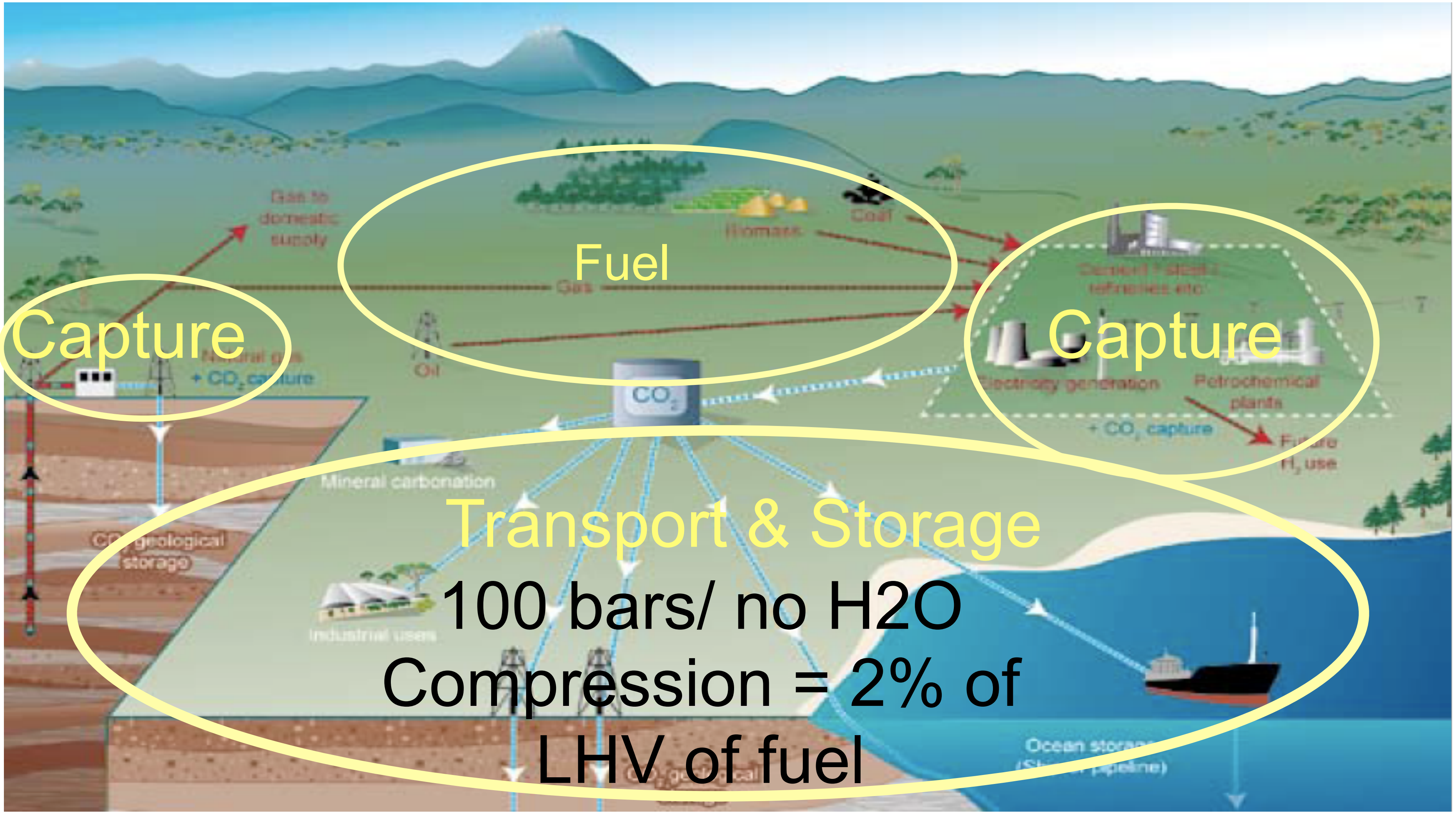
IPESE
INDUSTRIAL PROCESS AND ENERGY SYSTEMS ENGINEERING

CO2 Capture, Sequestration and Re-Use Part II Sequestration or Re-Use

Prof. François Marechal

CO_2 transport and storage (CCS)



(source : IPCC CCS Report)

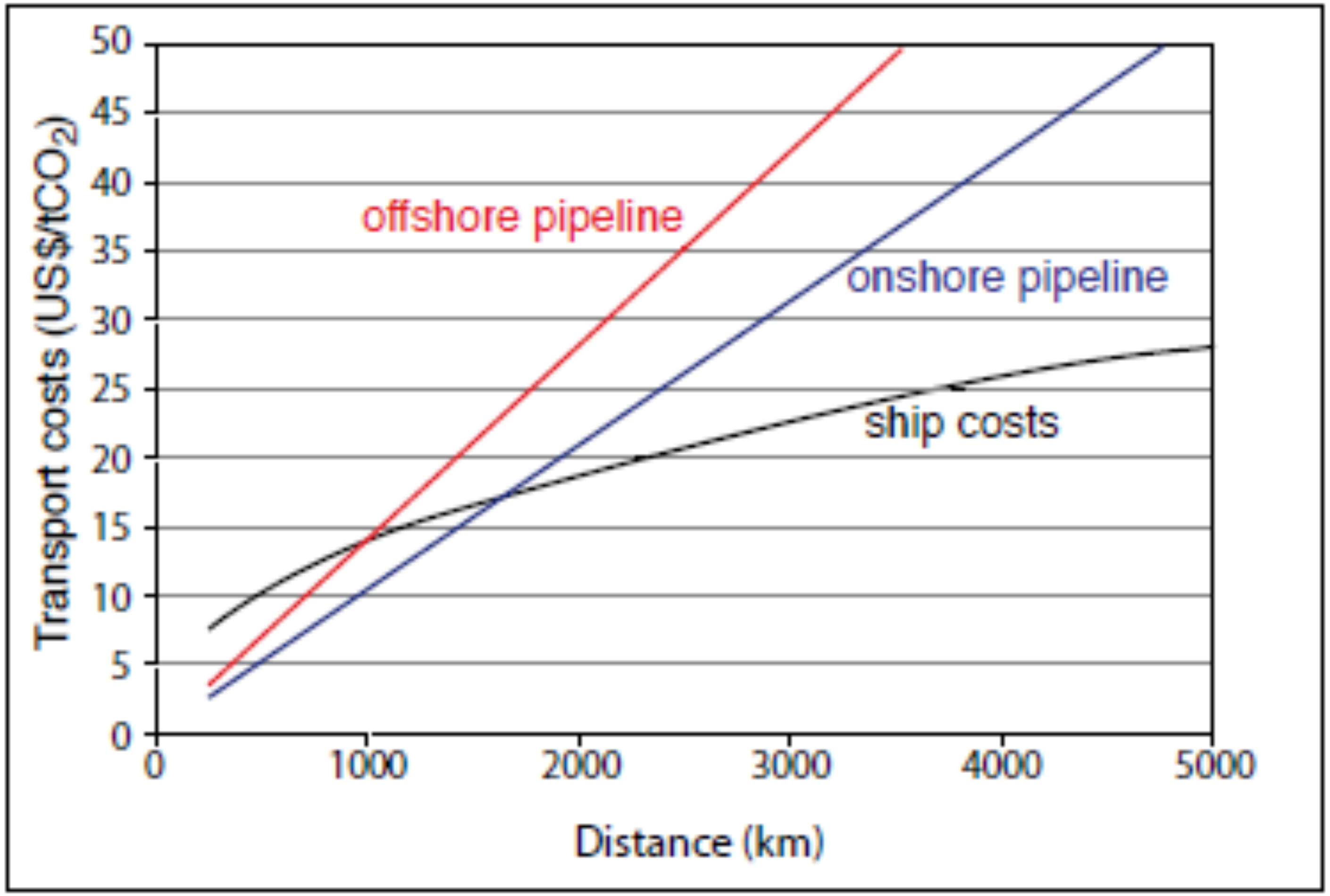
CO_2 transport

CO2 transport methods

- Pipelines
  - <1500km (small distance)
  - CO2 8MPa
  - > 20 Mt CO2/year

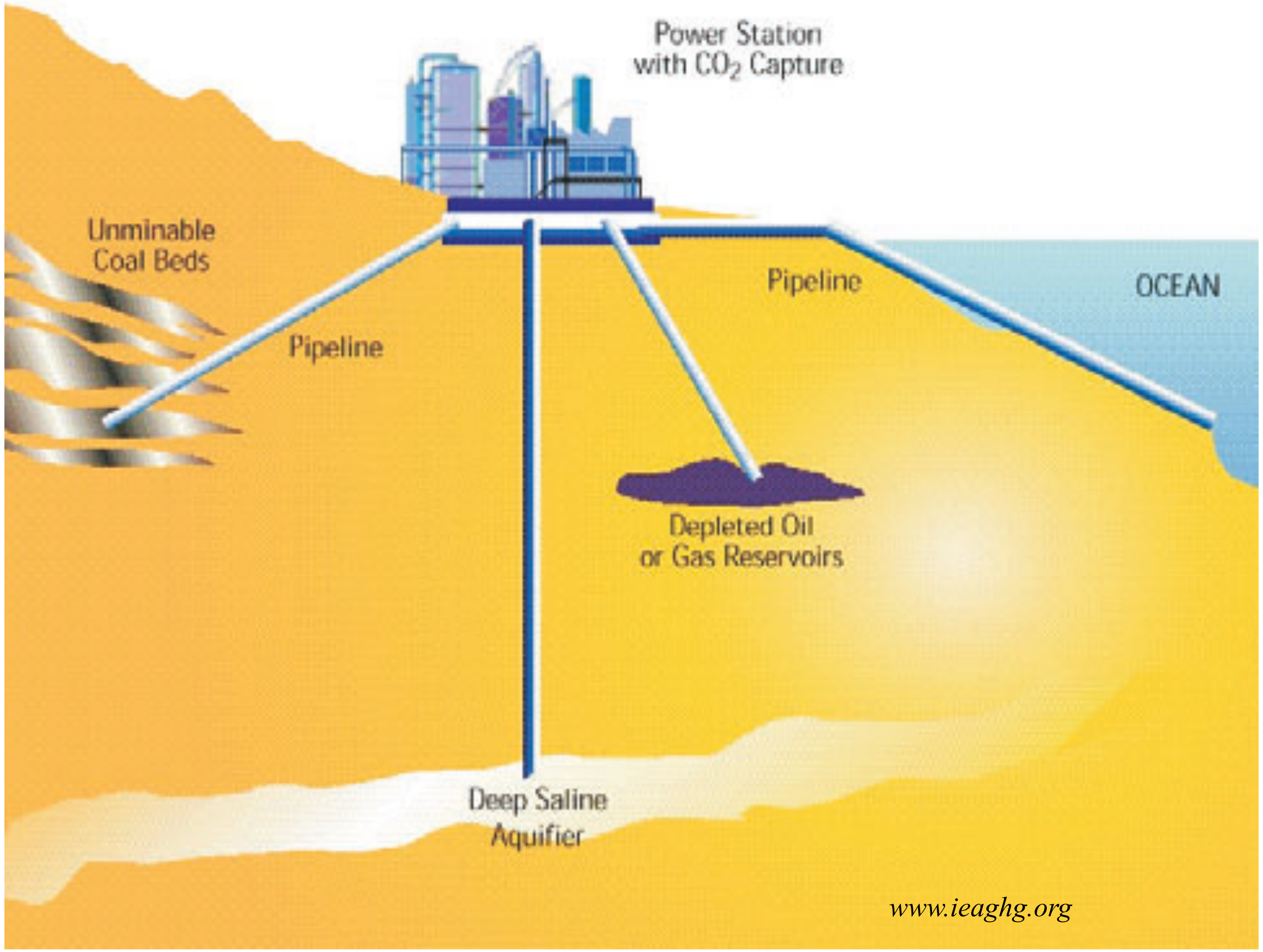
- Ship
  - > 1500 km (large distance)
  - CO2 liq. 0.7MPa
  - ~6 Mt CO2/year

- Road & rail tankers
  - CO2 -20°C, 2MPa
  - Very small scale
  - uneconomical for large-scale CO2 transportation



IPCC2005 CCS report

CO_2 storage



Power Station
with CO_2 Capture
Unminable
Coal Beds
Pipeline
Pipeline
OCEAN
Depleted Oil
or Gas Reservoirs
Deep Saline
Aquifier
www.ieaghg.org

CO_2 storage : Geological storage

Geological storage

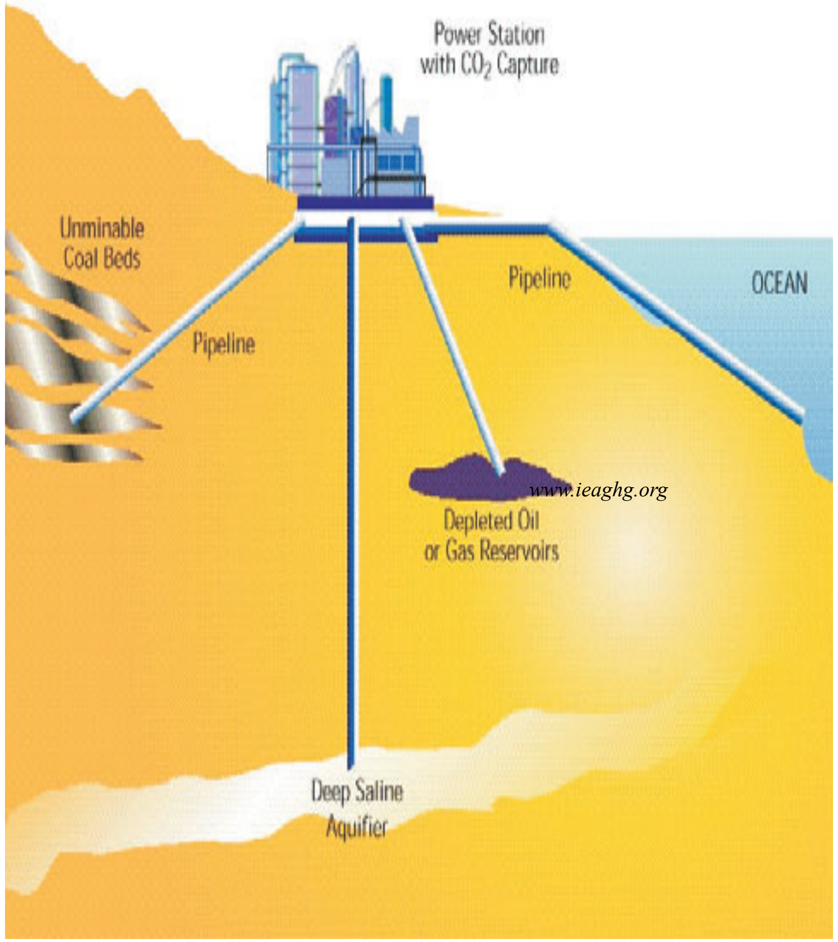
- Enhanced Oil/Gas Recovery (EOR/EGR)
  - CO2 is used to push gas out of gas/oil fields
  - In 2004 only 20% of the CO2 used for EOR is captured CO2 from energy conversion
  - Use of Water => produces toxics and radioactive elements
  - 3.15 t CO2 extracted (as fuel) per ton of CO2 sequestrated !
- Enhanced Coal Bed Methane recovery (ECBM)
  - CO2 substitutes the absorbed CH4 in deep coal mines and
  - is trapped into the pore matrix of the coal due to
  - the higher affinity of CO2 with coal than CH4
  - Twice as much CO2 as CH4 can be absorbed, so the balance is positive even if the CO2 released by CH4 combustion is accounted for

CO_2 storage

Geological storage

- Deep saline formations (storage in aquifers)
  - Dissolution in saline waters (not suitable for potable water)
  - CO2 chemically trapped by chemical reaction producing carbonates ($MeCO_3$)

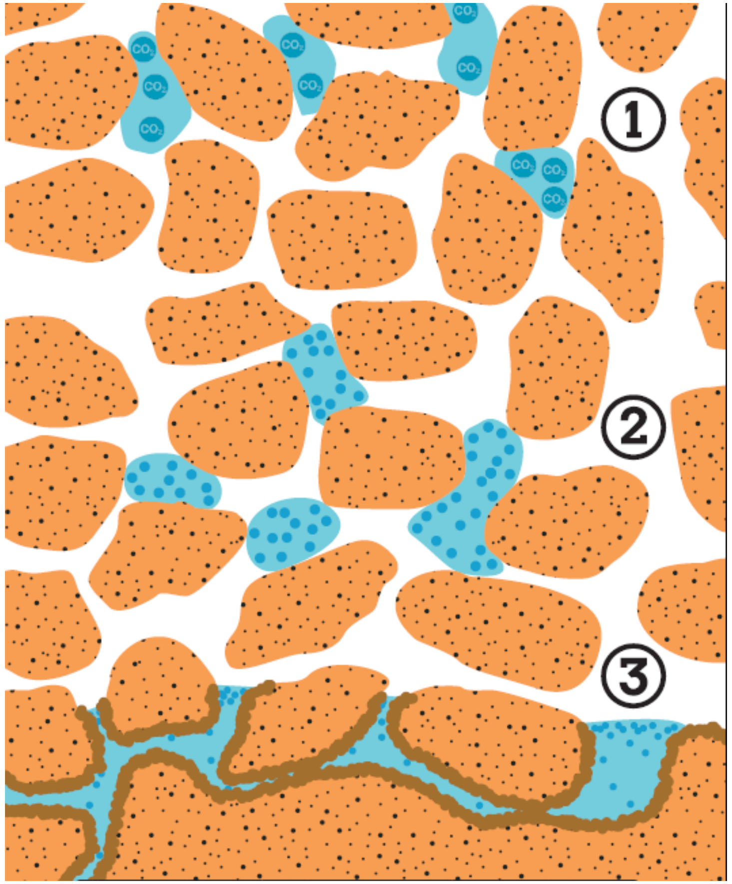
- Storage in mines & chemical storage
  - CO2 reaction with naturally occurring minerals (magnesium silicate)to produce carbonates that could be stored permanently



CO_2 storage

Trapping methods

- Residual trapping
  - Injected CO2 is trapped in the tiny pores of the rocks
- Dissolution trapping
  - Part of the CO2 dissolves into the surrounding water
- Mineral trapping
  - Heavy CO2-rich water sinks to the reservoir's bottom where over time it may react to form minerals (limestone, sandstone)



www.zeroemissionsplatform.eu

CO_2 storage capacity

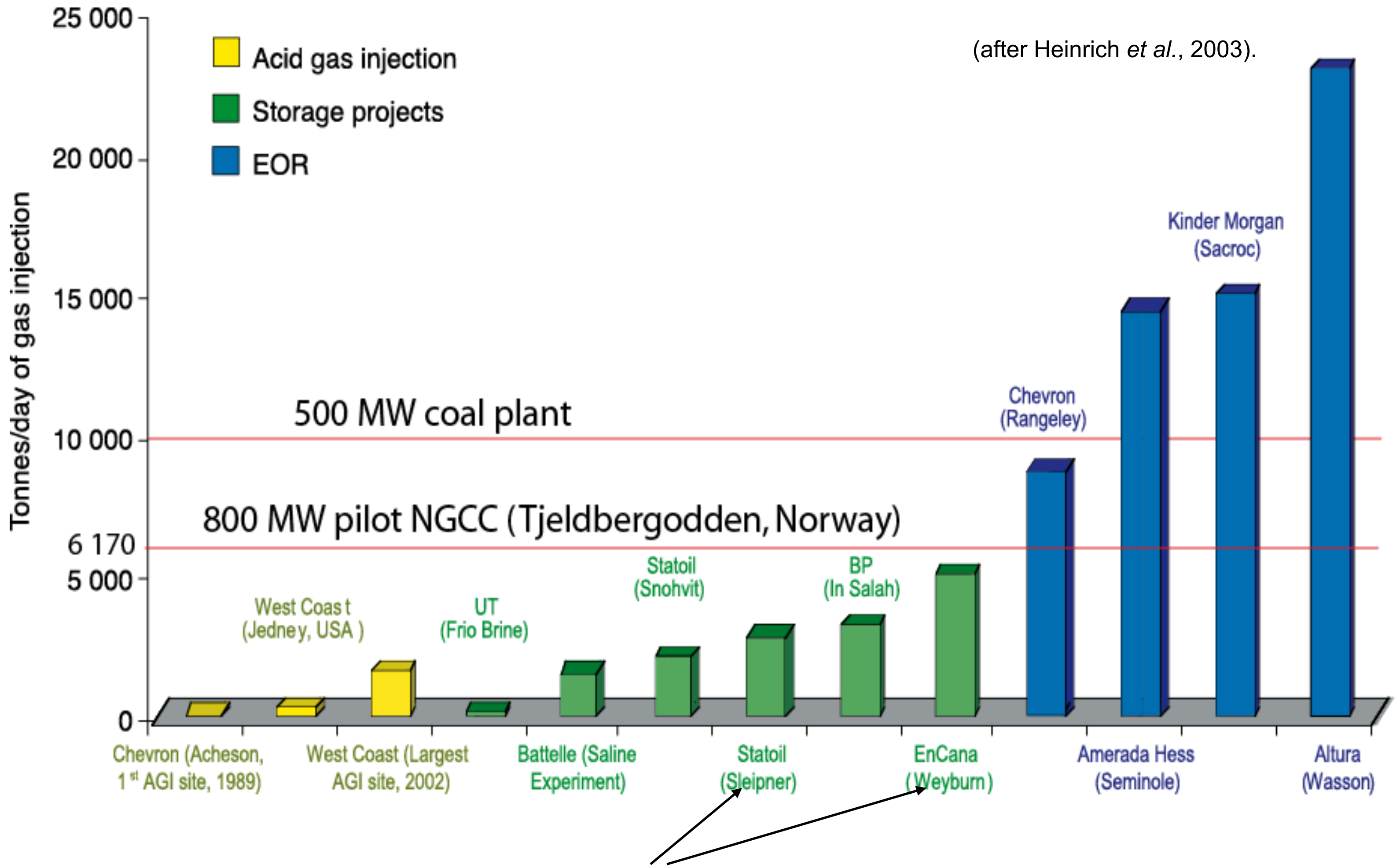
Geological storage capacity

Option	Lower estimate $GtCO_2$	Upper estimate $GtCO_2$
Oil/Gas fields	675	900
Unminable coal beds	3-15	200
Deep saline formation	1000	10000

IPCC2005 CCS report

- Economic potential for CCS: 200-2000 GtCO2
- Largely sufficient geological storage capacity
- Storage cost depends on:
  - Depth & permeability of storage formation
  - Number of wells needed for injection
  - Type of reservoir
  - Onshore/offshore
  - 0.5-8 \$/tCO2 + 0.1-0.3 \$/tCO2 monitoring
  - Including EOR 10-16\$/tCO2 net profit (depends on oil/gas prices)

CCS: gas injection projects



3 injection sites (1-2 Mt CO_2/yr) are running since several years :

Norway (1996), Canada (2000), Algeria (2004)

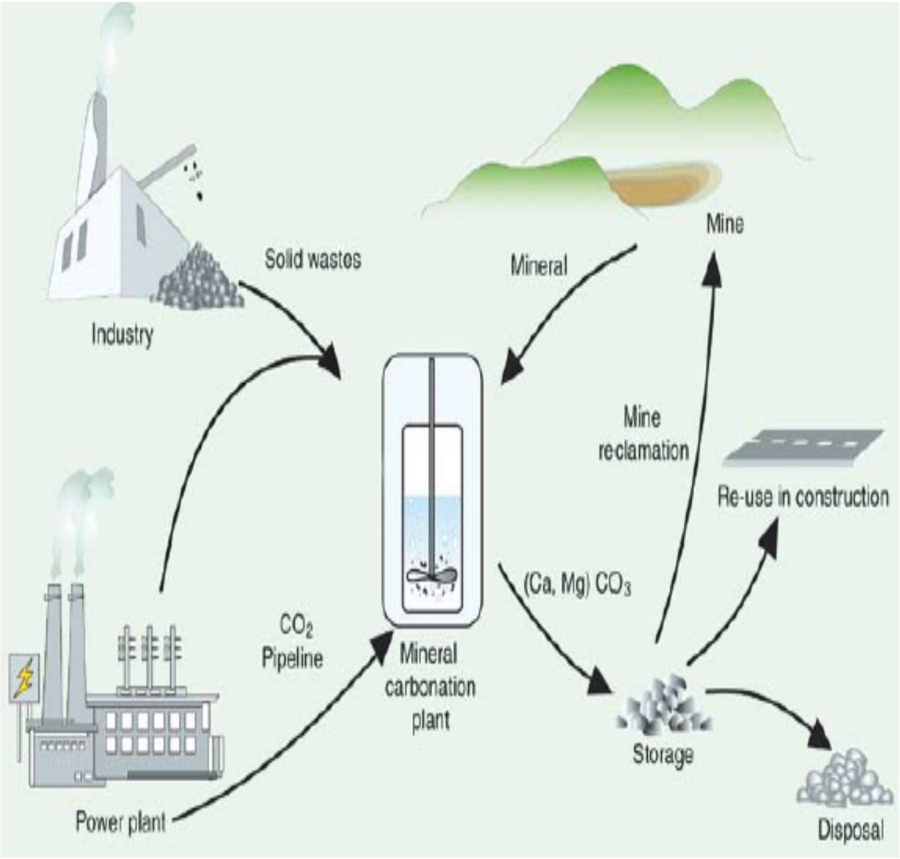
CO_2 storage by carbonation

Mineral Carbonation

- CO2 conversion to solid inorganic carbonates by chemical reaction

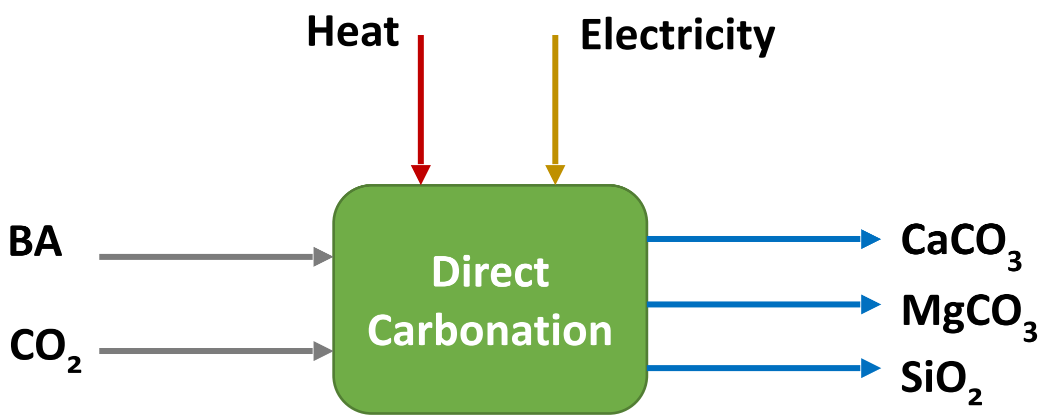
$$1t/CO_2 + [2-3t] \quad MO \rightarrow [3-4t] \quad MCO_3 + heat$$

- MO= Metal oxide (MgO, CaO) or Mg2SiO4, Mg3Si2O5(OH)4
- Magnesium carbonate (MgCO3) or calcium carbonate (CaCO3 limestone)
- =accelerated or assisted natural "weathering"
- Available silicate rocks are larger than needed to fix all fossil-derived CO2, however limited to technically exploitable reserves
- Heat ≈ 60 kJ/mol CO2 (to compare with 400 kJ/mol CO2 for combustion)
- CCS system with carbonation 60-180% more energy input per kWh than reference plant without capture
- Cost: 50-100$/tCO2 mineralized
- Considerable environmental
- impact mining & disposal



IPCC2005 CCS report

Wet Direct Carbonation Balance



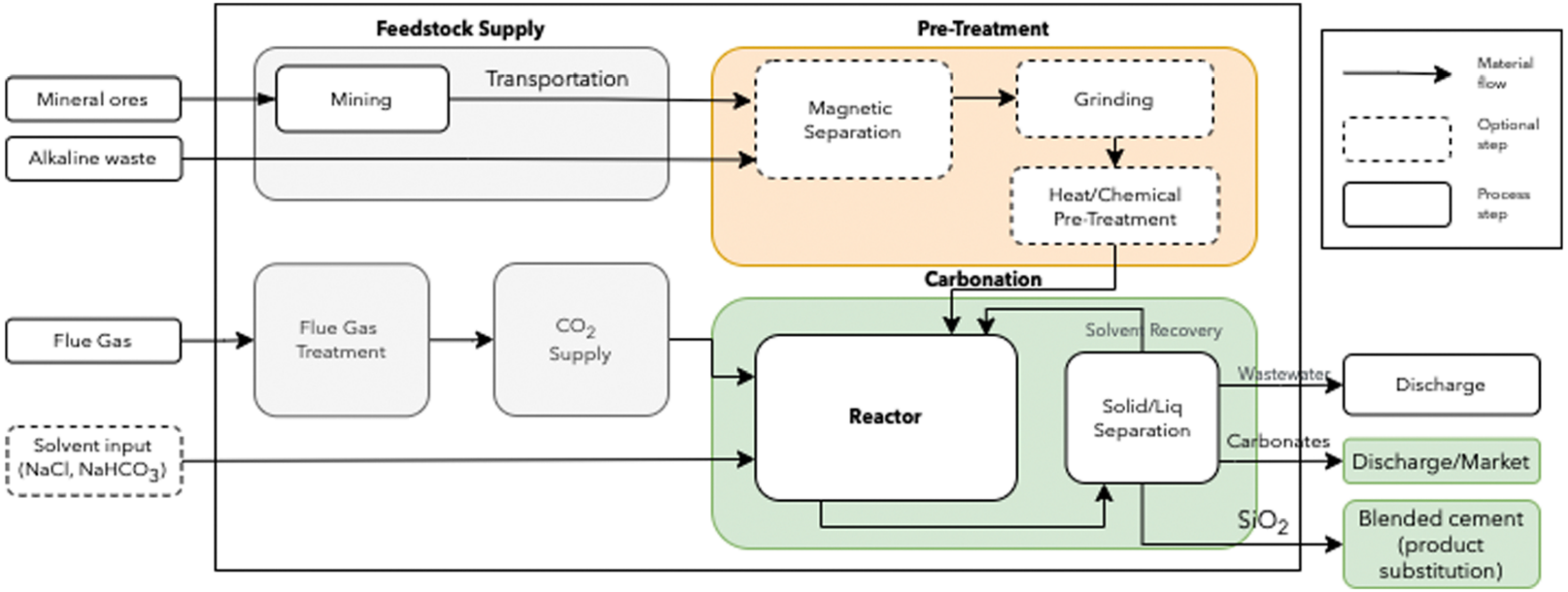
Carbonation Reactor	Inlet	Outlet	Unit
SiO2	10.5	11.9	t/h
MgSiO4	1.17	1.13	t/h
CaSiO3	5.2	2.6	t/h
∑ Feedstocks (BA)	16.9	15.6	t/h
CO_2	1.00	0	t/h
$CaCO_3$	0	2.22	t/h
$MgCO_3$	0	0.05	t/h
Heat pre-treatment (650°C)	161		kWh/tCO_2
Heat reaction (80 -150°C)	106		kWh/tCO_2
Electricity [1]	685		kWh/tCO_2

The Mass balance reference is 1t/h of stored CO2

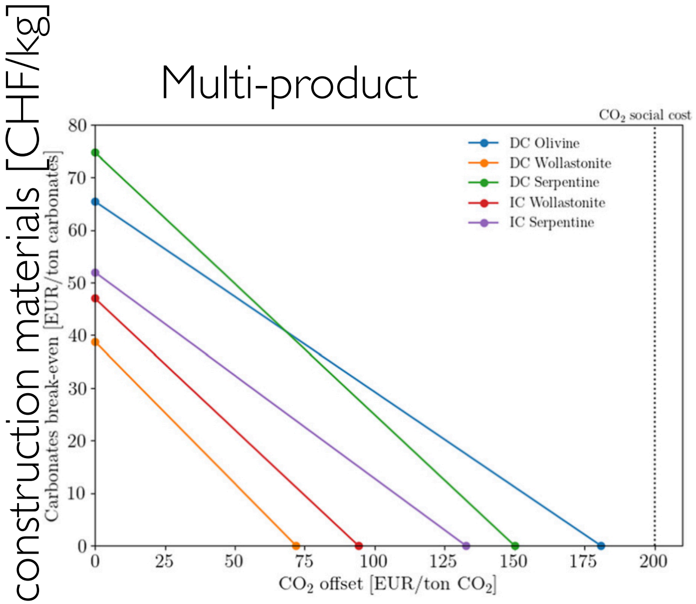
- **Incineration Bottom Ash (BA) feedstock**
  - SiO_2: 62 wt.%
  - $MgSiO_4$: 7 wt.%
  - $CaSiO_3$: 31 wt. %
- **Feedstock pre-treatment [1]**
  - Grinding, crushing, transport and magnetic separation
  - Heat treatment/Activation
- **CO2 supply [1]**
  - Separation and compression

References:
[1]: Ostavari, H. et al. Rock 'n' use of CO2: carbon footprint of carbon capture and utilization by mineralization. Sustainable Energy fuels, 2020, 4, 4482

Carbon mineralisation

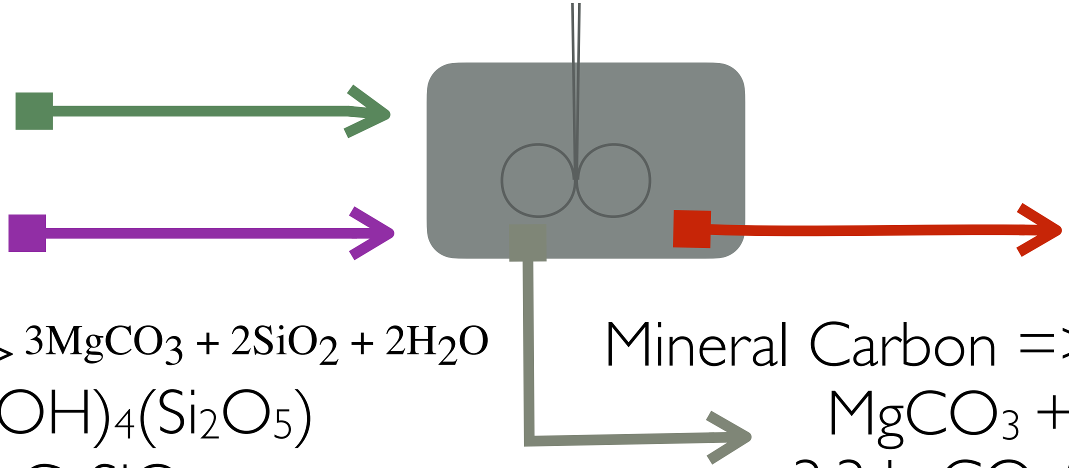


Multi-product



CO2 [CHF/kg]

CO_2



$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \Rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$

Serpentine $Mg_3(OH)_4(Si_2O_5)$

Wolastonite $CaSiO_3$

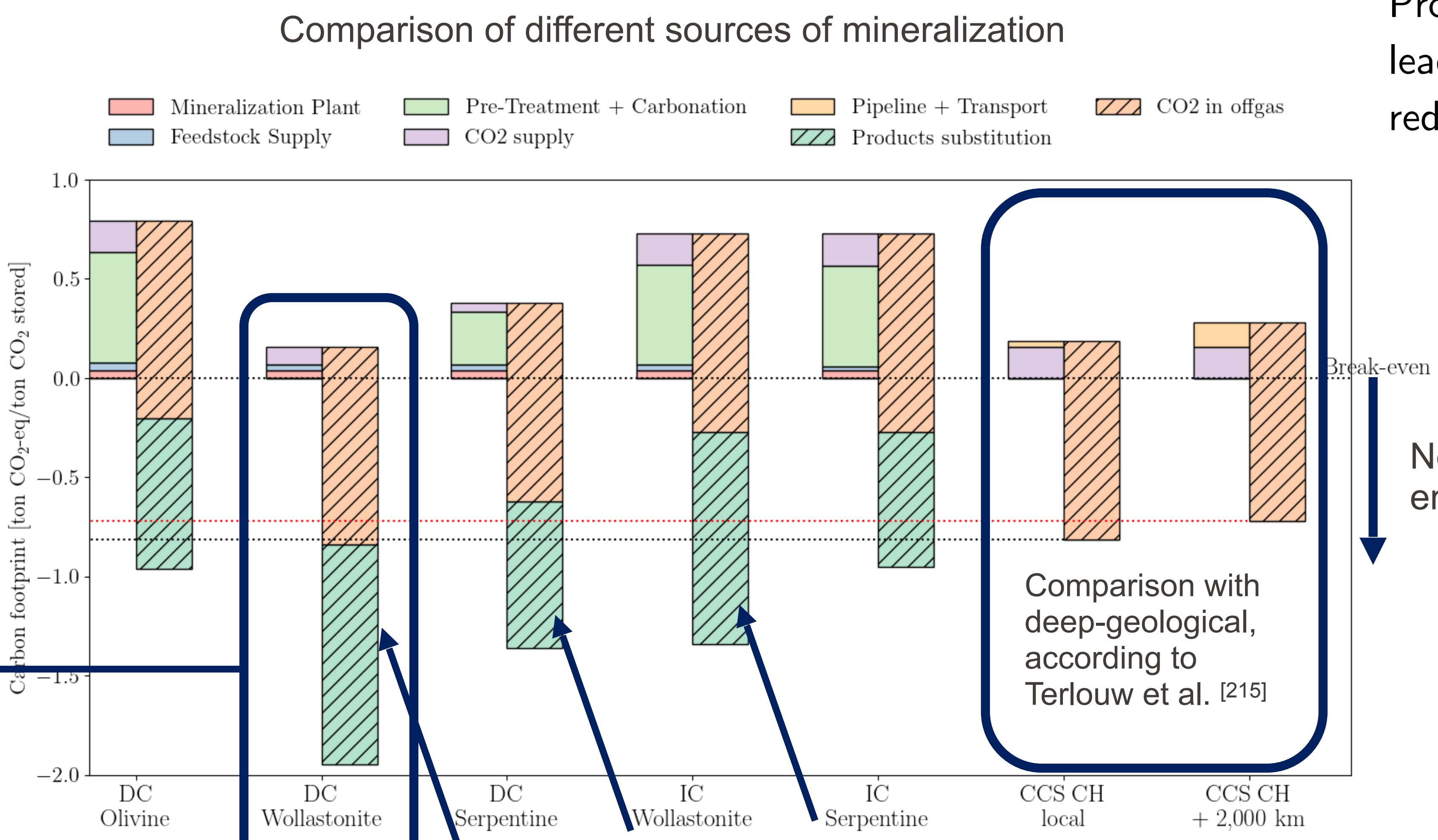
Mineral Carbon => construction

$MgCO_3 + SiO_2$

-3.3 $kgCO_2$/day/cap

Results: carbon footprint in the waste sector

Process integration leads to 35% cost reduction



Net-negative emissions

Wollastonite outperforms due to a simpler process

Net-negative emissions are possible, but are mostly dependent on the products **substitution credit**

CO2 can be used as a product

Table 7.2 Industrial applications of CO_2 (only products or applications at the Mtonne-scale): yearly market, amount of CO_2 used, its source, and product lifetime (Aresta and Tommasi, 1997; Hallman and Steinberg, 1999; Pelc et al., 2005). The figures in the table are associated with a large uncertainty.

Chemical product class or application	Yearly market ($Mt\ yr^{-1}$)	Amount of CO_2 used per Mt product ($MtCO_2$)	Source of CO_2	Lifetime[b]
Urea	90	65	Industrial	Six months
Methanol (additive to CO)	24	<8	Industrial	Six months
Inorganic carbonates	8	3	Industrial, Natural[a]	Decades to centuries
Organic carbonates	2.6	0.2	Industrial, Natural[a]	Decades to centuries
Polyurethanes	10	<10	Industrial, Natural[a]	Decades to centuries
Technological	10	10	Industrial, Natural[a]	Days to years
Food	8	8	Industrial, Natural[a]	Months to years

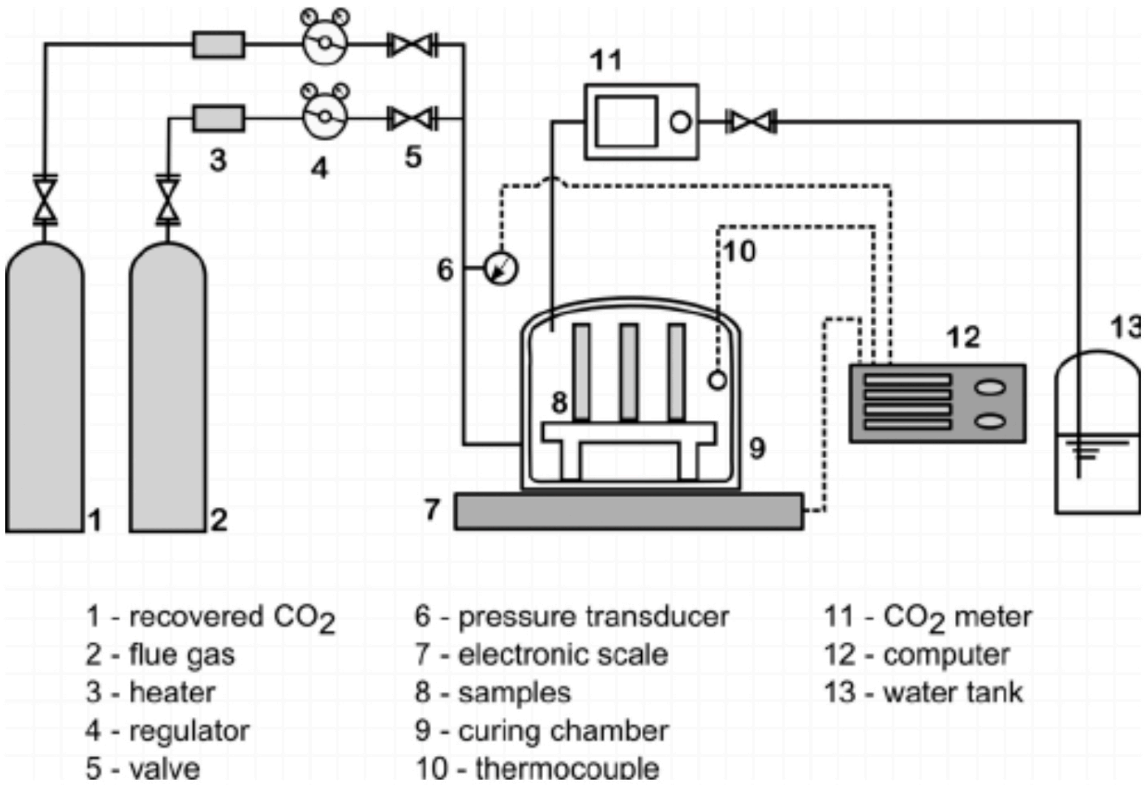
[a] Natural sources include both geological wells and fermentation.

[b] The fraction of used CO_2 that is still stored after the indicated period of time drops to zero.

It is important that the CO2 used as carbon is not going to release fossil C in the atmosphere at an other time e.g. short term plastic usage

IPCC Special Report on Carbon dioxide Capture and Storage
Chapter 7 : Mineral carbonation and industrial uses of carbon dioxide

Cement curing



Carbonation curing schematic for using either pressurized recovered CO 2 or pressurized flue gas.

Per unit CO2 sequestrated		CO_2 emitted	CO_2 avoided
Carbonation	Cu-OPC	1.4	3.35
	Cu-WOA	1.23	3.35
	Cu-ISS	2	3.35
	Cu-WCA	1.45	3.35
	Ex-WOA	0.56	3.35

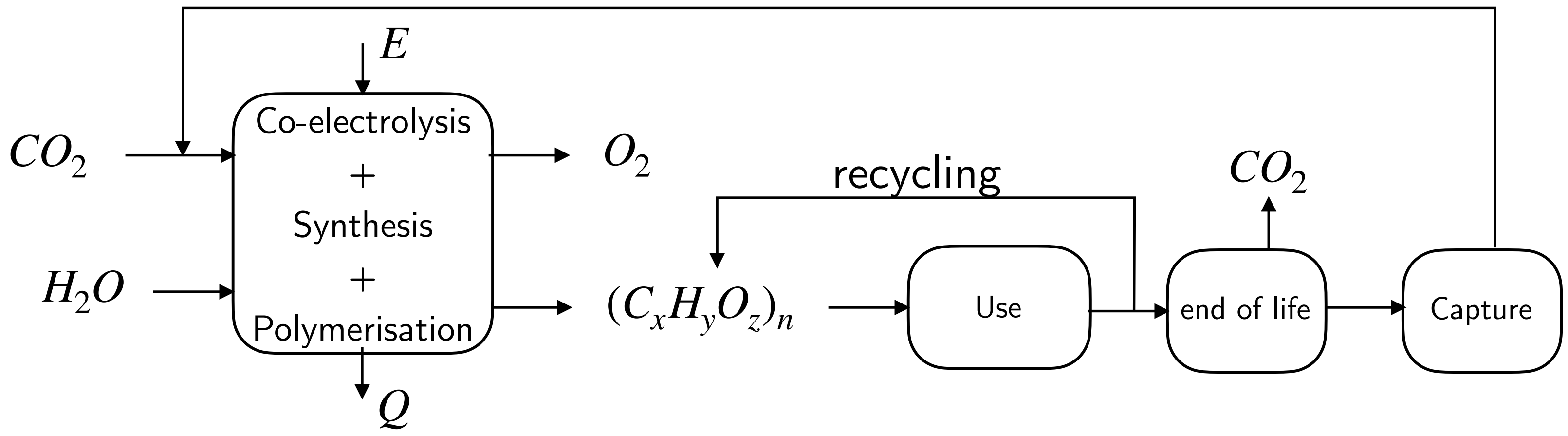
use as construction materials (substitution)

Can. J. Civ. Eng. Vol. 37, 2010

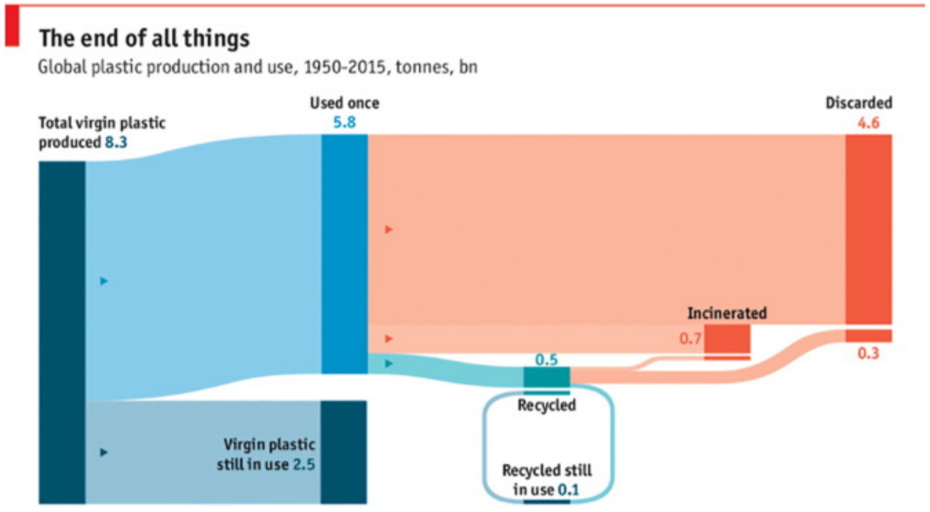
EPFL

Plastics

- 55 kg/cap/year produced from the waste of fuel production
  - 75 % single use (2.7 kg CO2/kg polymer = 111 kg/cap/year)
  - 25 % long term use (2.0 kg CO2/kg polymer = 27.5 kg/cap/year **sequestrated**)



Plastic world production: 55 kg plastics/capita/year

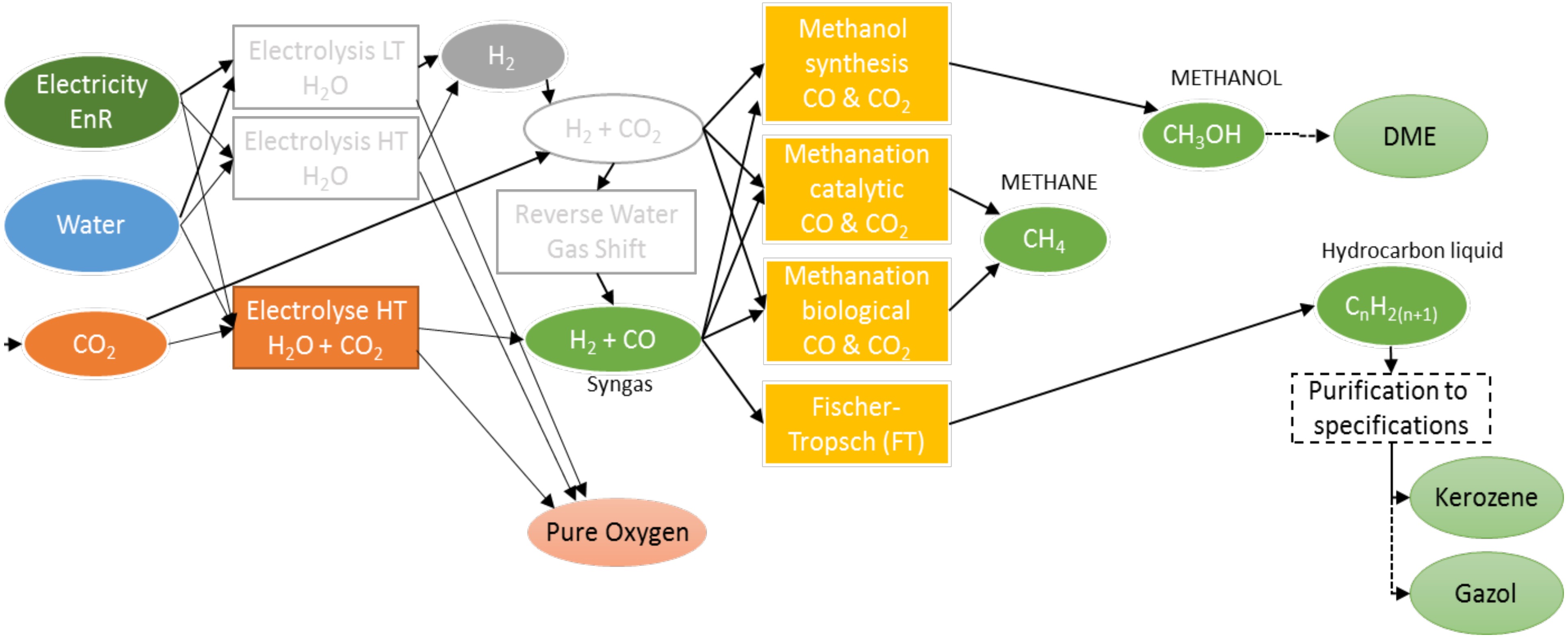


Source: "Production, use, and fate of all plastics ever made" by R. Geyer et al., *Science Advances*

CO_2 utilization : E-Fuels

Conversion of captured CO_2: as a source of Carbon

Power-to-chemicals/stored energy



Electricity has to be from renewable energy resources

CO2 reuse : Power2Gas concepts

Electrolysis : H_2O + E => H_2 +1/2 O_2 (e.g.Proton exchange membrane systems eff ≈ 60%)

+ Methanation (Sabatier Reaction)

- Typical Temperature : 250°C-400°C
- Catalyst : Ni
- Exothermic

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + energy \qquad \Delta H = -165.0kJ/mol$$

- Biological catalysis(1)
  - Typical Temperature : 40-70°C
  - Catalyst : thermophilic methanogen Methanothermobacter thermautotrophicus
  - www.electrochea.com
- Co-Electrolysis (SOEC) + Methanation or Fisher-Tropsh
  - Typical Temperature : 800°C

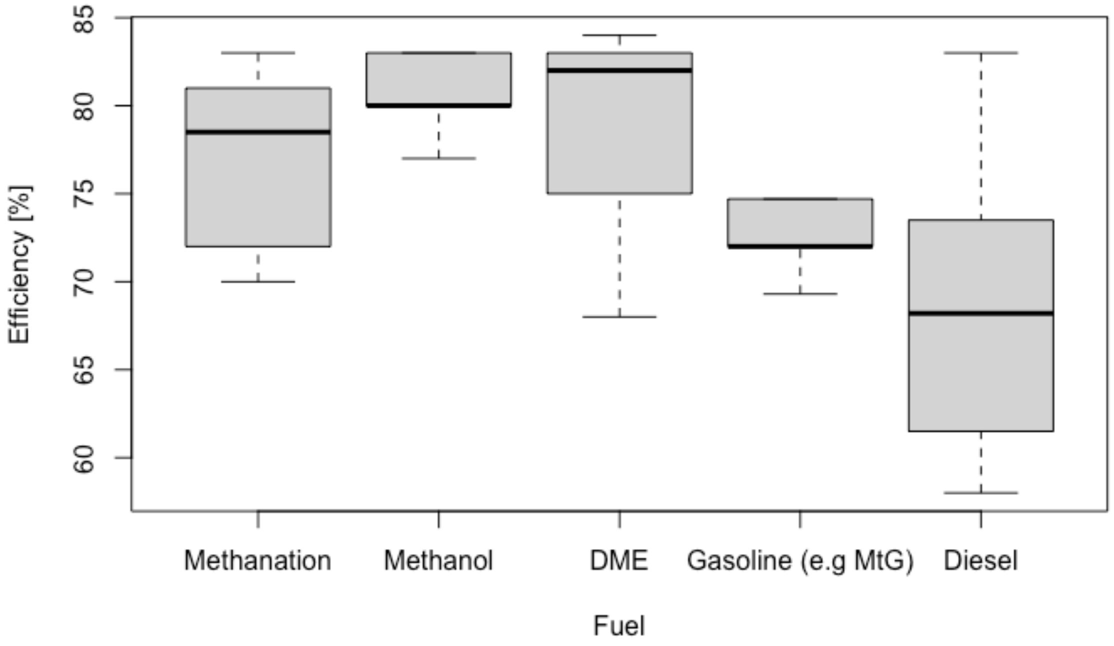
$$CO_2 + 2H_2O + energy \rightarrow CH_4 + 2O_2$$

(1) Matthew R. Martin, et al. “A Single-Culture Bioprocess of *Methanothermobacter thermautotrophicus* to Upgrade Digester Biogas by CO**2**-to-CH**4** Conversion with H**2**,” *Archaea*, vol. 2013, Article ID 157529, 11 pages, 2013.

(2) Diethelm, S., herle, J. V., Montinaro, D. and Bucheli, O. (2013), Electrolysis and Co-Electrolysis Performance of SOE Short Stacks. Fuel Cells, 13: 631–637. doi: 10.1002/fuce.201200178

Fuels production : Power2X

Efficiency



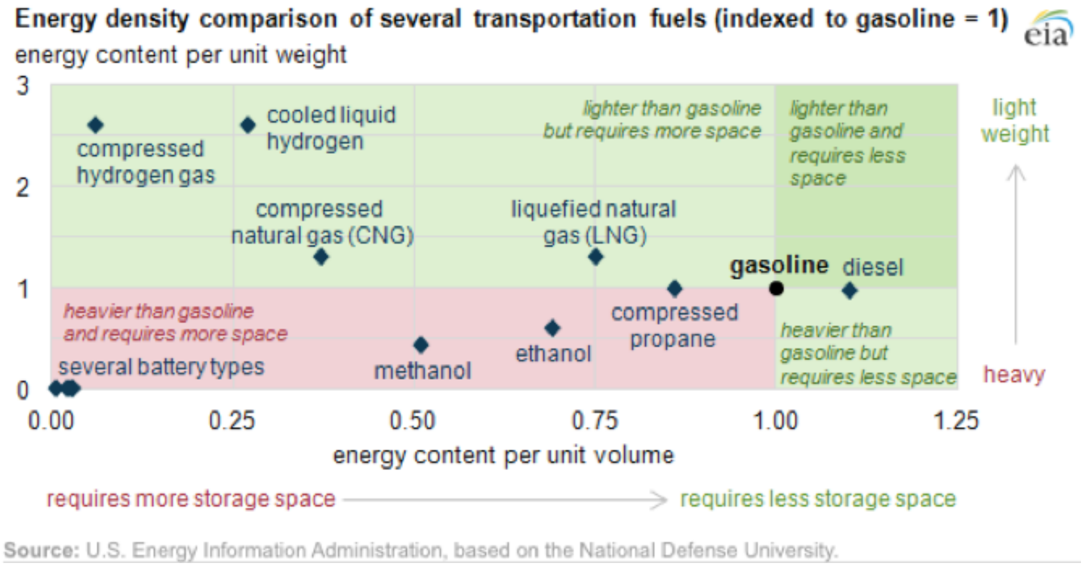
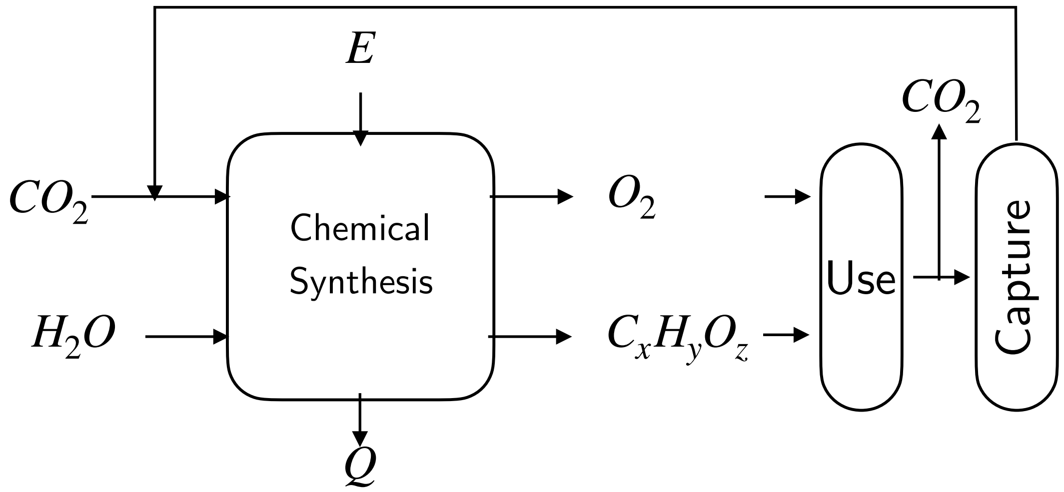


Figure 2.1: Energy density of various fuels (source: eia [39])

Life cycle efficiency

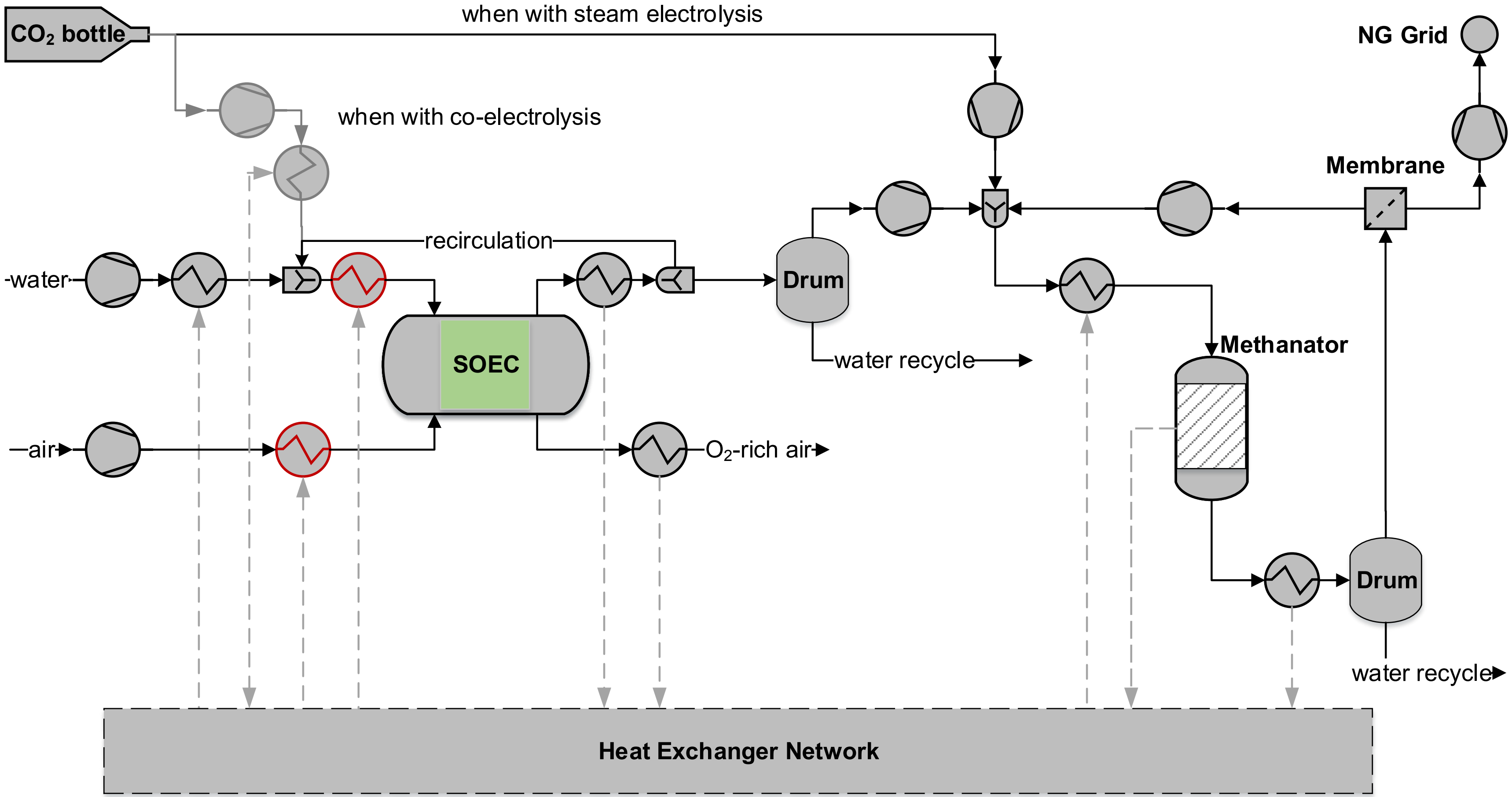
Per unit CO2 captured		CO_2 emitted	CO_2 avoided	KPI_{CO2}
Syn. Fuels	Methane	0.31	1.39	**-1.08**
	Methanol	0.23	1.49	**-1.26**
	DME	0.22	1.51	**-1.29**
	Diesel	0.22	1.20	**-1**
	Gasoline	0.20	1.20	**-0.96**

Based on El. Swiss mix



Electrolysis and Co-Electrolysis

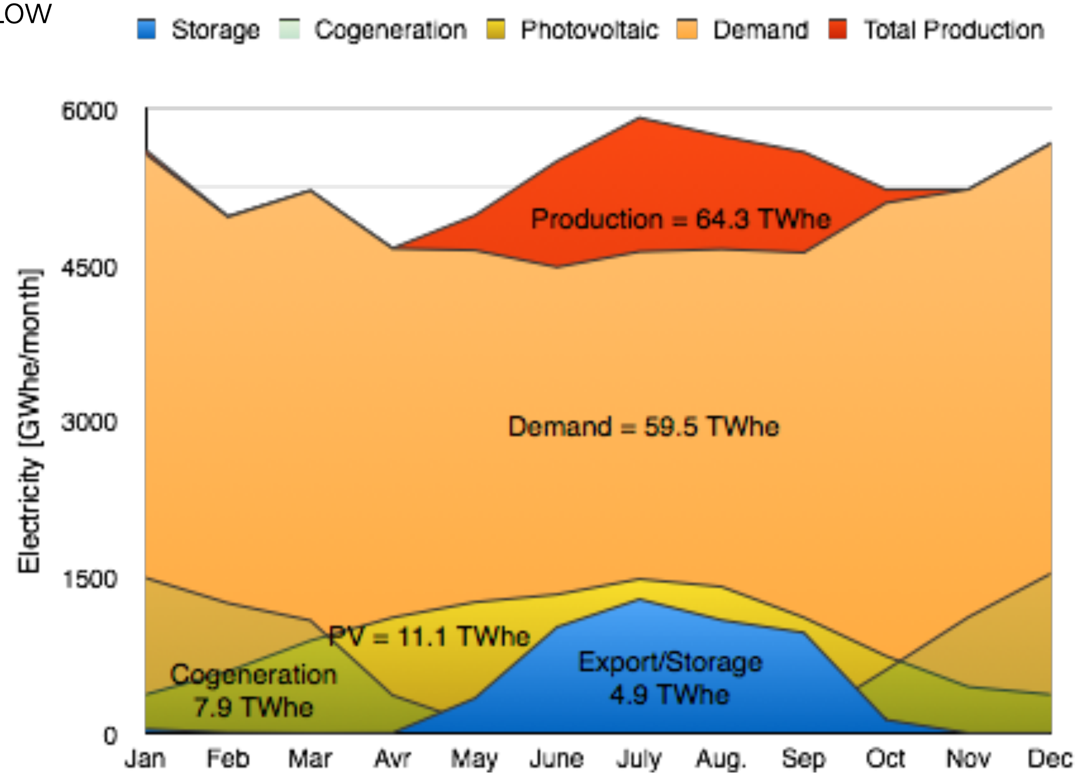
Efficiency reaches 80% of HHV



Electricity storage

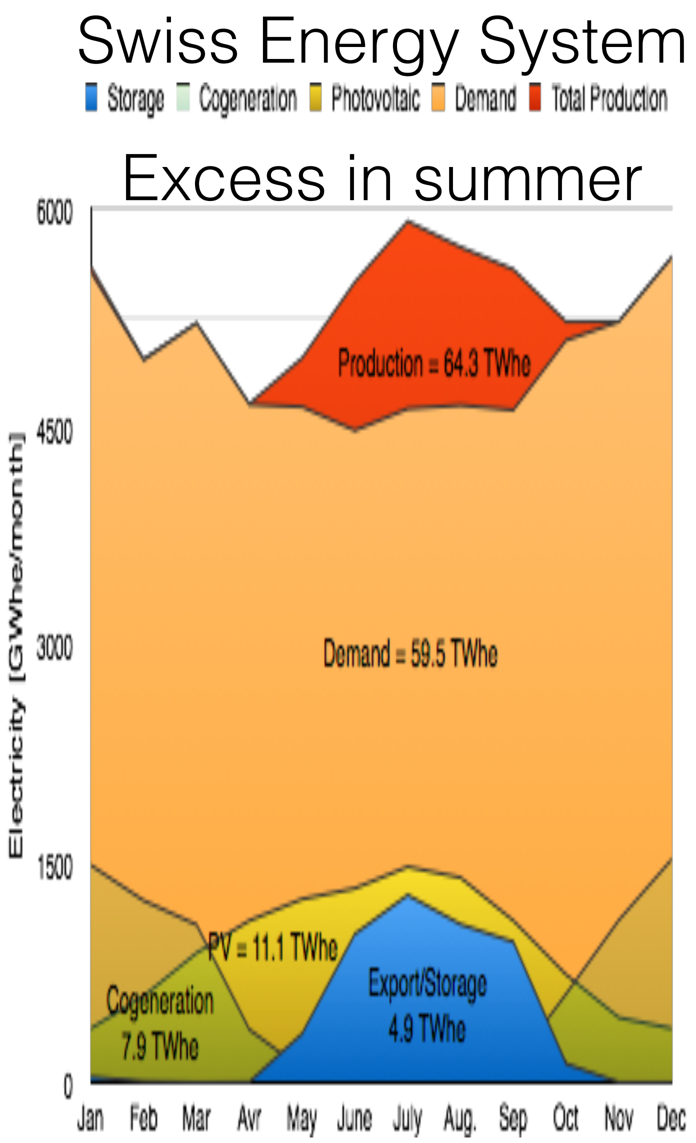
Who is going to use the extra amount in the Summer ?

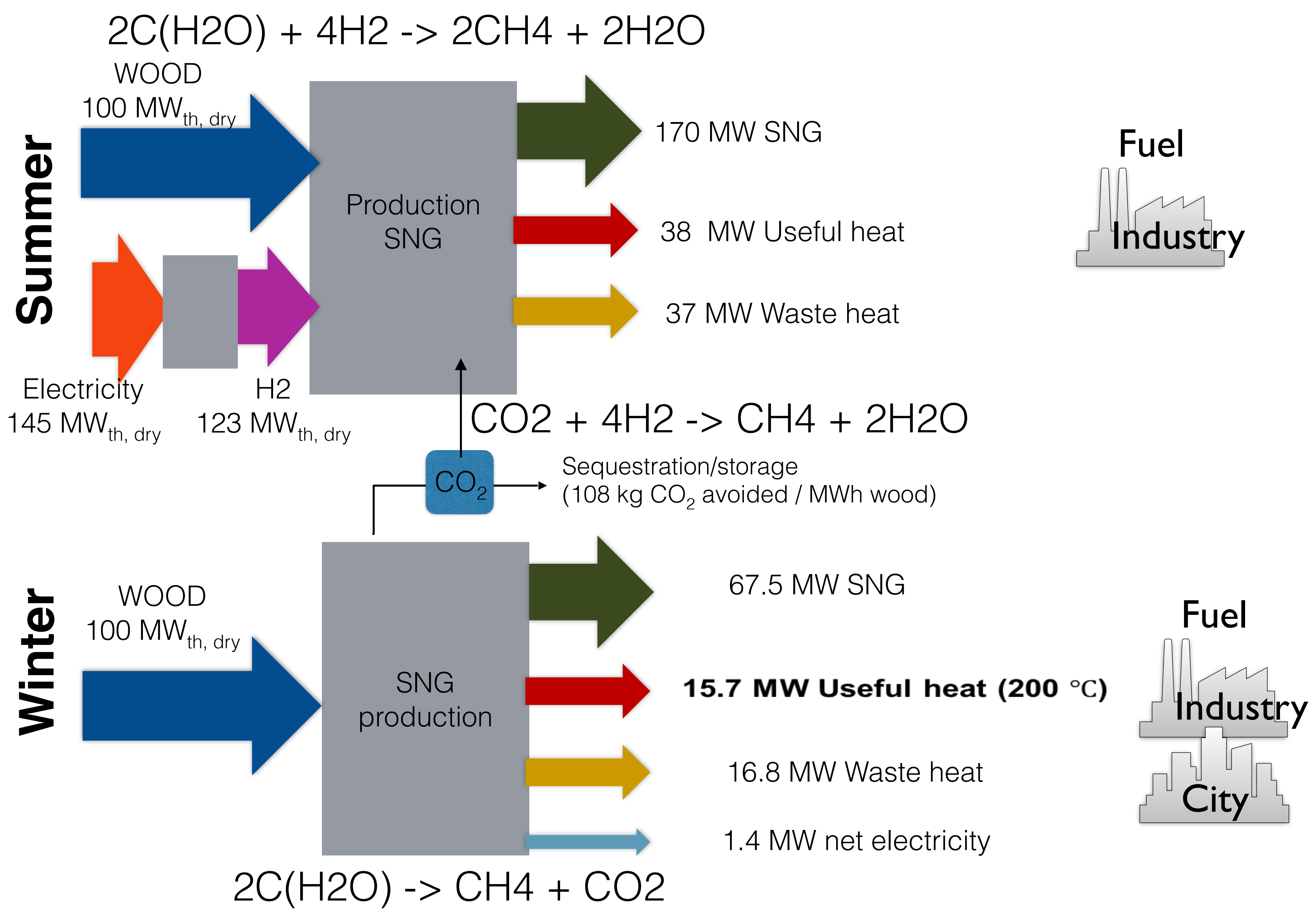
Scenario 2050 : OFEN / Low



http://www.energyscope.ch

Combined heat, fuel and storage from biomass





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