Electrolysis and H_2

Current uses of H_2

H_2 current uses

- Refineries (40%): hydrodesulphurisation, - cracking
- Ammonia production (fertiliser) (40%)
- Methanol and other chemicals (10%)
- Light industries (10%): where reducing atmosphere is needed
  - Metal treatment
  - Semiconductor industry
  - Glass making
  - Food (fats hydrogenation)
- 8 EJ (1.5% of world energy)

Annual H_2 production

- 631 10^9 m^3
  - 49% from natural gas
  - 29% from oil
  - 18% from coal

  96% from fossil sources

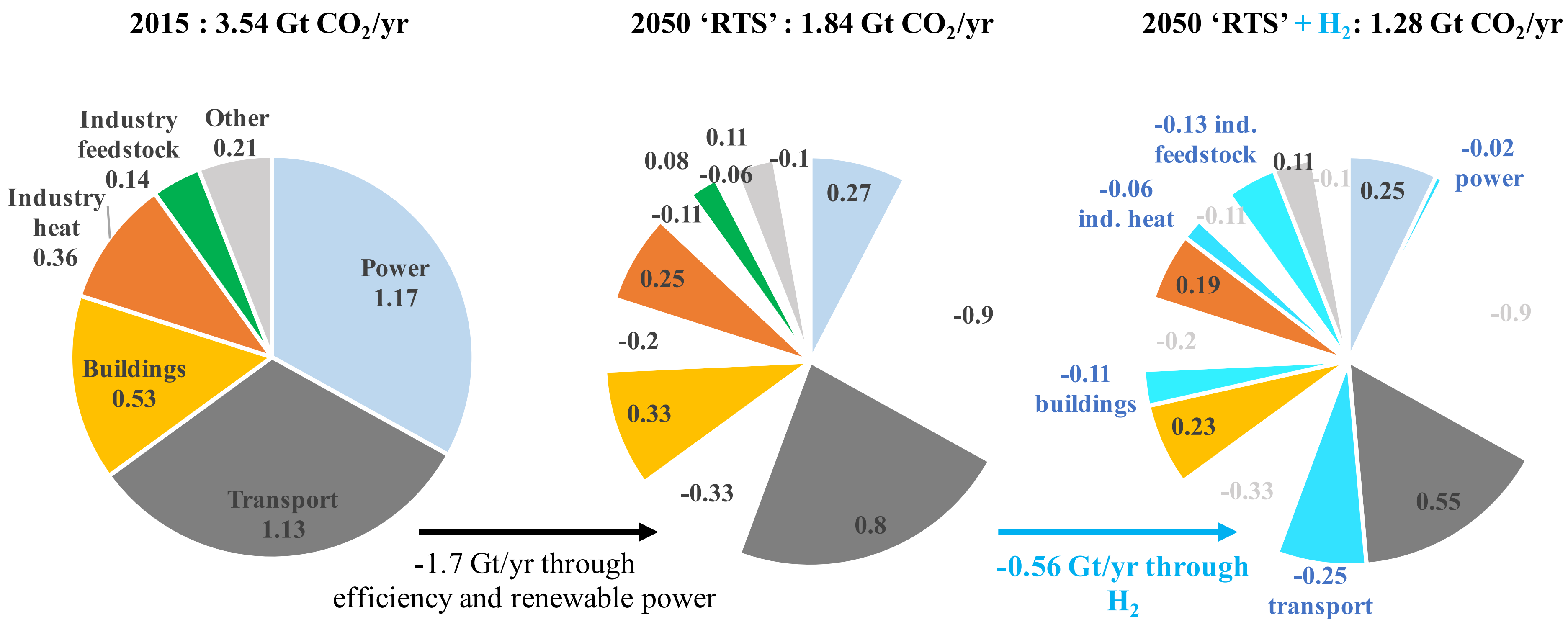
  - 4% from electrolysis

Potential future uses of H_2

Future H_2 uses

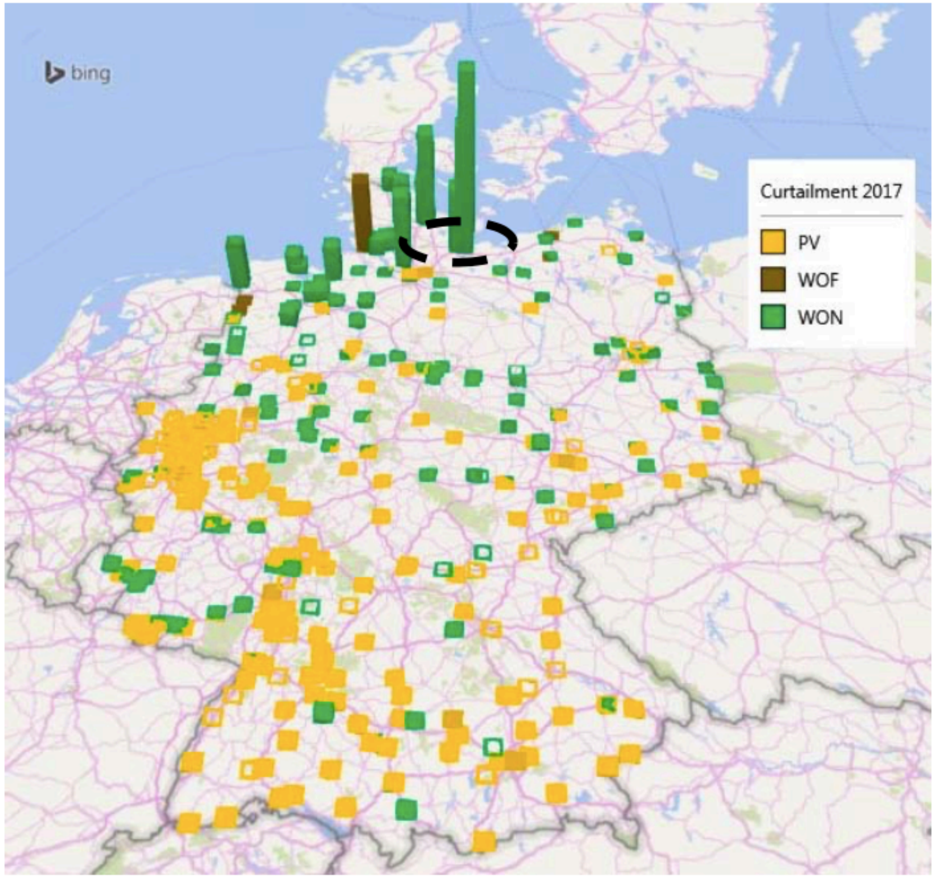
- Mobility : fuel cell vehicles
- Residential heating : natural gas network admixing
- Industry:
  - industry heating: replacing coal, natural gas
  - industry feedstock:
    - refineries
    - ammonia, methanol, other industries
    - steel making
  - light industries

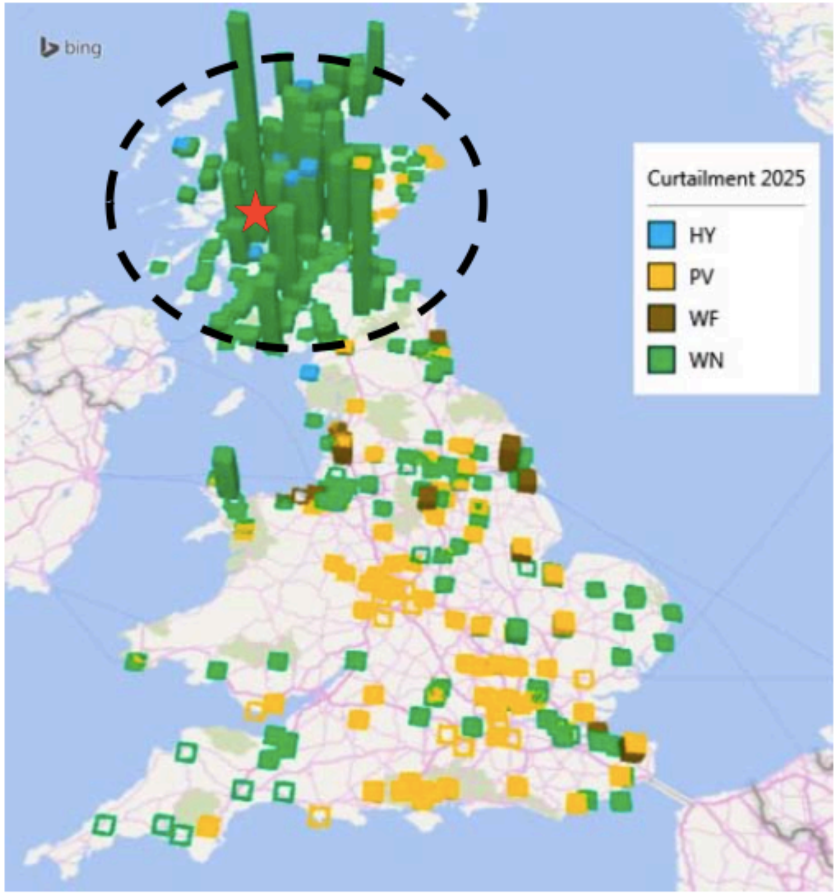
H_2 could strongly decarbonize energy supply



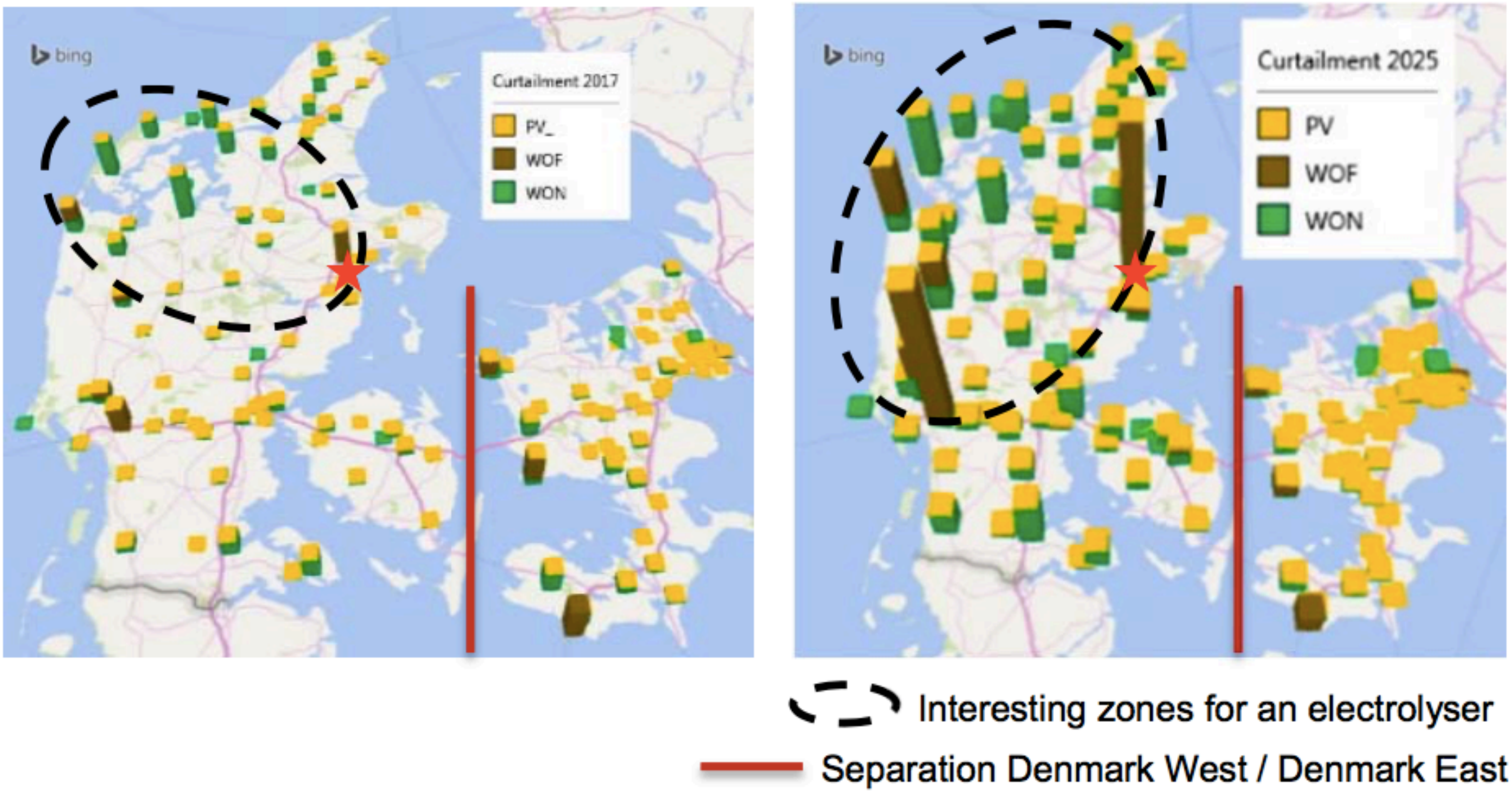
H_2 = potentially up to 24% of energy in 2050 in Europe.
7-fold increase from now.
This demands huge electrolysis capacities (100s of GWe), mainly from wind and PV.

Curtailment (excess electricity)





Germany, 2017, max bar height = 428 GWh.   UK, 2025, max bar height = 117 GWh.



DK: 2017 (left) and 2025 (right). Max bar height 2025 = 442 GWh

Electric Mobility

- **mobility** demand consumes ⅓ of primary energy and is a bigger bottleneck (fossil resource: gasoline, diesel, kerosene) than **electricity** demand (¼ of primary energy), for which many alternatives exist, and **heating** demand (≈40% of primary energy), which has enormous saving potential
- biofuels cannot cover, by far, the current demand

→ a substantial shift to transport electrification seems likely (FC vehicles, batteries, train, e-buses)

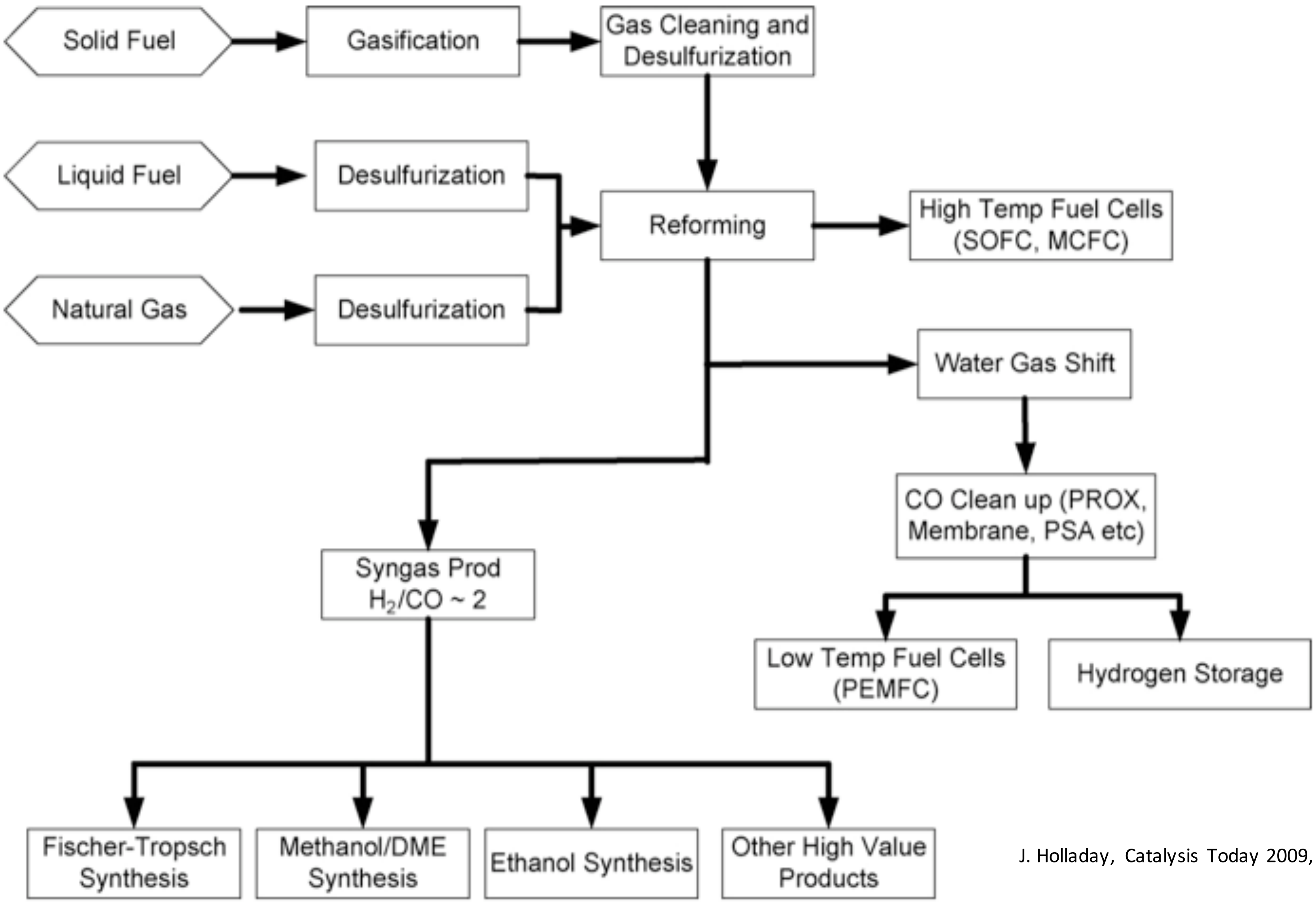
Electricity Storage

- the electrical grid has virtually no storage capacity
- seasonal electricity demand varies significantly
- the difference (summer-winter) is exarbated when replacing base-load (nuclear) with renewables like PV and hydro (summer-excess, winter-deficit)

→long term storage is required

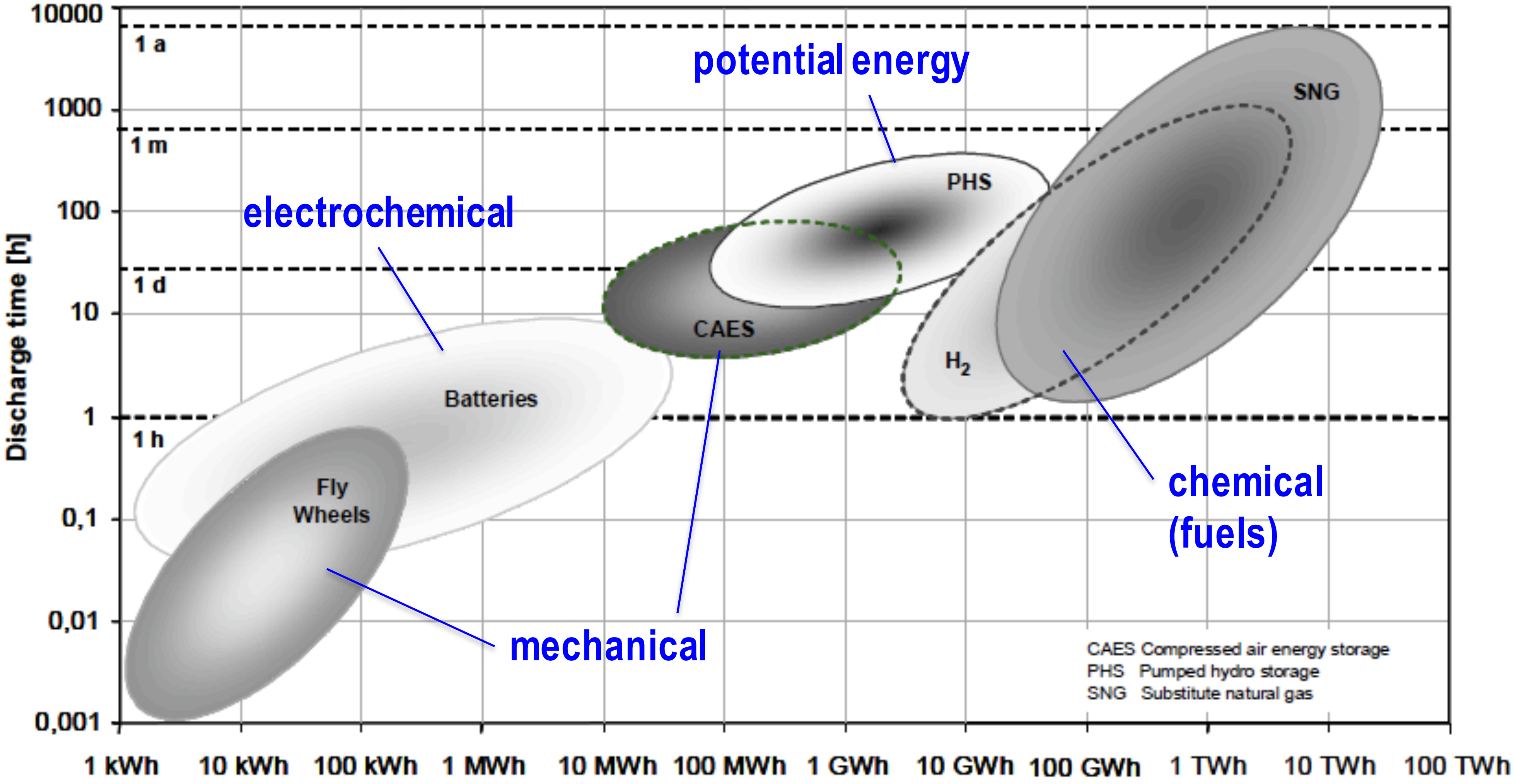
- as fuel by electrolysis (H_2, CH_4, …)

Overall pathways involving H_2



J. Holladay, Catalysis Today 2009, Vol 139, 244

Storage schemes overview



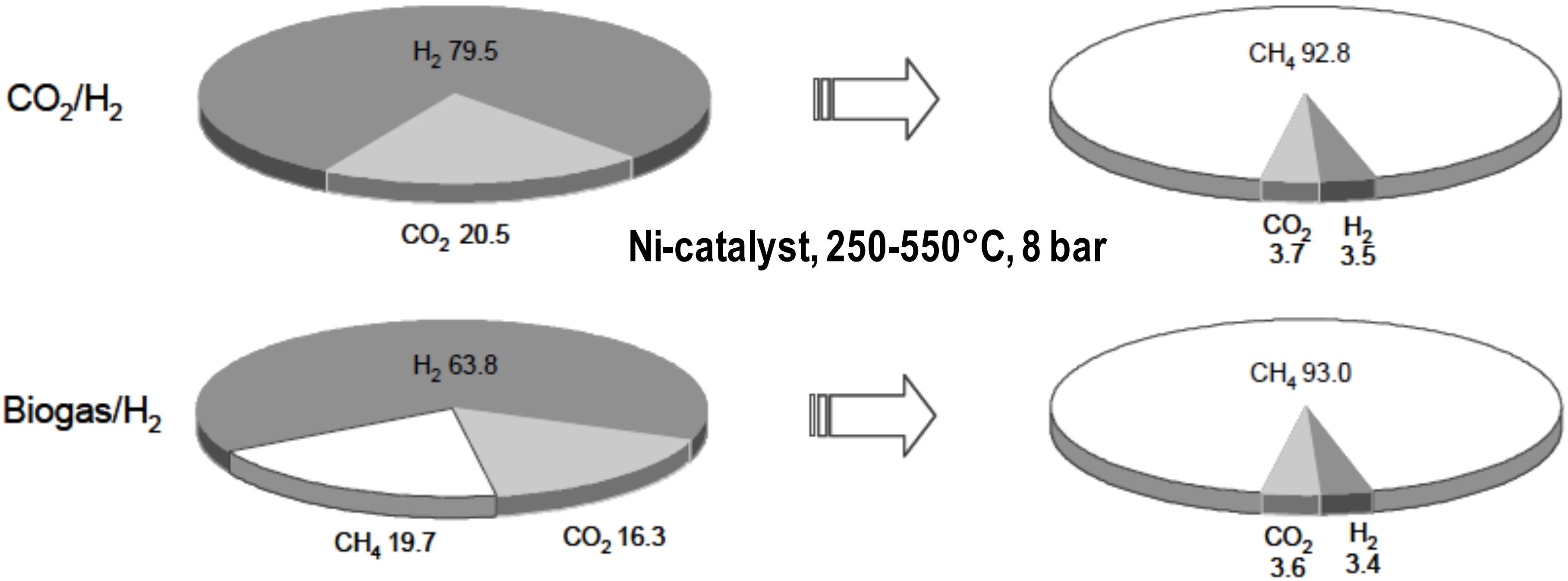
Storing Renewable Energy in the Natural Gas Grid, Methane via Power-to-Gas (P2G): A Renewable Fuel for Mobility
M. Specht, U. Zuberbühler, F. Baumgart, B. Feigl, V. Frick, B. Stürmer, M. Sterner, G. Waldstein, ZSW-Ulm

→ converting electricity to fuel gives the largest capacities

H_2/CO_2 - methanation

ΔH = -165 kJ/mol (exothermal)

$$4\ H_2 + CO_2 \quad \Leftrightarrow \quad CH_4 + 2\ H_2O$$



✔ **NG grid quality: <5% H_2, <6% CO_2**

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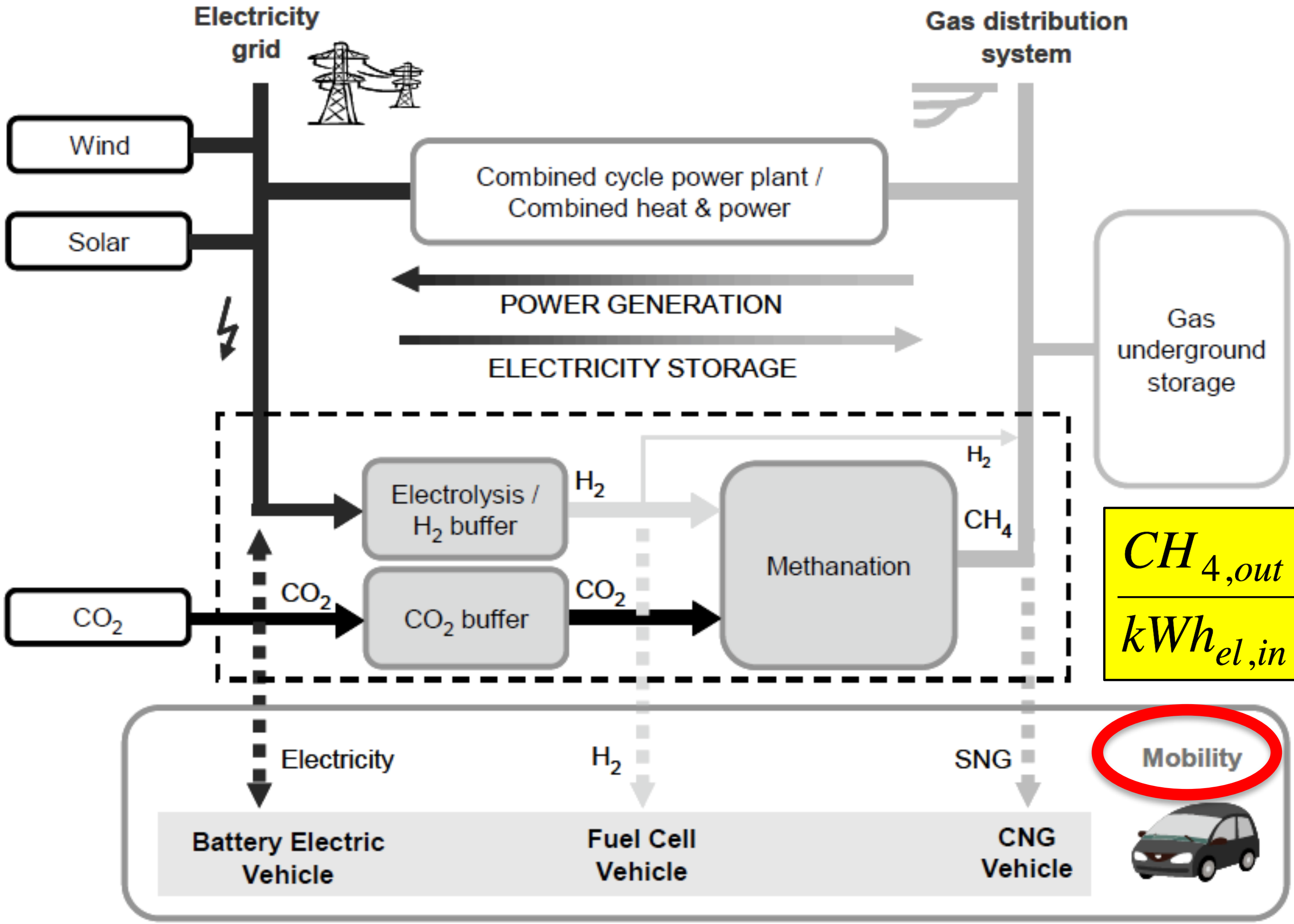
‘Power-to-Gas’ concept



$$\frac{CH_{4,out}}{kWh_{el,in}} \geq 60\%$$

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Motivation / Rationale

- tap/store available renewable seasonal/intermittent electricity reserve (hydro, PV, wind)
- chemical fuel storage is long term, high density, versatile
  - esp. mobility fuels are a bottleneck, and imported
- the electricity grid is nearly saturated
- the natural gas grid has large capacity reserve and is associated with low distribution losses (1/10th of elec. grid distribution)

Other pipelines

- existing
- under construction, projected or planned
- natural gas fields

Liquefied natural gas (LNG) receiving terminal

- in operation
- under construction or projected

Better than 'water-only' electrolysis: steam+CO_2 co-electrolysis

$$H_2O \Rightarrow H_2 + \frac{1}{2}O_2$$

$$CO_2 \Rightarrow CO + \frac{1}{2}O_2$$

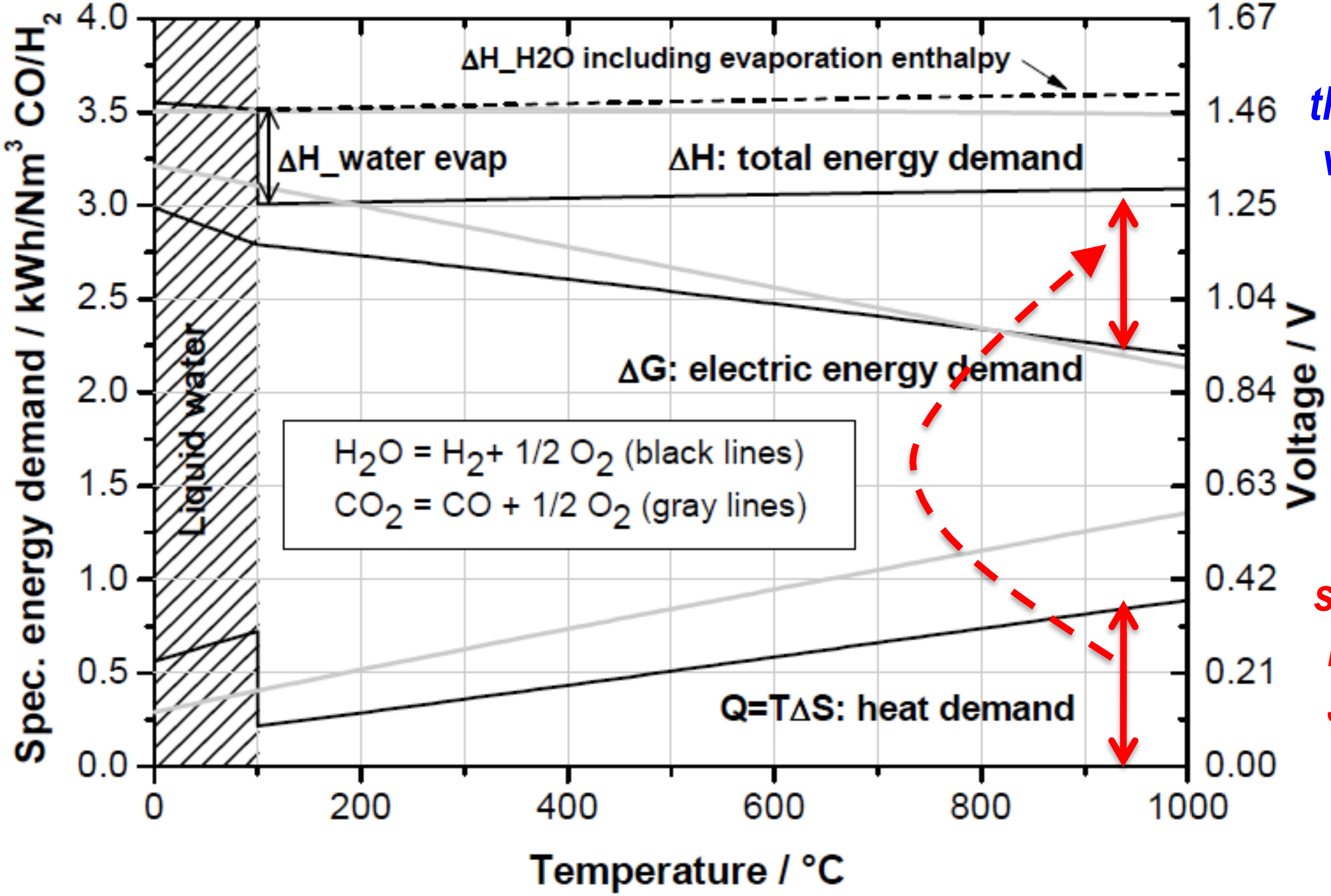
→ **SYNGAS**

- syngas is upgradable to CH_4 (→ gas grid), as well as to MeOH, liquid synfuels
- the 'H_2-only' cycle has storage/distribution/infrastructure issues
- **no need for extra step** of $H_2 + CO_2 \Leftrightarrow H_2O + CO$
- operation at higher temperature confers:
  - more favorable thermodynamics
  - more favorable kinetics

→ hence less electrical input

Thermodynamics

at 700°C, electrical input is reduced by 1/3 compared to liquid water electrolysis

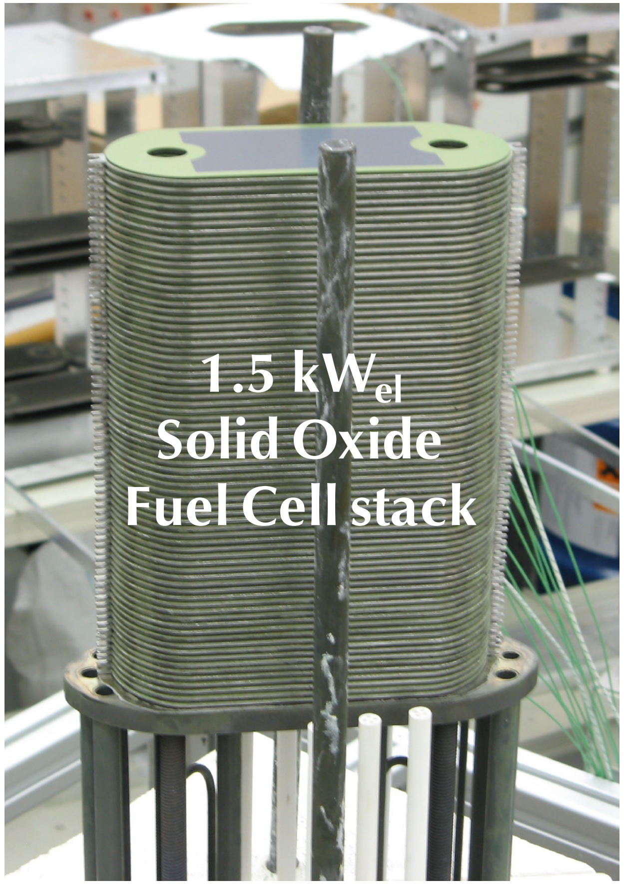


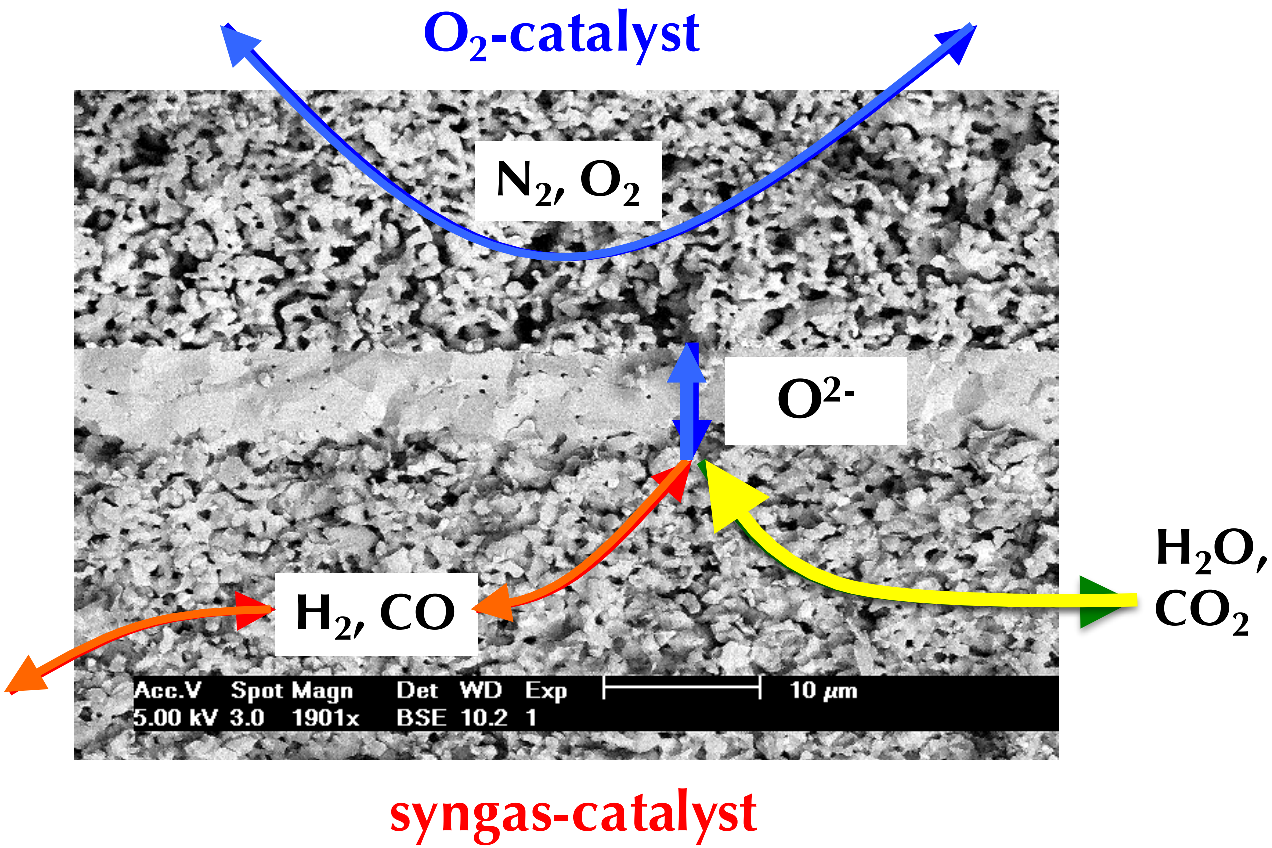
thermoneutral voltage 1.3 V

self-sustained heating from Joule losses

Q. Fu, ROLE OF ELECTROLYSIS IN REGENERATIVE SYNGAS AND SYNFUEL PRODUCTION,in Syngas: Production, Applications and Environmental Impact, Editor: A. Indarto and J. Palgunadi , 2011 Nova Science Publishers, Inc.

How is it done? :
inverse fuel cell

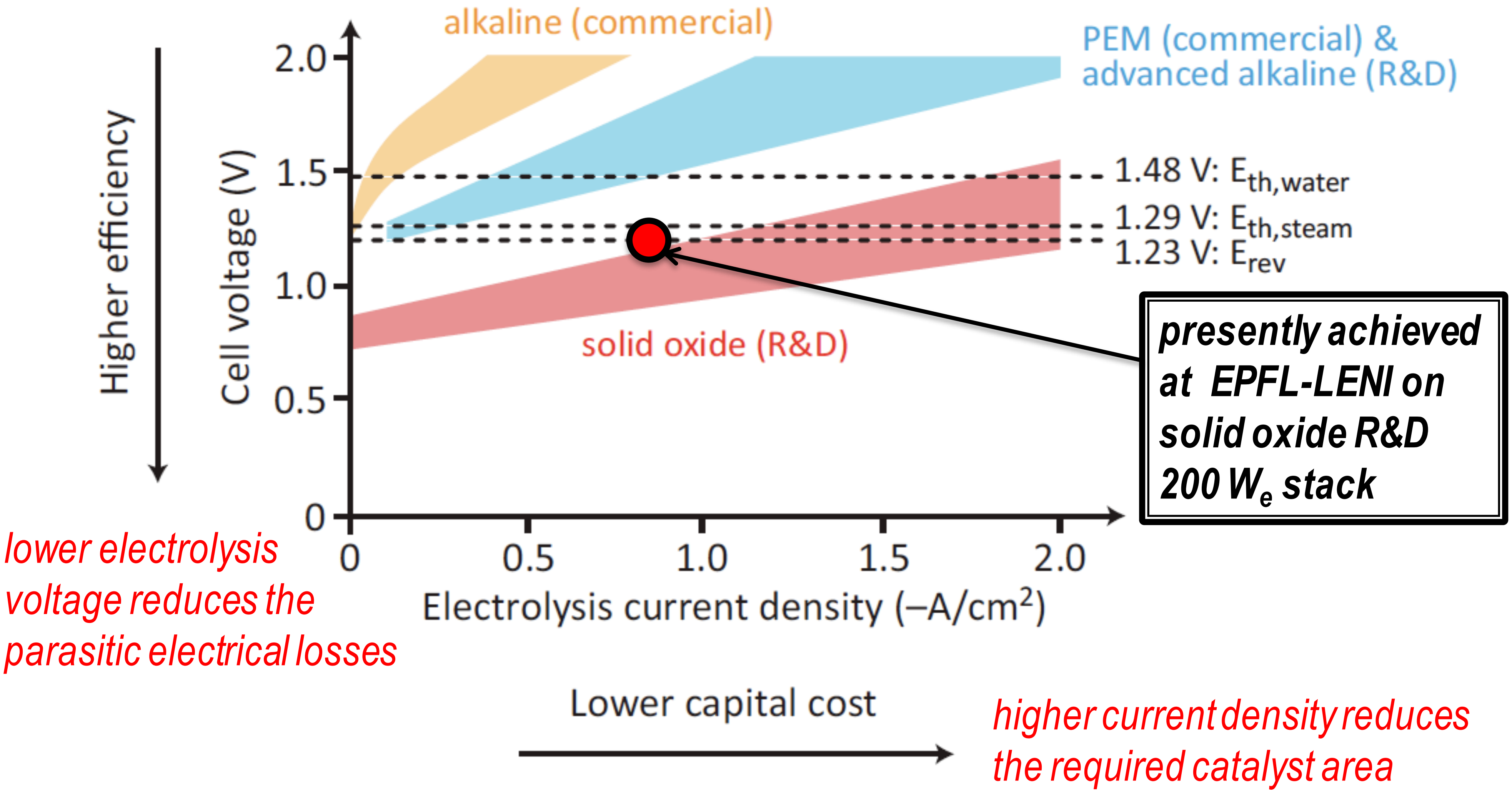




<u>Operating regime</u> :
700-800°C
1 bar (to 5 bar)

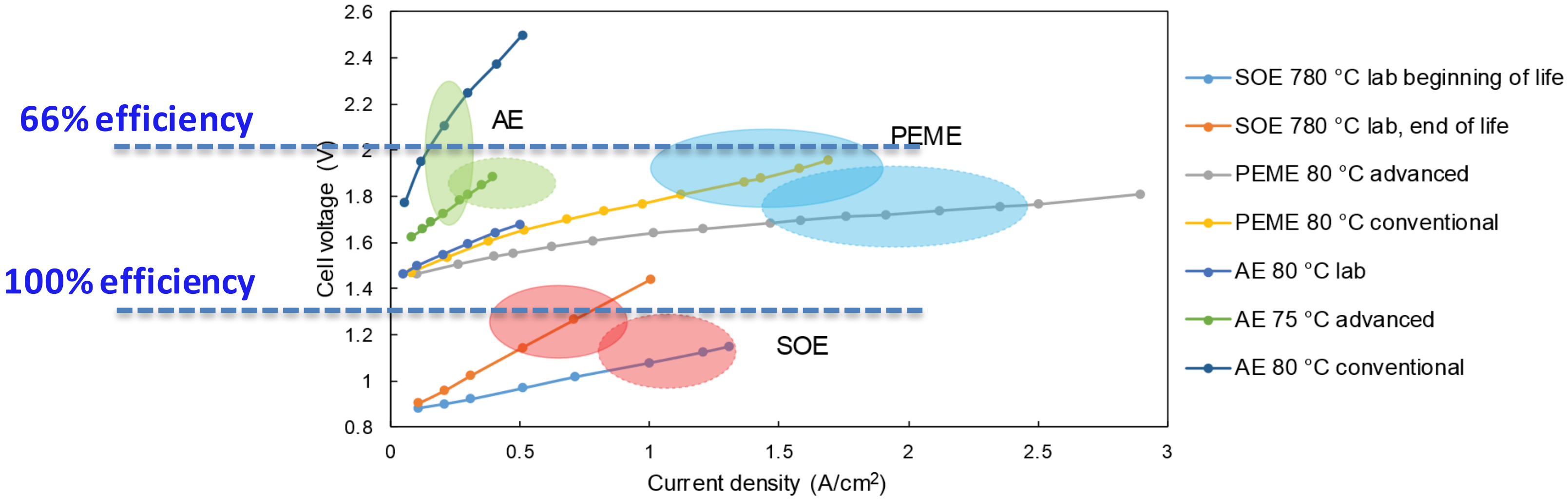
FUEL CELL
ELECTROLYSER

Electrolysis technology comparison

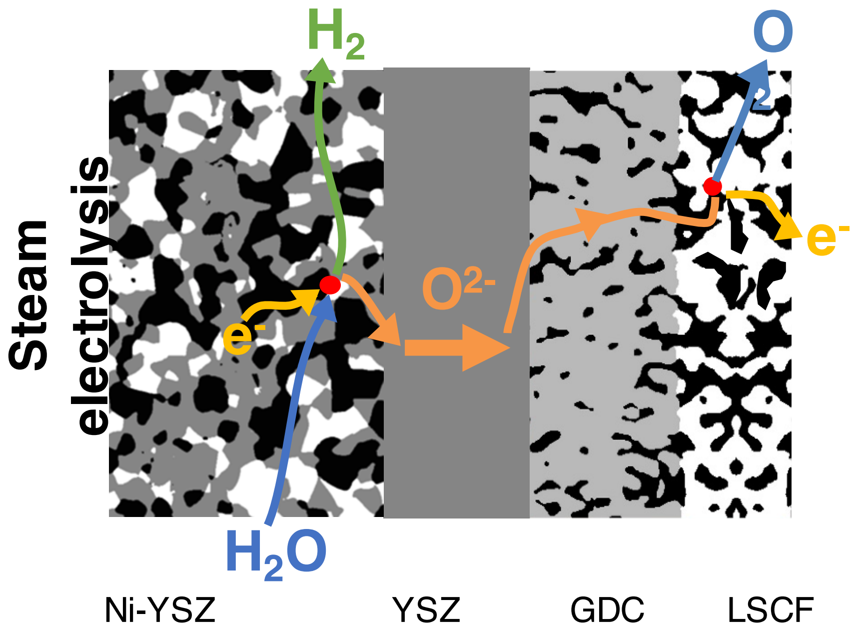


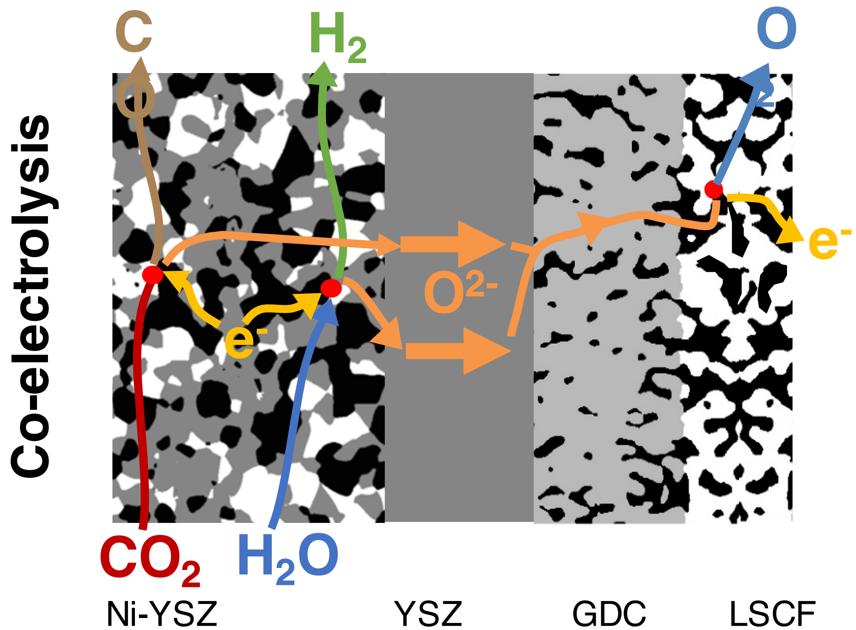
Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy
Christopher Graves, Sune D. Ebbesen, Mogens Mogensen, Klaus S. Lackner
Renewable and Sustainable Energy Reviews 15 (2011) 1–23

Electrolysis of water (alcaline, PEM) and steam (solid oxide - SOEC)



- Solid-oxide electrolysis (650 – 900 °C)





Electrolysis key figures

	Alcaline	PEM	Solid oxide
medium	liq. H_2O	liq. H_2O	steam (+ CO_2)
temperature	80°C	80°C	800°C
current, A/cm^2	0.25 – 0.5	0.5 – 1.5	0.8*
voltage, V	1.7 - 2.0	1.5 – 2.0	1.25*
stack efficiency	≤ 85%	≤ 85%	≈ 100%
system efficiency *	≤ 75%	≤ 75%	≤ 90%
kWh_{el} / m^3 H_2	≈ 5	≈ 5	≈ 3.5
lifetime	10-20 yrs	1-2 yr	1 yr

** losses: insulation, compression, inverter*

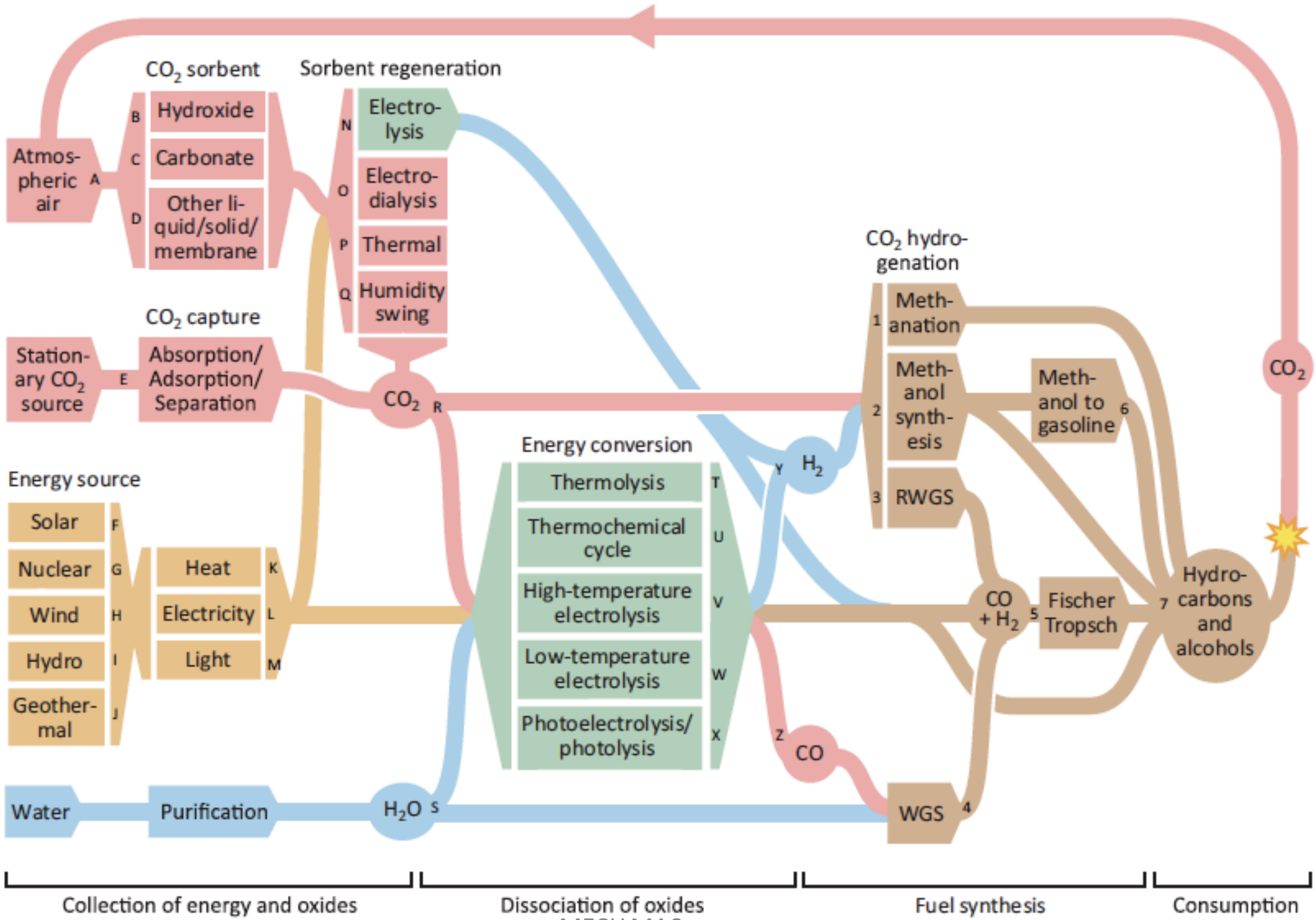
actual achieved figures at EPFL-LENI

Electrolysis efficiencies: lit. data

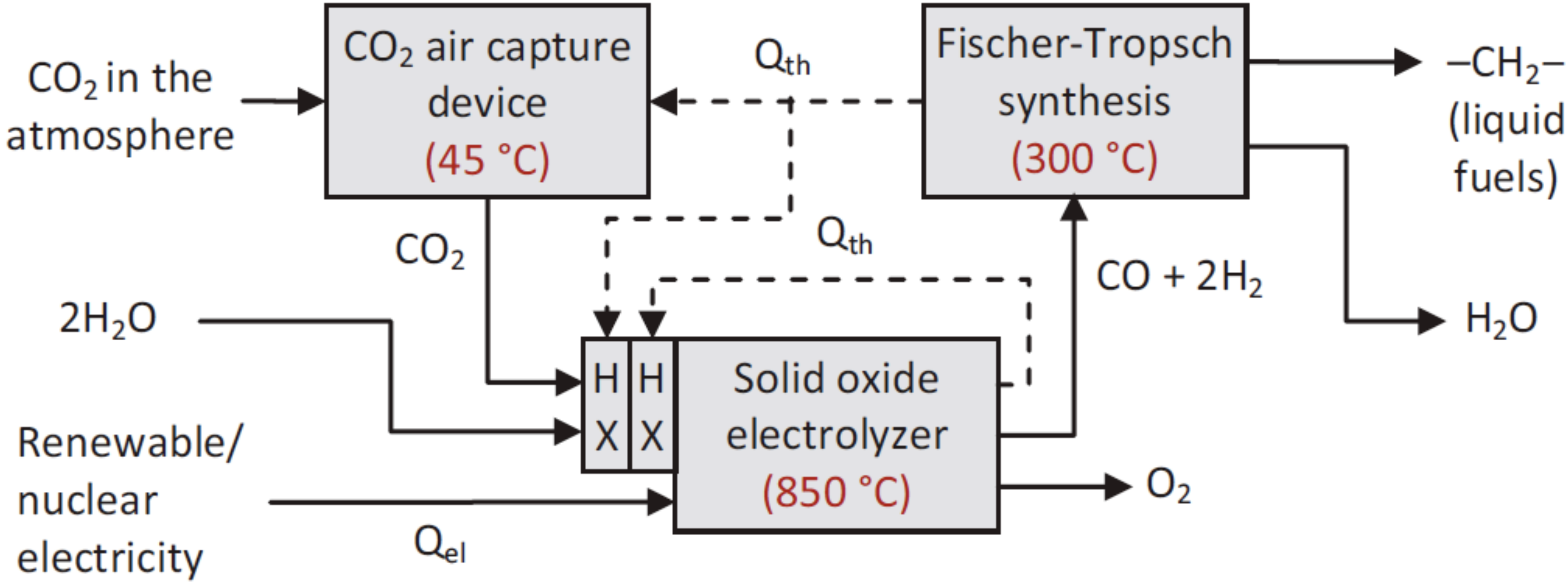
- theoretical : 39 kWh_{el}/kg H_2 (HHV 142 MJ/kg)
- alkaline electrolysis : 55-69 kWh_{el}/kg (56-73%)
  - 25°C, 30 wt% KOH solution, 2 V, 0.1-0.3 A/cm^2
- polymer membrane electrolysis : 55-70%
  - inverse polymer electrolyte fuel cell
  - 60°C, no separation required, 1.6 V, 1.6 A/cm^2
- ceramic membrane electrolysis (SOEC):
  - inverse solid oxide fuel cell, 800-1000°C, 1.2-1.5 V, 1 A/cm^2
  - 85-90% (electrical only), 60% with external heat source
- cost : alkaline < polymer < SOEC

CO_2-to-fuel pathways: general overview

C. Graves et al./Renewable and Sustainable Energy Reviews 15 (2011) 1–23



Thermal process integration example



Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy
Christopher Graves, Sune D. Ebbesen, Mogens Mogensen, Klaus S. Lackner
Renewable and Sustainable Energy Reviews 15 (2011) 1–23

Swiss context (gas industry)

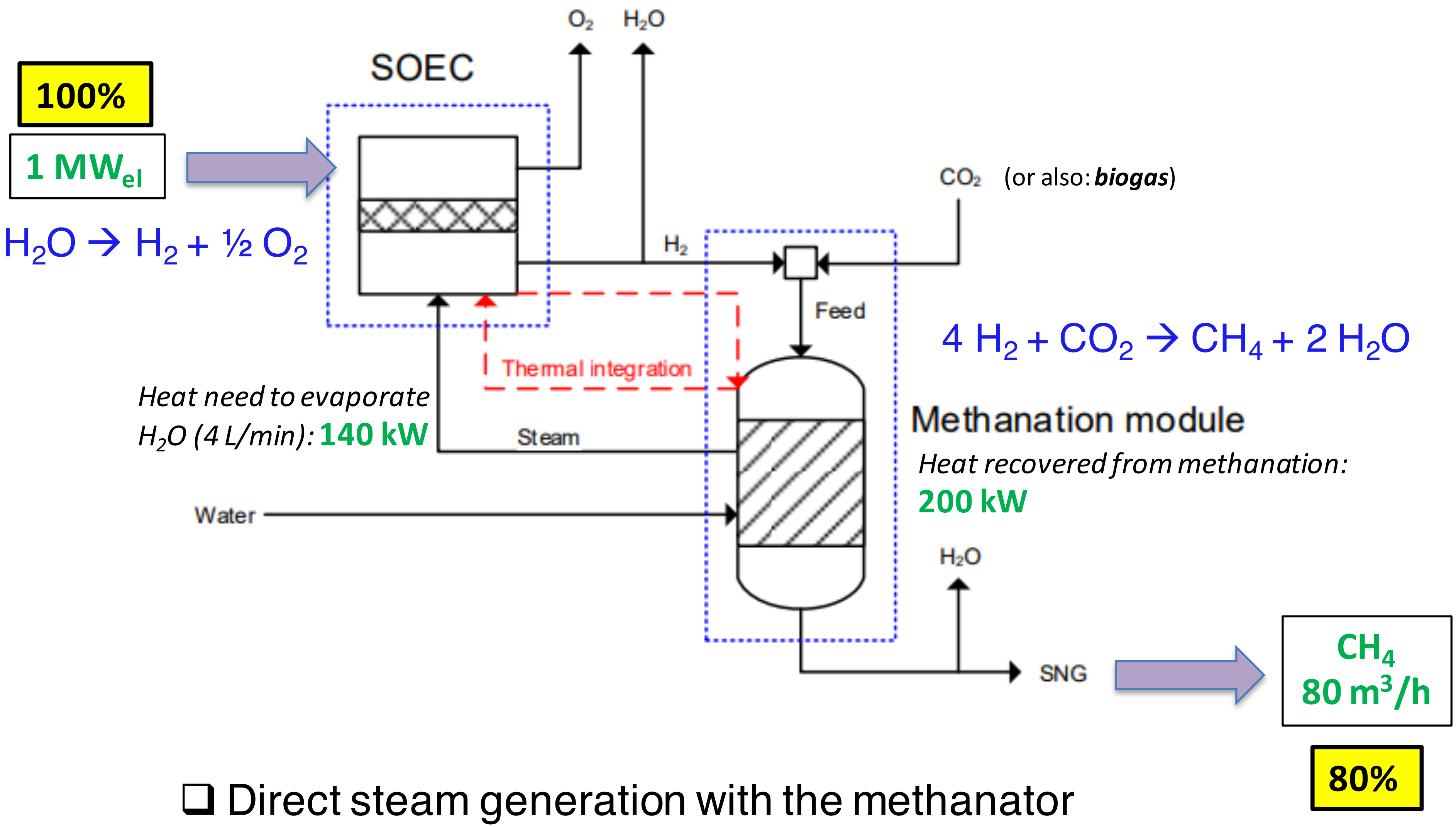
- **Power-to-methane** conversion for storage of renewable electricity
- High **efficiency** electrolysis of steam (H_2O) to H_2
  (>90%, vs. 50-60% for water electrolysis)
- Steam is generated by recovering heat from the downstream exothermal **methanation** process

$$3 \text{ to } 4\ H_2 + CO_2(/CO) \rightarrow CH_4 + 1 \text{ to } 2\ H_2O$$

- The integrated process steam electrolysis + methanation can reach **80%** energy **efficiency** electrical power → renewable methane CH_4
- The **CO_2 utilisation** can stem from air capture + separation, or from concentrated CO_2 streams, e.g. **biogas**, combustion (wood/waste),…

- « *30% renewable gas in the Swiss gas grid by 2030* » (10.5 TWh):
  - upgrading current Swiss biogas production to bio-methane via SOEC can reach ≈**20%** of this target (2.3 TWh)
  - upgrading future potential Swiss biogas production to bio-methane via SOEC can reach **100%** of this target (10.9 TWh); this would require ≈800 electrolysers of 1 MW_{el} (800 MWe). This is of the same order as current hydro-pumping storage.

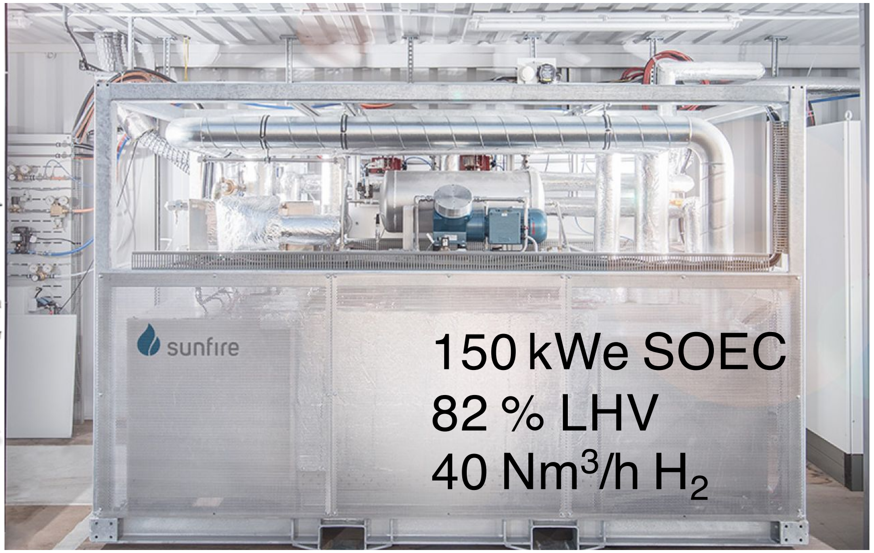
SOE (Solid Oxide Electrolysis) based Power-to-CH_4



❑ Direct steam generation with the methanator

Solid-oxide system development & manufacturers

SUNFIRE POWERCORE



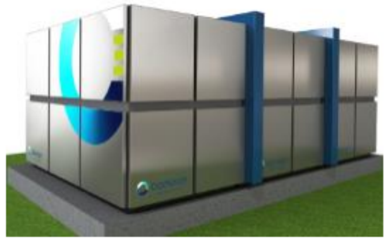
150 kWe SOEC
82 % LHV
40 Nm^3/h H_2

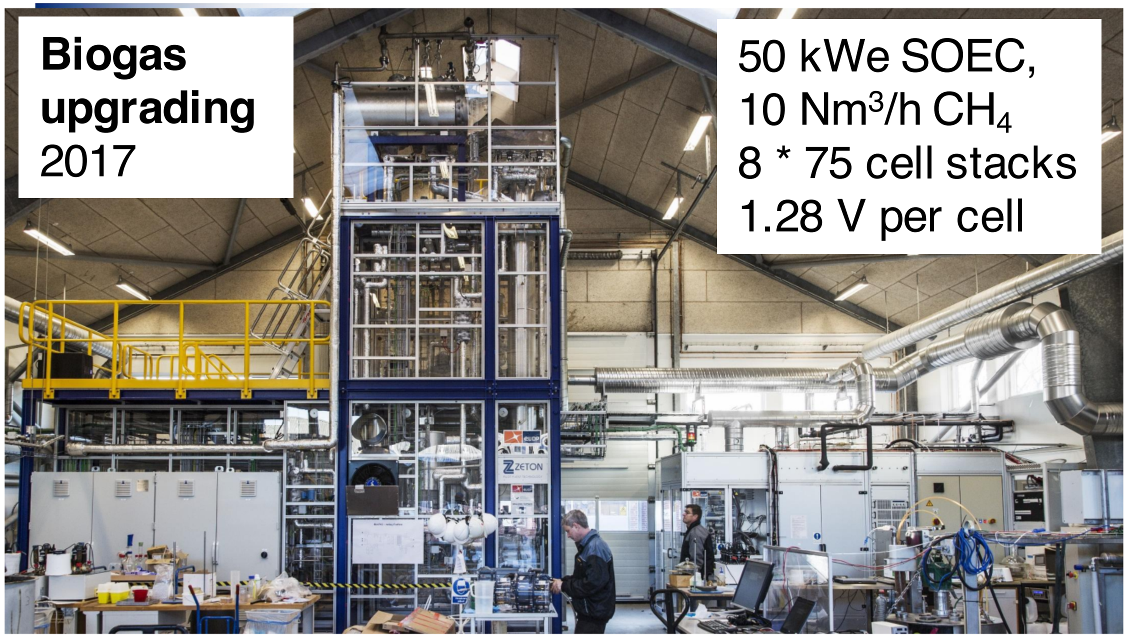
Convion C50
50kW, NG, Biogas

Validation 2015

CONVION SOFC

X00 concept
175 kWe, Biogas
ηe > 53 %
2016



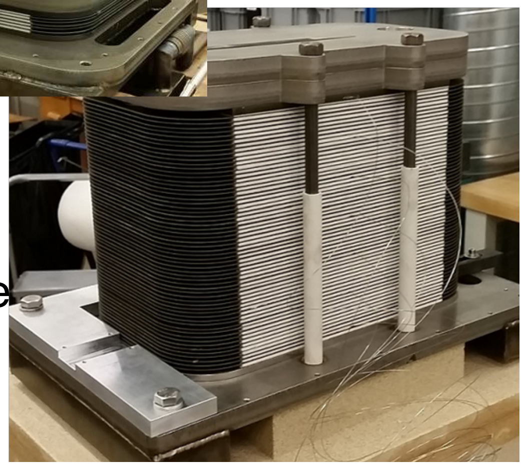


Biogas upgrading
2017

50 kWe SOEC,
10 Nm^3/h CH_4
8 * 75 cell stacks
1.28 V per cell

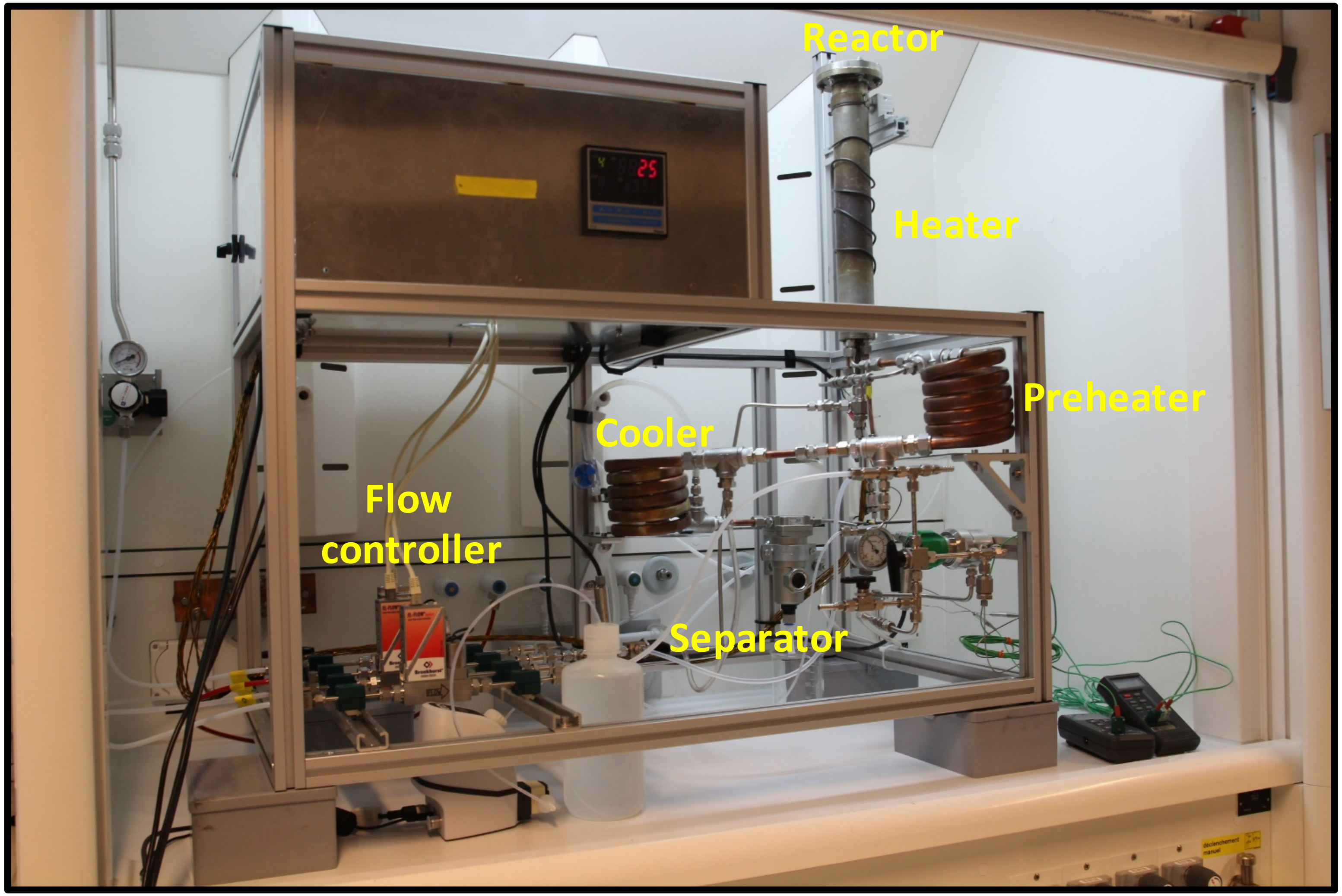
HALDOR TOPSØE

SOLIDPower 5-kW SOFC stack



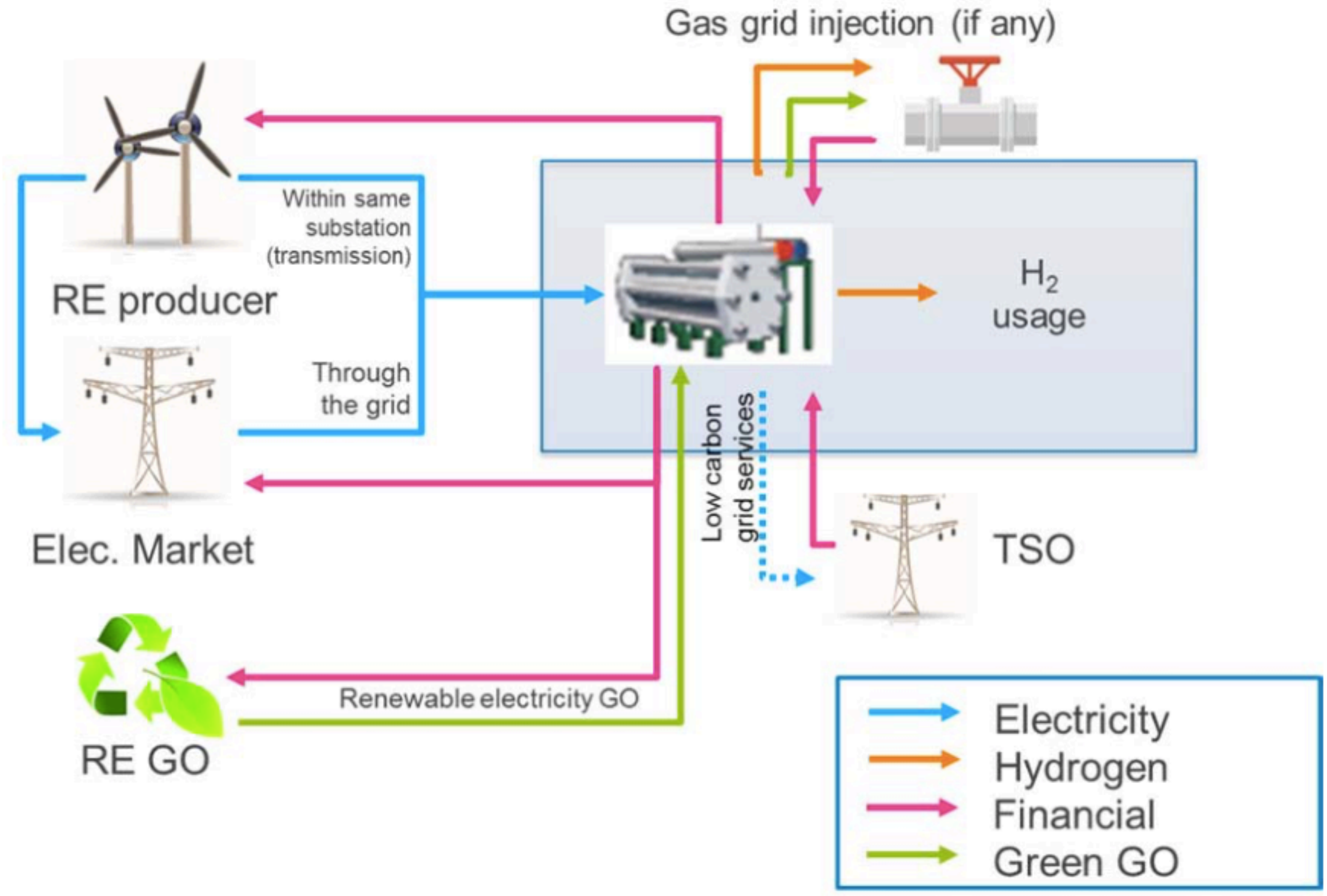
Electrolysis
2019: 20 kWe
2020: 100 kWe

Methanation reactor at EPFL-GEM laboratory



Pietsch, P., Wang, L., Van herle, J., Dynamic modeling and optimal design of small-scale evaporator-integrated methanator, master thesis, 2018.

Electrolyser business models



H_2 distribution energy cost

Production → Storage → Distribution → Transfer → Use

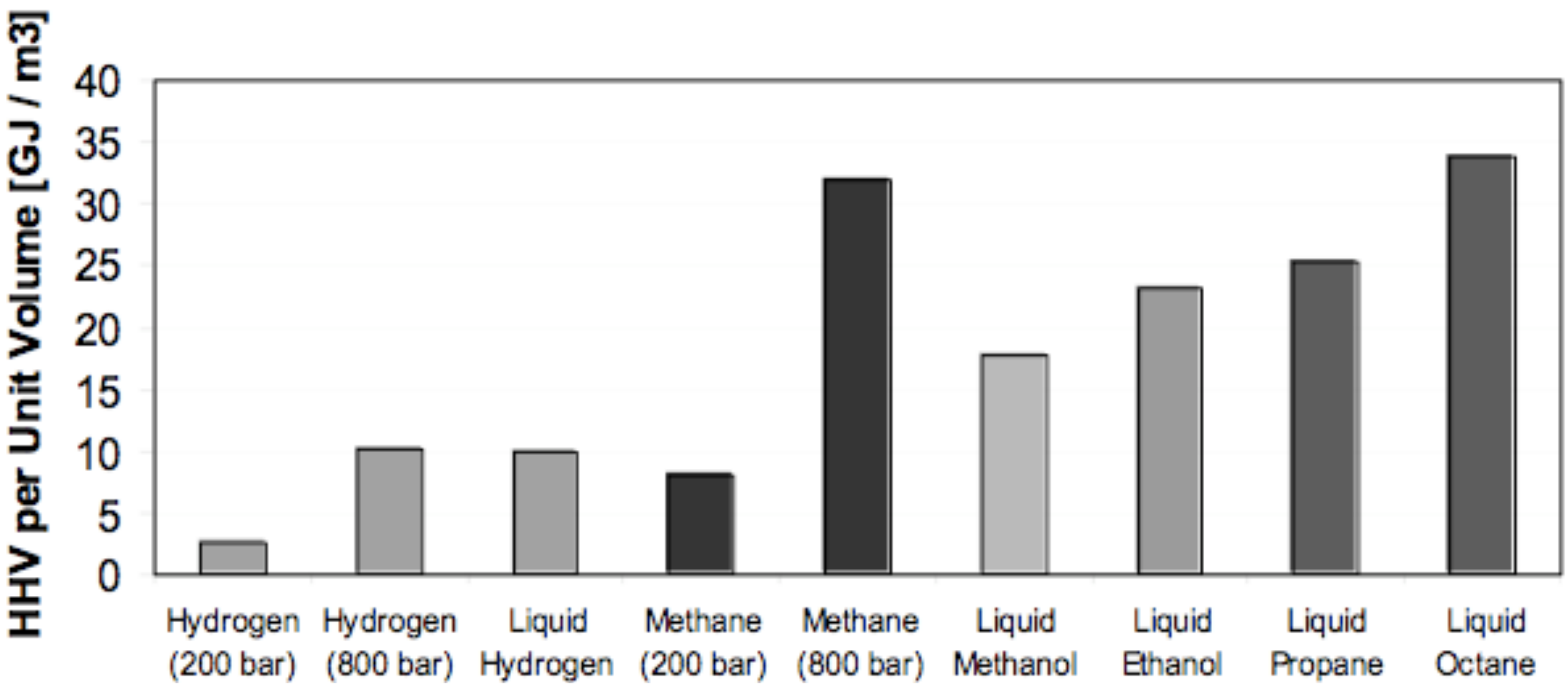
source (well) → *sink (service)*

Oil	**:**	**-12%**
Gas	**:**	**-5%**
H_2	**:**	**- ? %**

H_2 vs. hydrocarbons: properties

	H_2	Natural gas (CH_4)	Gasoline
Boiling point	-252.7 °C	-160°C	40-200°C
Melting point	-259 °C	-182°C	-40°C
Gas density	0.089 kg/m^3	0.707 kg /m^3	4 kg /m^3
Liquid density	0.071 kg/L	0.41-0.5 kg/L	0.72-0.78 kg/L
Lower HV	120.2 MJ/kg, 8.6 MJ/L as liquid	47 MJ/kg 21 MJ/L as liquid	42 MJ/kg
Higher HV	142 MJ/kg, 12.7 MJ/m^3 10.1 MJ/L as liquid	53 MJ/kg, 40 MJ/m^3 24 MJ/L as liquid	46 MJ/kg 36 MJ/L
Autoignition	585°C	632°C	220°C
Flammability in air	4-75%	5-15%	1-7.6%
Flame temperature	2045°C	1875°C	2200°C

HHV by volume



U. Bossel, H_2-economy

Storage of hydrogen

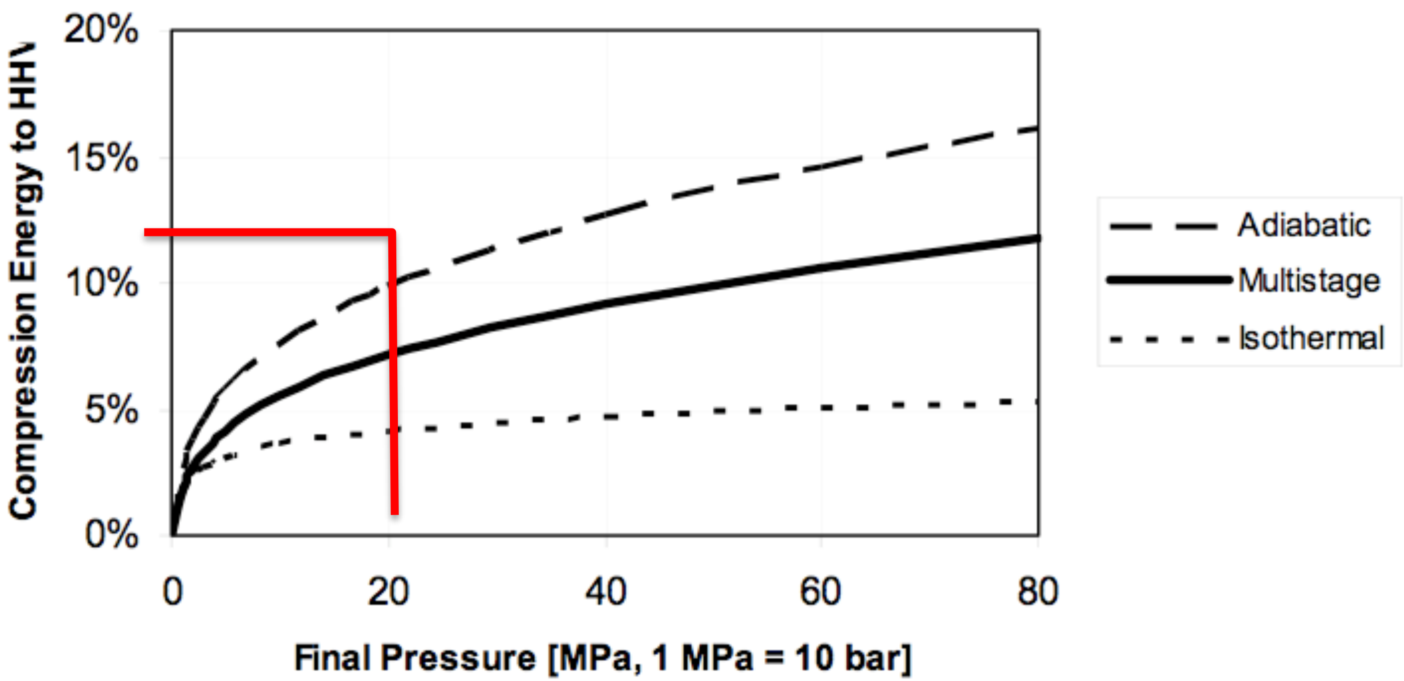
- as compressed gas
- as liquified gas
- as metal hydride
  - physically bound (absorbed, H_2 interstitial)
  - chemically bound (NaH, $NaBH_4$)

Compressed gas energy cost

- ideal isothermal : $work_{id}$ (J/kg) = $p_0 V_0 \ln(p_1/p_0)$
- adiabatic : $work_{ad} = (\gamma/\gamma-1)\, p_0 V_0\, ((p_1/p_0)^{(\gamma-1)/\gamma}-1)$

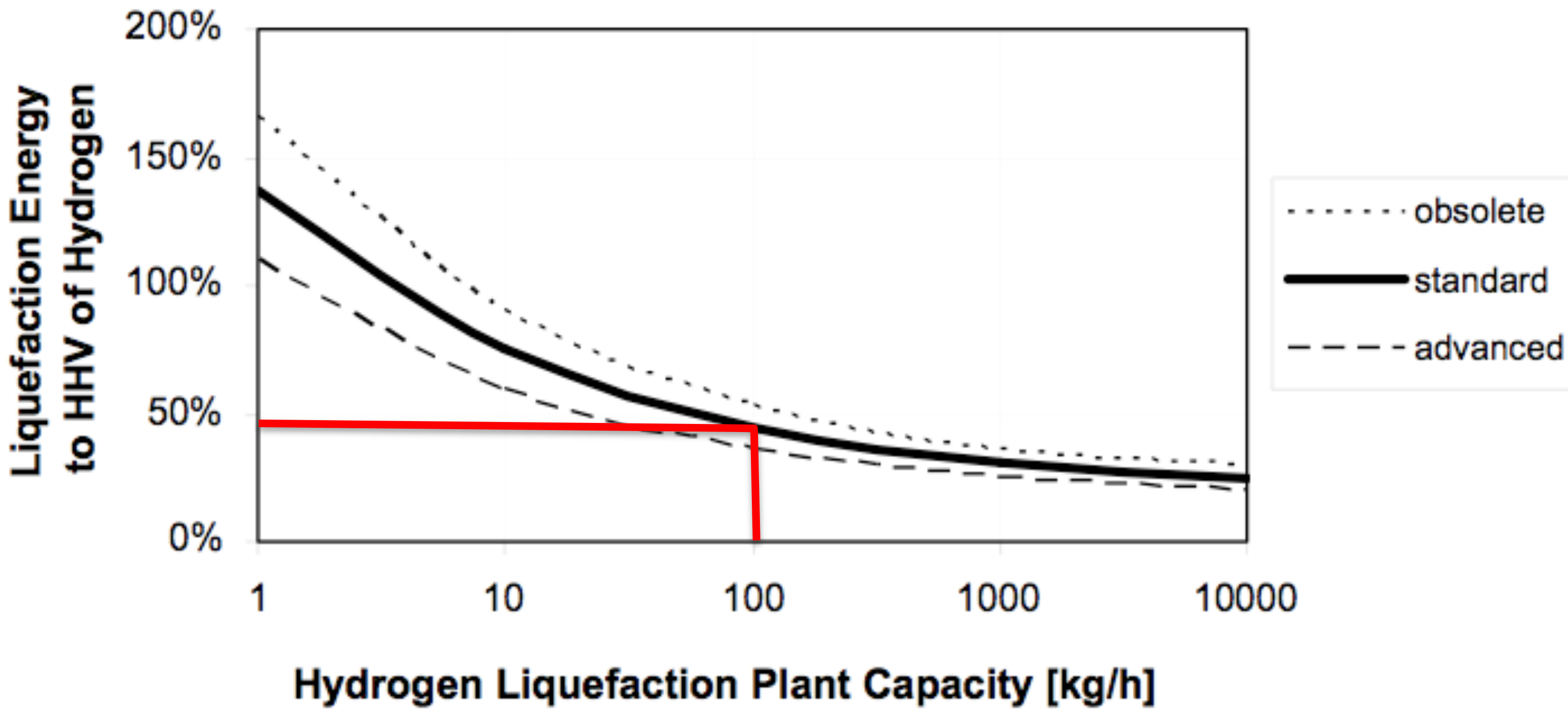
  V_o initial volume(m^3/kg) (11.11 m^3/kg for H_2, 1.39 m^3/kg for CH_4)

  p_0 initial pressure, p_1 final pressure, $\gamma = C_p/C_v$ (1.41 for H_2, 1.31 for CH_4)
- @200 bar (W_{ad}): for CH_4 2 MJ/kg, for H_2 **14 MJ/kg**



H_2 liquefaction

298 K → 20 K	MJ need per kg liquid H_2	Reference
theoretical requirement	14.2 (10% of HHV)	Carnot
usual scale	54	182 kg / h, Linde plant (D)
large scale	36	2000 kg / h, USA
ultimate scale	30-25	12000 kg/h, study case



Metal hydride storage
(*physically* *absorbed*)

- $LaNi_5$, ZrC_2 dissolve H_2 in their crystal structure, under pressure and with heat release
- equivalent to compression at 30 bar
- storage of 55-60 g H_2/L (cf. LH_2 = 70 g/L)
- hydride density = 7 kg/L

→therefore, only 1 kg of H_2 (=1 gallon or 4 L of gasoline) is stored in >100 kg of hydride!

→impossible mobile storage for vehicles

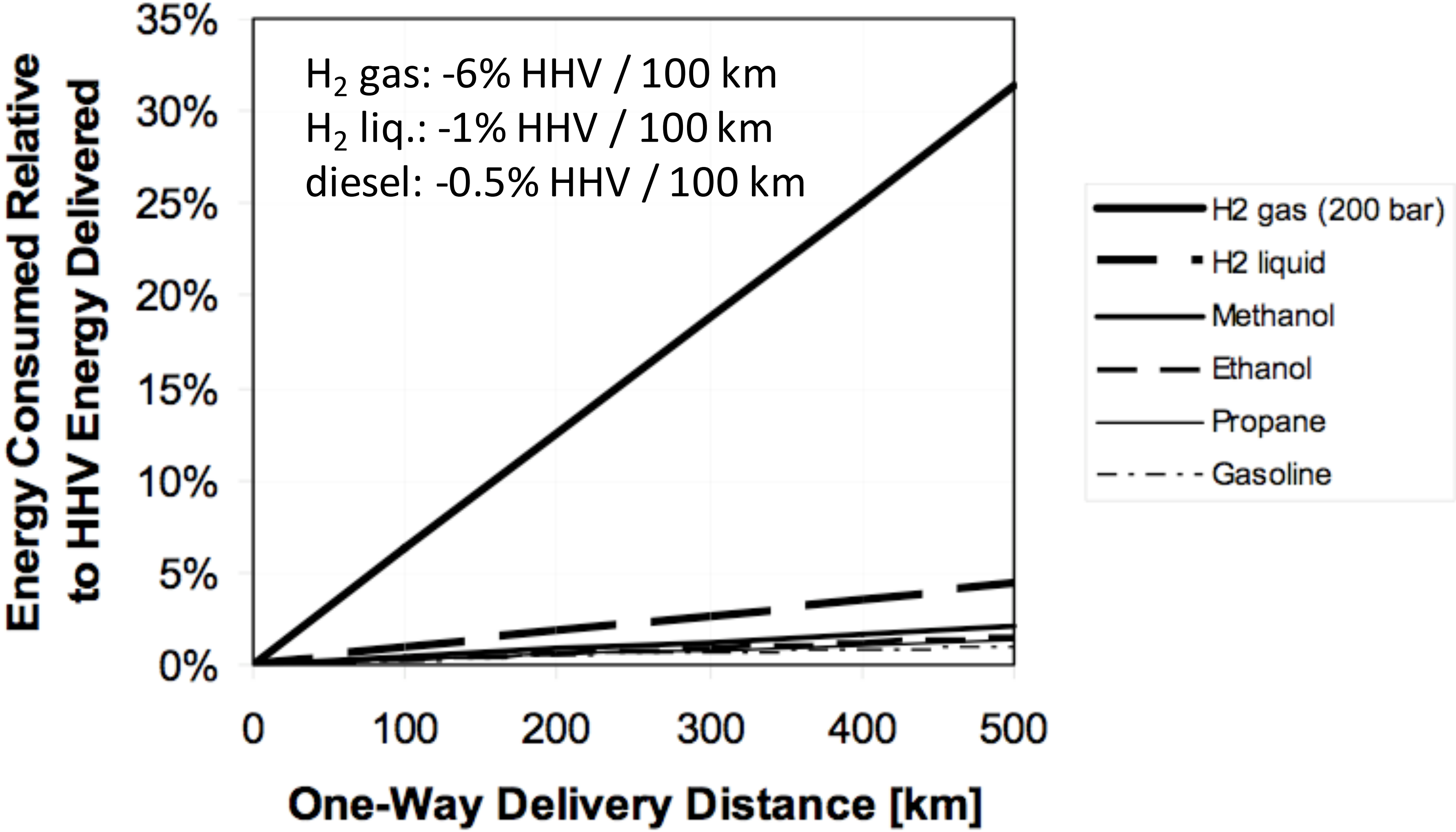
Metal hydride storage
(*chemically* ***bound***)

- LiH, NaH, CaH_2, $LiBH_4$, $NaBH_4$, $LiAlH_4$
- fabrication: $NaCl + \frac{1}{2}H_2O \rightarrow NaH + \frac{1}{2}Cl_2 + \frac{1}{4}O_2$ 500kJ/mol at high T; then cooled, granulated, packed sealed
- release by hydrolysis: $NaH + H_2O \rightarrow NaOH + H_2$ -85kJ/mol
- in fact, water is the H_2 source
- high energy density (comparable to wood)
- 60% efficiency

Hydrogen Distribution

1. by road (delivery trucks)
2. by pipeline
3. by on-site generation (electrolysis) at filling station

1. By road transport



2. By pipeline

- NG pipelines are **incompatible** for H_2 use (diffusion loss, brittleness, compressor,…)
- energy carried: $Q(W) = V(m^3/s).\rho(kg/m^3).HHV(MJ/kg)$ = section $A\ (m^2)$*flow $f(m/s).\ \rho(kg/m^3).HHV(MJ/kg)$
- with $\rho_{CH4}=0.71$ vs $\rho_{H2}=0.09$, and $HHV_{H2}=142$ vs $HHV_{CH4}=53$, the H_2-velocity has to be 3.1 times higher
- pumping power $P(W)=A.f.\Delta p=A.f.½(L/D)\rho f^2\zeta$
- ratio $P_{H2}/P_{CH4}=(\rho_{H2}/\rho_{CH4}).(f_{H2}/f_{CH4})^3=(0.09/0.71).(3.1)^3 = 3.85$
- f_{CH4}=10m/s, one compressor every 150 km consumes ca. 0.3% of the passing energy stream

→ for H_2,ca. 0.3%*3.85 = 1.16%

3. By onsite electrolysis

- filling station, 1000 cars/day, 60 L gasoline/car (=2.4 GJ = 17 kg H_2), i.e. 17 tonnes H_2 /day = 2400 GJ/day
- fuel cell vehicles need only 70% of gasoline equivalent →1750 GJ/day
- electrolyser efficiency 78%, ac/dc 95% →2300 GJ/day (107 m^3/day H_2O)
- compression to 400 bar requires 300 GJ/day
- total need of 2600 GJ/day = 30 MW (1 nuclear power plant for every 30 filling stations!)
- 2600 GJ/day consumed, 1750 GJ/day delivered : 150% HHV

→ 67% efficiency

Energy cost of filling (H_2 transfer)

- stored at 100 bar (p_1), car uses 400 bar (p_2)
- multistage compression (ca. 2*isoth. compression):

work (J/kg) $\approx 2 * p_0 V_0 \left(\ln(p_2/p_0) - \ln(p_1/p_0) \right)$

$p_0 V_0$ = 1.11 MJ/kg

work = 1.54 MJ/kg (1.1% of HHV)

→ in reality, this will rise to 3% HHV