to large scale too.**	**1. Flue gas characteristics:** **1.1** Percentage of CO2 [Vol %]: 20-40%. **1.2** Typical operating pressure: 10-80 bar. **2. Work with a gasification system**	**1. Flue gas characteristics:** **1.1** Percentage of CO2 [Vol %] 4-15%. **1.2** Typical operating pressure: 1 bar. **2. suitable for retrofitting** **3. Applicable to the majority of existing coal-fired power plants**	**1. Manage emissions from distributed sources** **2. Treats percentage of CO2 in volume around 0.04%** **3. Can be installed almost everywhere but large volume are needed**

The decision support tool (DST) assesses and compares widely available CO2 capture technologies in terms of **three main criteria: ENGINEERING, ECONOMICS**, and **ENVIRONMENT**. There are various key performance indicators (KPIs) under each criterion which play important roles. Then, you can express your **preferences in terms of a score system (1 to 9)** in two points. **First**, inserting which criteria, economic, engineering, or environment is preferable with respect to others. your preferences will be used to calculate and provide the first set of weights to each criterion. Inside each criterion, there are KPI factors that must be **evaluated** by you following the same procedure to obtain the second set of weights of each KPI. In this way you will show your preferences in two phases of the process and based on that, the suitability of each technology will be analyzed. A database associated with each KPI is built and used to score each technology accordingly. Lastly, CO2 capture technology options are evaluated and **ranked** to screen and recommend suitable possibilities considering all important criteria

Decision-support tool

- Following the Analytical Hierarchy Process



4. Analytical Hierarchy Process - KPIs for Environment criteria

Table 4.1

Environment																		
Please rate importances of these KPIs																		
(j - k)																		
Criterion j	Extreme favors		Very Strong favors		Strongly favors		Slightly favors		Equal		Slightly favors		Strongly favors		Very Strong favors		Extreme favors	Criterion k
(LCA score	○ 9	○ 8	○ 7	○ 6	○ 5	○ 4	○ 3	○ 2	○ 1	○ 2	● 3	○ 4	○ 5	○ 6	○ 7	○ 8	○ 9	- Safety Issue)
(LCA score	○ 9	○ 8	○ 7	○ 6	○ 5	○ 4	○ 3	○ 2	● 1	○ 2	○ 3	○ 4	○ 5	○ 6	○ 7	○ 8	○ 9	- Public acceptance)
(Safety Issue	○ 9	○ 8	○ 7	○ 6	○ 5	○ 4	○ 3	● 2	○ 1	○ 2	○ 3	○ 4	○ 5	○ 6	○ 7	○ 8	○ 9	- Public acceptance)

Table 4.2

KPIs	KPIs Weight
LCA score	0.210
Safety Issue	0.550
Public acceptance	0.240

Inconsistency	0.016

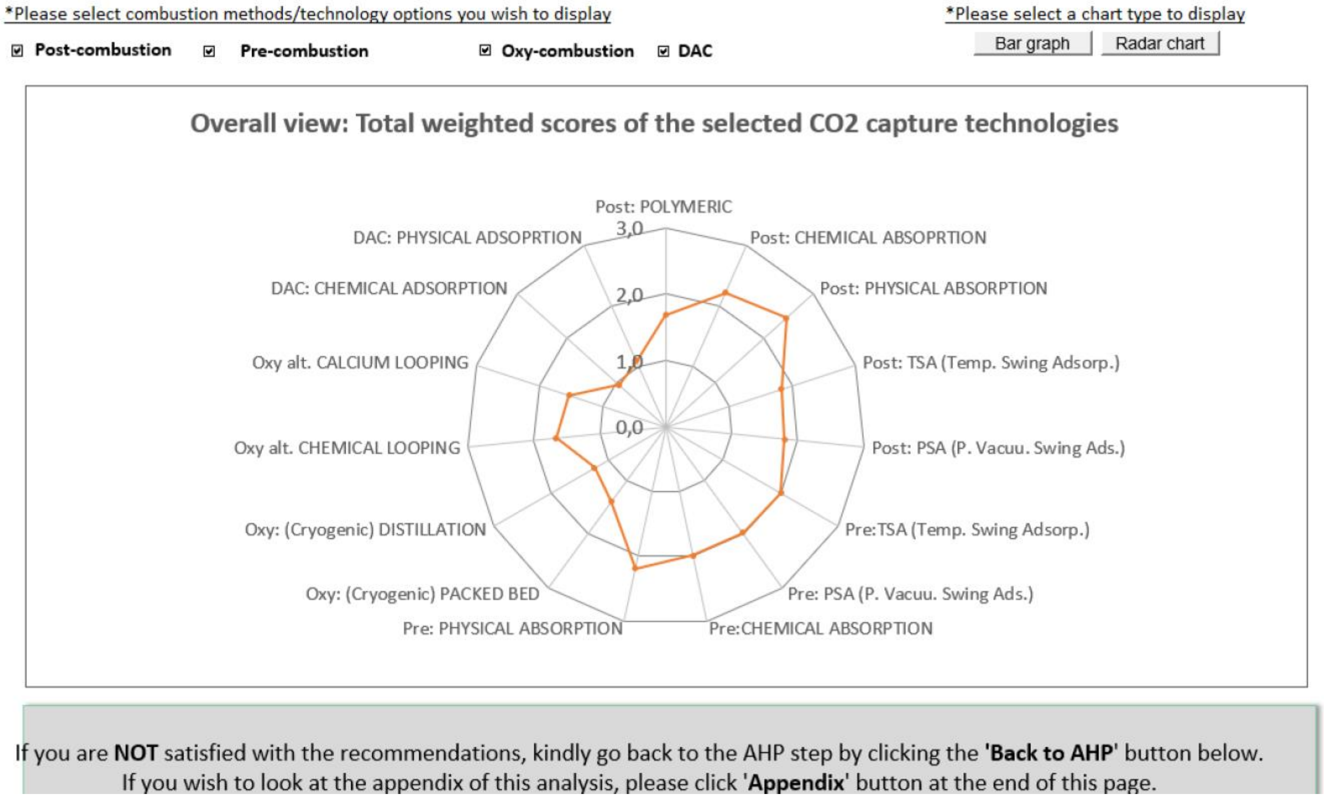
Total Inconsistency	0.074

If you are satisfied with the criteria weights and KPI weights of each criterion, please click the **'Go to Results' button** to display analyzed results. If you wish to re-evaluate your preferences, please click the **'Back to Top' button** to scroll up and you may repeat the rating process.

As explained in the AHP theory page, **Pairwise matrices** can be displayed when you click the 'Show Pairwise Matrix' button provided below.

Decision-support tool

- Results display



*Please select combustion methods/technology options you wish to display

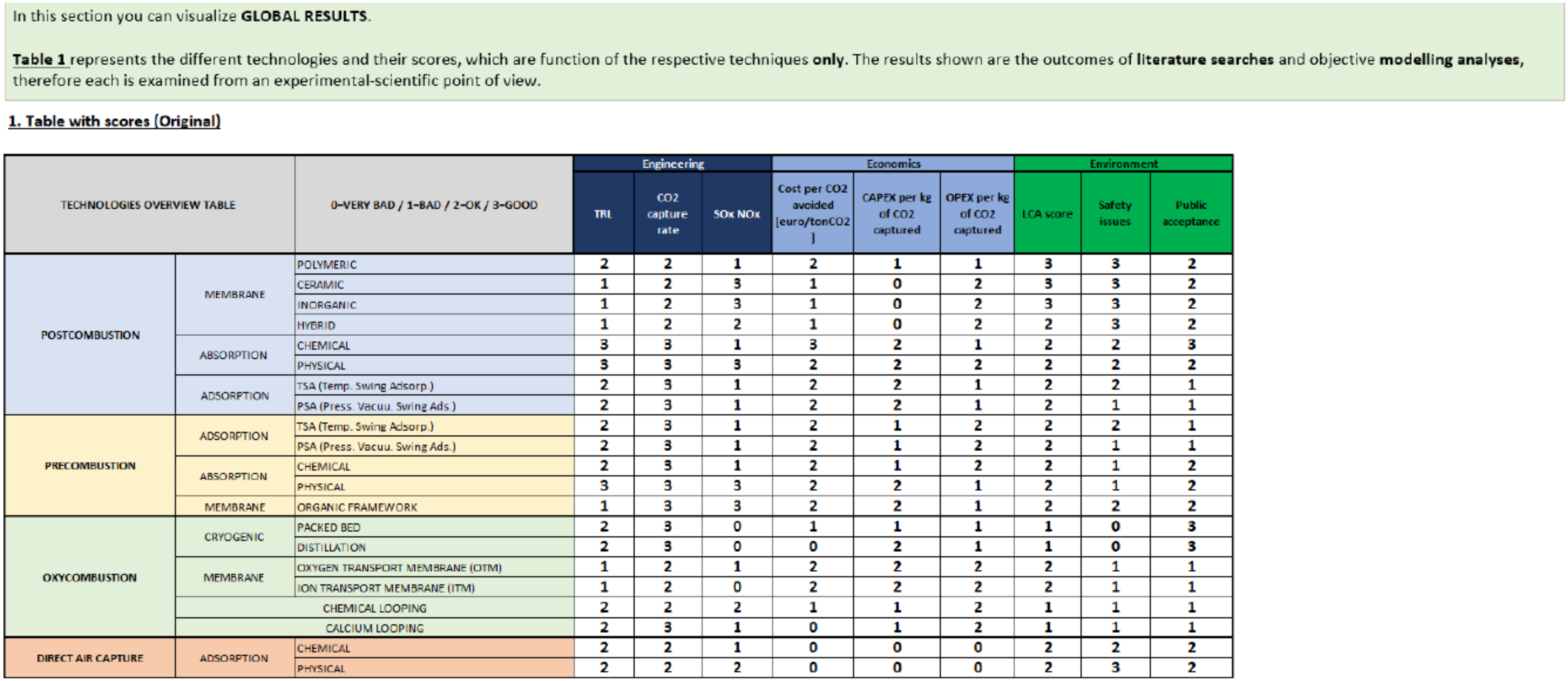
☑ **Post-combustion** ☑ **Pre-combustion** ☑ **Oxy-combustion** ☑ **DAC**

*Please select a chart type to display

If you are **NOT** satisfied with the recommendations, kindly go back to the AHP step by clicking the '**Back to AHP**' button below.
If you wish to look at the appendix of this analysis, please click '**Appendix**' button at the end of this page.

Decision-support tool

- Information support



In this section you can visualize **GLOBAL RESULTS**.

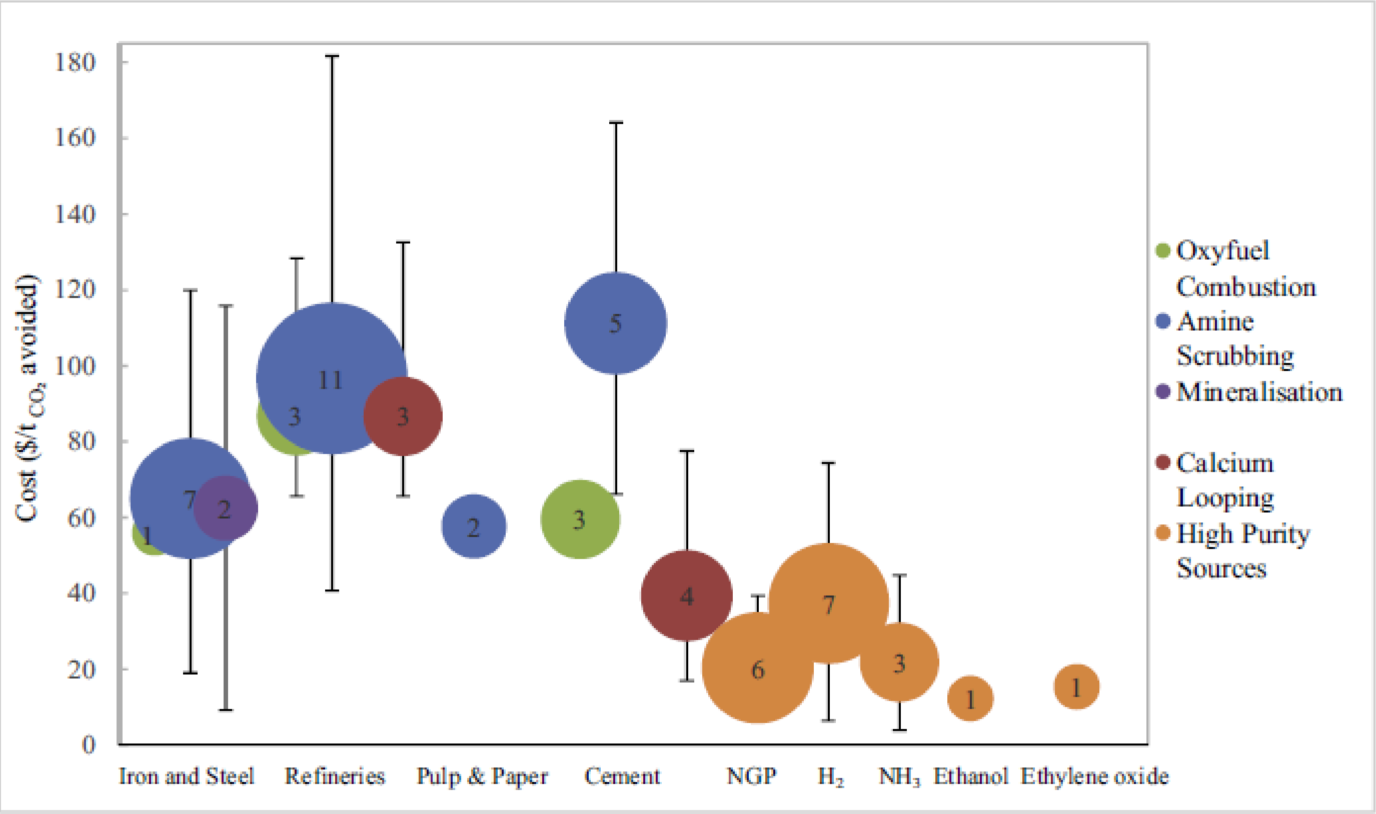
Table 1 represents the different technologies and their scores, which are function of the respective techniques **only**. The results shown are the outcomes of **literature searches** and objective **modelling analyses**, therefore each is examined from an experimental-scientific point of view.

1. Table with scores (Original)

TECHNOLOGIES OVERVIEW TABLE		0-VERY BAD / 1-BAD / 2-OK / 3-GOOD	Engineering			Economics			Environment		
			TRL	CO2 capture rate	SOx NOx	Cost per CO2 avoided [euro/tonCO2]	CAPEX per kg of CO2 captured	OPEX per kg of CO2 captured	LCA score	Safety issues	Public acceptance
POSTCOMBUSTION	MEMBRANE	POLYMERIC	2	2	1	2	1	1	3	3	2
		CERAMIC	1	2	3	1	0	2	3	3	2
		INORGANIC	1	2	3	1	0	2	3	3	2
		HYBRID	1	2	2	1	0	2	2	3	2
	ABSORPTION	CHEMICAL	3	3	1	3	2	1	2	2	3
		PHYSICAL	3	3	3	2	2	2	2	2	2
	ADSORPTION	TSA (Temp. Swing Adsorp.)	2	3	1	2	2	1	2	2	1
		PSA (Press. Vacuu. Swing Ads.)	2	3	1	2	2	1	2	1	1
PRECOMBUSTION	ADSORPTION	TSA (Temp. Swing Adsorp.)	2	3	1	2	1	2	2	2	1
		PSA (Press. Vacuu. Swing Ads.)	2	3	1	2	1	2	2	1	1
	ABSORPTION	CHEMICAL	2	3	1	2	1	2	2	1	2
		PHYSICAL	3	3	3	2	2	1	2	1	2
	MEMBRANE	ORGANIC FRAMEWORK	1	3	3	2	2	1	2	2	2
OXYCOMBUSTION	CRYOGENIC	PACKED BED	2	3	0	1	1	1	1	0	3
		DISTILLATION	2	3	0	0	2	1	1	0	3
	MEMBRANE	OXYGEN TRANSPORT MEMBRANE (OTM)	1	2	1	2	2	2	2	1	1
		ION TRANSPORT MEMBRANE (ITM)	1	2	0	2	2	2	2	1	1
	CHEMICAL LOOPING		2	2	2	1	1	2	1	1	1
	CALCIUM LOOPING		2	3	1	0	1	2	1	1	1
DIRECT AIR CAPTURE	ADSORPTION	CHEMICAL	2	2	1	0	0	0	2	2	2
		PHYSICAL	2	2	2	0	0	0	2	3	2

Cost of CO_2 capture

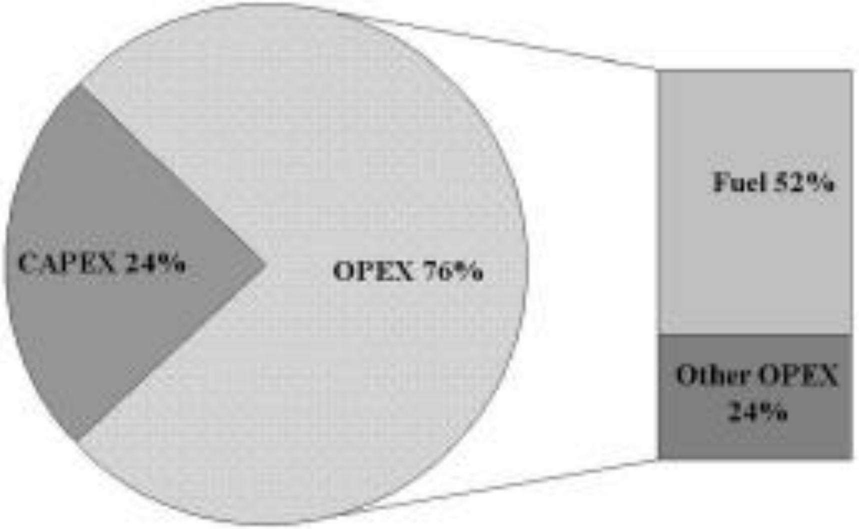
- Estimated cost for different industries



Leeson et al, 2017, DOI: 10.1016/j.ijggc.2017.03.020

Cost of CO_2 capture

- Cost mostly related to the energy penalty!



Abu-Zahra M., 2009. Carbon dioxide capture from flue gas. PhD Thesis at the Technical University of Delft, The Netherlands

CO_2 market

- European Emissions Trading System (ETS)
- CO_2 price now reaches 25 €/t!

https://ember-climate.org/data/carbon-price-viewer/

CO_2 market

- La Libre Belgique, 04/05/21
  - A noter qu’on voit des fumées de tours de refroidissement = de l’eau!

Les droits d'émission pour une tonne de CO_2 dépassent les 50 euros en Europe, une première

Conjoncture

La Libre Eco avec Belga

Publié le 04-05-21 à 13h17 - Mis à jour le 04-05-21 à 14h03

Les droits d'émission de CO_2 dépassent les 50 euros pour la première fois en Europe.

© Shutterstock

CO_2 market

- European Emissions Trading System (ETS)
- CO_2 price now reaches 65 €/t!

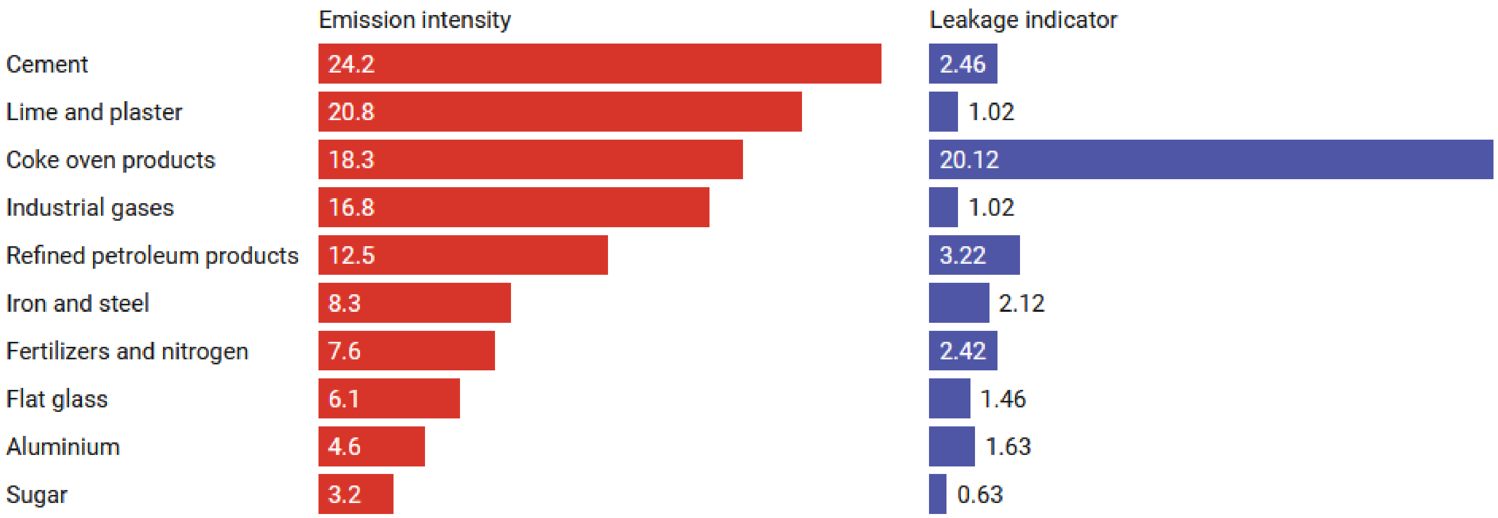
https://ember-climate.org/data/carbon-price-viewer/

Most intensive industries

- Risk of leakage?
  - Carbon border adjustment

Top 10 EU economic sectors with the highest emissions

The industries with the highest emissions also tend to have a high risk of carbon leakage, meaning foreign imports might be substituted for domestic production to avoid a charge for emissions. An indicator over 0.2 is considered at risk for carbon leakage.

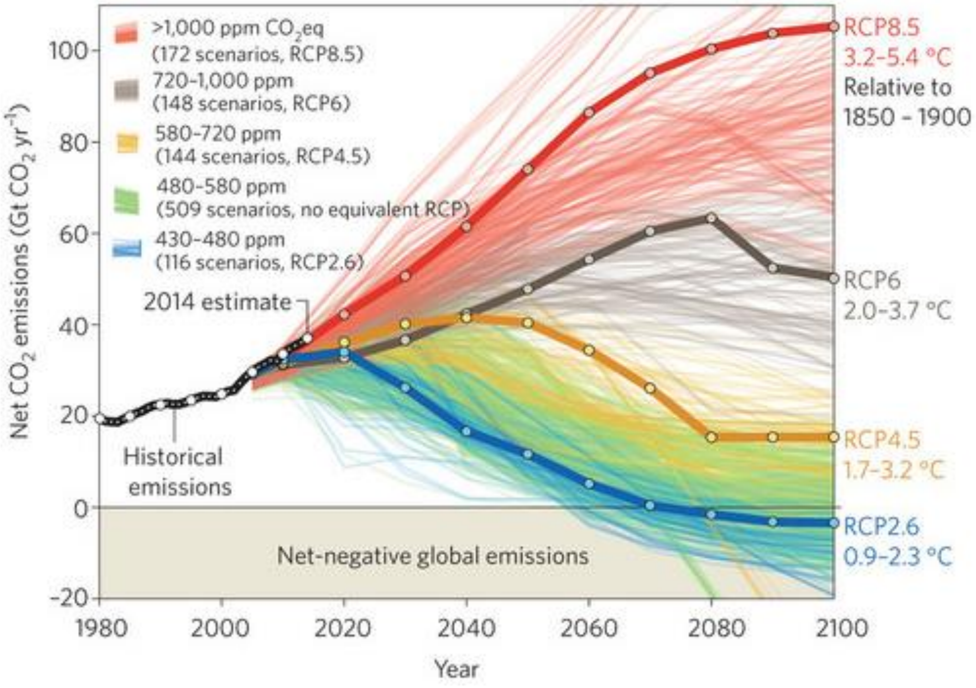


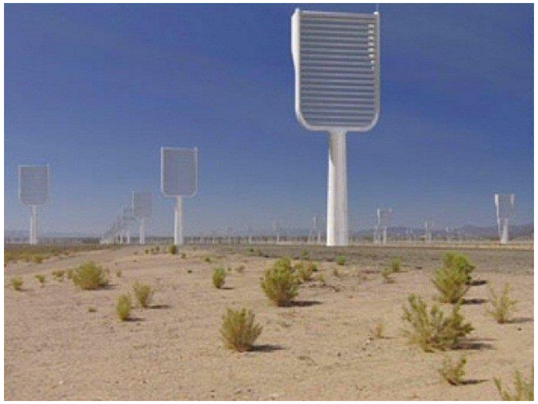
Emission intensity is the volume of emissions per unit of GDP. Coke oven products include coke, which is made from coal and used for fuel in furnaces and to manufacture iron and steel.

Chart: The Conversation/CC-BY-ND • Source: European Commission • Get the data

Future (?) challenge: Remove CO_2 from the air

- Negative CO_2 emissions





  - Use of biomass with CCS
  - Direct air capture
    - Expected costs vary between 100 and 800 $/ton

Fuss et al, Nature, 2014, doi:10.1038/nclimate2392
K.S. Lackner, CNCE ASU, 2017.

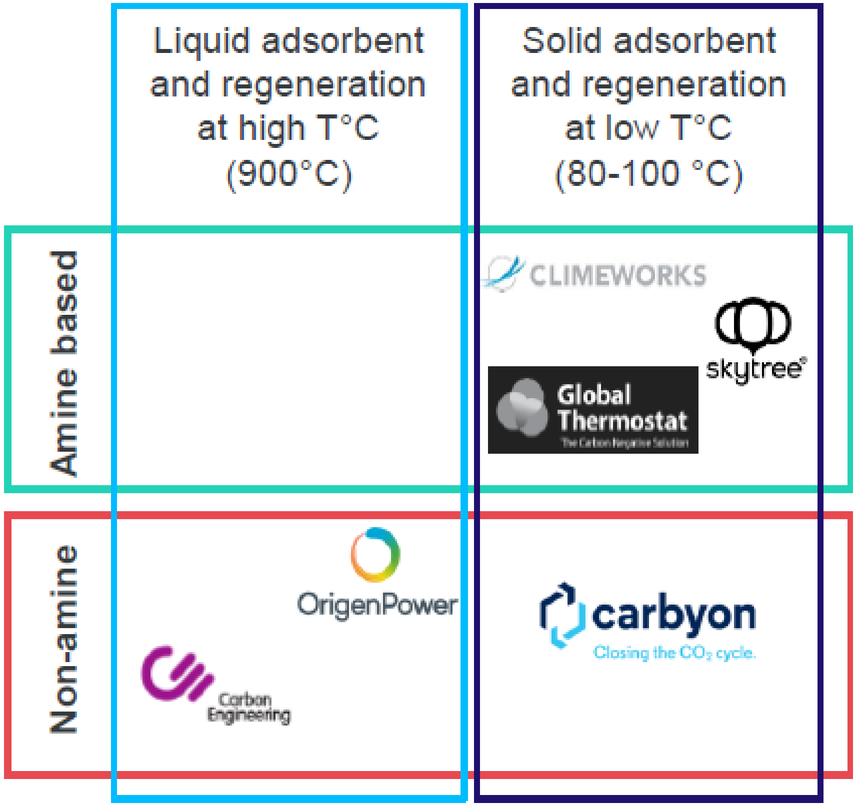
Direct air capture

- Direct air capture motivations
  - Compensate for mobile CO_2 emissions: 30 to 50% of current emissions
  - Close the carbon cycle of synthetic fuels
  - Reduce the need for transporting CO_2
    - No Nimby effect, you can go wherever you want, incl. close to use or storage sites
- Compensate for CO_2 leakage from geologic storage
- Long-term considerations: remove C from the atmosphere

www.pnas.org/cgi/doi/10.1073/pnas.1108765109

Direct air capture

- A growing business…

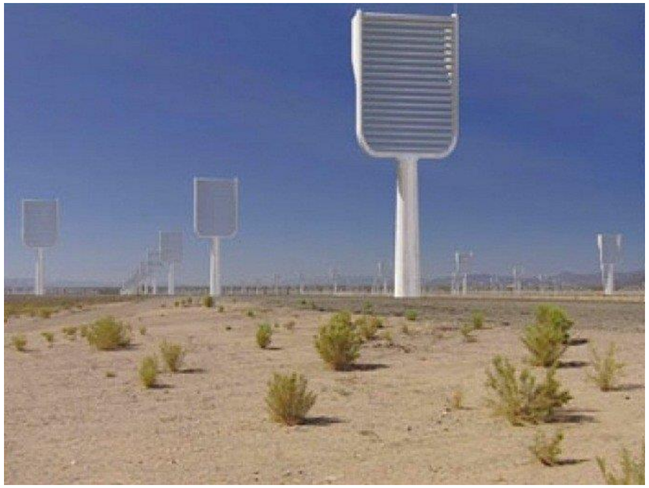


	Liquid adsorbent and regeneration at high T°C (900°C)	Solid adsorbent and regeneration at low T°C (80-100 °C)
Amine based		CLIMEWORKS skytree® Global Thermostat
Non-amine	OrigenPower Carbon Engineering	carbyon Closing the CO₂ cycle.

Engie research, Emerging sustainable technologies, 2020

Direct air capture

- A growing business…



Exclusive: Carbon Engineering CEO discusses recent funding for DAC technology

By Molly Burgess | 24 April 2019

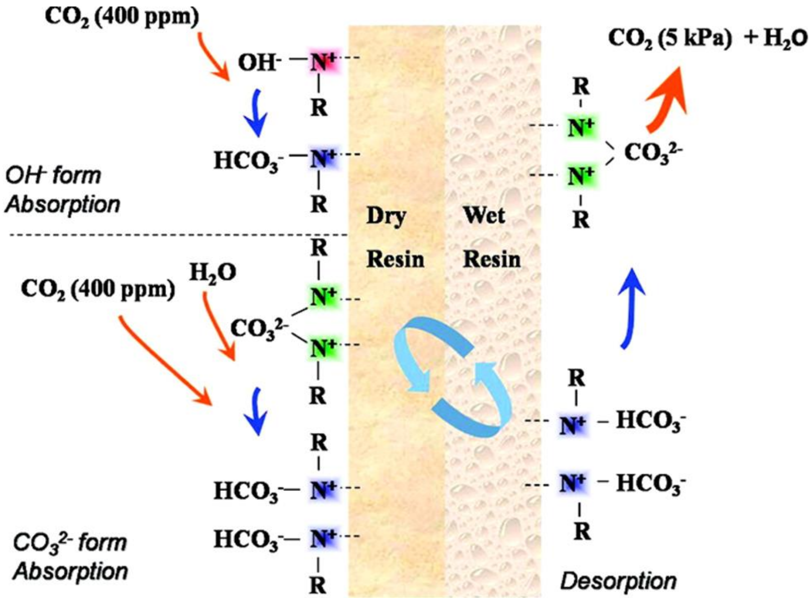
Last month, Carbon Engineering, a Canadian clean energy company announced the completion of an equity financing round of $68m, marking the largest private investment made into a Direct Air Capture (DAC) company to date.

Direct air capture

- Orca project, in Iceland
  - Climeworks (Swiss start-up)
  - 4000 tpa CO_2
  - CAPEX: ~15 M€
  - Geothermal energy
  - CO_2 liquefaction
  - Underground mineralization

Direct air capture

- ~ 410 ppm in the air
  - Adsorption
  - Temperature-swing, or humidity-swing
  - Prototyping on-going



Wang et al, Environ. Sci. Technol., 45, 6670–6675, 2011

Pros and Cons of DAC technologies

- Pros:
  - Capture CO2 from the air in any location
  - Serves as a backstop technology for managing climate change
  - Can provide CO2 as a feedstock for CO2 utilization applications
- Cons:
  - DAC is currently expensive ($ 300 – 600/ tCO2)
  - DAC requires large amount of energy

DAC in Research, development and demonstration (RD&D)

- The companies most actively engaged in DAC mostly favour chemical approaches, using either liquid solvents or solid sorbents.

- Since heat and power are required to regenerate the key chemical agents, the goal of many companies and researchers is to improve
    - CO_2 loadings,
    - reduce input energy requirements and costs, and
    - improve concentrations of CO_2

Direct air capture

- Climeworks – Antecy
  - Modular collectors, 50 tpa CO_2
  - TSA, regeneration at 80-100°C
  - Original: amine sorbents
  - Antecy: non-amine sorbents
  - Produces CO_2 with high purity (99%)
  - Collaboration with fuel production (Audi), with mineralisation (Carbfix)

DAC technologies today

- Carbon Engineering
    - Pursuing a liquid solvent based approach
    - This enables a continuous process @ steady-state
    - https://carbonengineering.com/our-technology/

- Climeworks
    - has three pilot plants currently in operation (one in Switzerland, one in Iceland and one in Italy)
    - The sorbent is amine supported on solid porous granules arranged in a proprietary filter. The regeneration is based on a combined temperature- and pressure-swing process
    - https://climeworks.com/

DAC technologies today

- Global Thermostat
  - Has a demonstration plant operating in California and a pilot plant in Huntsville, Alabama
  - The sorbent is amine supported on a porous ceramic monolith structure.
  - Regeneration is based on temperature-vacuum swing
  - https://globalthermostat.com/about-carbon-capture/

- Center for Negative Emissions
  - DAC based on an anionic exchange resin, regenerated using moisture swing
  - https://cnce.engineering.asu.edu/

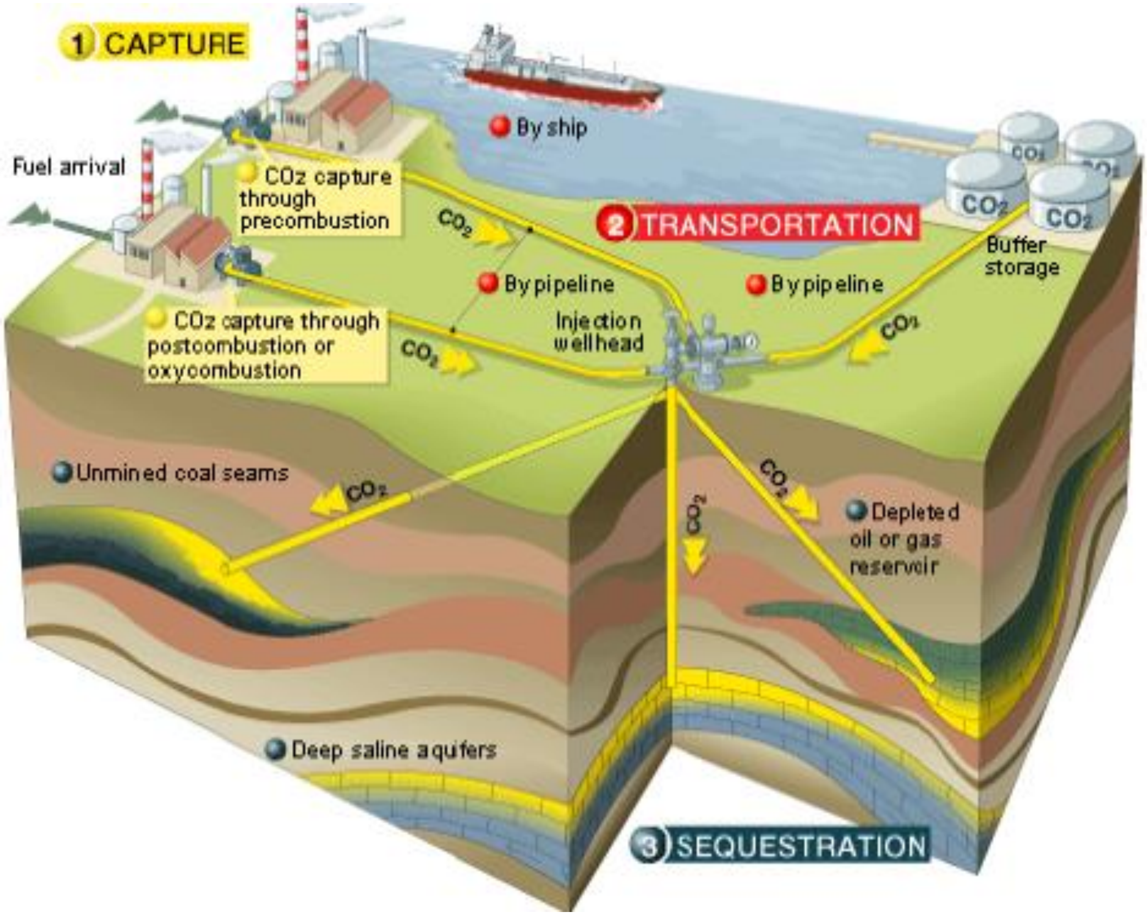
3. Storage of CO_2

CHEMICAL ENGINEERING

LIÈGE université

Integrated chain

Capture – Transport – Storage



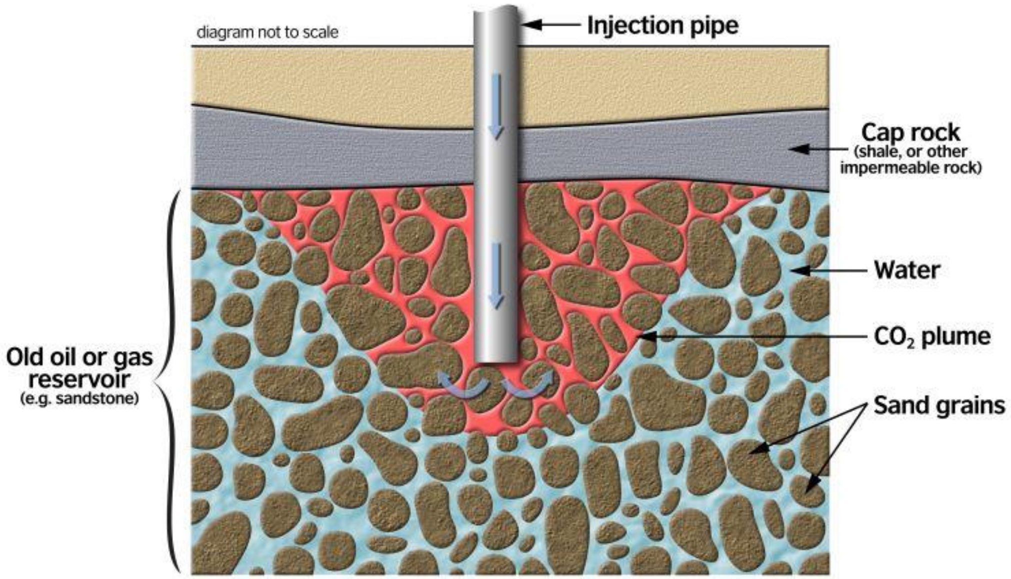
Transport of CO_2

- By ship:
  - 100 000 tons transported/year (~1000 tCO_2/ship)
  - Liquefied CO_2 (-30°C, 15 bar)
  - Similar technology to LPG, but to be improved
- By pipeline:
  - Supercritical CO_2 (100 bar)
  - > 6500 km of pipelines since the 1970ies (EOR)

www.sccs.org.uk; IEAGHG, "CO_2 Pipeline Infrastructure", 2013/18, December, 2013

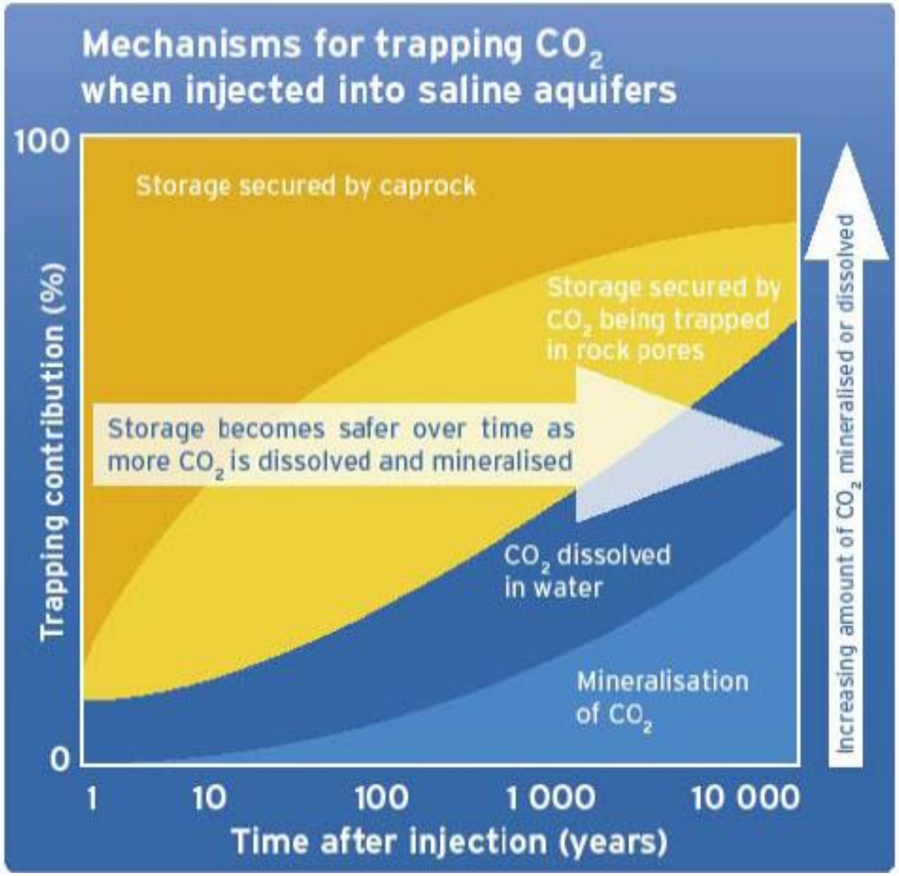
Possible storage sites

- Saline aquifers: large capacity, geology less well-known, reservoir properties under study
- Depleted gas and oil fields: Limited capacity, but geology is well-known, storage safety has been proven
- Coal seams: limited capacity, low permeability, possibility to recover methane



What happens to stored CO_2?

- CO_2 diffuses in the geological formation and is trapped under the cap
- It then get stuck in smaller porosities
- It dissolves and gets mineralized
- Long time-scale!



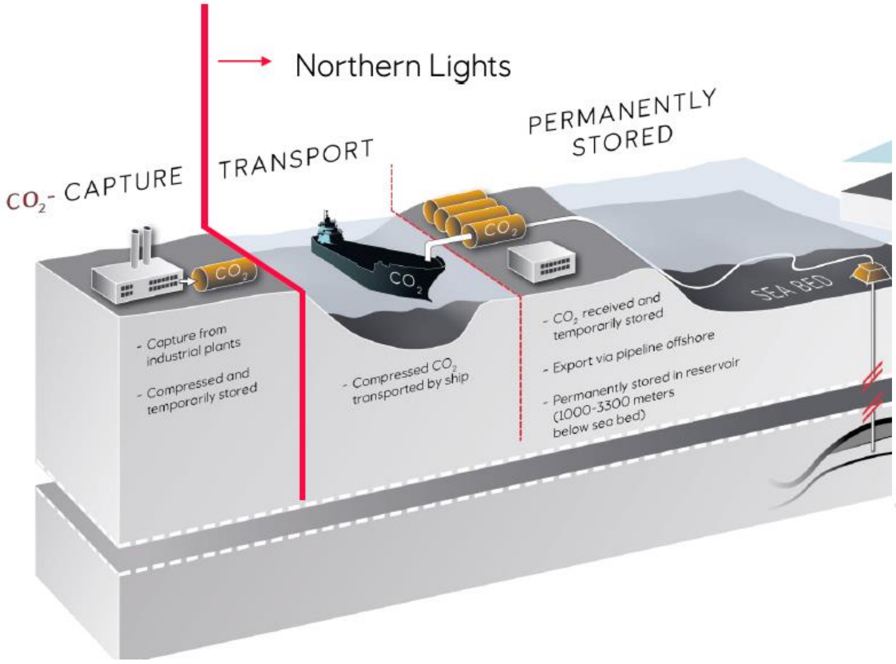
Some examples

- In-Salah, Algeria
  - 3.8 Mt CO_2 injected 2004 - 2011
  - Former gas reservoir (1900 m deep)
  - Injection paused, soil integrity being studied
  - Constant monitoring

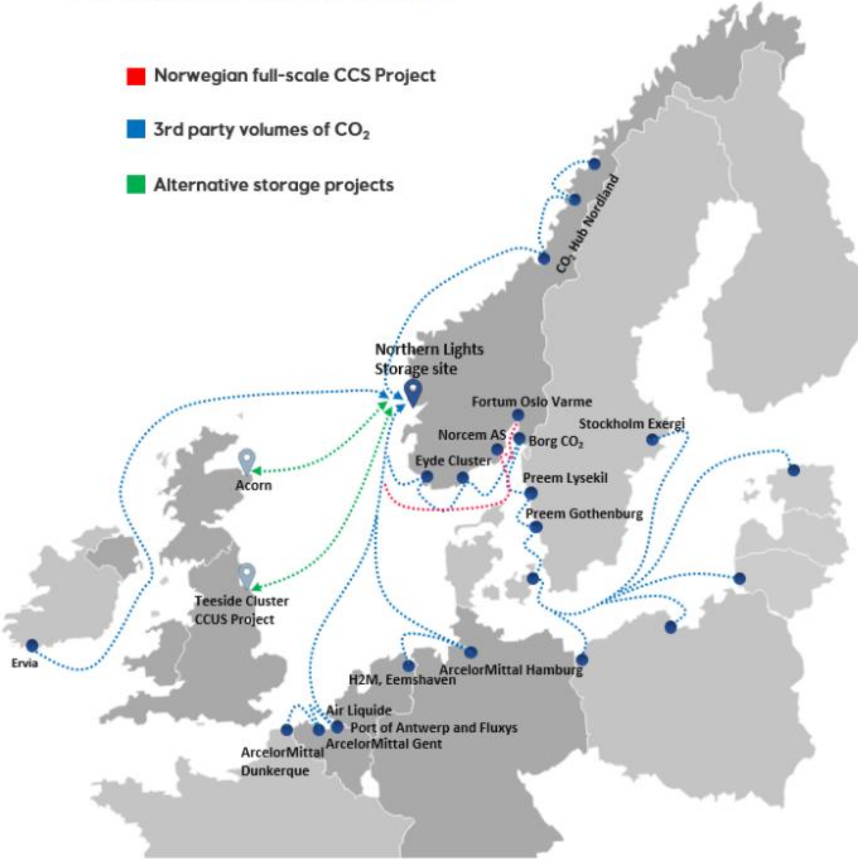
- Sleipner, Norway
  - ~ 1 Mtpa from 1996
  - Saline aquifer (800-1000 m deep)
  - Offshore of Norway's coast
  - > 17 Mt injected

Northern lights

- Norway, off-shore field, saline aquifer
- Up to 5 Mt CO_2/y



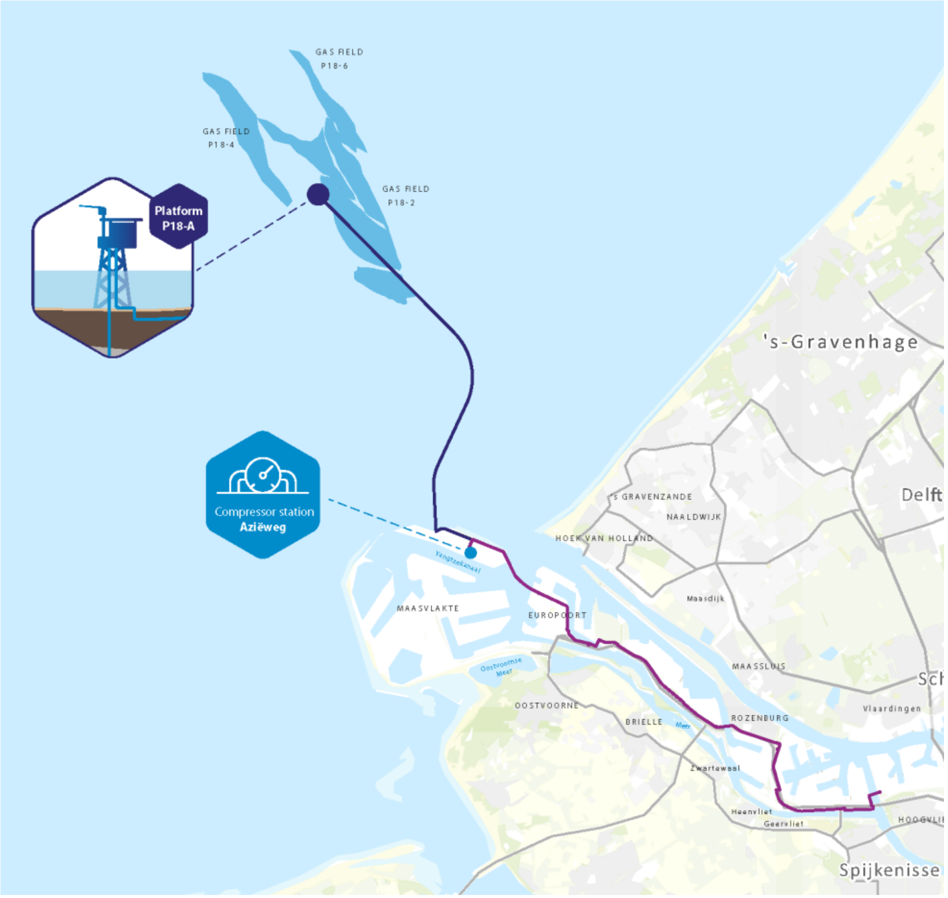
- A ship based solution means access for CO2 emitters across Europe



https://northernlightsccs.eu/en

Porthos

- Rotterdam, off-shore depleted gas field
- 2.5 Mt CO_2/y



Antwerp@C

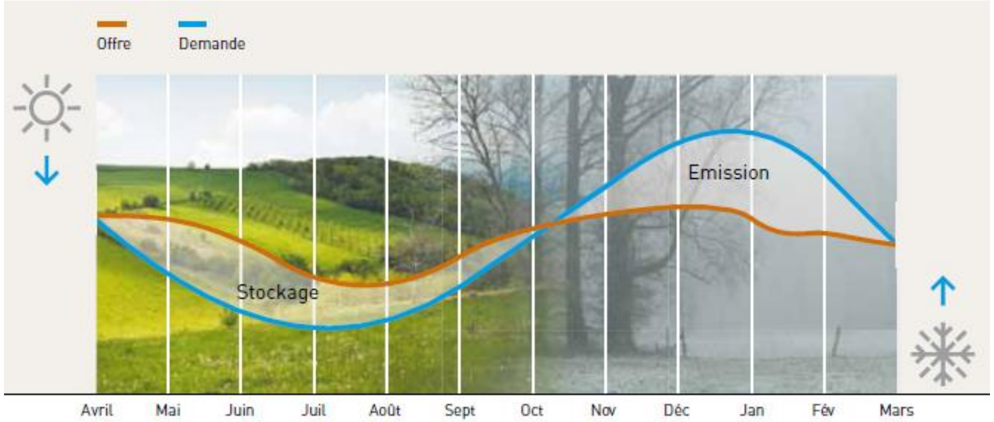
- No storage capacity offshore of Belgium
  - Antwerp@C studies the infrastructure for connection to Norway and The Netherlands
  - => Pipelines, intermediate storage, liquefaction unit…

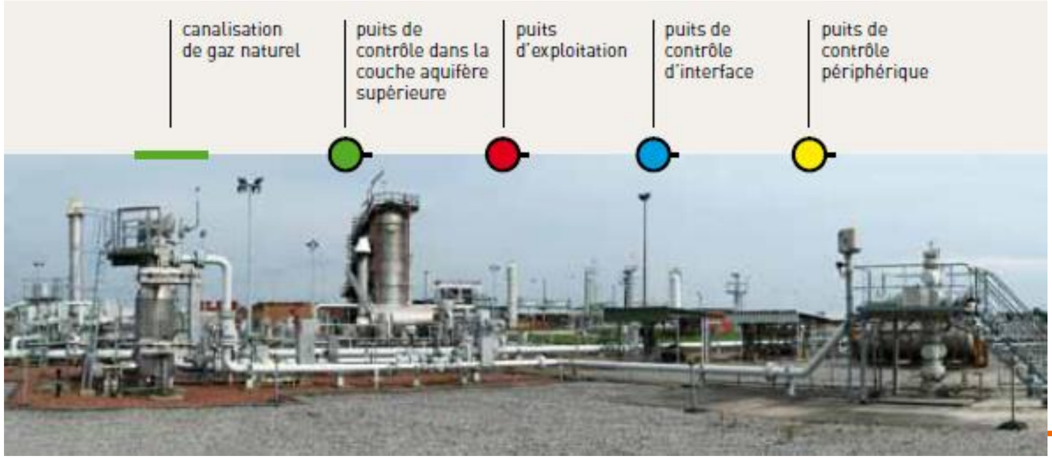
Antwerp@C

8 players in chemical & energy sector investigate feasibility of carbon capture, utilisation and storage in Port of Antwerp

Is it dangerous?

- Not a new technology: seasonal storage of natural gas
  - Example: Loenhout (Anvers)



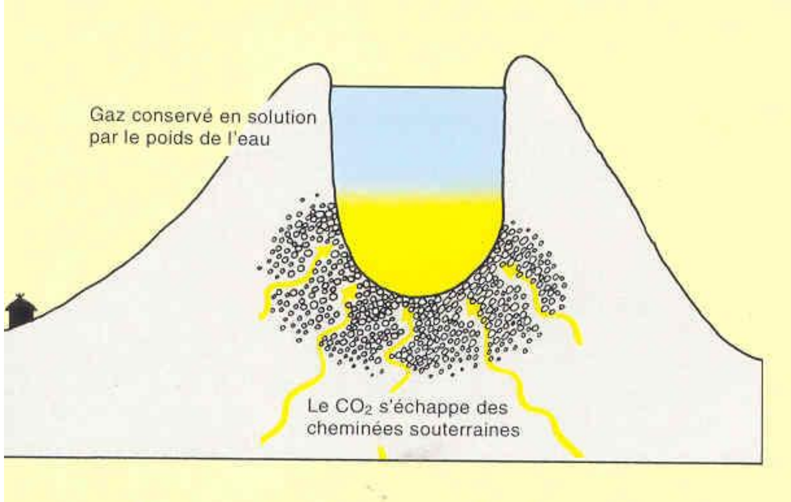


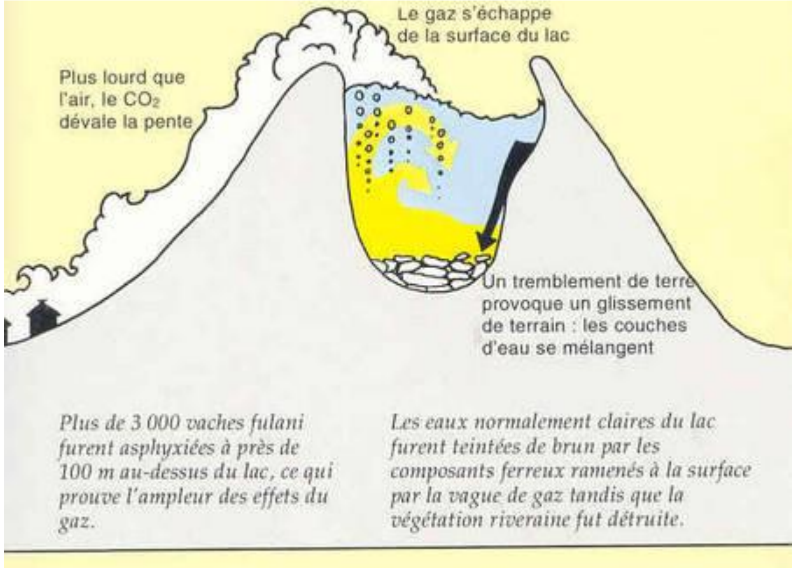
Source : www.fluxys.com

Is it dangerous?

- Case of lake Nyos
    - Cameroun, 1986
    - CO_2 from volcanic source
    - Almost 1700 fatalities

=> Risk management!





Plus de 3 000 vaches fulani furent asphyxiées à près de 100 m au-dessus du lac, ce qui prouve l'ampleur des effets du gaz.

Les eaux normalement claires du lac furent teintées de brun par les composants ferreux ramenés à la surface par la vague de gaz tandis que la végétation riveraine fut détruite.

4. Re-use of CO_2

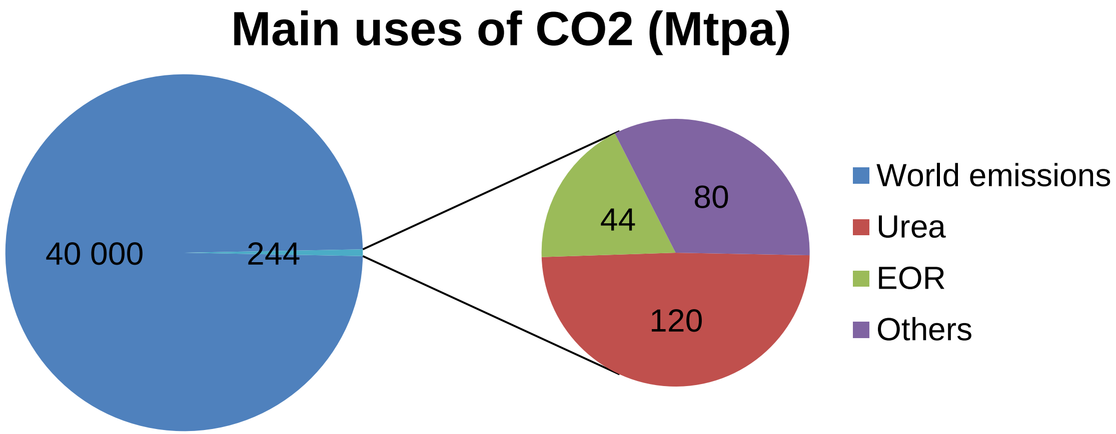
CO_2, waste or feedstock?

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

- CO_2 capture is expensive
    - Captured CO_2 ~ 40 US$/t
    - ETS Market (European price for CO_2) ~ 7-8 €/tCO_2 between 2011 and 2018
    - Now ~ 25 €/tCO_2

CO_2, waste or feedstock?

- How to improve the economics of CO_2 capture?
  - Consider CO_2 as a resource, not as waste

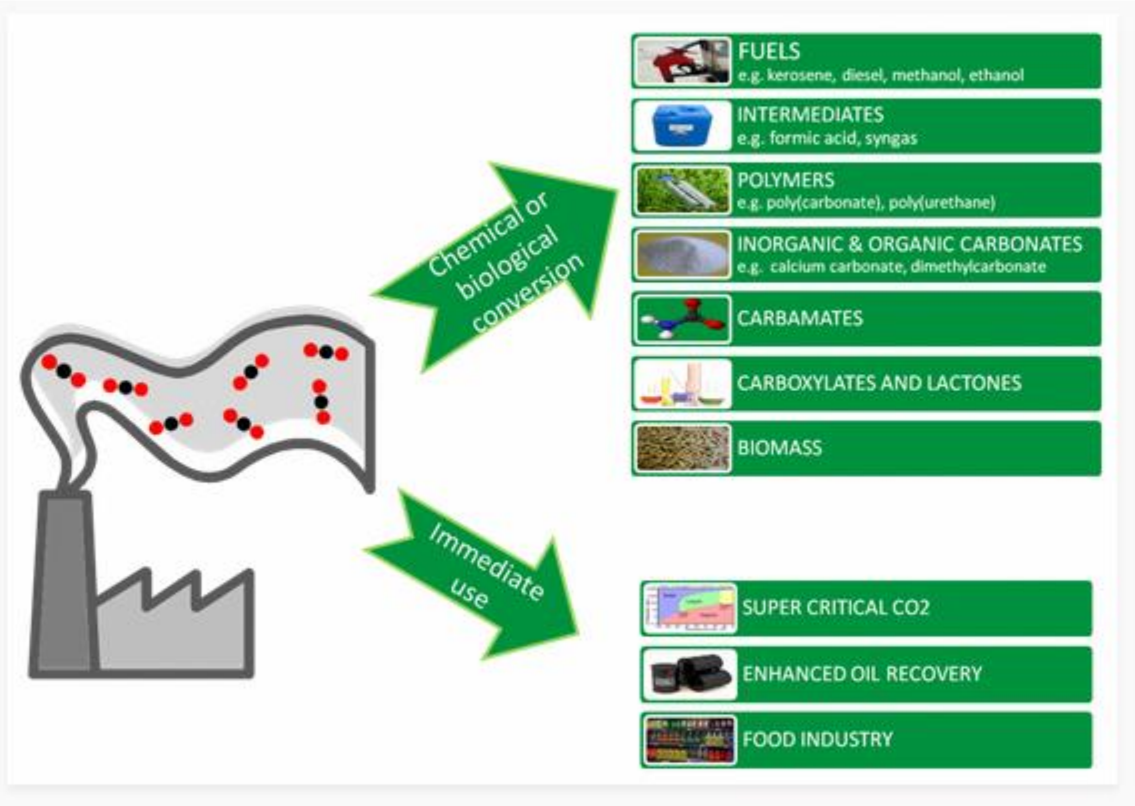


- So far, sources for CO_2 are high-purity ones
  - Industrial (Ethanol, Ammonia, Ethylene, Natural gas…)
  - Natural (Dome)
  - CO_2 from power plants (~2.4 Mtpa)

Global CCS Institute. Global Status of CCS 2016: Summary Report.
Koytsumpa et al, 2016. https://doi.org/10.1016/j.supflu.2017.07.029

Main CO_2 re-use pathways

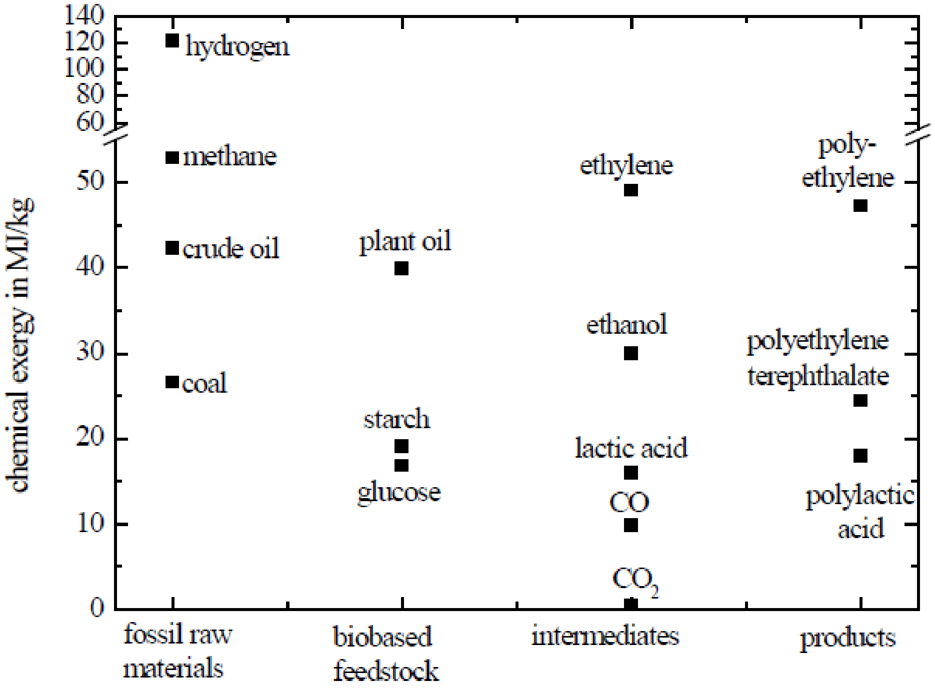
Many different products, as CO_2 can be seen as a carbon source => leads to almost all petrochemical products!



Source: CO2Chem

Main CO_2 re-use pathways

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

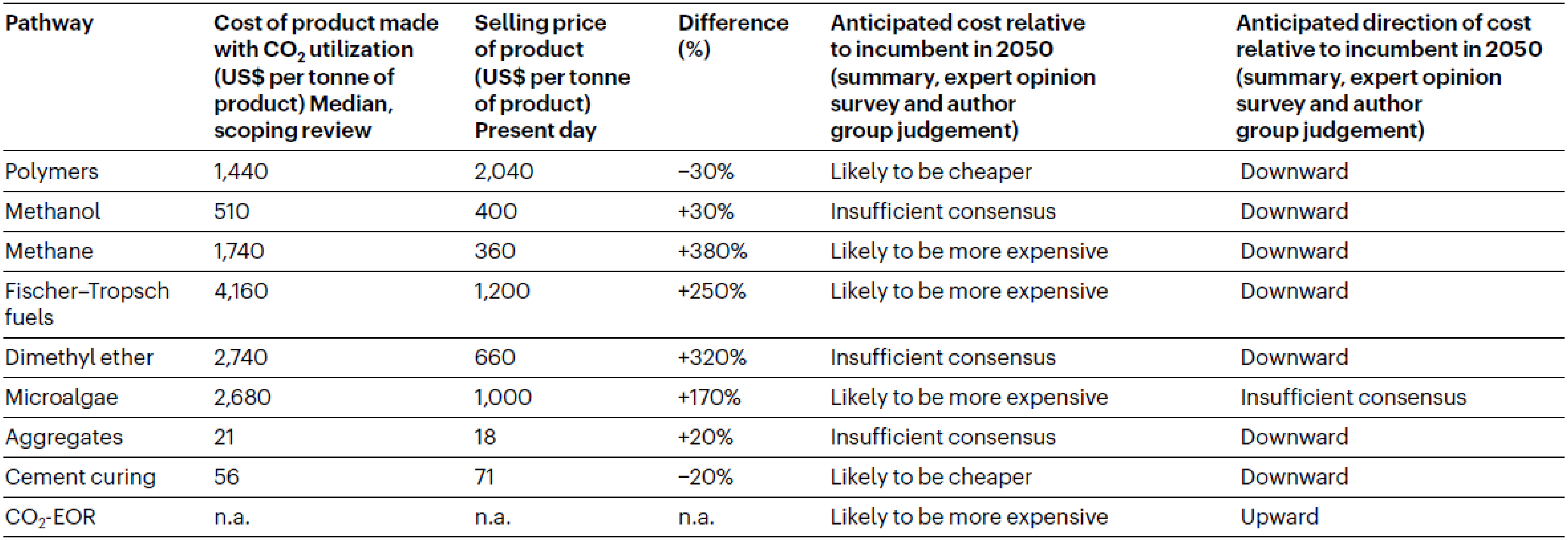


=> At large scale, need to make sure that energy comes from renewables!

Frenzel et al, 2014. Doi:10.3390/polym6020327

Large potential for CO_2 re-use!

- Up to 18 Gt CO_2/y by 2050



Pathway	Cost of product made with CO_2 utilization (US$ per tonne of product) Median, scoping review	Selling price of product (US$ per tonne of product) Present day	Difference (%)	Anticipated cost relative to incumbent in 2050 (summary, expert opinion survey and author group judgement)	Anticipated direction of cost relative to incumbent in 2050 (summary, expert opinion survey and author group judgement)
Polymers	1,440	2,040	−30%	Likely to be cheaper	Downward
Methanol	510	400	+30%	Insufficient consensus	Downward
Methane	1,740	360	+380%	Likely to be more expensive	Downward
Fischer–Tropsch fuels	4,160	1,200	+250%	Likely to be more expensive	Downward
Dimethyl ether	2,740	660	+320%	Insufficient consensus	Downward
Microalgae	2,680	1,000	+170%	Likely to be more expensive	Insufficient consensus
Aggregates	21	18	+20%	Insufficient consensus	Downward
Cement curing	56	71	−20%	Likely to be cheaper	Downward
CO_2-EOR	n.a.	n.a.	n.a.	Likely to be more expensive	Upward

Hepburn et al., 2019. The technological and economic prospects for CO2 utilization and removal. Nature 575, 87-97. https://doi.org/10.1038/s41586-019-1681-6

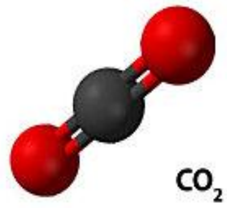
The FRITCO$_2$T Platform

Chemical Transformation

Synthetic Fuels

Mono/Polymers, Composite and Biomaterials

Mineralization



Sourcing

Capture & Purification

Physical Use

Pharmaceutics & Cosmetology

Direct CO_2 use (solvent, foaming…)

Transversal

Process sustainability (LCA and economics)

www.chemeng.uliege.be/FRITCO2T

NB: Carbon sequestration in soils

- Suquestration as soil organic carbon
- Technical potential: 0.79 - 1.54 Gt C/y

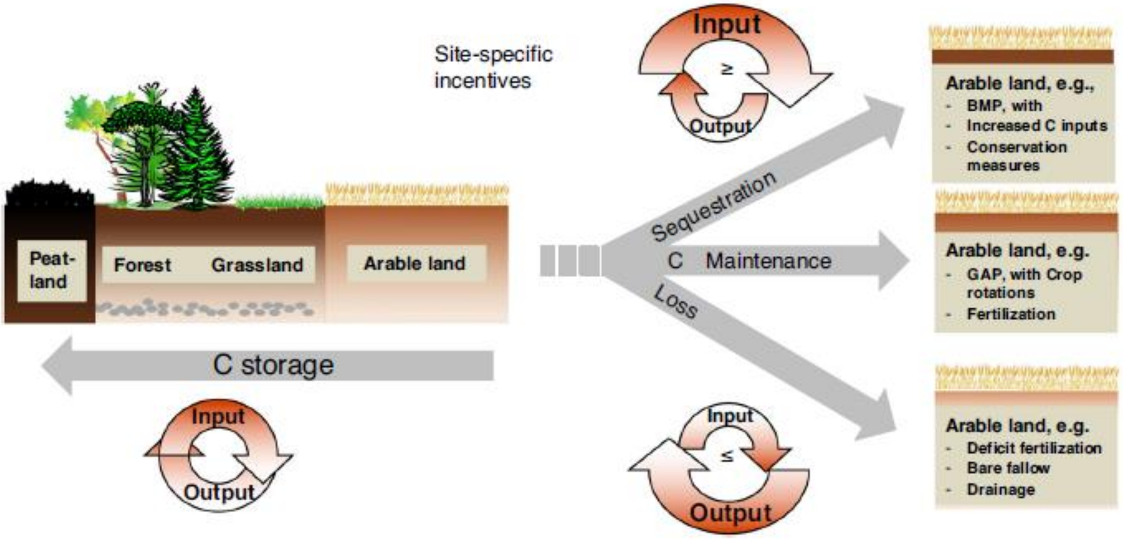


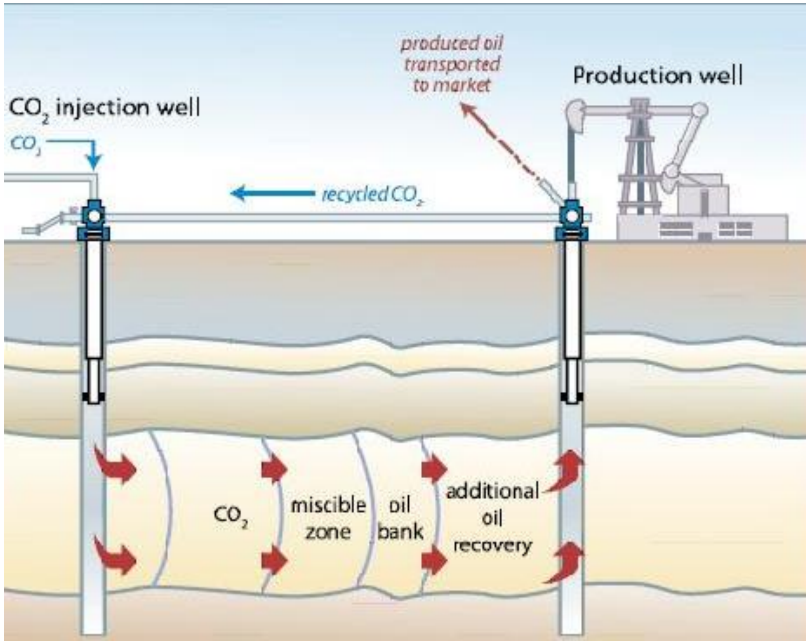
Fig. 1 Conceptualization of C sequestration potentials in arable land. Usually C is lost after land-use conversion from native ecosystems (e.g., peatlands, forests, grasslands) to arable land. Future C storage in agricultural fields then depends on agricultural management practices, with options to regain C by increasing the organic matter input relative to ongoing CO_2 release at best management practice options (BMP), to maintain C stocks by continued good agricultural practice (GAP), or to lose additional C by intensifying agriculture without additional C input, usually followed by soil degradation.

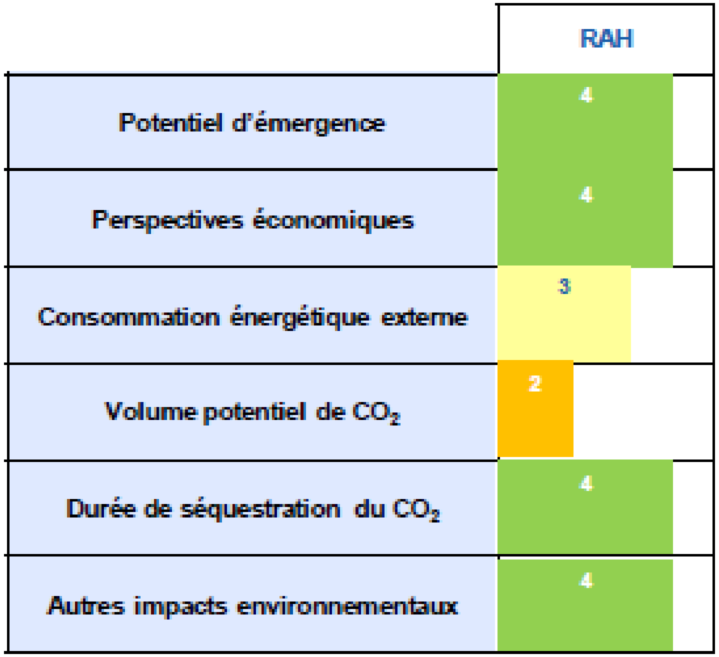
https://www.nature.com/articles/s41467-020-18887-7

Direct use of CO_2

Enhanced oil recovery (EOR):

- 66 $MtCO_2$/a (increasing, mostly North America)
- Energy consumption for compression and injection





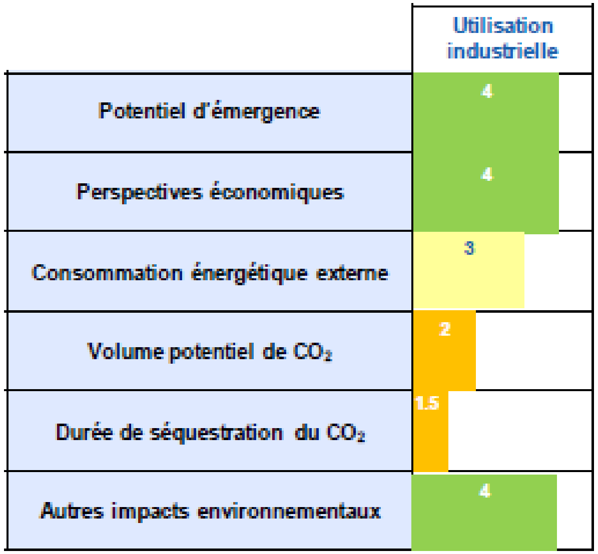
	RAH
Potentiel d'émergence	4
Perspectives économiques	4
Consommation énergétique externe	3
Volume potentiel de CO_2	2
Durée de séquestration du CO_2	4
Autres impacts environnementaux	4

Panorama des voies de valorisation du CO2, Rapport ADEME, June 2010

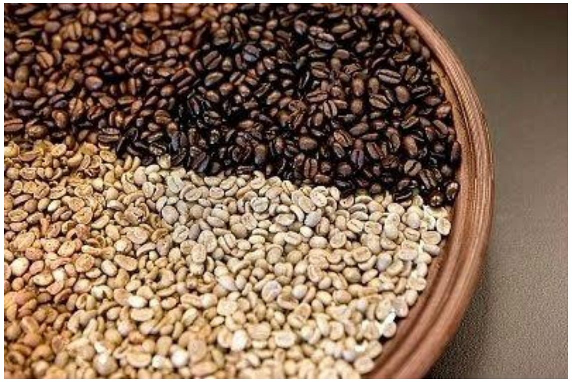
Direct use of CO_2

Other direct industrial uses of CO_2

- High purity grade is required (99,99%)
- Lower growth potential (20 $MtCO_2$/an)
- Only short-term CO_2 storage

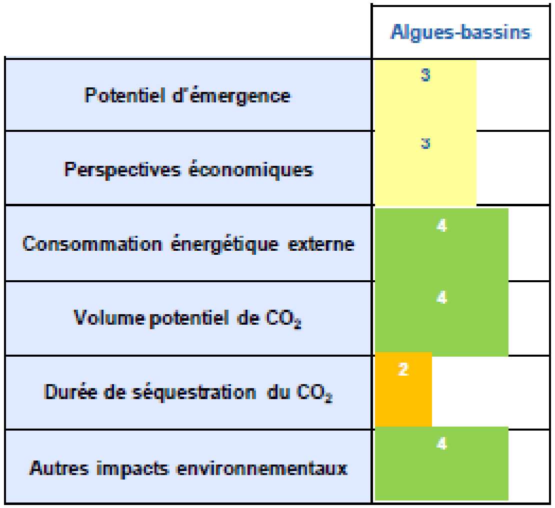


	Utilisation industrielle
Potentiel d'émergence	4
Perspectives économiques	4
Consommation énergétique externe	3
Volume potentiel de CO_2	2
Durée de séquestration du CO_2	1.5
Autres impacts environnementaux	4



Biological transformation of CO_2

- Photosynthesis
  - Greenhouses
  - Microalgae



	Algues-bassins
Potentiel d'émergence	3
Perspectives économiques	3
Consommation énergétique externe	4
Volume potentiel de CO_2	4
Durée de séquestration du CO_2	2
Autres impacts environnementaux	4

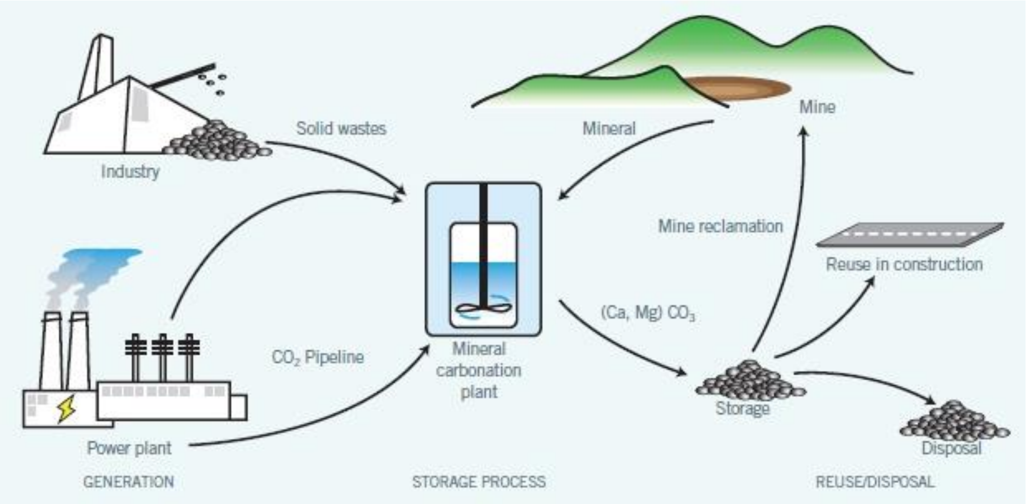
- Drawbacks:
  - Area for cultivation (+- 120 t CO_2/ha)
  - Energy for post-processing

Biological transformation of CO_2

- Leads to a large variety of products…

Chemical transformation to lower energy

- Mineralization - Carbonatation
  - $CaO + CO_2 \rightarrow CaCO_3$
  - $MgO + CO_2 \rightarrow MgCO_3$
  - $Mg_2SiO_4 + 2\ CO_2 \rightarrow 2\ MgCO_3 + SiO_2$




Source: Hemcrete, 2015

- Use of Mg or Ca oxides as feedstock, coming from minerals or industrial wastes
- Spontaneous but slow reaction

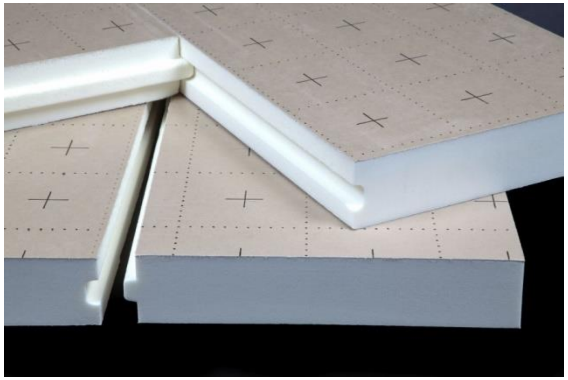
Chemical transformation to lower energy

- Eg.: Recoval process
  - Formation of Ca and Mg carbonates
  - Recoval uses steel slag

Carbstone, ORBIX, 2019

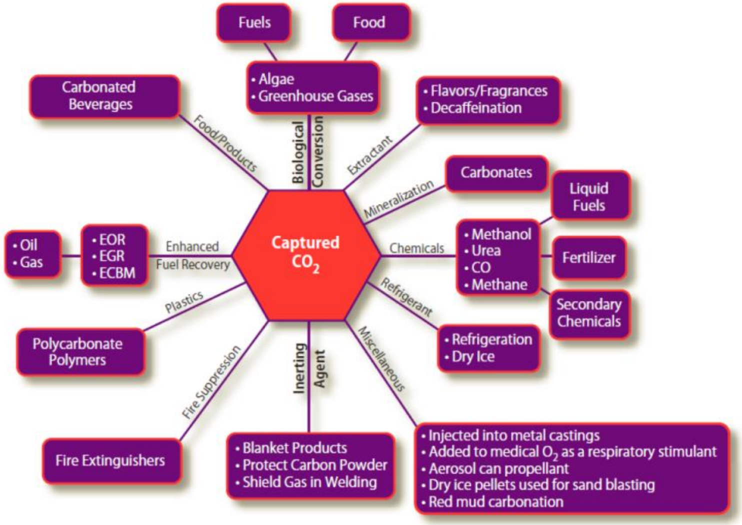
Chemical transformation to higher energy

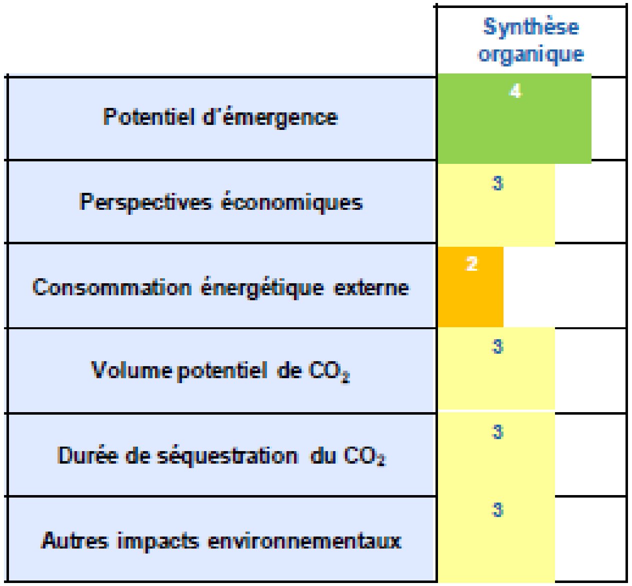
- Some products made from CO_2



CO_2 to chemicals

- CO_2 can be a useful source of carbon for organic chemistry, it’s just that you need energy!
  - Small molecules: formic acid, urea, …
  - Monomers and polymers: polycarbonates, polyols, polyurethanes…
  - Limited potential volume: ~6% of crude oil for petrochemistry
  - Fuels
- High added value possible
- Need for efficient and selective catalysts





	Synthèse organique
Potentiel d'émergence	4
Perspectives économiques	3
Consommation énergétique externe	2
Volume potentiel de CO_2	3
Durée de séquestration du CO_2	3
Autres impacts environnementaux	3

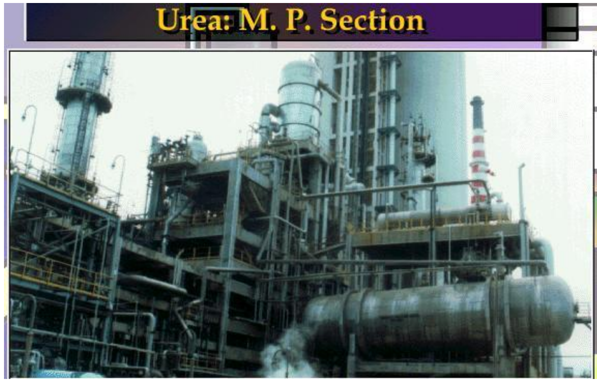
CO_2 to chemicals

- Formic acid
  - Main route: CO + H_2O + methanol catalyst
  - Alternative: CO_2 + H_2
    - Low TRL
    - Low market volume => is it useful to develop a new process?

Blair and Berman, University of Central Florida, WO 2014/089537 A1

CO_2 to chemicals

- Urea
  - $2\ NH_3 + CO_2 \leftrightarrow H_2N\text{-}COONH_4$
  - $H_2N\text{-}COONH_4 \leftrightarrow (NH_2)_2CO + H_2O$
  - Already large use (120 $MtCO_2$/an)



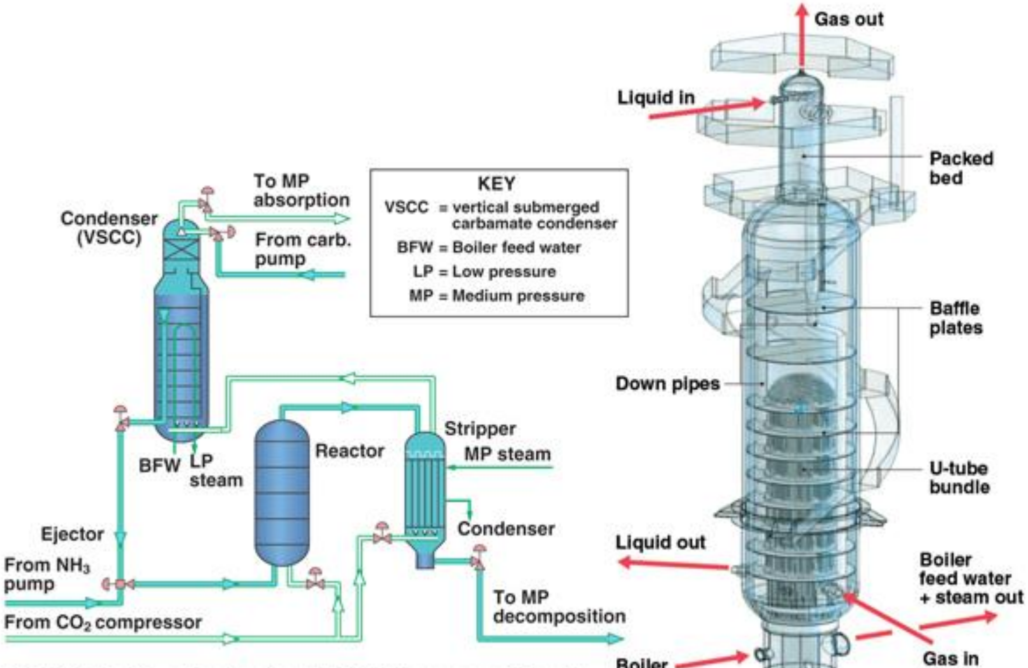
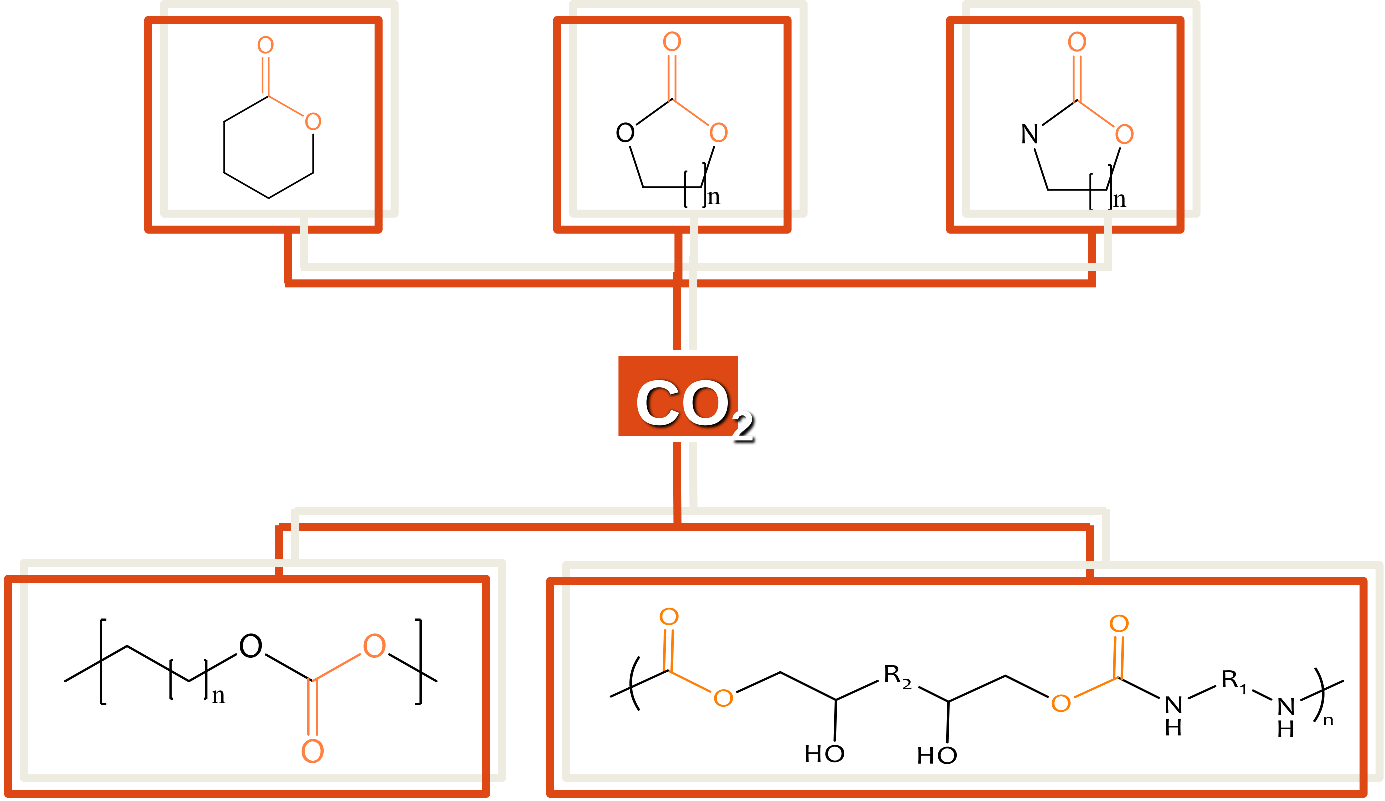


FIGURE 2. Toyo-Engineering's ACES21 process (above) for making urea integrates two condensers and a scrubber into a single condenser (right), which has a vertical, submerged carbamate-condensing section

CO_2 to chemicals

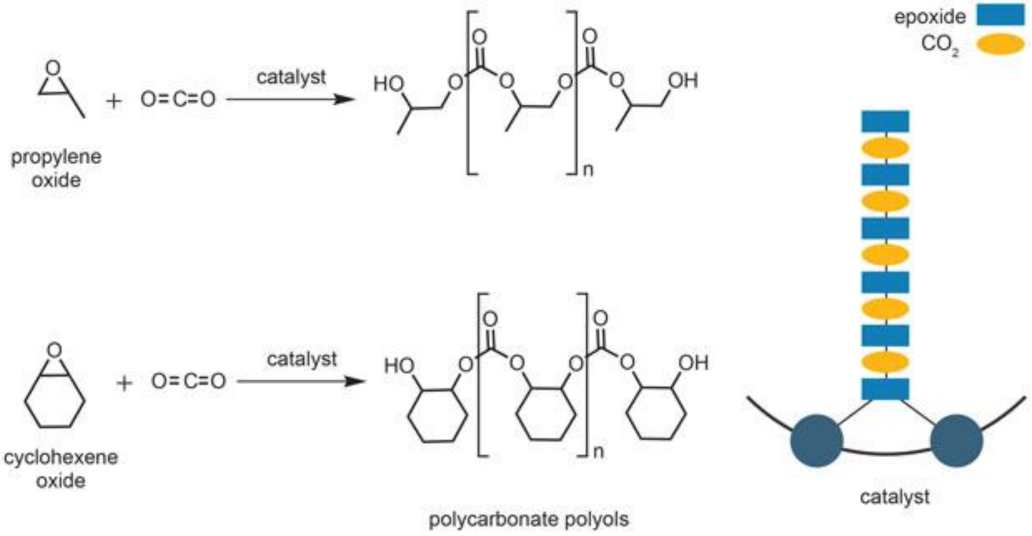
- Monomers



Gennen & al., ***Chemsuschem***, 2015, 11, 1845-1849; Alves & al., ***RSC Adv***., 2015, 5, 53629-53636; Alves & *al.*, ***Catal. Sci. Technol***., 2015, 5, 4636-4643, Poussard & al., ***Macromolecules***, 2016, accepted

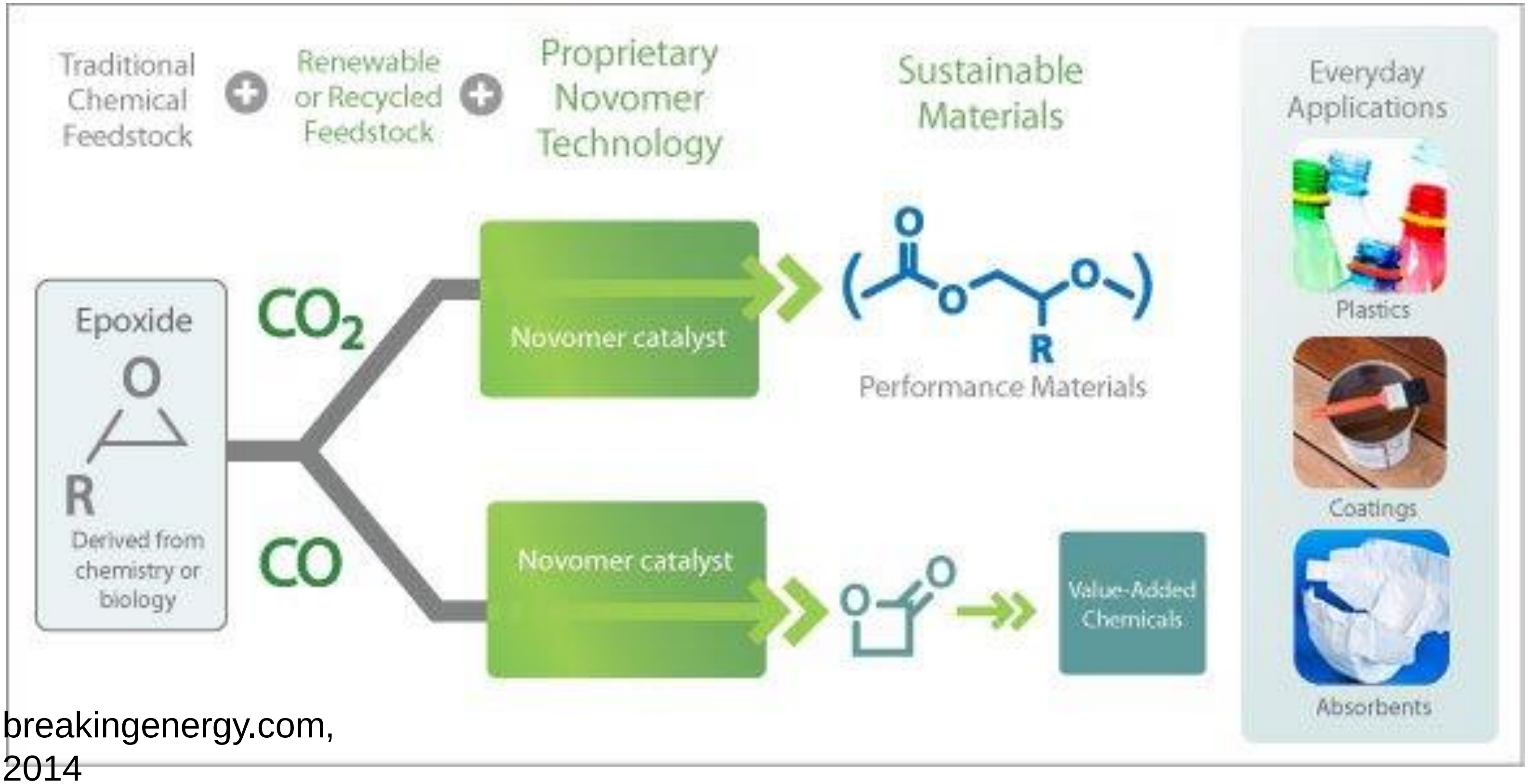
CO_2 to chemicals

- Polycarbonates
  - CO_2 + epoxides



CO_2 to chemicals

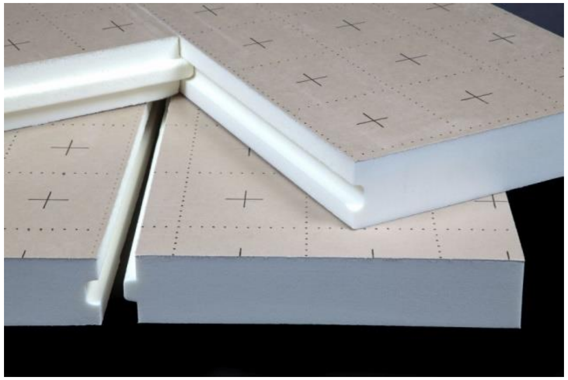
- Other polyols…
  - Up to 40 wt% CO_2 in the final plastic



breakingenergy.com, 2014

CO_2 to chemicals

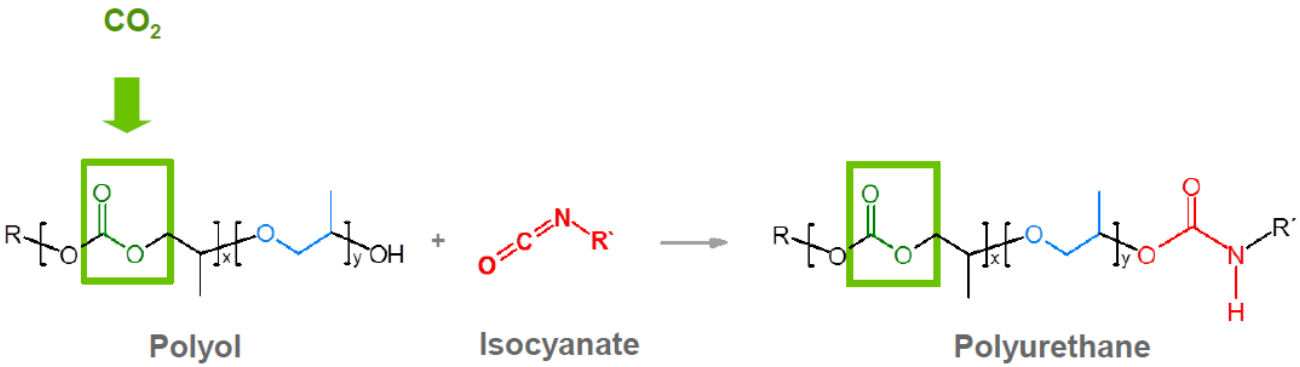
- Polyurethanes
  - 18 Mtpa market
  - 5000 t/a pilot reactor
  - 20% CO_2 in the final plastic



CO2-production-line at Bayer Material Sciences' site in Dormagen, Germany. ChemEurope.com, June 2015

CO_2 to chemicals

- Polyurethanes
  - Polyols + Isocyanate
    => Dream material

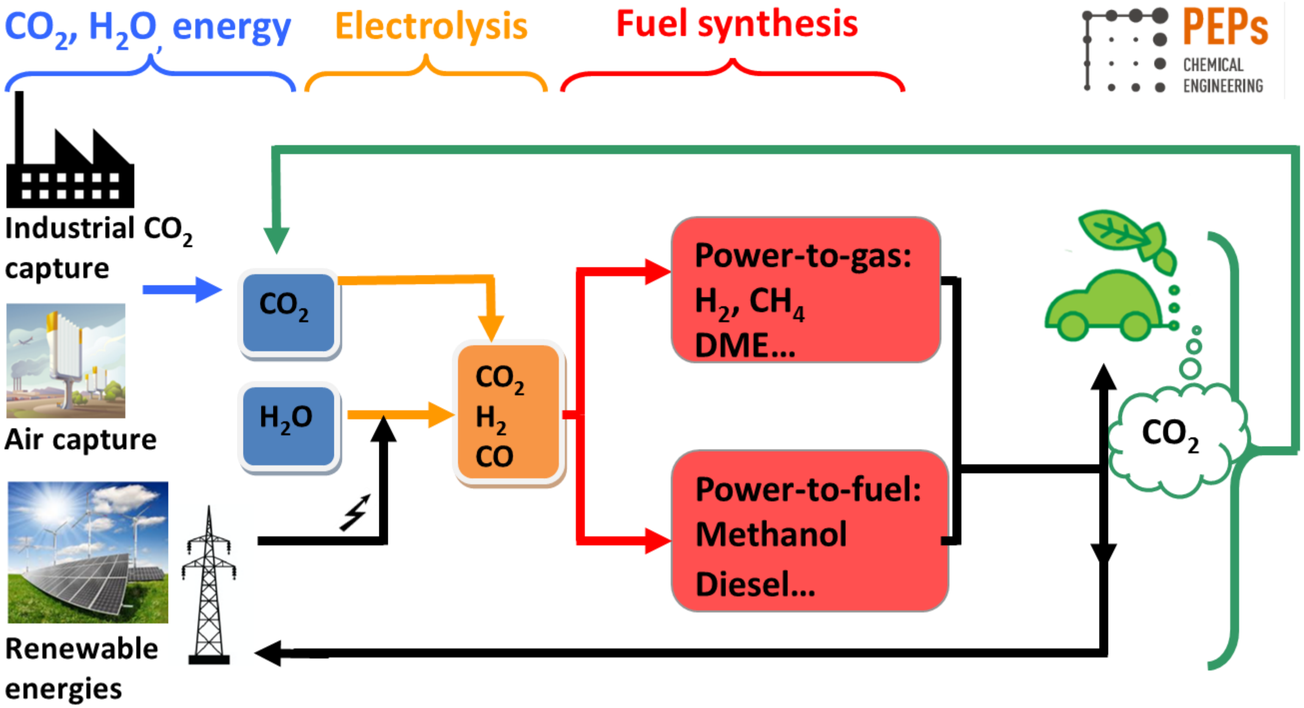


- 1 step further: remove isocyanates → NIPU market
  - Grignard B et al., Green Chem., 2016, 18, 2206

Sources: Bayer pilot plant; C. Gürtler, Covestro
5th Carbon Dioxide Utilisation Summit

CO_2 to fuels

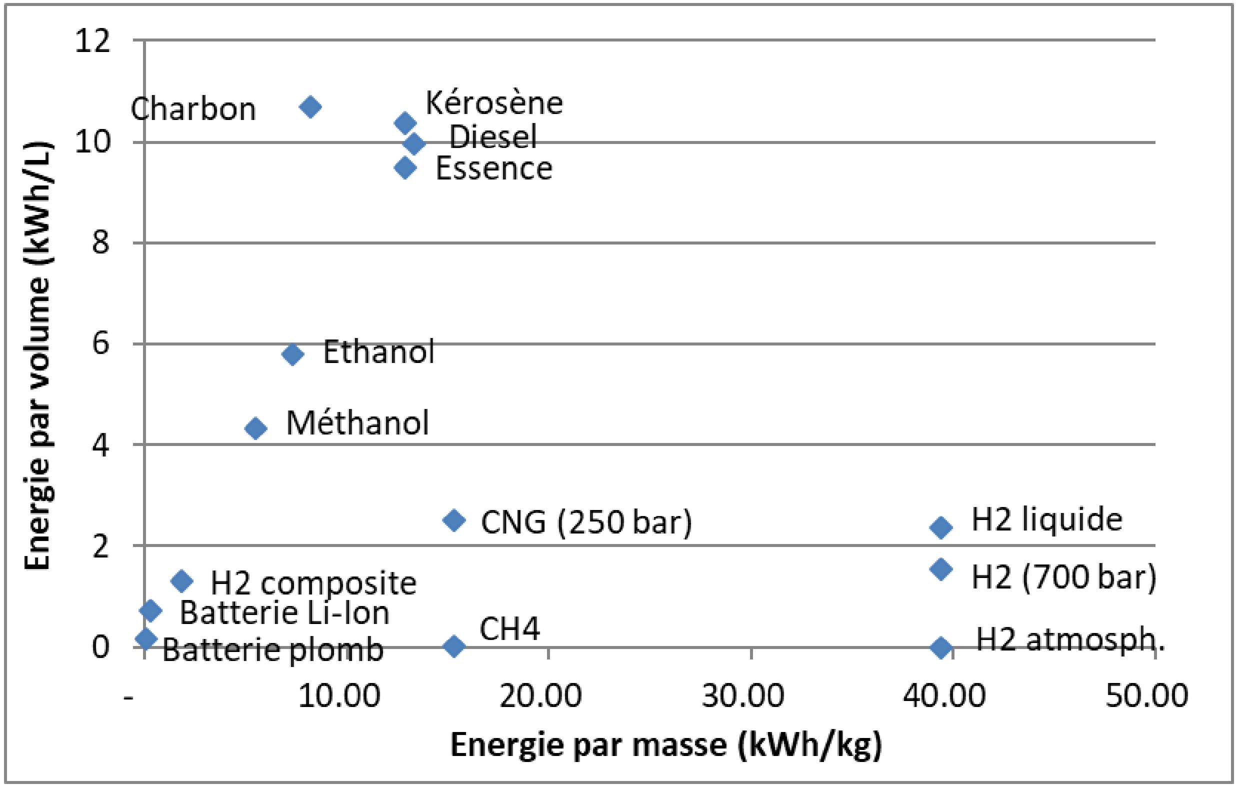
- Decisive advantage: a fantastic energy density!
- => Power-to-liquid, power-to-gas



=> Sustainability is possible with carbonated fuels!

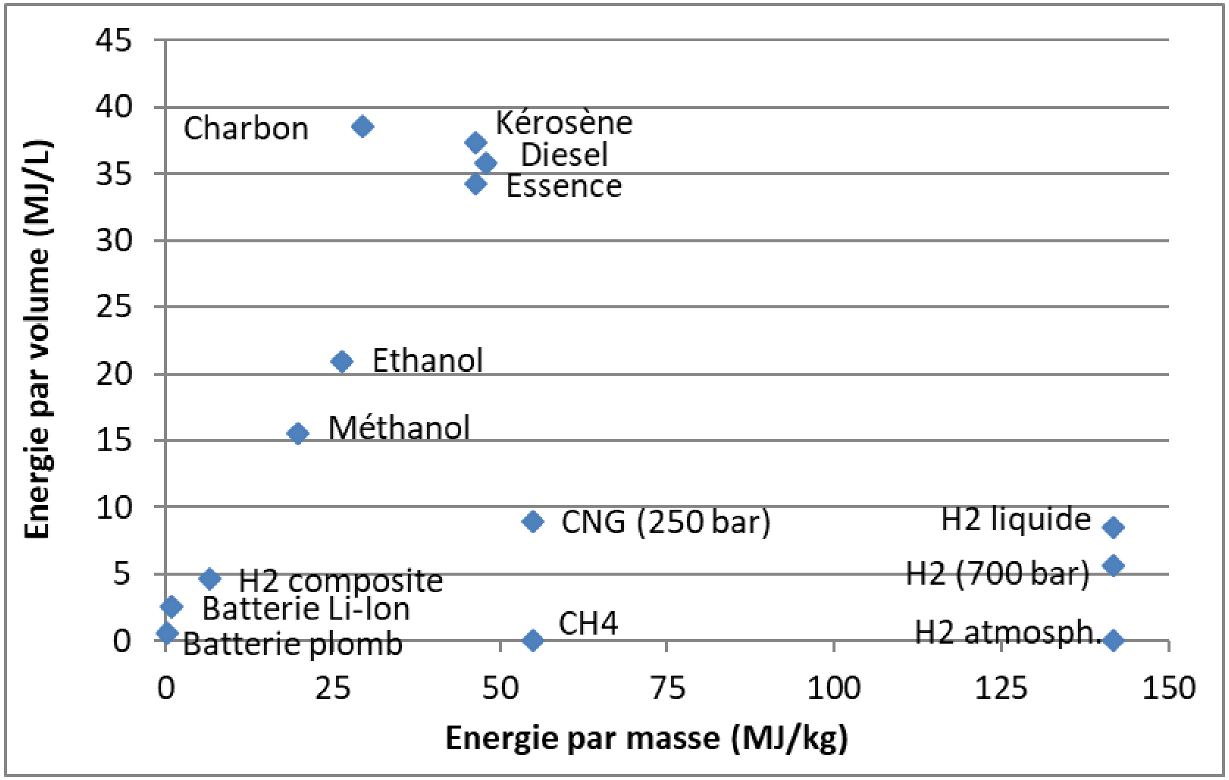
CO_2 to fuels

- Decisive advantage of chemical storage: a fantastic energy density!
  - => Interseasonal energy storage becomes possible



Energy storage

- Decisive advantage of chemical storage: a fantastic energy density!
  - => Interseasonal energy storage becomes possible



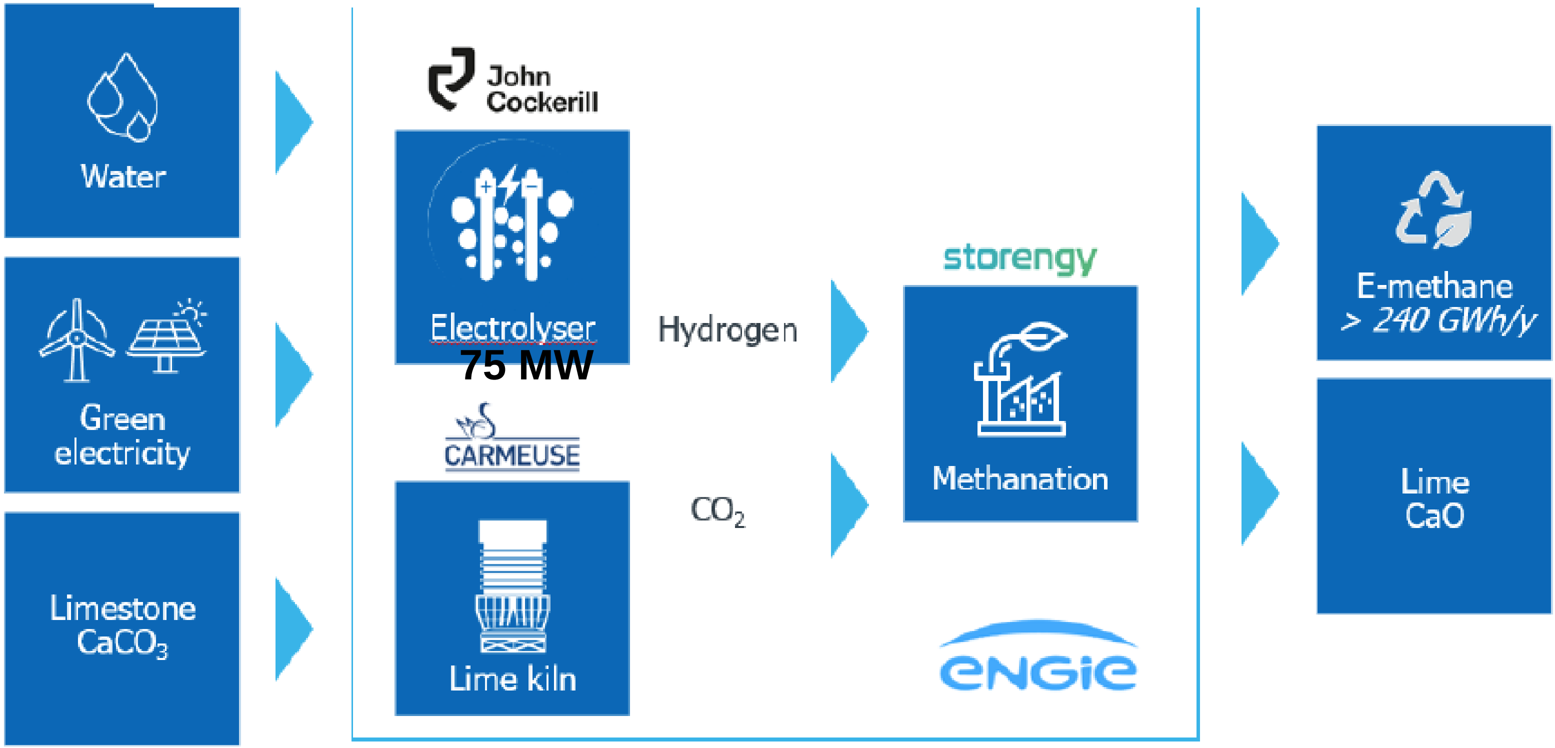
CO_2 to fuels

- Methane
  - $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$
  - Sabatier reaction
  - ΔH° = -165 kJ/mol

- Commercial uses:
  - Great Plain synfuel plant (see CO_2 capture chapter)
  - Methanation in ammonia synthesis
  - Considered for producing fuel on Mars
    - $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$
    - CH_4 used as fuel
    - H_2O electrolyzed for regenerating H_2 and producing O_2
  - Jupiter1000 in Marseille (Fos-sur-mer)
  - Power-to-gas in Germany
    - E.g. Audi e-gas plant, 54% efficiency (without heat reuse)

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

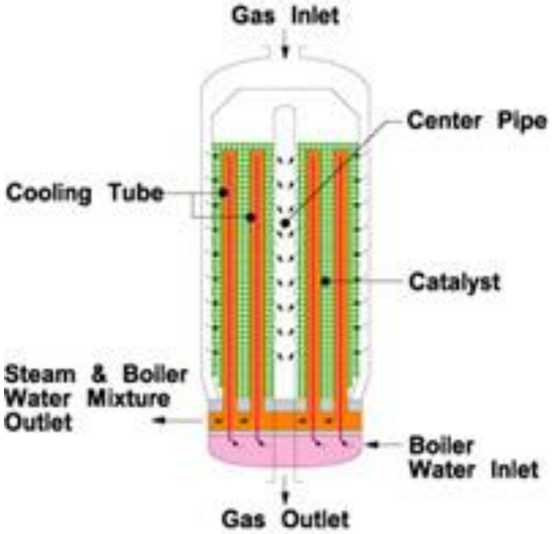
Recent announcement - Methane



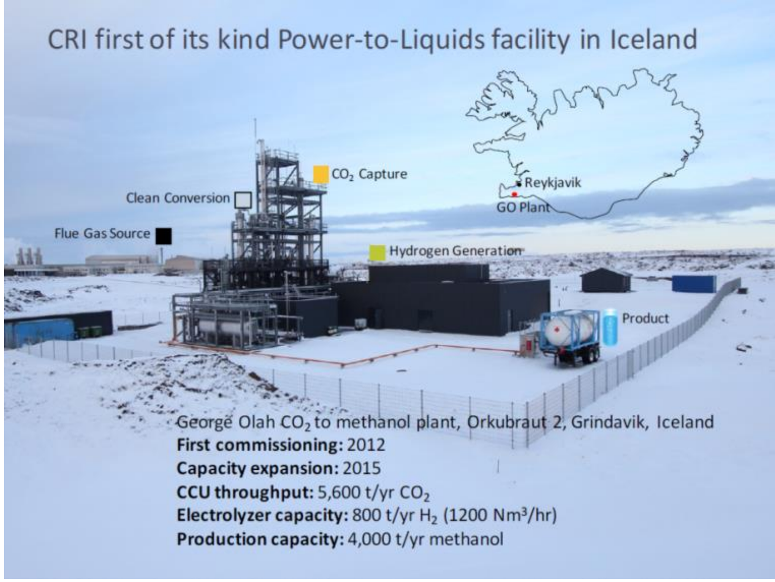
CO_2 to fuels

- Methanol
  - $CO + 2\ H_2 \rightarrow CH_3OH$
  - $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

Haldor Topsoe, > 10 000 t/d



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



CRI first of its kind Power-to-Liquids facility in Iceland

George Olah CO_2 to methanol plant, Orkubraut 2, Grindavik, Iceland

First commissioning: 2012

Capacity expansion: 2015

CCU throughput: 5,600 t/yr CO_2

Electrolyzer capacity: 800 t/yr H_2 (1200 Nm^3/hr)

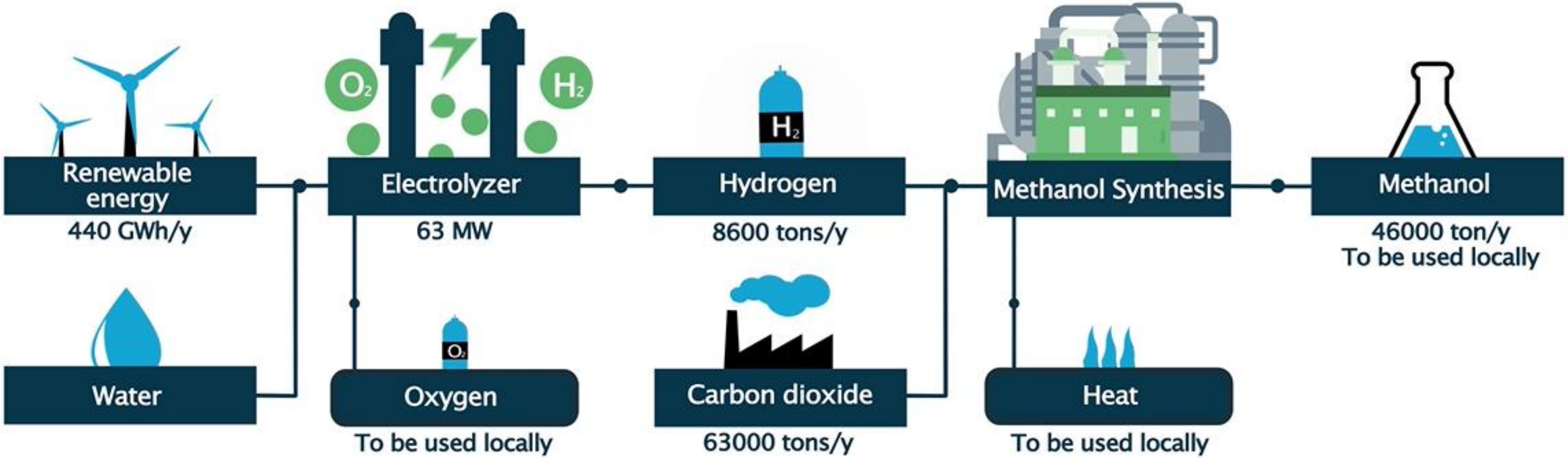
Production capacity: 4,000 t/yr methanol

12 t/d renewable methanol - CRI

Recent announcement

The North-C-Methanol project

https://northccuhub.eu/



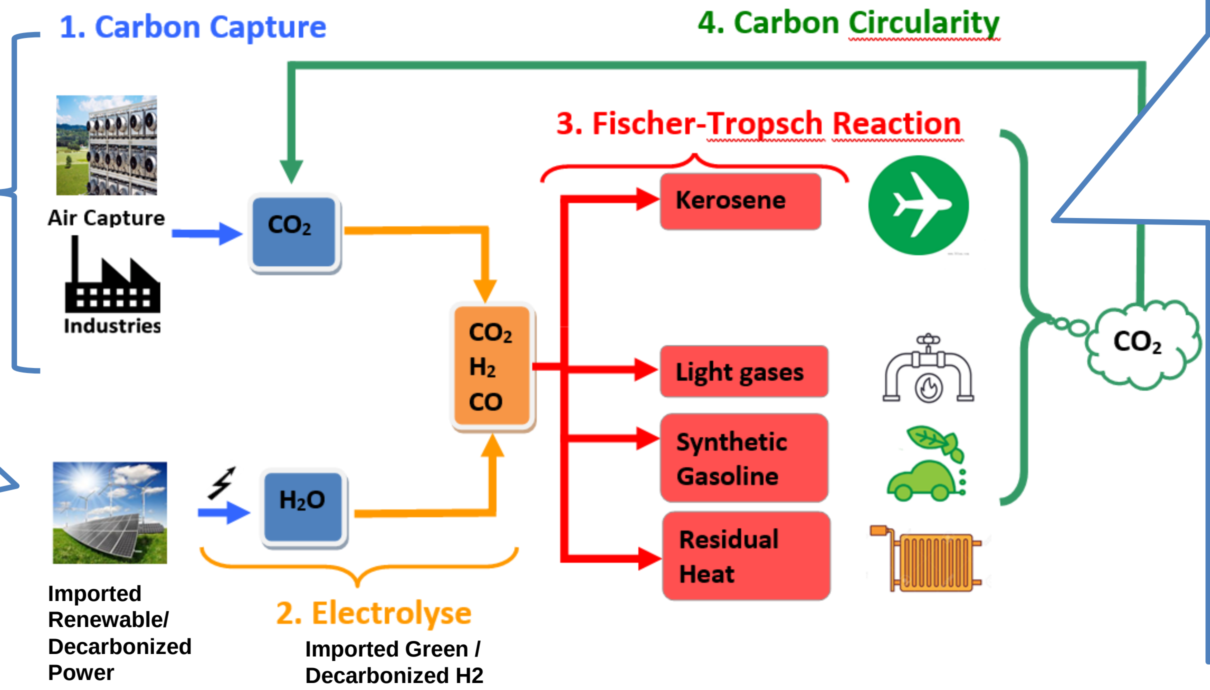
Antwerp: power-to-methanol: 8000 ton/y

NKL Project

- Neutral-Kero-Lime

1Mt CO2/year

0.15Mt H2/year (i.e. ~1GW continuous = 1 nuclear unit in base load)



250.000 m³/year (~40% conso Liege Airport)

Other products

- 117kt of petrol ;
- 16.5 kt other (methane, ethane...) ;
- heat: 1,282 GWh i.e. ~1.5x current capacity of the existing heat network in Herstal (~800GWh/year)

CO_2 to fuels

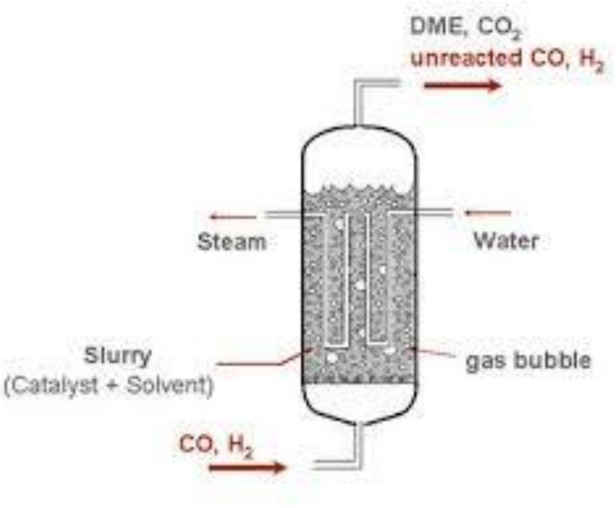
- Syngas
  - Water-gas shift
    - $CO_2 + H_2 \rightarrow CO + H_2O$
  - (Dry) Reforming
    - $CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2$
  - Co-electrolysis:
    - $H_2O \rightarrow H_2 + 0.5\ O_2$
    - $CO_2 \text{ -> } CO + 0.5\ O_2$

NETL, WGSR

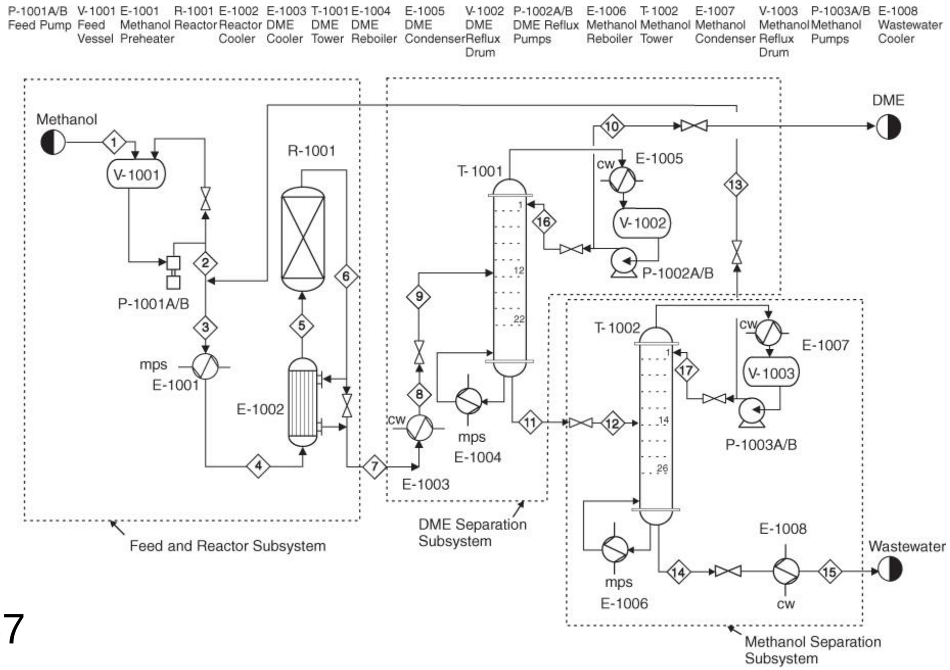
Wikipedia, SOEC

CO_2 to fuels

- DME (CH_3-O-CH_3)
  - 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



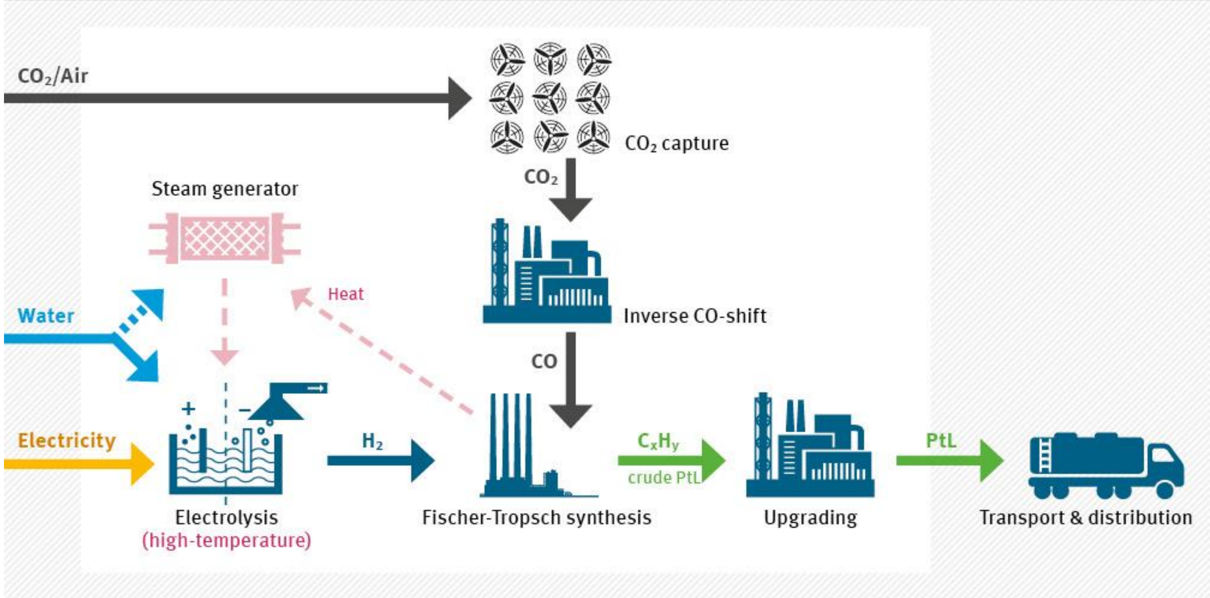
Turton et al., Prentice Hall, 2012

CO_2 to fuels

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

Figure 3

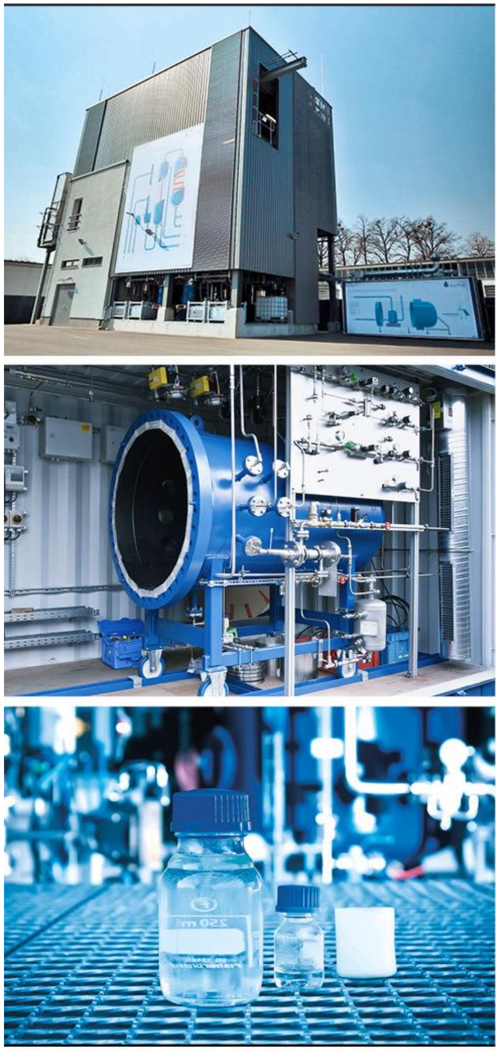
PtL production via Fischer-Tropsch pathway (high-temperature electrolysis optional)



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

CO_2 to fuels

- Transport applications of CO2-sourced fuels
  - Ferries (Methanol, Stena, 24 MW)
  - Trucks (DME, Volvo)
  - Cars (GEM fuels, Gely…)

CO_2 to fuels

- Potential market is larger than for petrochemistry!
  - But high energy cost and lower added-value products
  - => Need for renewable energy to make it sustainable

- Critical issues
  - Variability of energy source
  - Capital cost
  - Conversion efficiency
    - Power-to-methanol @ CRI => 4000 T/a, Efficiency ~50%
    - Power-to-diesel @ Sunfire => 58 m^3/a, Efficiency ~70%

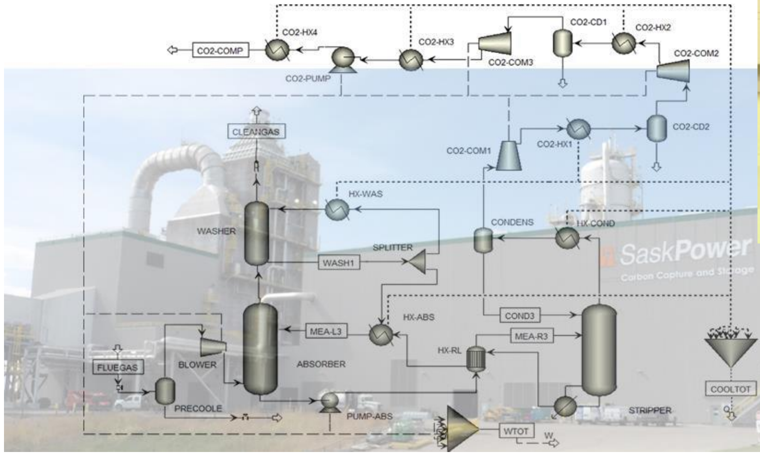
CCU activities – Chemeng ULiège

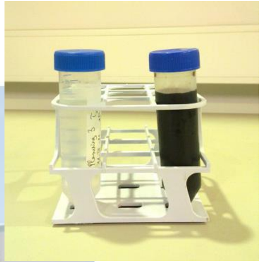
- CO_2 capture: Point-source and Direct air capture
  - Process modeling, design and optimisation (Aspen but not only)
  - Experimental study of sorbents/solvents stability

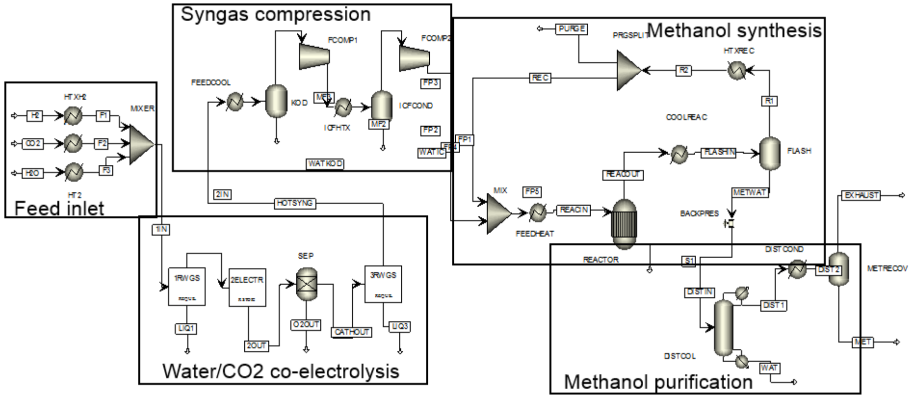
- e-Fuel synthesis
  - Process modeling with techno-economical analysis
    - Power-to-methanol, jet fuels, …
  - Experimental study of fuel synthesis based on 6.6 kW capacity of low-T electrolysis

- Energy system planning and modeling
  - Optimization of power grid with power-to-fuel for long-term electricity storage

CCU activities – Chemeng ULiège



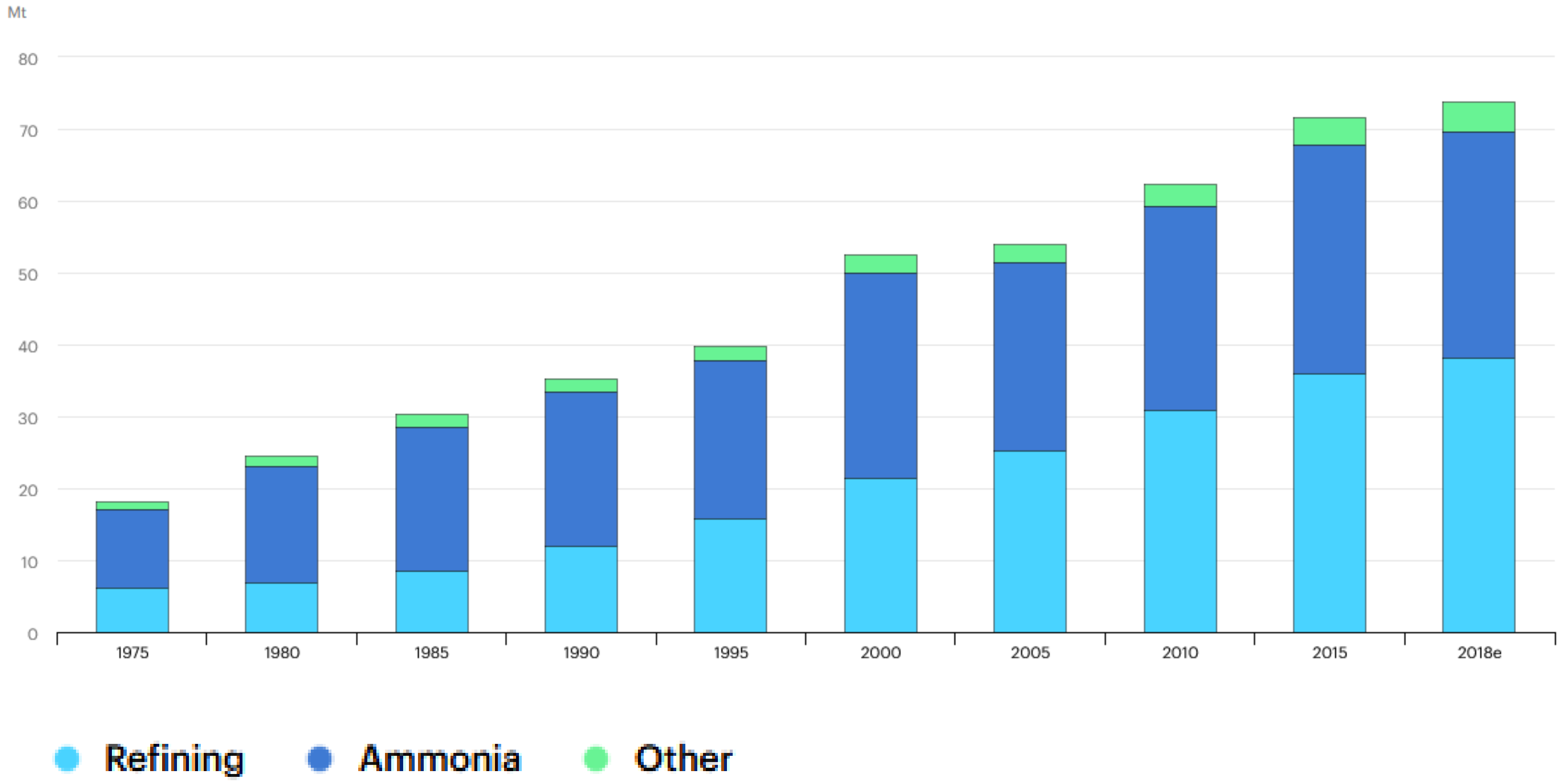




Léonard et al., 2016. Computer aided chemical engineering *38*, 1797.
DOI: 10.1016/B978-0-444-63428-3.50304-0

Hydrogen is not new!

- Historic demand for H_2



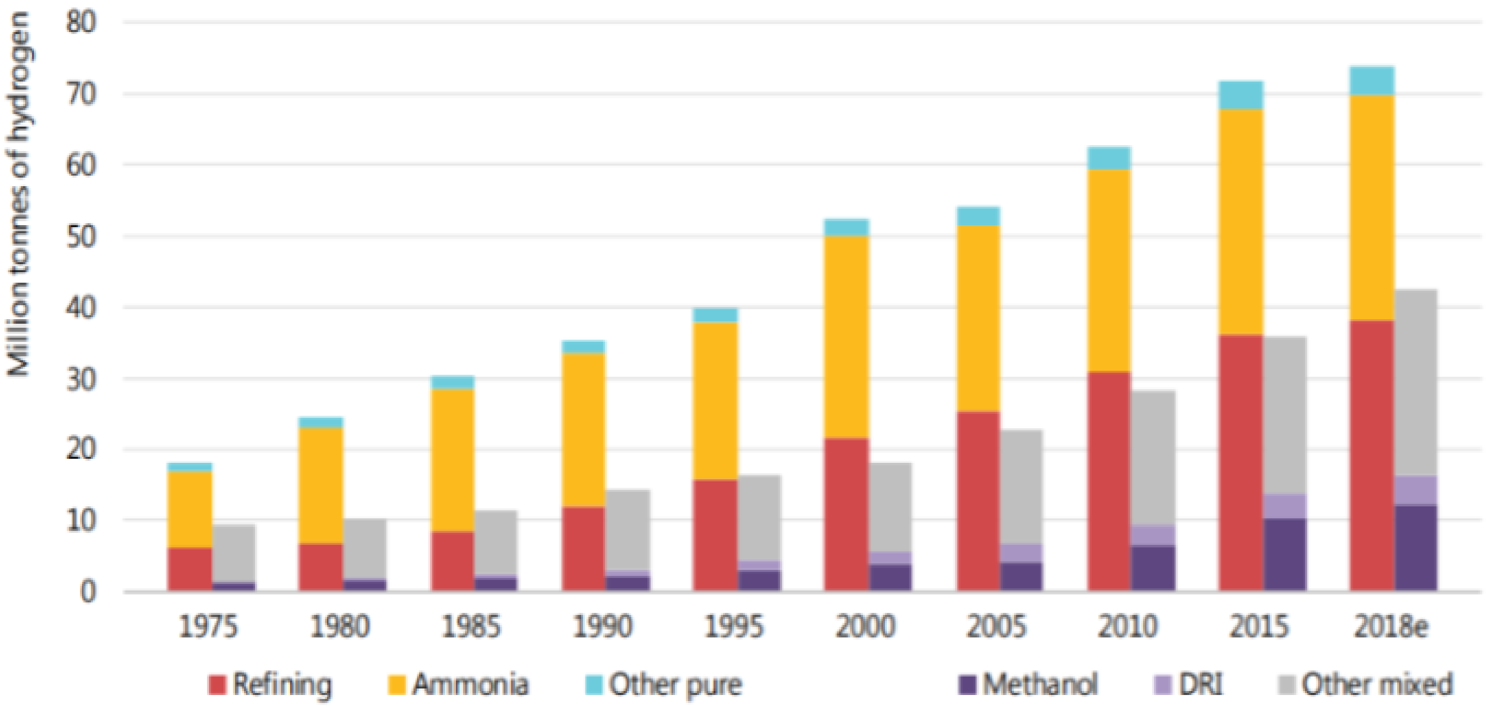
CHEMICAL ENGINEERING

Source: IEA, *Global demand for pure hydrogen, 1975-2018*, IEA, Paris https://www.iea.org/data-and-statistics/charts/global-demand-for-pure-hydrogen-1975-2018

LIÈGE université

Hydrogen is not new!

Figure 1. Global annual demand for hydrogen since 1975



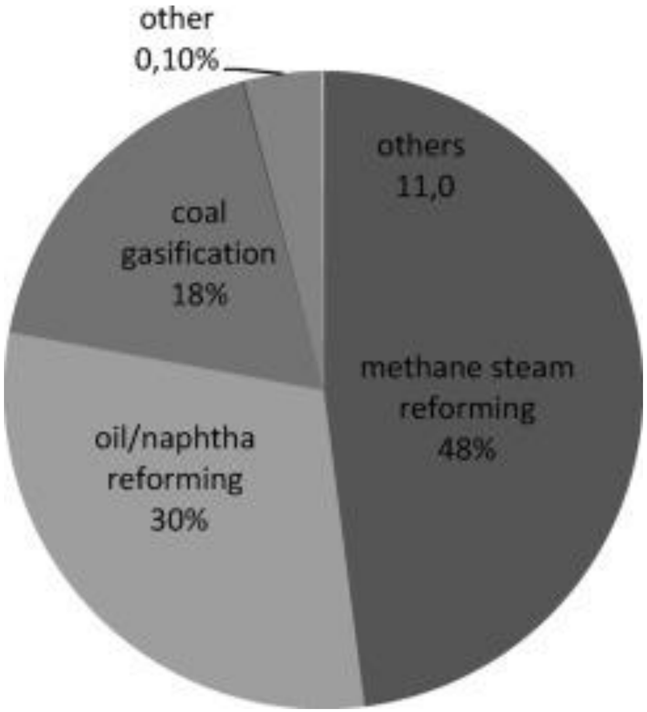
Notes: DRI = direct reduced iron steel production. Refining, ammonia and "other pure" represent demand for specific applications that require hydrogen with only small levels of additives or contaminants tolerated. Methanol, DRI and "other mixed" represent demand for applications that use hydrogen as part of a mixture of gases, such as synthesis gas, for fuel or feedstock.

Source: IEA 2019. All rights reserved.

Source: IEA, *Global demand for pure hydrogen, 1975-2018*, IEA, Paris https://www.iea.org/data-and-statistics/charts/global-demand-for-pure-hydrogen-1975-2018

Hydrogen generation

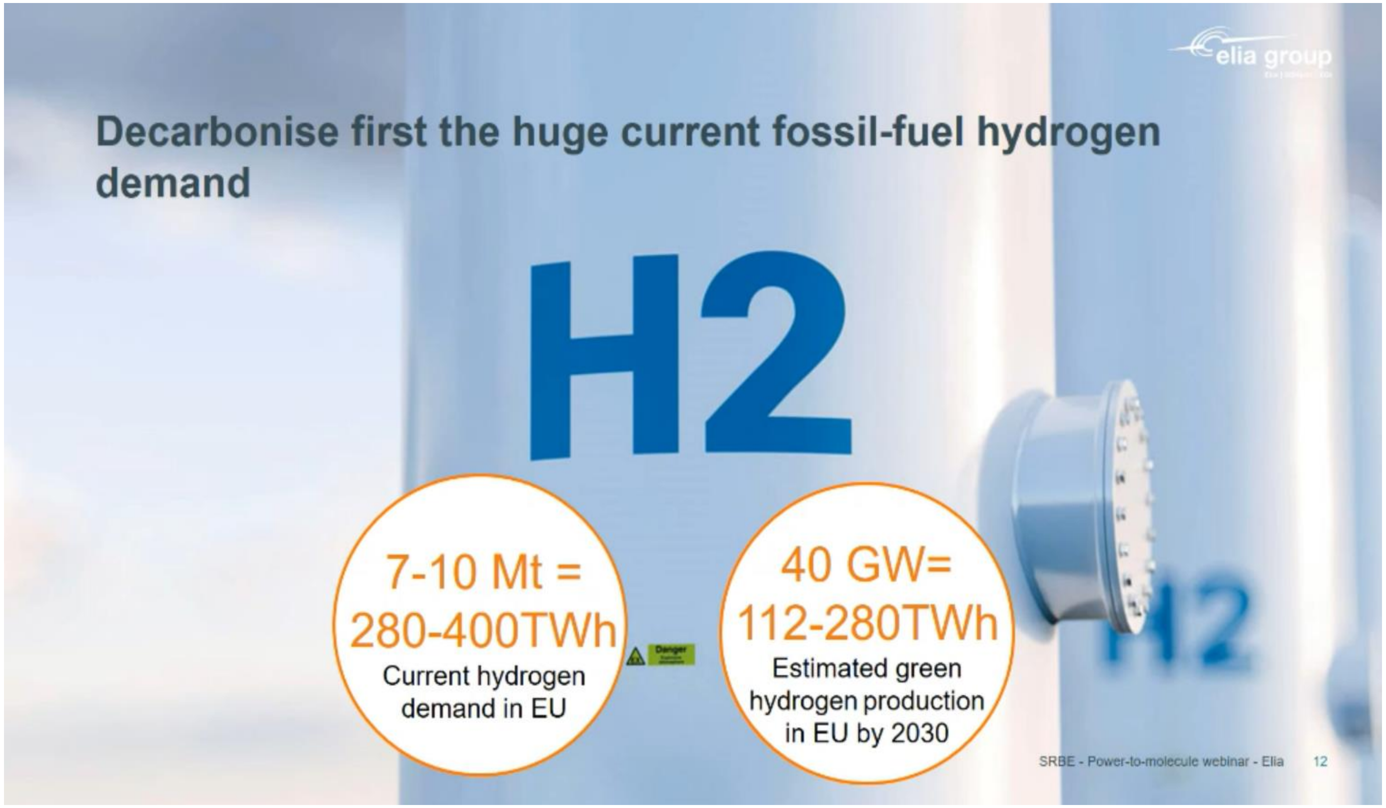
- Current processes for H_2 strongly rely on fossil fuels



Source: https://doi.org/10.1016/j.ijhydene.2016.08.219

Producing green H_2 is already a big challenge!

- H_2 = 40 kWh/kg



Decarbonise first the huge current fossil-fuel hydrogen demand

7-10 Mt =
280-400TWh
Current hydrogen demand in EU

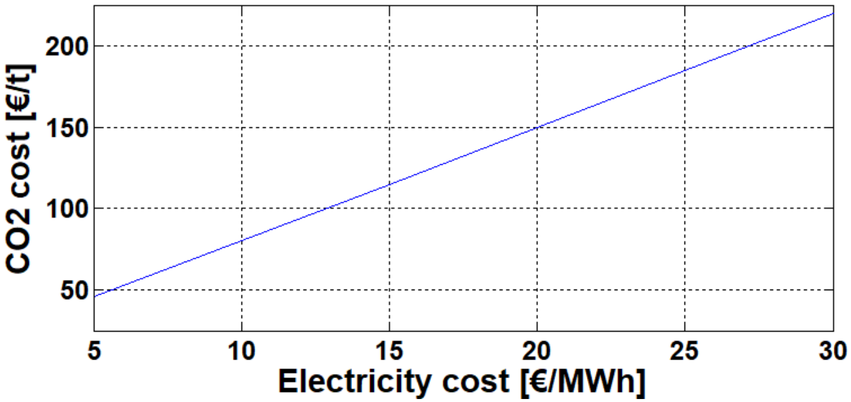
40 GW=
112-280TWh
Estimated green hydrogen production in EU by 2030

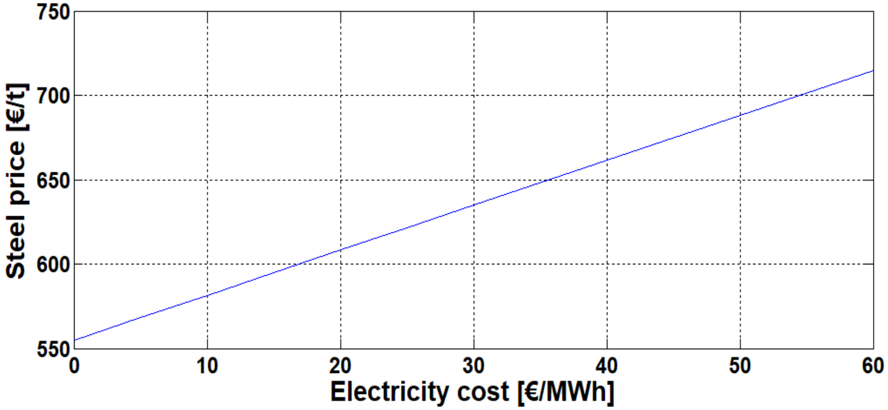
SRBE - Power-to-molecule webinar - Elia 12

Source: Nicolas Gielis, Elia, Power-to-molecules SRBE Webinar, Nov-Dec 2020

Producing green H_2 is already a big challenge!

- Assuming 85% efficiency, the H_2 needs in green industry would be:
  - For a typical ammonia plant (540 kt NH_3/year) => 700 MW power
  - For a typical steel making plant (1 Mt steel/year) => 400 MW power
  - Break-even costs (left: ammonia; right: steelmaking)

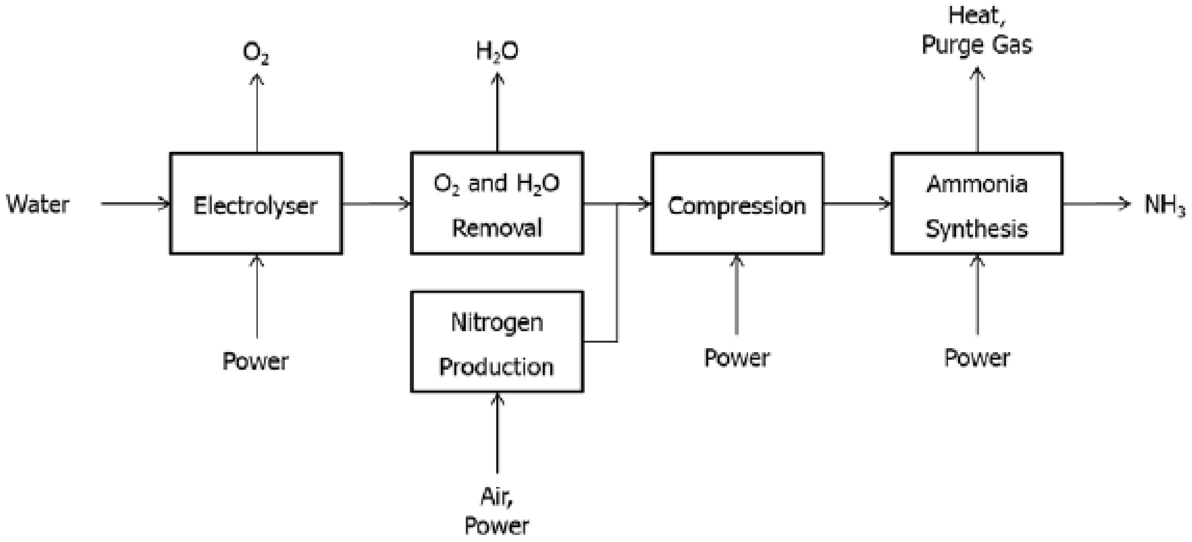




Source: Hoxha J.-L., Caspar M., Donceel A., Fraselle J., Philippart de Foy M., Poncelet R., Léonard G., 2020. Feasibility study of low-carbon ammonia and steel production in Europe. Eceee Industrial Summer Study Proceedings.

The case of ammonia

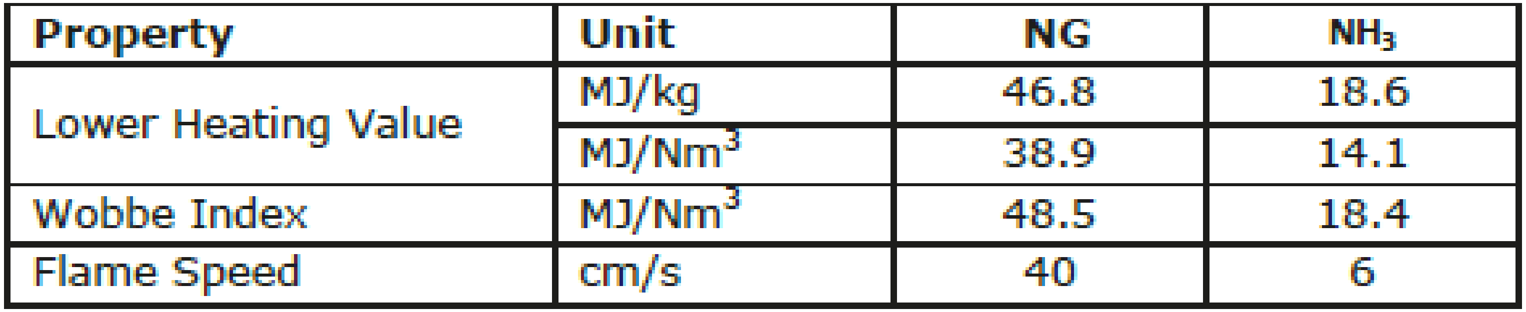
- Ammonia may be a smart way to transport H_2
- But:
  - Toxicity
  - Volatility
- Process block diagram



Source: Power-to-ammonia, Institute for Sustainable Process Technology, 2017

The case of ammonia

- Ammonia may be a smart way to transport H_2
- It can be used directly as a fuel



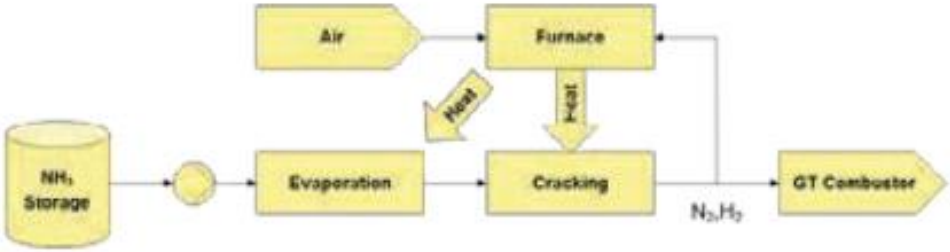
Property	**Unit**	**NG**	**NH_3**
Lower Heating Value	MJ/kg	46.8	18.6
	MJ/Nm^3	38.9	14.1
Wobbe Index	MJ/Nm^3	48.5	18.4
Flame Speed	cm/s	40	6

- Drawbacks:
  - Not mature technology, not much research on that
  - NOx => need for rich mixture

Source: Power-to-ammonia, Institute for Sustainable Process Technology, 2017

The case of ammonia

- Ammonia may be a smart way to transport H_2
- It can be converted back to H_2 before combustion



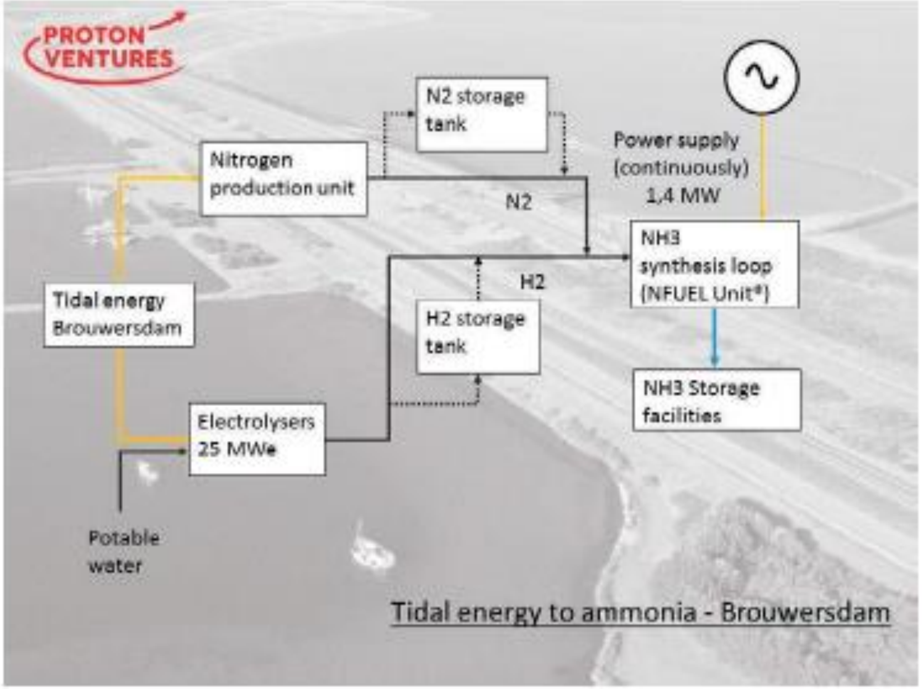
NH_3 cracking (NH3_CR)

- Drawbacks:
  - Need for H_2 gas turbines (new to market)
  - NOx => need for rich mixture

Source: Power-to-ammonia, Institute for Sustainable Process Technology, 2017

The case of ammonia

- Power-to-ammonia rises interest
- But few studies so far…
  - Case study of tidal electricity to green NH_3
  - Import coalition



Source: Power-to-ammonia, Institute for Sustainable Process Technology, 2017

5. Conclusions and perspectives

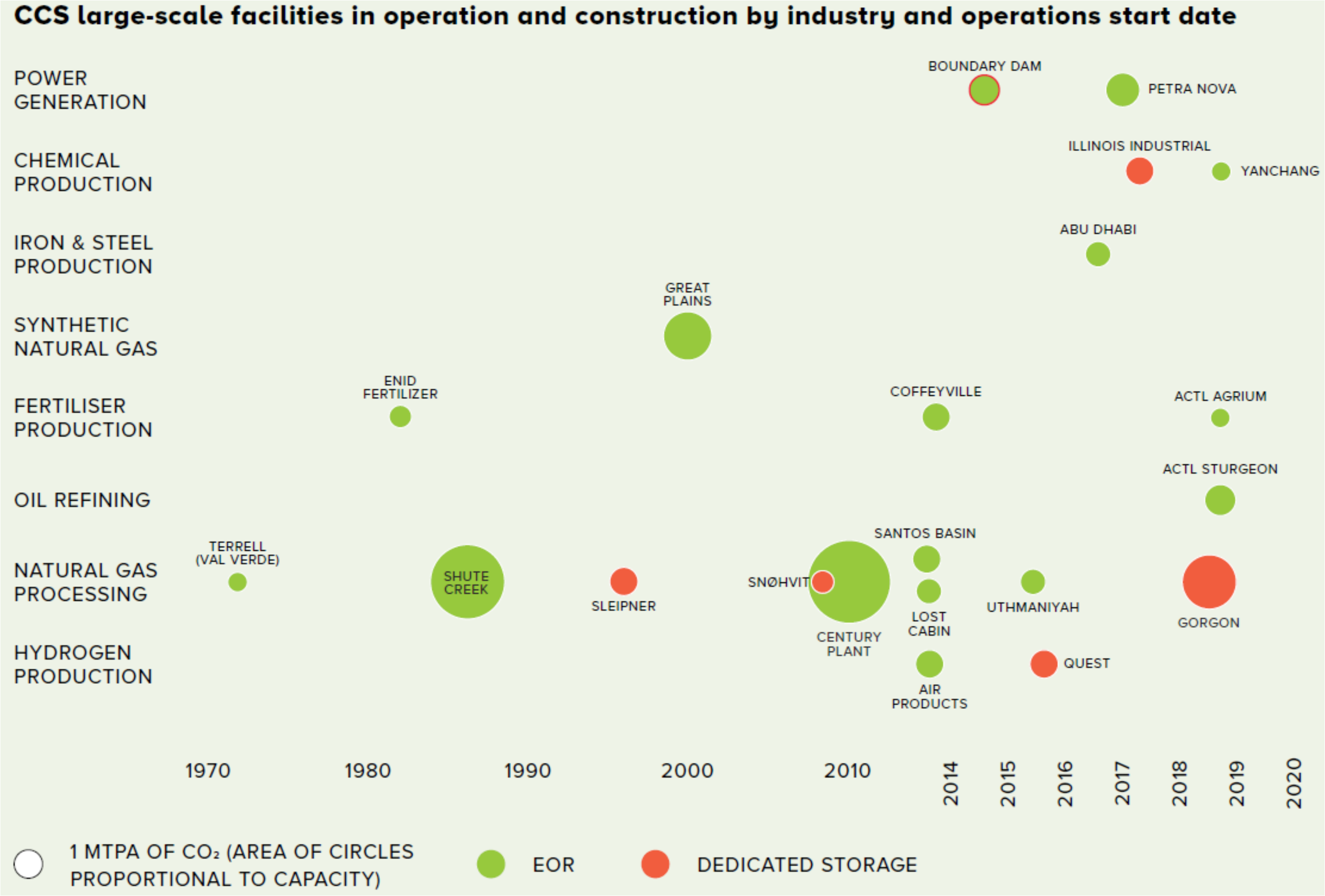
State of technology CCUS

- Capture of CO_2
    - Mature but not commercially applied yet
    - Improvements needed to lower costs & energy penalties, extend lower limit for CO_2 concentration in stream for capture
    - Current estimates *circa* \$50-100/t CO_2 → < \$40 with further development

- Transport of CO_2
    - Commercially applied
- Storage
    - Commercially applied (mostly EOR), interest rising
- Re-use
    - Maturity depends on technology, from TRL 1 to 9

- Big acceleration due to Paris COP21 agreement
    - European Green Deal

CCS: not many sites in Europe!



Global CCS Institute 2017

Conclusions and perspectives

Large potential but many challenges for CO_2!

- Society
  - Acceptation of new technologies

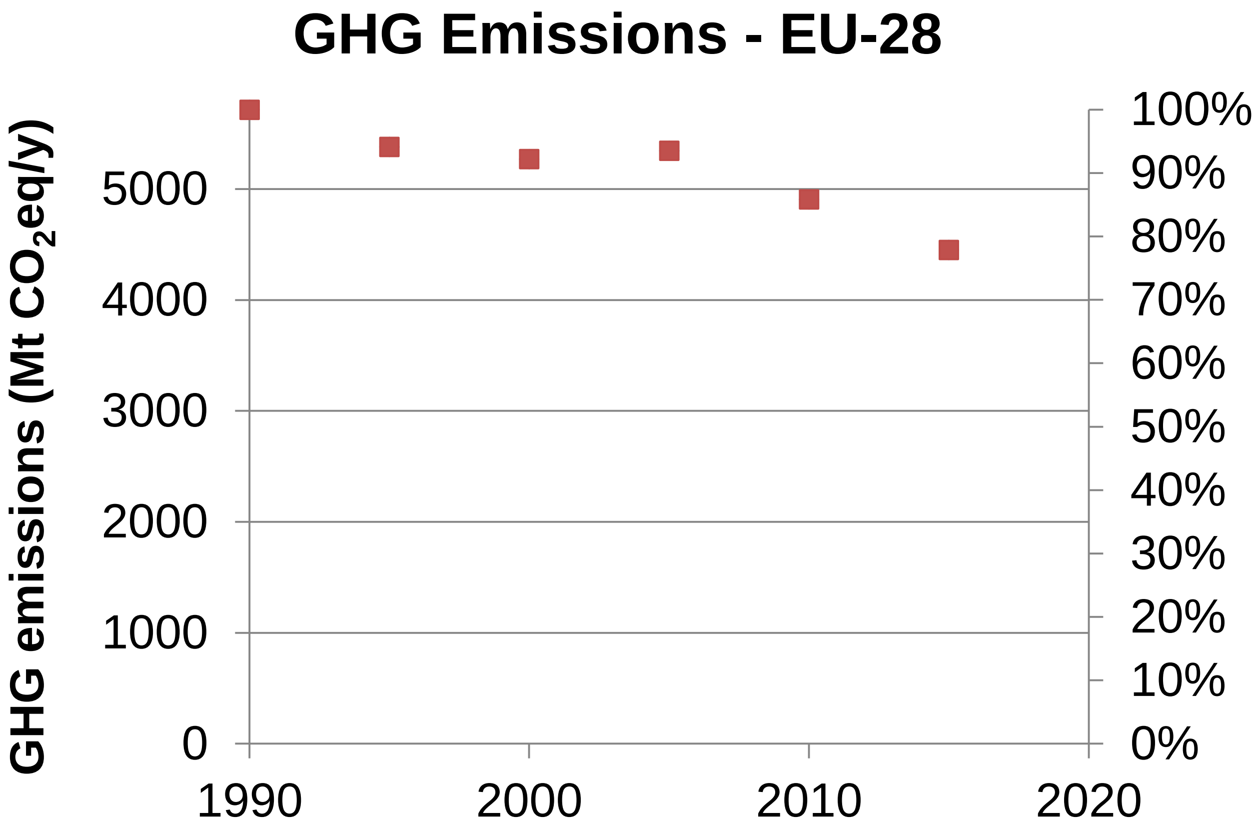
- R&D and industries
  - Develop these technologies, efficient & cheap
  - Integrate them to existing processes!
  - Be able to process huge flow rates

- Politics
  - Large-scale demonstration projects are needed, but they are expensive!
  - Efficient legislative framework is needed to promote new technologies
  - Cost of CO_2 capture ~30-40 €/t vs. ETS market
  - Carbon tax?
  - Label on low-CO_2 or CO_2-sourced goods? ...

NEUTRALIZED BY
GREEN ENERGY
0% CO2
CERTIFIED

The 2020 European goal was achieved!

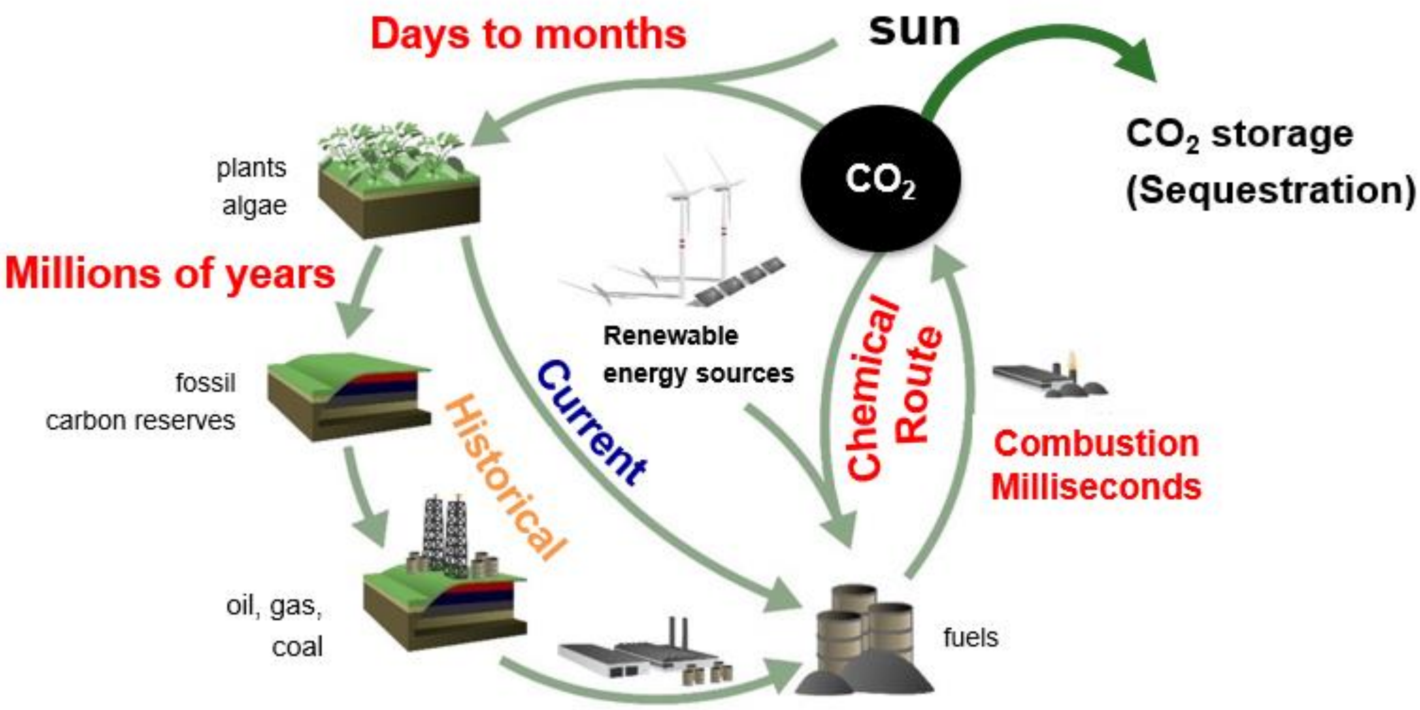
- Thanks to energy policies, or relocation of emissions ?



Eurostat, 2017. Greenhouse gas emission statistics - emission inventories

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!



Saeys et al., KVAB, Green Chem

Thank you for your attention!

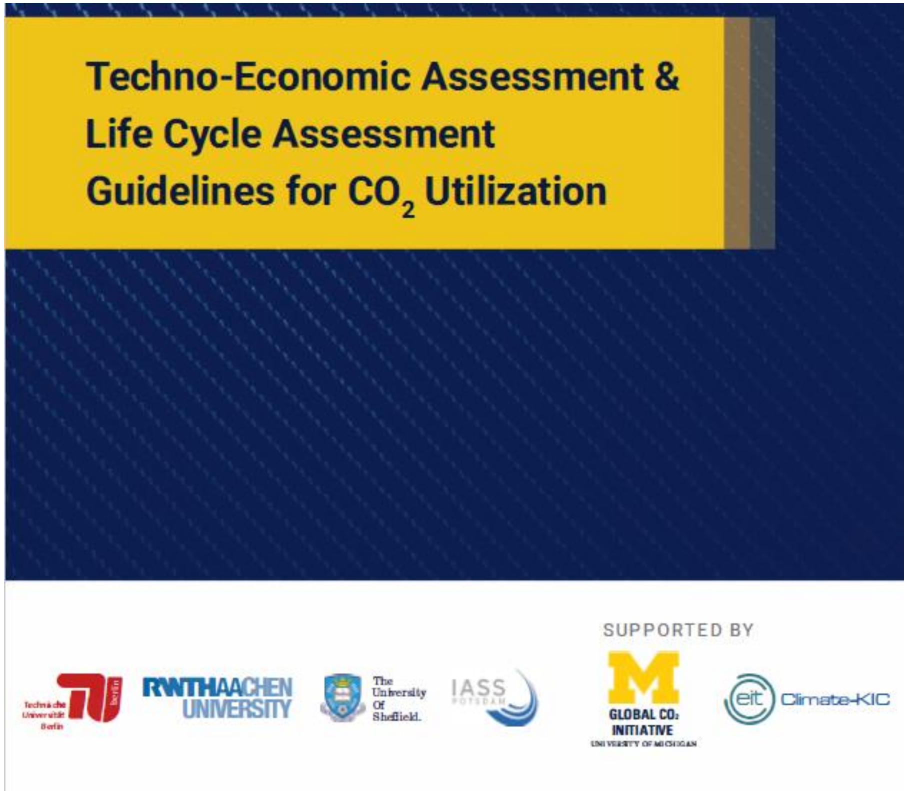
g.leonard@uliege.be

CHEMICAL
ENGINEERING

LIÈGE
université

LCA – TEA guidelines

- DOI: 10.3998/2027.42/145436
- http://hdl.handle.net/2027.42/145436

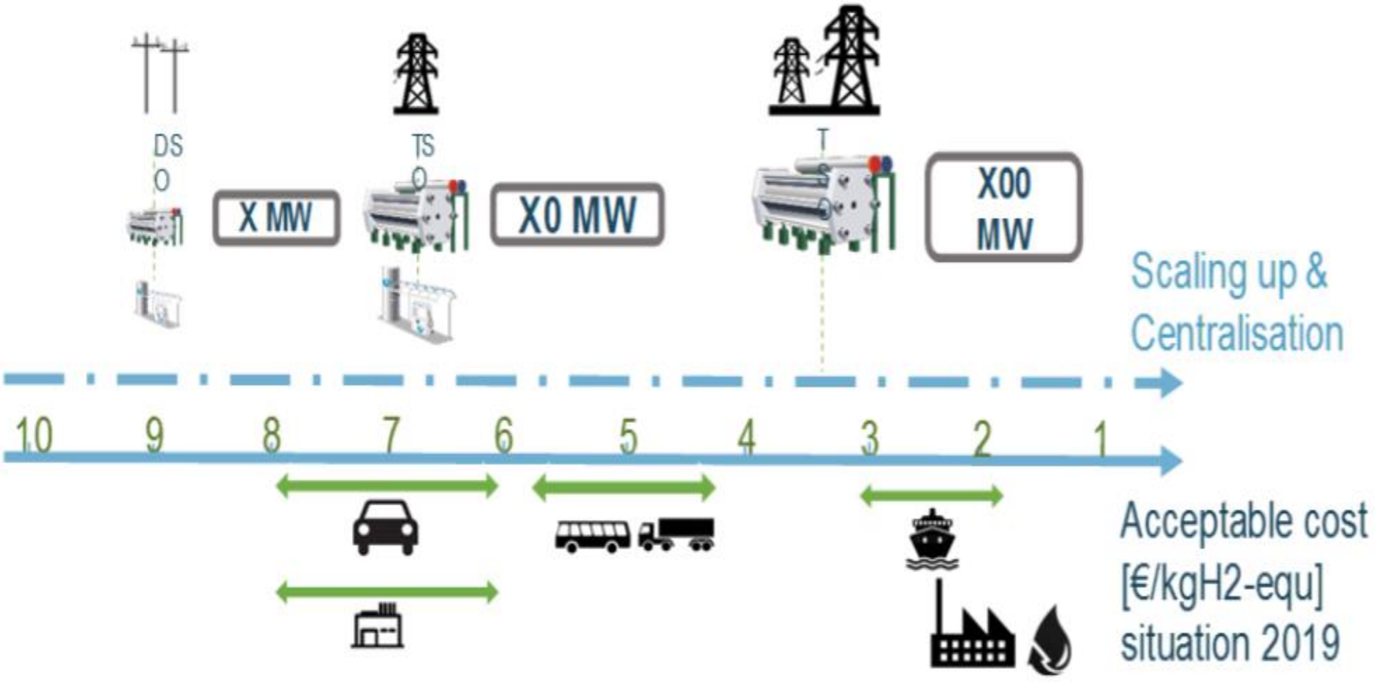


Techno-Economic Assessment &
Life Cycle Assessment
Guidelines for CO_2 Utilization

SUPPORTED BY

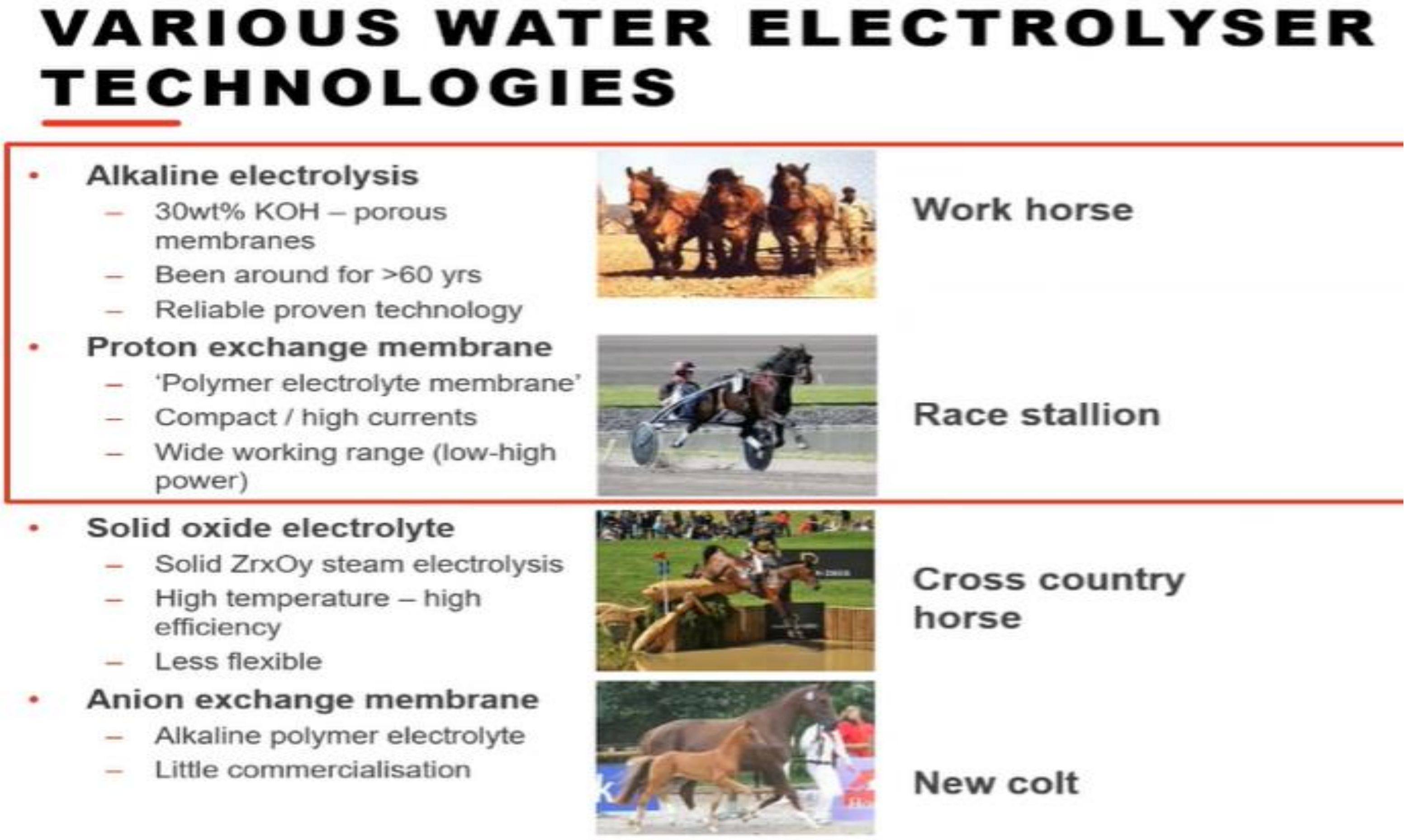
Hydrogen costs

- Economies of scale



Source: Waterstofnet, Nov-Dec 2020

Electrolysis



VARIOUS WATER ELECTROLYSER TECHNOLOGIES

- **Alkaline electrolysis**
  - 30wt% KOH – porous membranes
  - Been around for >60 yrs
  - Reliable proven technology

Work horse

- **Proton exchange membrane**
  - 'Polymer electrolyte membrane'
  - Compact / high currents
  - Wide working range (low-high power)

Race stallion

- **Solid oxide electrolyte**
  - Solid ZrxOy steam electrolysis
  - High temperature – high efficiency
  - Less flexible

Cross country horse

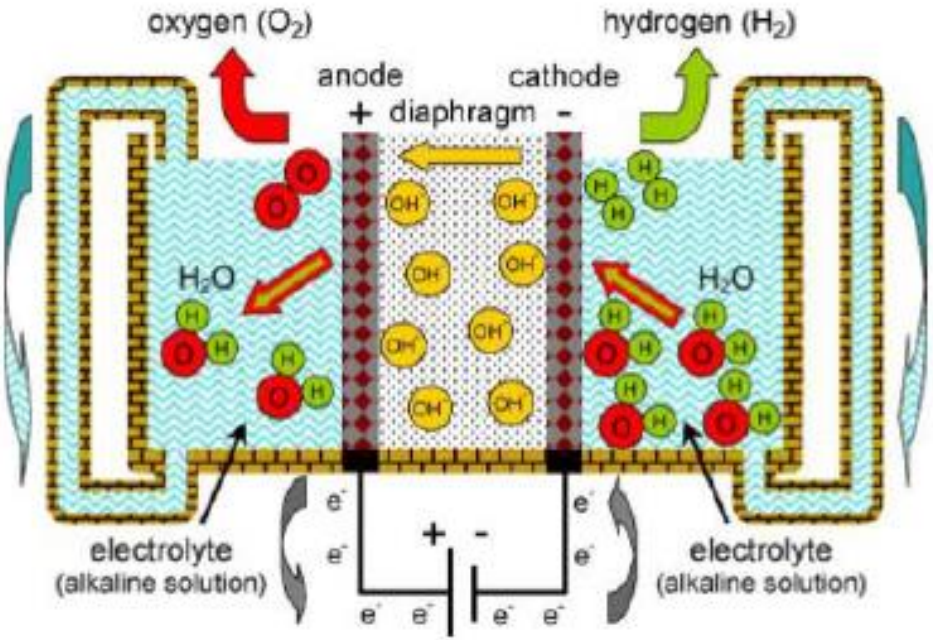
- **Anion exchange membrane**
  - Alkaline polymer electrolyte
  - Little commercialisation

New colt

Source: Baudoin De Lannoy, Hydrogenics Europe, Power-to-molecules SRBE Webinar, Nov-Dec 2020

Electrolysis

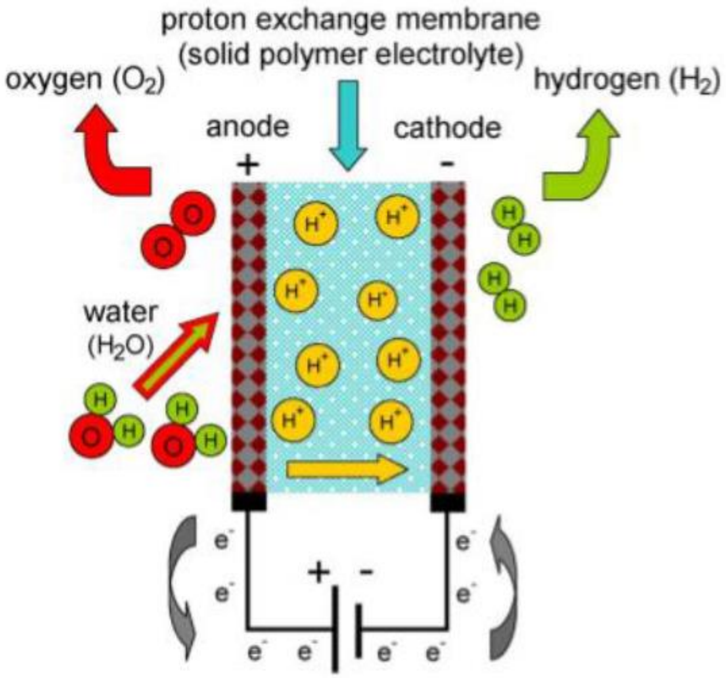
- Conventional technologies
  - Alcaline



A. Barbucci, 2016, *Electrolysers and Fuel Cells,* University of Genova, Dept. of Chemical Engineering

Electrolysis

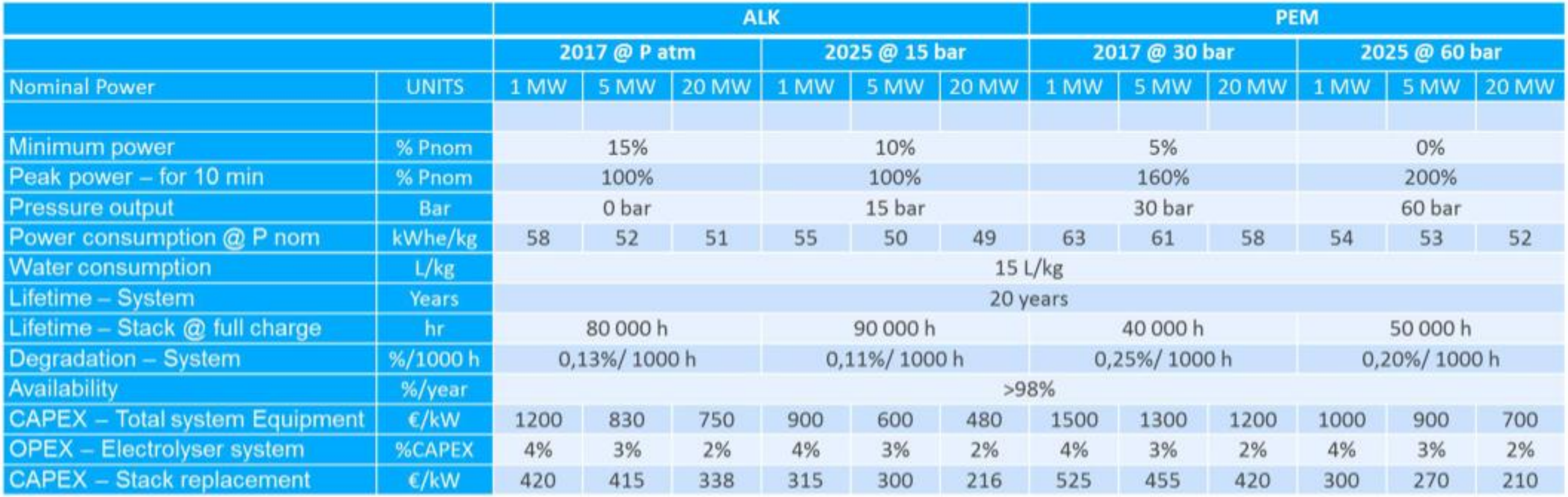
- Conventional technologies
  - PEM



A. Barbucci, 2016, *Electrolysers and Fuel Cells,* University of Genova, Dept. of Chemical Engineering

Electrolysis

- Conventional technologies
  - Comparison



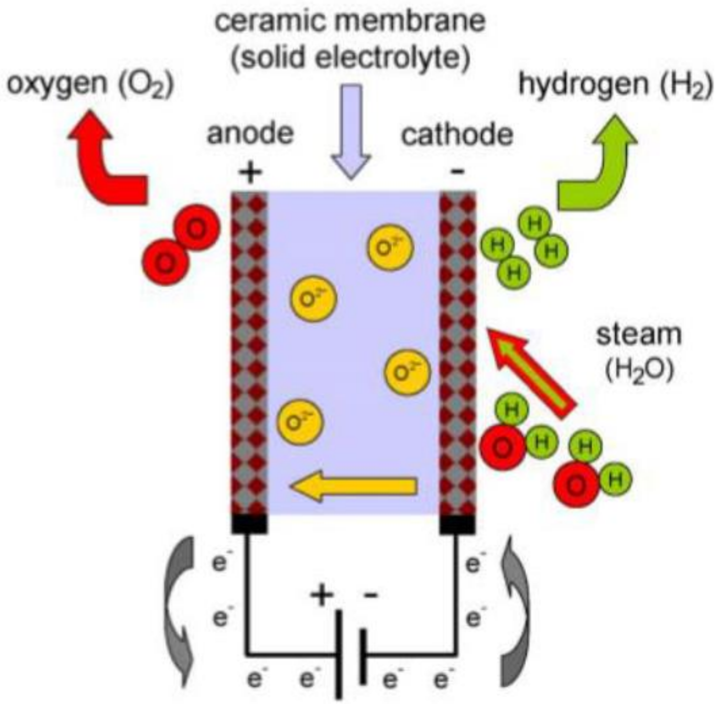
		ALK						PEM					
		2017 @ P atm			2025 @ 15 bar			2017 @ 30 bar			2025 @ 60 bar		
Nominal Power	UNITS	1 MW	5 MW	20 MW	1 MW	5 MW	20 MW	1 MW	5 MW	20 MW	1 MW	5 MW	20 MW
Minimum power	% Pnom	15%			10%			5%			0%		
Peak power – for 10 min	% Pnom	100%			100%			160%			200%		
Pressure output	Bar	0 bar			15 bar			30 bar			60 bar		
Power consumption @ P nom	kWhe/kg	58	52	51	55	50	49	63	61	58	54	53	52
Water consumption	L/kg	15 L/kg											
Lifetime – System	Years	20 years											
Lifetime – Stack @ full charge	hr	80 000 h			90 000 h			40 000 h			50 000 h		
Degradation – System	%/1000 h	0,13%/ 1000 h			0,11%/ 1000 h			0,25%/ 1000 h			0,20%/ 1000 h		
Availability	%/year	>98%											
CAPEX – Total system Equipment	€/kW	1200	830	750	900	600	480	1500	1300	1200	1000	900	700
OPEX – Electrolyser system	%CAPEX	4%	3%	2%	4%	3%	2%	4%	3%	2%	4%	3%	2%
CAPEX – Stack replacement	€/kW	420	415	338	315	300	216	525	455	420	300	270	210

Table 3: Summary of electrolyser selected cost and performance data

Study on early business cases for H2 in energy storage and more broadly power-to-H2 applications, 2017. Report by Tractebel and Hinicio for FCH-JU

Electrolysis

- New technologies
  - Solid oxide – High temperature (steam)



A. Barbucci, 2016, *Electrolysers and Fuel Cells,* University of Genova, Dept. of Chemical Engineering

Electrolysis

- The point of working at high temperature…
  - Use of waste heat
  - No need for expensive catalysts
  - Reversible operation

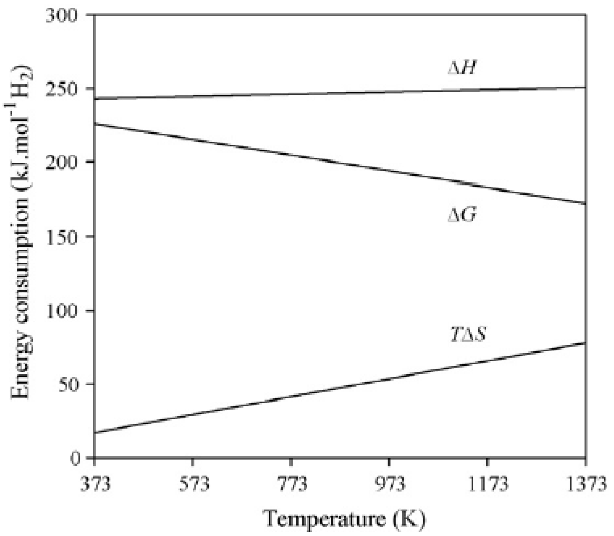


Fig. 1. Thermal ($T\Delta S$), electrical (ΔG) and total (ΔH) energy consumption during steam electrolysis as a function of temperature. The gas compositions are taken to be 50 mol% H_2/50 mol% H_2O and 100 mol% O_2. Irreversible losses are not taken into account.

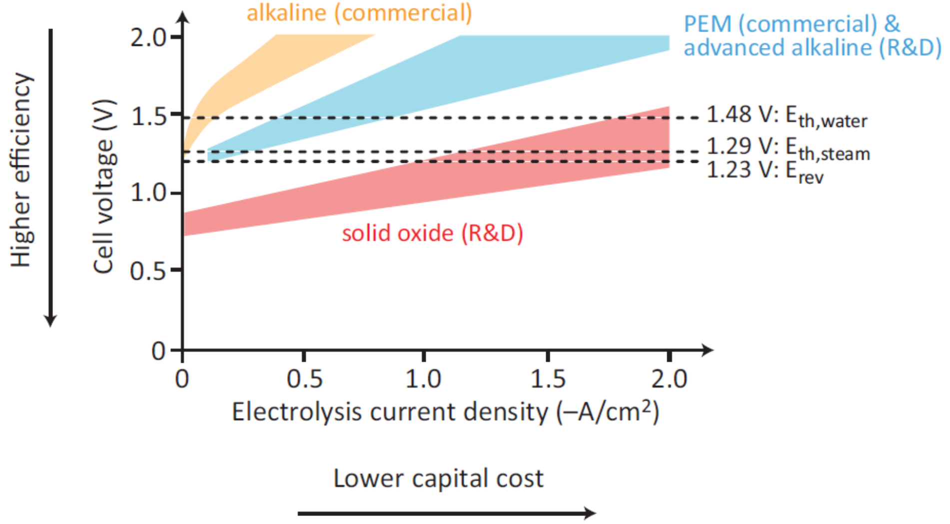
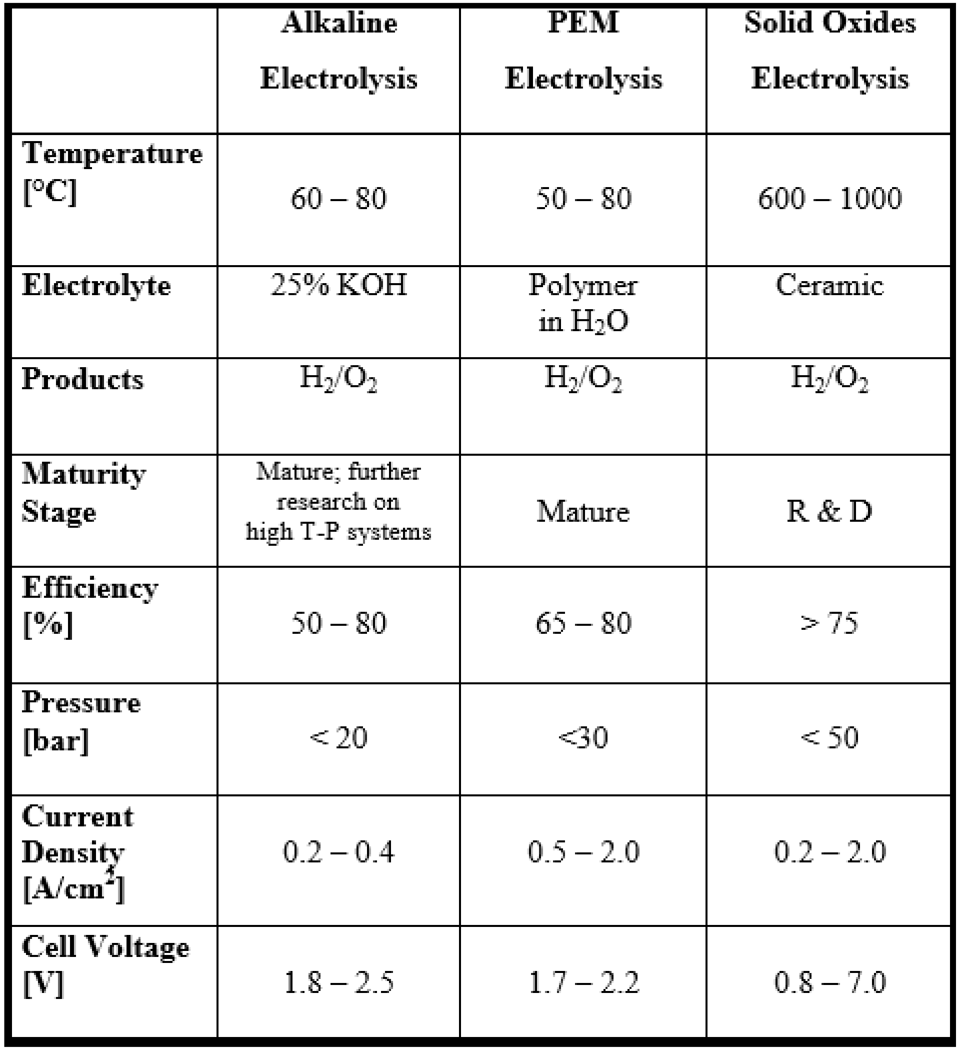


Fig. 5. Typical ranges of polarization curves for different types of state-of-the-art water electrolysis cells. $E_{th,water}$ and $E_{th,steam}$ are the thermoneutral voltages for water and steam electrolysis, respectively. E_{rev} is the reversible potential for water electrolysis at standard state. These curves are representative based on [31,35–37,94–99,107–109,160,187,232,240,241].

Left: doi:10.1016/j.jpowsour.2006.12.081
Right: doi:10.1016/j.rser.2010.07.014

Electrolysis

- Comparison



	Alkaline Electrolysis	PEM Electrolysis	Solid Oxides Electrolysis
Temperature [°C]	60 – 80	50 – 80	600 – 1000
Electrolyte	25% KOH	Polymer in H_2O	Ceramic
Products	H_2/O_2	H_2/O_2	H_2/O_2
Maturity Stage	Mature; further research on high T-P systems	Mature	R & D
Efficiency [%]	50 – 80	65 – 80	> 75
Pressure [bar]	< 20	<30	< 50
Current Density [A/cm²]	0.2 – 0.4	0.5 – 2.0	0.2 – 2.0
Cell Voltage [V]	1.8 – 2.5	1.7 – 2.2	0.8 – 7.0

Cold start up time (min)	15 [32] 20 [65]	<15 [32] 5 [65]	>60 [32]

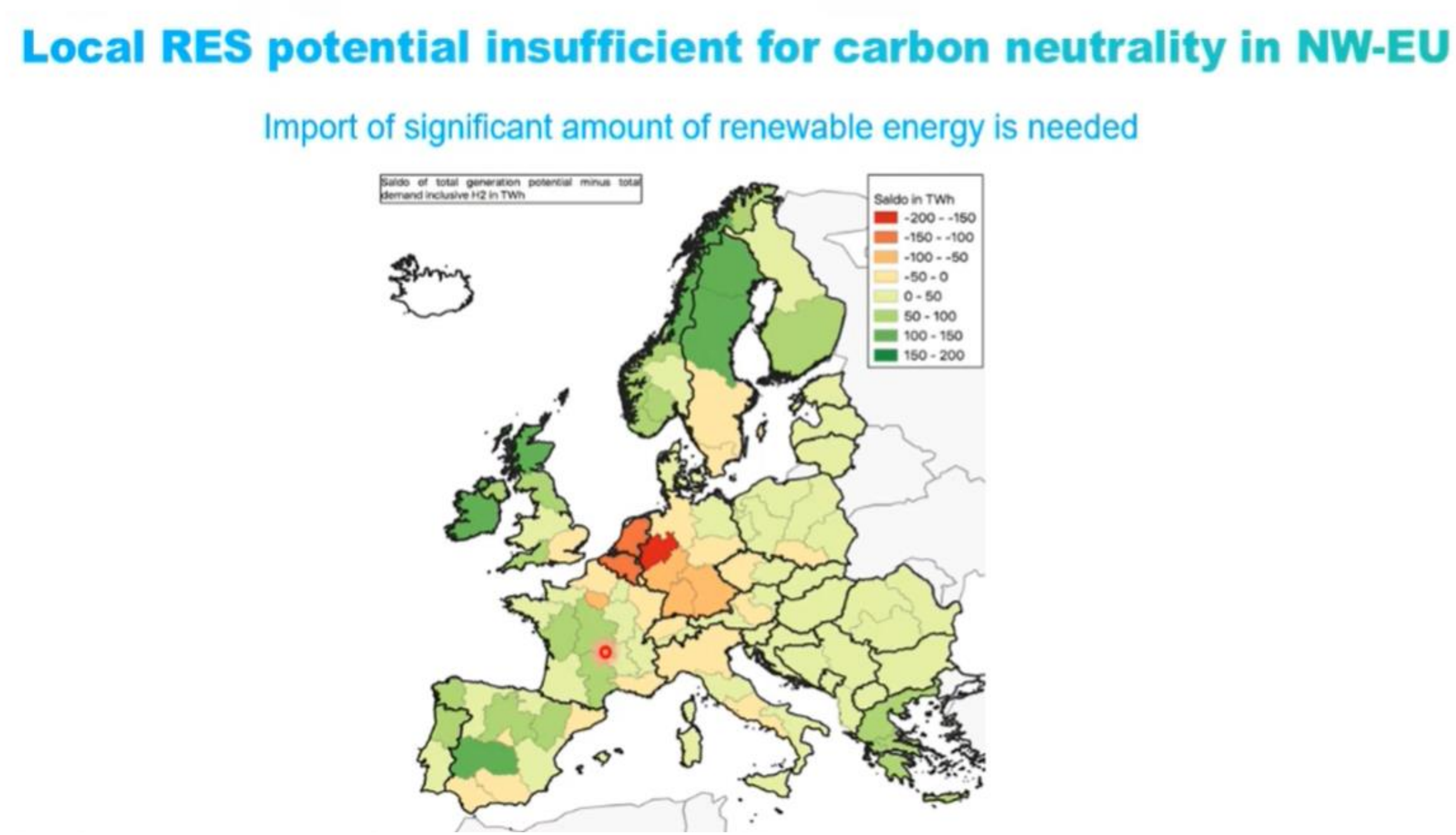
CHEMICAL ENGINEERING

Bruno L. and Franco M., Master's thesis, ULiège-UniGenova, 2017
https://doi.org/10.1016/j.rser.2017.08.004

LIÈGE université

Recent work: H_2 Import Coalition

- If not producing H_2 in Europe, then import it!



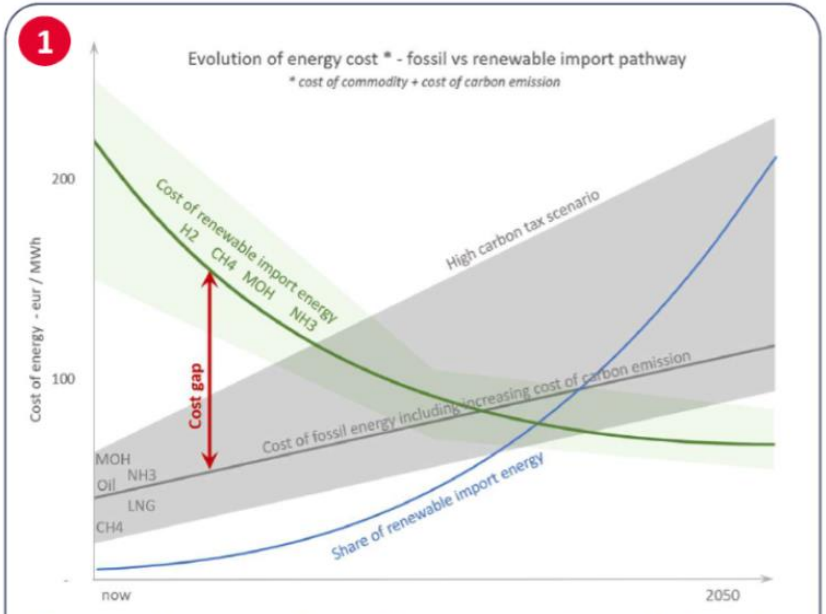
Local RES potential insufficient for carbon neutrality in NW-EU

Import of significant amount of renewable energy is needed

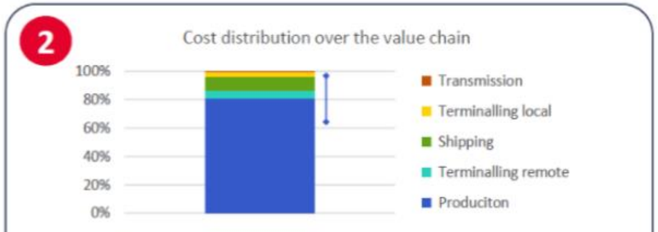
D. Marenne, Engie, Power-to-molecules SRBE Webinar, Nov-Dec 2020

Recent work: H_2 Import Coalition

- If not producing H_2 in Europe, then import it!
- But not as H_2, as storage and transport are more difficult
- Comparison of import areas and energy carriers



The renewable import pathway will become competitive on the longer term thanks to significant cost reduction potential. → Financial incentives are required on the short term in order to support industrial scale up.



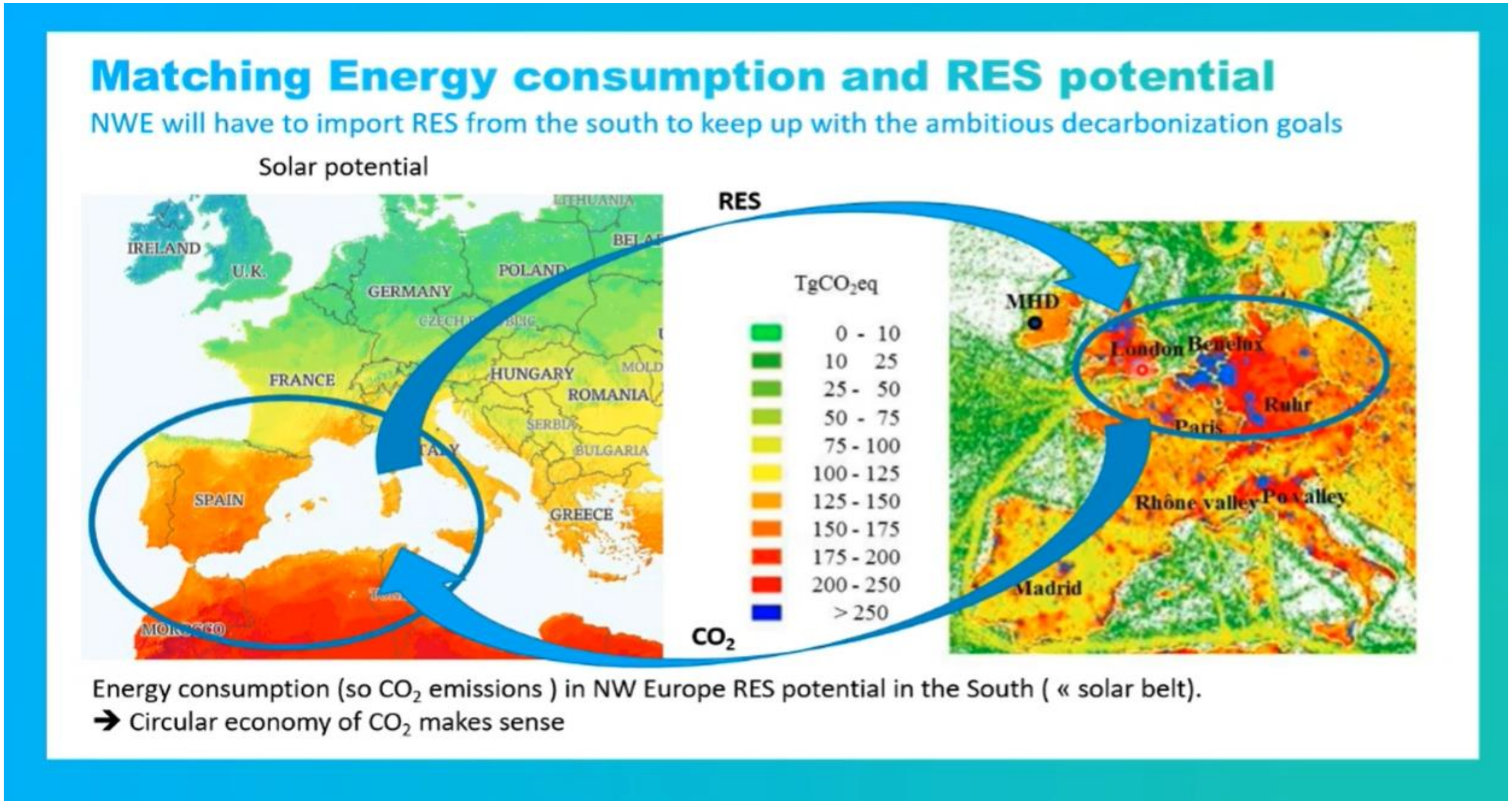
Renewable electricity accounts for the vast majority of the overall molecule cost : 60%-95% depending on the scenario
→ Preference for production locations with low LCOE[1]

No silver bullet: no clear winner scenario. Market demand (Use case scenarios) will strongly influence the outcome.
→ multiple carriers and locations remain feasible

H2 Import Coalition, 2020

Recent work: H_2 Import Coalition

- If not producing H_2 in Europe, then import it!



Matching Energy consumption and RES potential

NWE will have to import RES from the south to keep up with the ambitious decarbonization goals

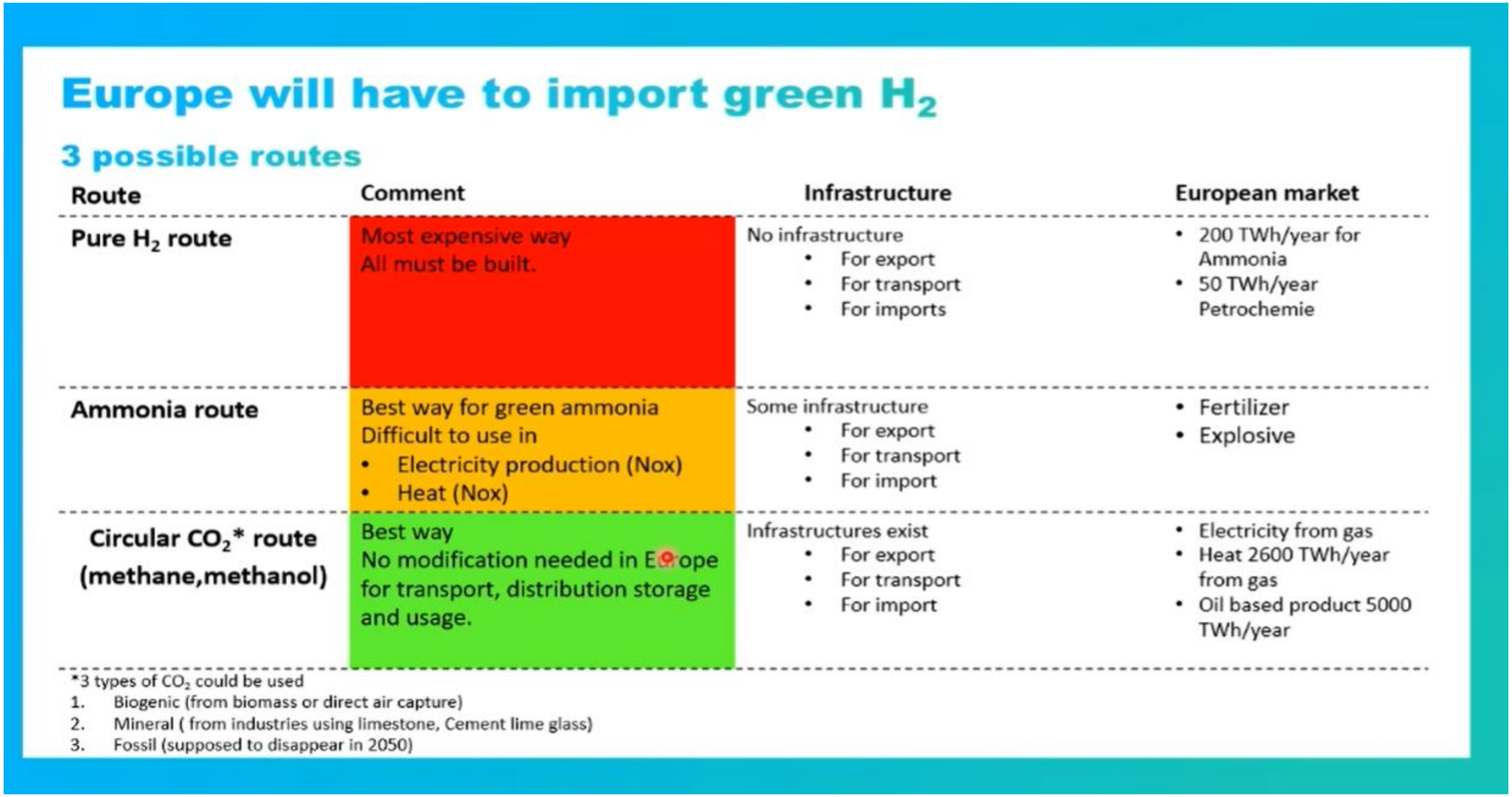
Energy consumption (so CO_2 emissions) in NW Europe RES potential in the South (« solar belt).

➔ Circular economy of CO_2 makes sense

D. Marenne, Engie, Power-to-molecules SRBE Webinar, Nov-Dec 2020

Recent work: H_2 Import Coalition

- If not producing H_2 in Europe, then import it!



Europe will have to import green H_2

3 possible routes

Route	Comment	Infrastructure	European market
Pure H_2 route	Most expensive way All must be built.	No infrastructure • For export • For transport • For imports	• 200 TWh/year for Ammonia • 50 TWh/year Petrochemie
Ammonia route	Best way for green ammonia Difficult to use in • Electricity production (Nox) • Heat (Nox)	Some infrastructure • For export • For transport • For import	• Fertilizer • Explosive
Circular CO_2* route (methane,methanol)	Best way No modification needed in Europe for transport, distribution storage and usage.	Infrastructures exist • For export • For transport • For import	• Electricity from gas • Heat 2600 TWh/year from gas • Oil based product 5000 TWh/year

*3 types of CO_2 could be used

1. Biogenic (from biomass or direct air capture)
2. Mineral (from industries using limestone, Cement lime glass)
3. Fossil (supposed to disappear in 2050)

D. Marenne, Engie, Power-to-molecules SRBE Webinar, Nov-Dec 2020

Be-Hyfe project