DIFFER
Dutch Institute for
Fundamental Energy Research

CO_2-NEUTRAL FUELS

- THE CHALLENGE -

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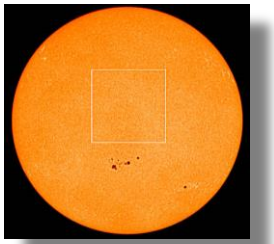
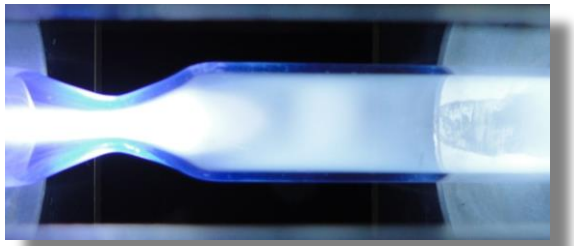
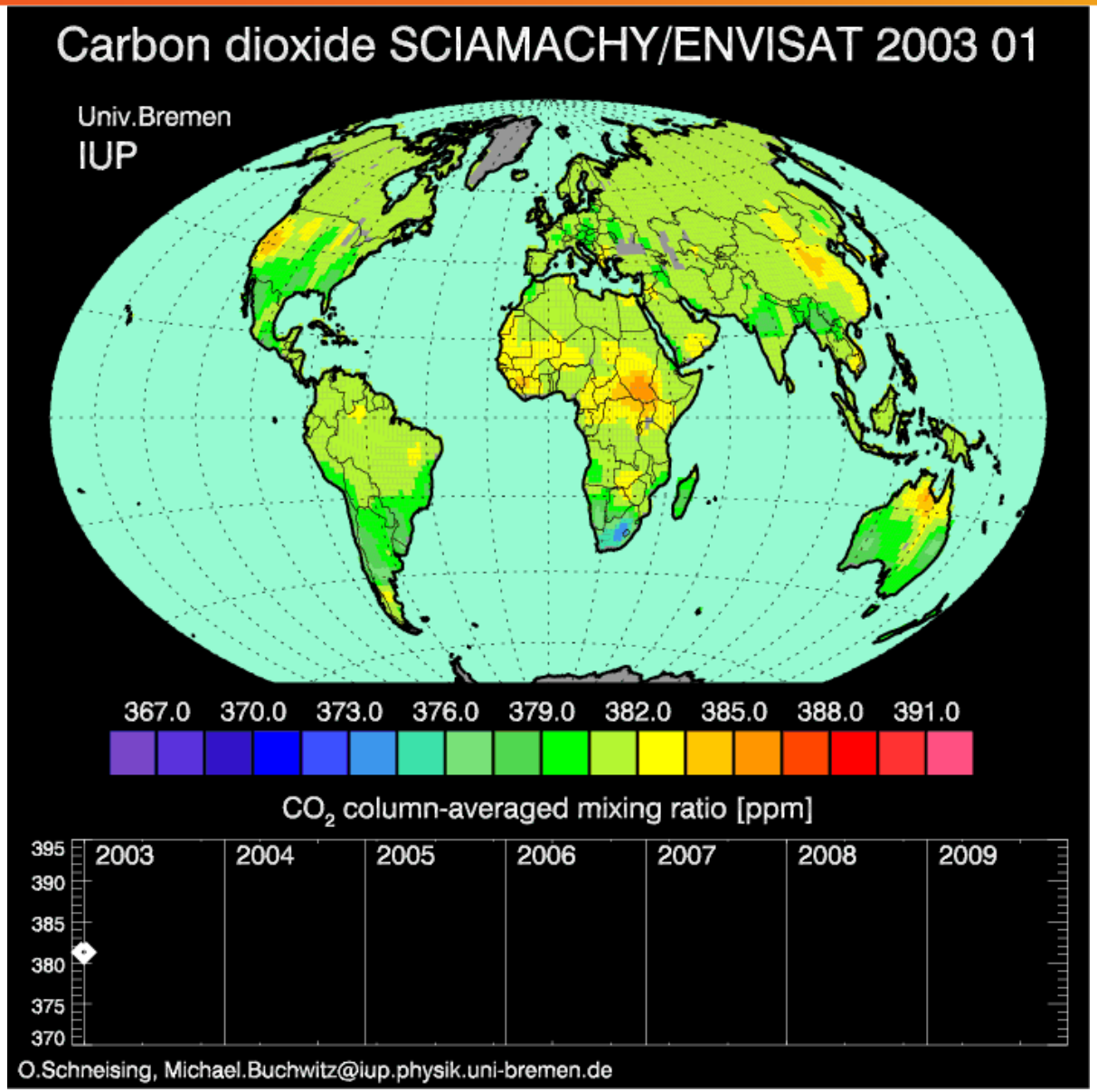



Joint EPS-SIF International School on Energy, Varenna, 17-23 July 2014

DIFFER is part of FOM and NWO

Global CO_2 concentration distribution



Global issues require global data

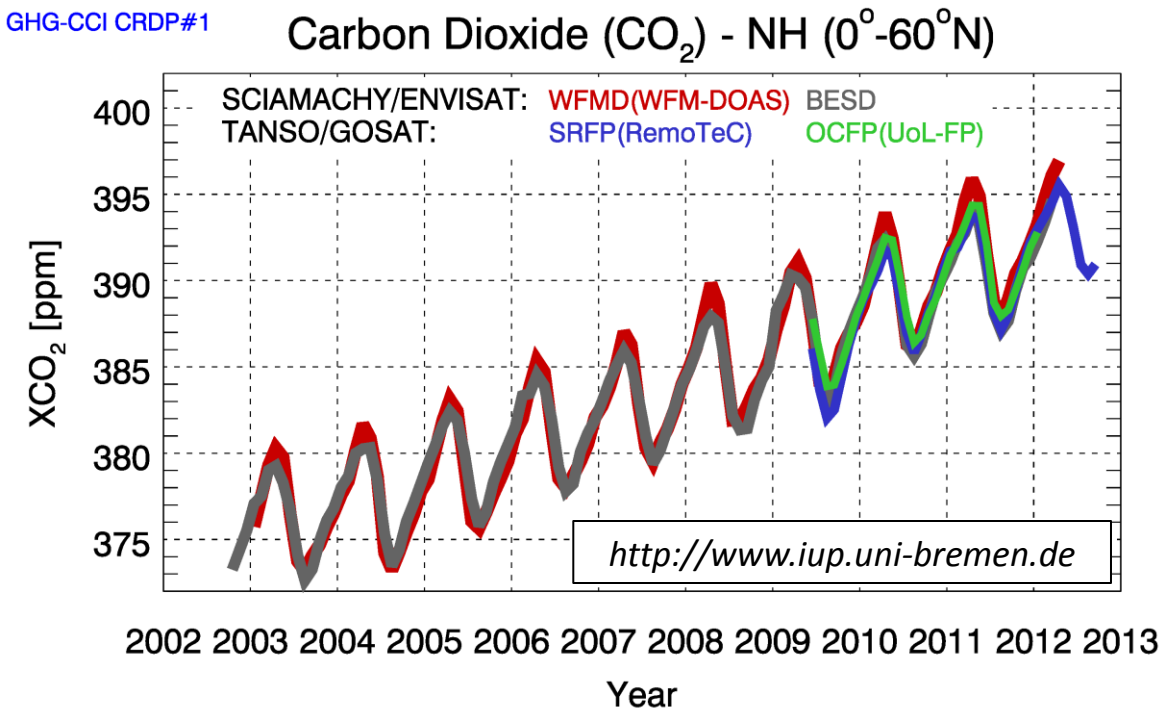
SCIAMACHY spectrometer on ESA ENVISAT

- Objective: Validation of atmospheric chemistry models
  Understanding the biogeochemical cycles (H, C, N,..)
  - Paul Crutzen (Nobel Prize Chemistry 1995)
  - Principal Investigators: J P Burrows, A P H Goede
- Mission duration: 2002 – 2012
  - 10 year CO_2 global data set

Data continuity

- NASA OCO-2 mission launched 2 July 2014
- ESA CarbonSat decision mid 2015.

SCIAMACHY Northern Hemisphere CO_2



Natural cycle ~ 10 ppm CO_2 swing

- photosynthesis uptake during growing season
- respiration during bio-mass decay

} **Carbon cycle closed** near-equilibrium over past ~ 1 Myr

Man made annual rise ~ 2 ppm/yr

- 90%: burning fossil carbon (>100 Myr old bio-mass) cement production
- 10%: land change

} **unsustainable**

Outline CO_2 Neutral Fuels

Why – What drives their development?

- Climate change, environmental pressure
- Natural resources
- Energy security

What - Renewable hydro-carbon based fuels

- Building on existing infra structure (storage, transport, distribution, use)
- Recycling CO_2 emitted

→ Closing the carbon cycle

How - Renewable Energy (RE) driven conversion of feedstock H_2O/CO_2

- RE System approach: intermittency, supply-demand mismatch
- Energy storage in chemical bonds: Power to Gas, Power to Liquid
- System integration (electricity and gas grid)
- Carbon capture and utilisation

→ CO_2 neutral fuels

Climate Change: IPCC 5th Assessment 2013

Man-made CO_2 emission

- Atmospheric concentration risen: 280 ppm pre-industrial to 400 ppm this year
- Increased radiative forcing from 0.57 to 2.29 W/m^2 since industrialisation
- Result 0.5°C global average surface temperature rise
- + 0.5°C due to climate system inertia expected later this century

IPCC defines Carbon budget: **1000 Gt** total **C** emission to limit global average surface temperature rise to 2°C

- already spent **545 Gt C** (1750-2011)
- yearly **10 Gt C** emission (2012)

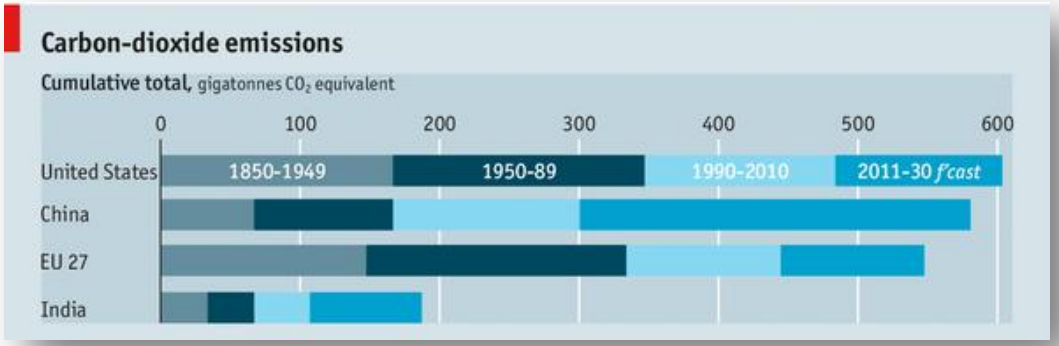
→ Business as usual: **2047 ±14yr**

→ Stabilisation scenario: **2069 ±18yr** (Mora et al., Nature Oct. 2013)

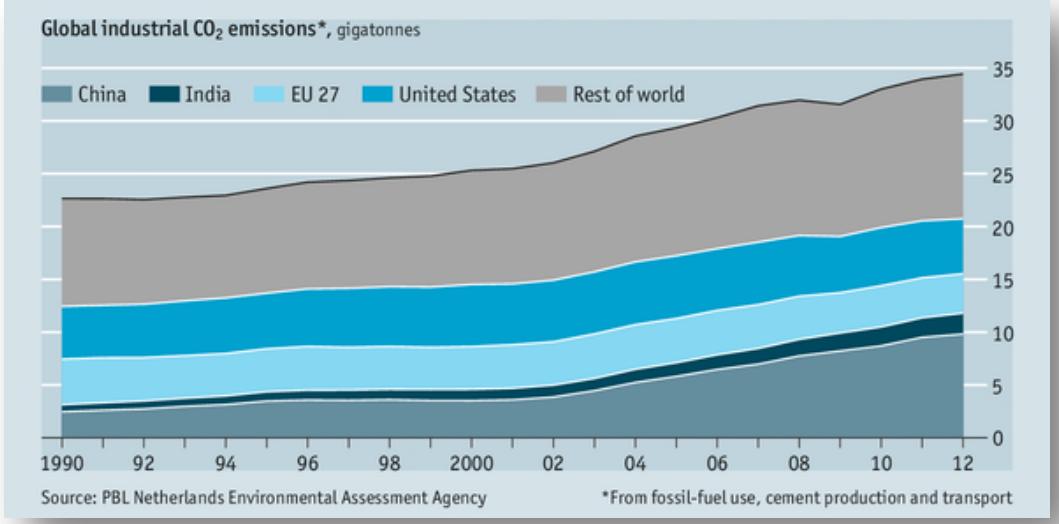
Time scale to dangerous climate change is 30 to 50 years

Climate Change is a Global Challenge

Cumulative CO_2 emissions US, China, EU, India



- **Bulk of emissions** so far by US and EU (1850 - 1989)
  - EU share is now ~13% and diminishing (-1.3% in 2012)



- Developing countries account for over half of **CO_2 emissions today**
  - India's emissions rose by over 7% in 2012

Yearly CO_2 emissions per country [$GtCO_2$]

Fossil Fuel reserves

Fossil fuels, albeit finite, are still relatively abundant in terms of world energy reserves:

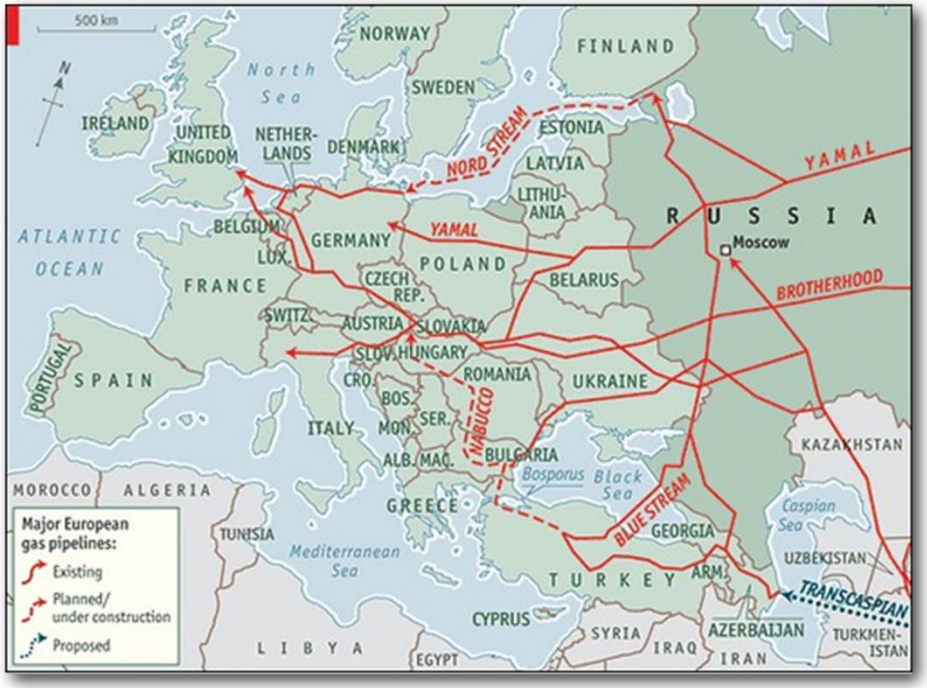
- Coal reserves 300 yrs (China)
- Gas expanded from 50 to 200 yrs due to fracking shale beds
- Oil demand has peaked in rich world
  - increased efficiency in petrol/diesel engines and emergence of hybrid and electric cars
  - switch to gas to power lorries, buses, ships and domestic/industrial heating systems

Time scale fossil fuel depletion is factor 10 larger

Not the driver for the energy transition!

Energy Security

- Ruled by geo-political factors, out of scope for physics
- Time scale uncertain, as recent events have shown
- Renewable Energy Sources are less geo-politically constrained, hence favour energy security



Source: Economist 4 April 2014

Outline CO_2 Neutral Fuels

Why - Sustainability

- Climate change
- Natural resources
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What - Renewable hydro-carbon based fuels

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- Recycling CO_2 emitted

→ Closing the carbon cycle

How - Renewable Energy (RE) driven conversion of feedstock H_2O/CO_2

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→ CO_2 neutral fuels

CO_2 Neutral Fuels

What are CO_2 neutral fuels?

- Bio-fuels
- Solar fuels
  - direct conversion solar photons into fuel (artificial leafs)
  - indirect: renewable electricity drives conversion feedstock H_2O/CO_2
- Both followed by carbon capture after use in order to close the carbon cycle

Bio-fuels: Exploiting the natural Carbon cycle

courtesy of dr. Thomas Haas

Syngas fermentation is the 3rd generation biotechnology

EVONIK INDUSTRIES

Generation	Raw Material	Bio Technology
1st gen	Plant oils Wheat Corn Sugar	Direct fermentation
2nd gen	Biomass residues from agricultures and forestry	Lignocellulose hydrolysis Integrated fermentation
3rd gen	Municipal waste Plant residues Industrial waste gases	Syngasfermentation

Bio-fuels: a limited option

- **1st generation bio-fuels**
  - 2007 US President Bush target 950 Mltr bio-fuel per year by 2011 (energy security)
  - 2008 Science: more GHG emitted by corn cultivation for ethanol than petrol
  - 2011 EPA reduced target to 30Ml/yr cellulosic ethanol and 57.7 Ml/yr corn ethanol

  food vs fuel debate
- **2nd generation bio-fuels**
  - Bio-mass with no nutritional value (agricultural waste, fast growing trees, shrubs/grasses)
  - woody cellulose into drop-in fuel: expensive to break-down and difficult to up-scale
  - Algae (10 to 100x more fuel per area)

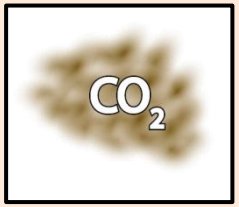
  However, US oil refineries 2500 Ml oil/day , 500 Ml bio-fuel requires 1 M Tonnes of bio-mass

  →Only certain areas in Brazil, Asia and US able to produce such amounts of bio-mass

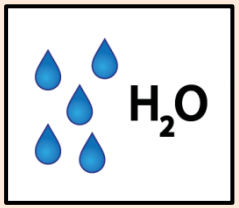
  flora vs fuel debate, ***there simply is not enough***
- **3rd generation bio-fuels**
  - Gasification of municipal waste to produce Syngas followed by Fischer-Tropsch ethanol
  - Pyrolysis (no oxygen) for direct conversion into oils

Solar Fuels: Mimicking natural Carbon cycle

Capture
direct air
point source



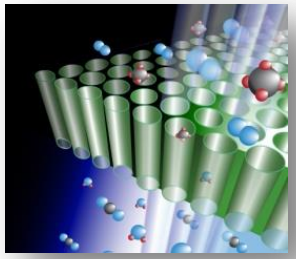
Purification

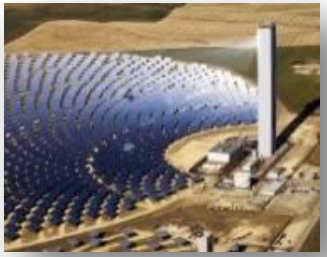


Direct conversion

Photo-chemical
0.2–6%

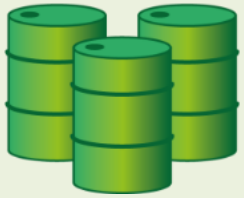
Thermo-catalytic
2–3 %





CO_2-neutral fuels

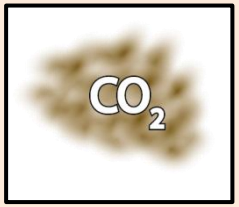
H_2 CO



CH_4 CH_3OH

Solar Fuels: Mimicking natural Carbon cycle

Capture
direct air
point source



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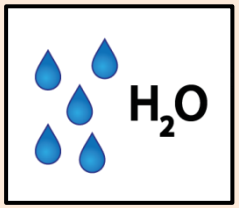


Indirect conversion

PV
25%

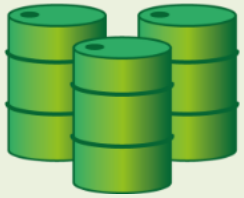
Wind
30%

Electrolysis
70–80%

Plasmolysis
>50%

CO_2-neutral fuels

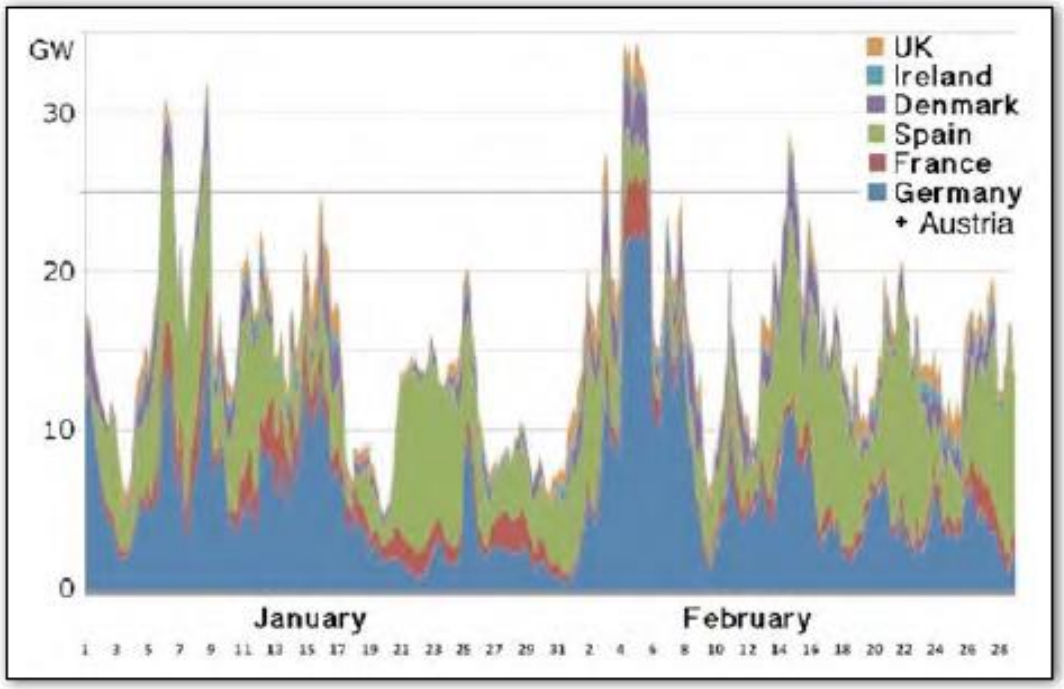
H_2 CO



CH_4 CH_3OH

Overall energy efficiency: 18–20%

Renewable energy: the need for storage



Wind power over Western Europe Jan-Feb 2011
Peaks and troughs are correlated
Bobin, Eur. Phys. News 44 (2013)

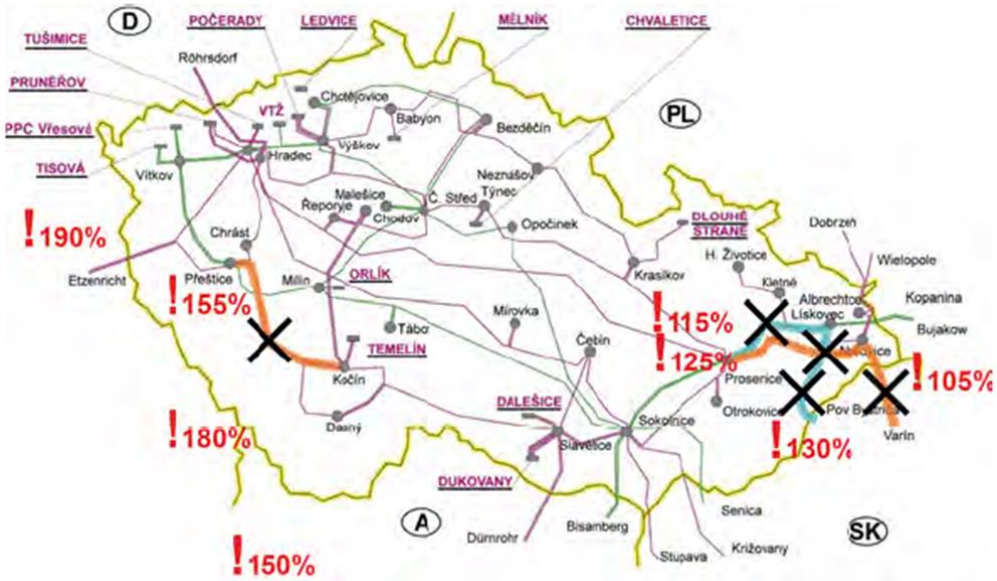
Energy storage needed to enhance the capacity factor of renewables
(Installed wind power capacity Europe 96 GW in 2011)

Smart grids and ICT will play an important role in future energy system, but can not bridge gap of several days of calm or strong wind

North –South electrical power flow

Electrical power flow in Central and Eastern EU

- Generation: main locations of wind and solar in North / Middle of EU
- Surplus wind power diverted to East EU



Stability issues for Electricity Grid

X = tripping of lines in Nov 2011-Feb 2012

! = congested lines, flow in % of safety limit

Source: Z. Boldiš, Eur. Phys. News 44 (2013)

Renewable Energy System (RES)

Wind, PV, concentrated solar, hydro, tidal, wave, geo-thermal, are characterised by:

ill-matched Supply and Demand both geo-graphically and temporarily

this limits large scale implementation of RES (fraction RES > 20-30%)

When directed at electricity production, intermittent peak power flow requires:

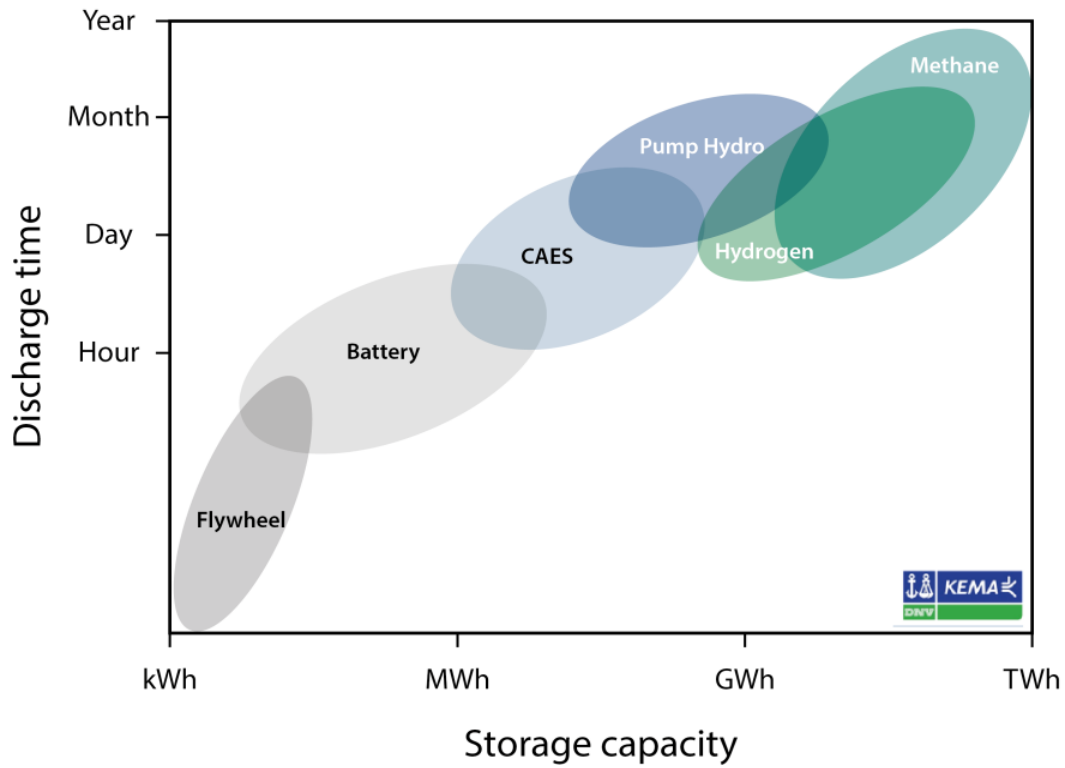
- over-capacity on transmission grid (capital investment)
- Wind power curtailment (Spain lost M€ 90 in 2012)
- Cross border export surplus wind electricity at negative price (Denmark, NL)
- Over capacity RE needed to provide base load (present capacity factor ~15%)
- Back-up power needed to cover several days/weeks of RE undersupply

Renewable Energy System must include energy storage element

Energy Storage options

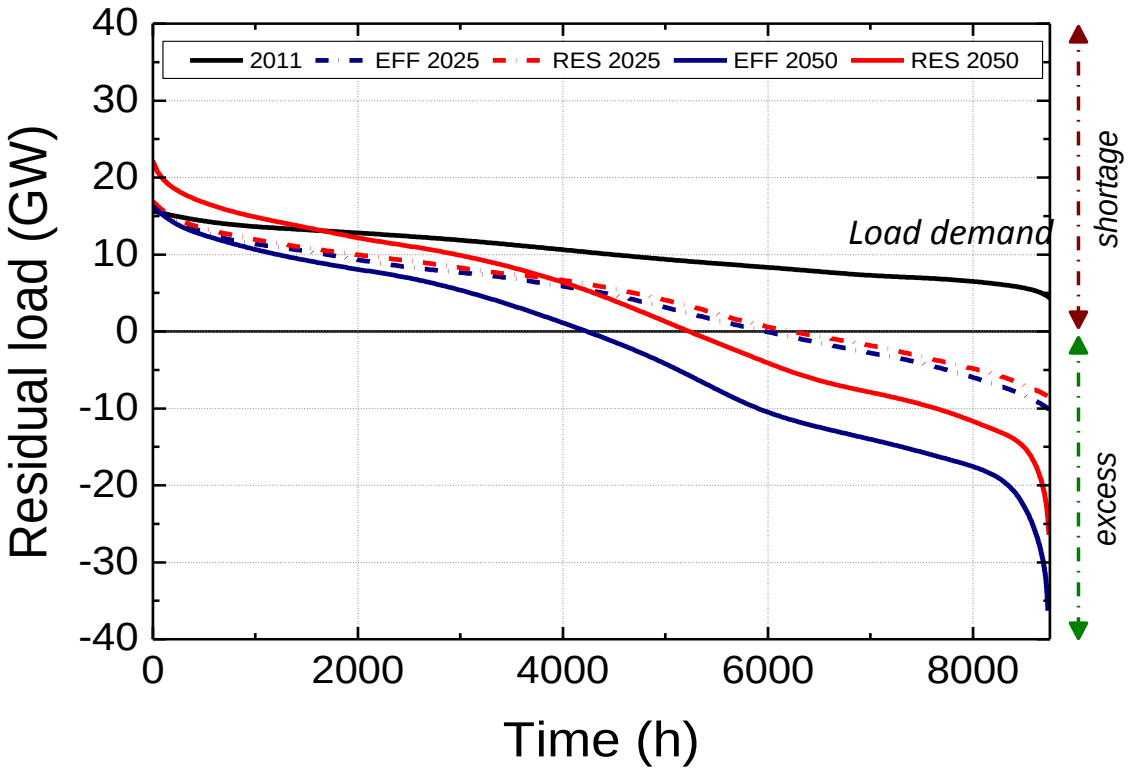
Energy Storage capacity needed at EU level to bridge **1 day** electrical power demand **~10TWh**
To cover several days to weeks of energy demand/supply:

- Long-term, large scale storage in chemical bonds (H_2, hydro-carbons)



Power discharge duration curve for various forms of electricity storage

Storage of Surplus Renewable Energy



The various scenarios show how load is relieved by introducing Renewable Energy (RES) and Energy Efficiency (EFF) in 2025 and 2050.

Surplus RE

Germany

- 2035: 34.5 TWh
- 2050: 160-260 TWh

Netherlands

- 2025: 1.5TWh (12GW wind)
- 2050: 30-55TWh

In order to balance supply and demand, these curves determine **energy storage** capacity required.
(Source ECN)

Transport: gas >10x cheaper than electricity

Comparison of specific investment costs for transport of energy from the Netherlands to the United Kingdom by:

- a high-voltage transmission line
- gas pipe line

	Power: BritNed	Gas: BBL
Length	260 km	230 km
Investment	600 M€	500 M€
Capacity	1 GW	20 GW
Specific investment costs	€ 230 /kW/100km	€ 11 /kW/100km

Source: GasUnie, the Netherlands.

Nord Stream gas pipeline: € 9/kW/100km (Russia to Europe via Baltic)

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→ Closing the carbon cycle

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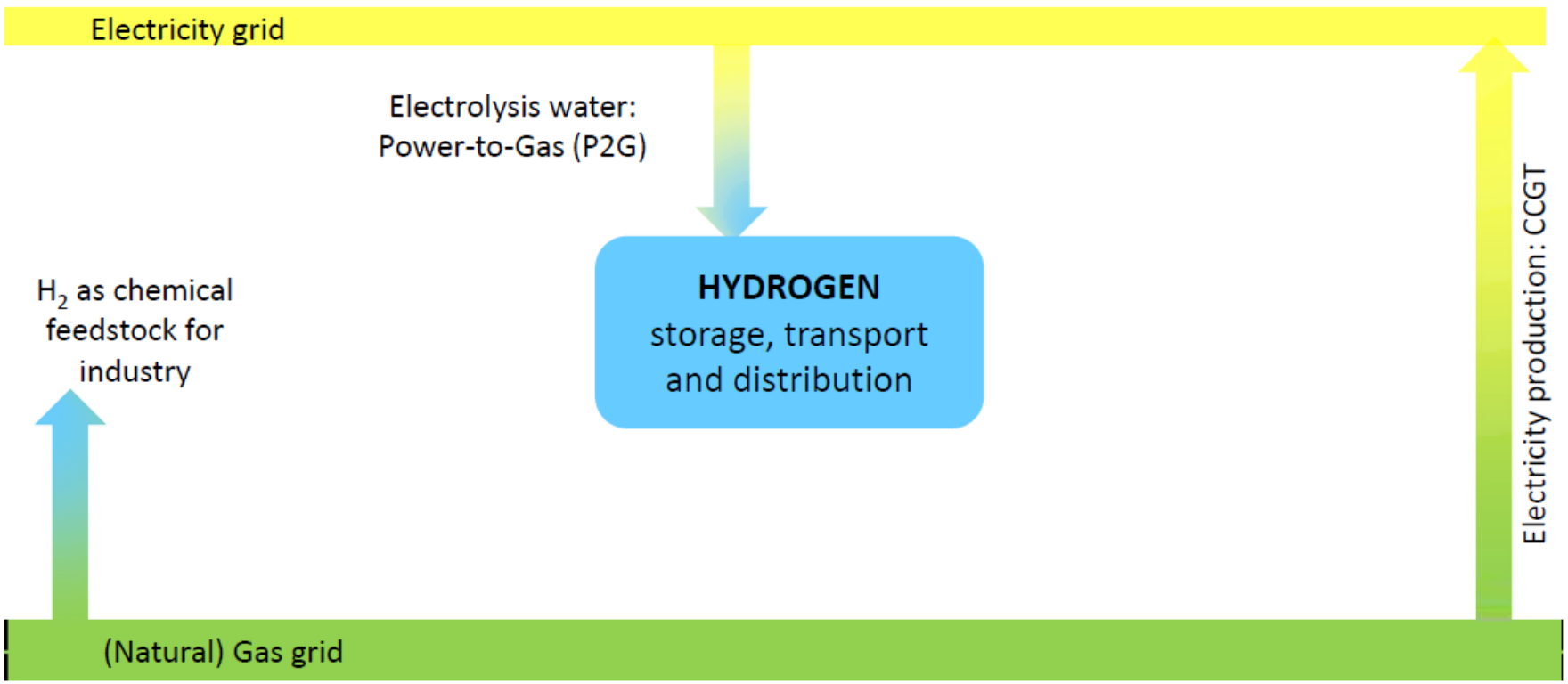
→ CO_2 neutral fuels

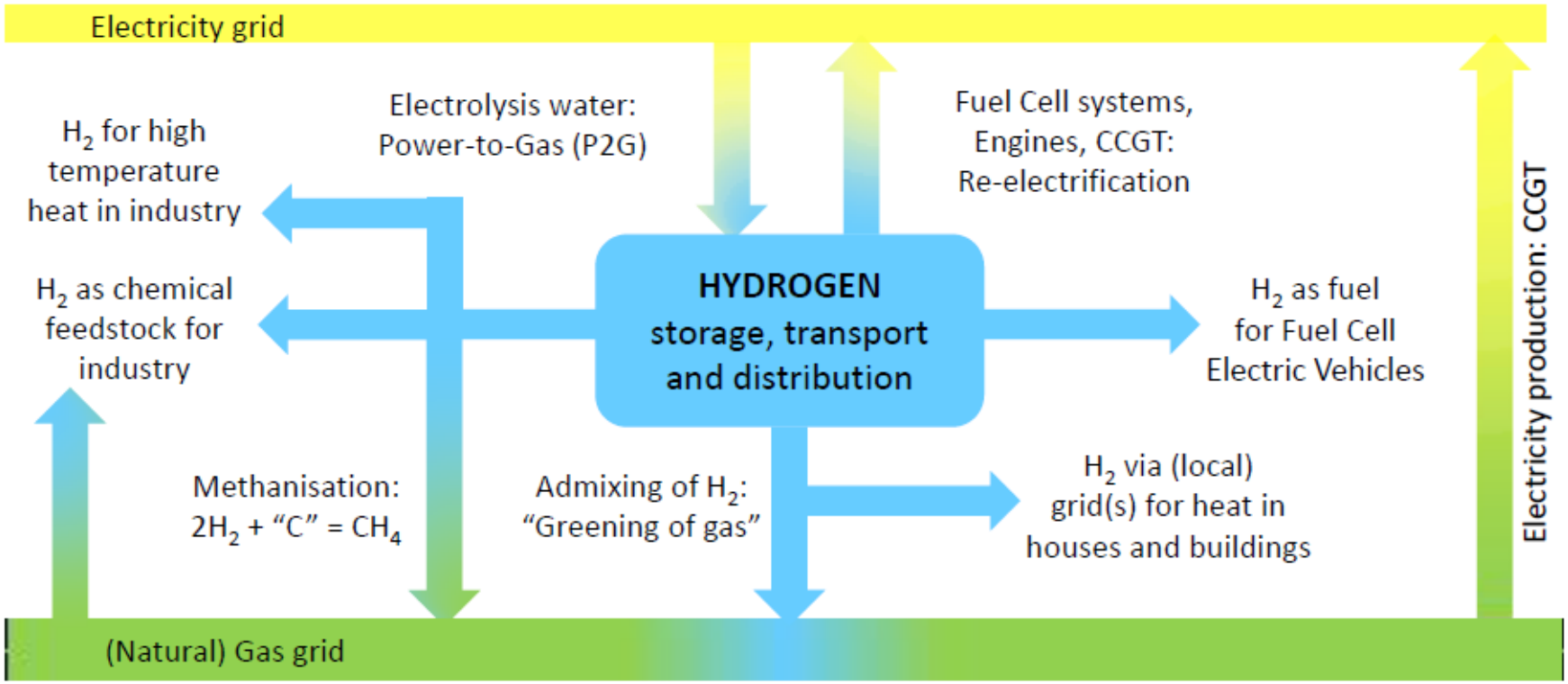
Electrical Power to Hydrogen

carbon free energy system → no CO_2 emission



source ECN

Hydrogen based energy system

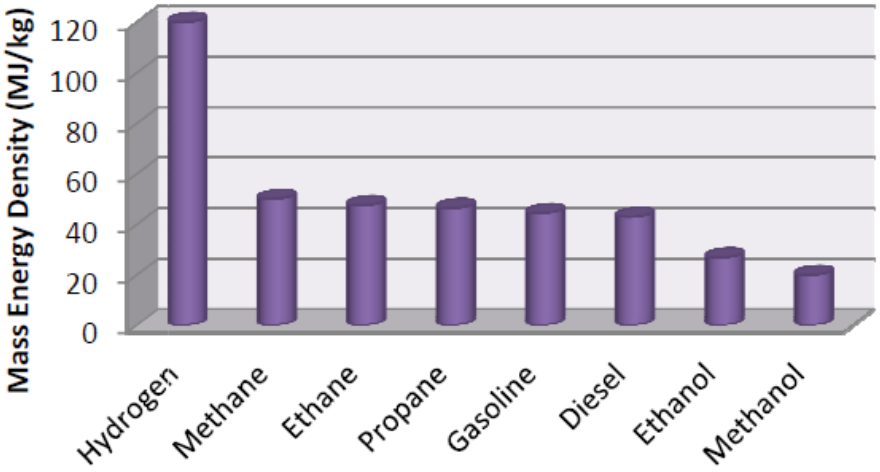


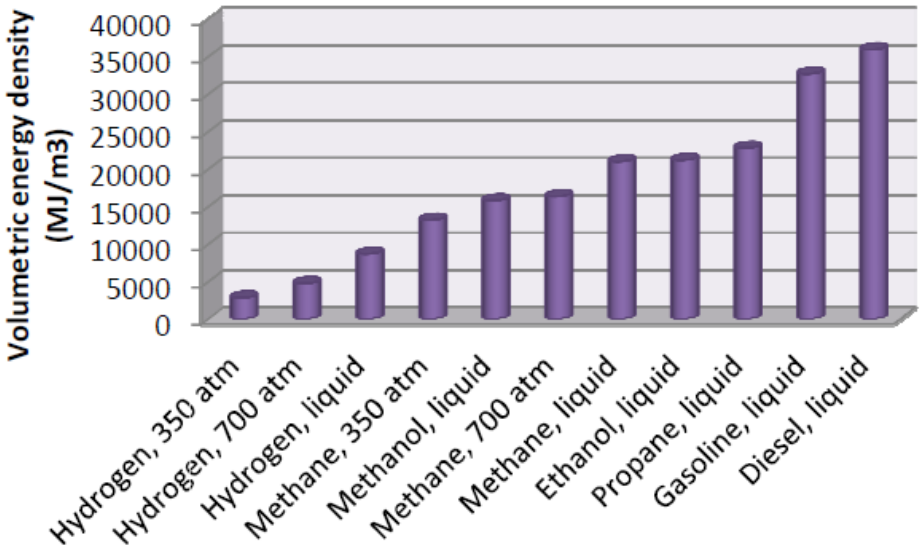
Allowed admixing of hydrogen in NL gas net < 0.02%, D < 10% under certain conditions

source ECN

Characteristics of Hydrogen as a fuel

- Low density (0.9 kg/m^3 at 0˚C and 1 bar)
  - For practical application: either compress (700 bar) or liquefy (liquid at 20K with density 70.8 kg/m^3) or bind (metal hydrides). However, energy penalty!
  - Highly diffusive and buoyant (leaks x10 N_2)
  - Chemically corrosive under pressure and temperature
- Low volumetric energy density
  - Cost and safety for automotive application
- Lack of fuel infrastructure limits application



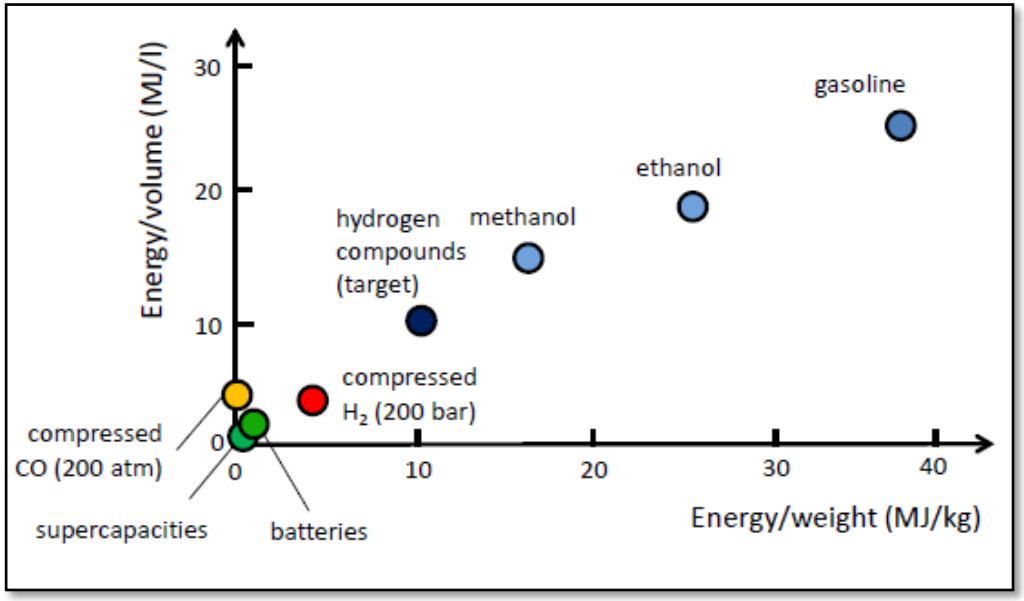


Source: EERA Joint Program Energy Storage (2013)

Hydrogen powered airplane

Source: Peter Styring, Univ Sheffield

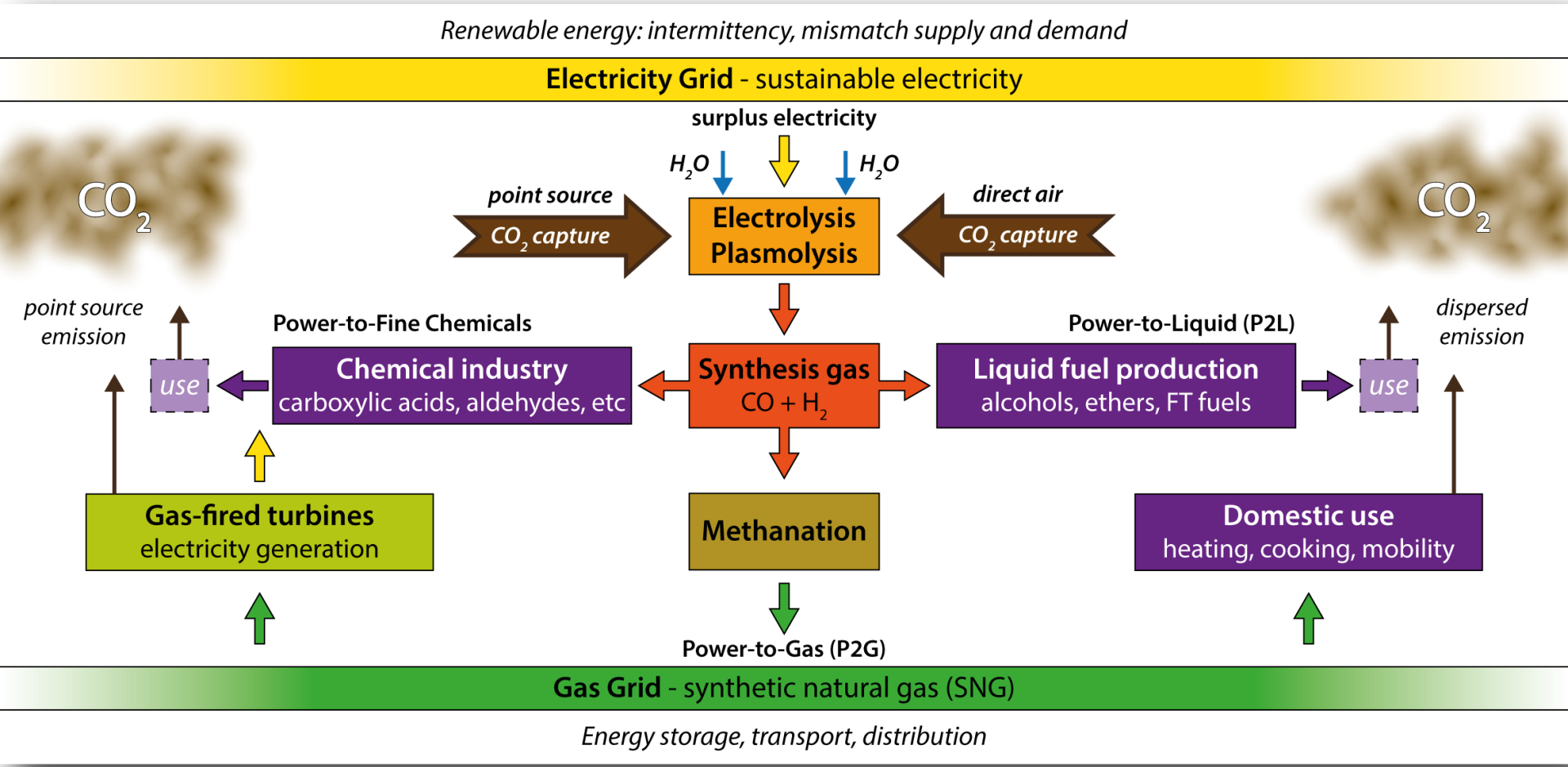
Energy storage by hydro-carbons



- **Ideal for energy storage**
  - High energy density per volume and per mass
- Use of **existing infrastructure**
  - Transport, distribution and use requires no new investment or technology
- Integration of electricity and gas fuel system: **Power-to-Gas (P2G)**
  - Large storage capacity in existing gas grid (NL gas grid ~ 552TWh)
- Integration of electricity and liquid fuel system: **Power-to-Liquid (P2L)**

Electrical Power to hydro-carbons

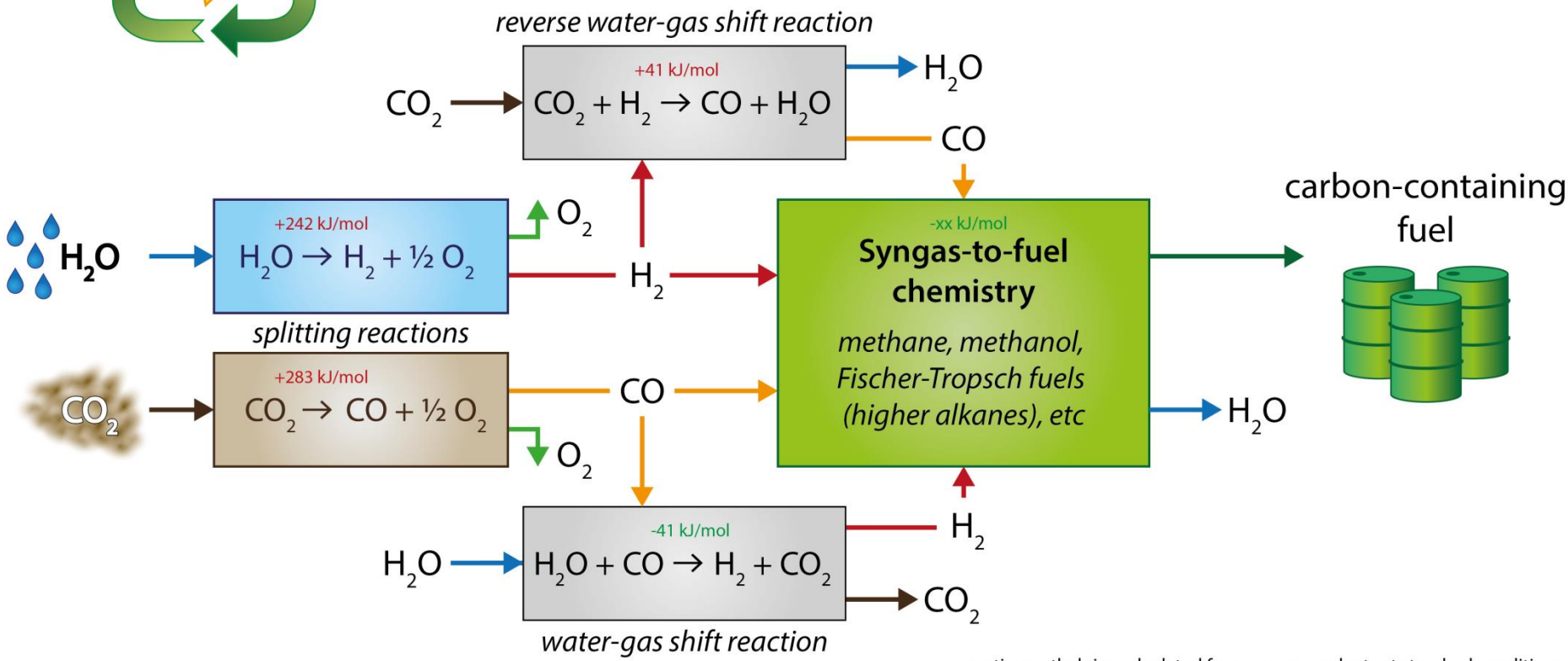
- **Closed carbon cycle based on synthetic hydro-carbon fuels**



From H_2O and CO_2 to CO_2-neutral fuels

sustainable energy

- H_2 generation by electrolysis >6 €/kg H_2
  (steam reformation fossil fuel <1 €/kg H_2)
- CO_2 capture 40 €/tonne point source;
  (direct air capture 400 €/tonne)



reaction enthalpies calculated for gaseous products at standard conditions

Syngas-to-fuels chemistry

- **Methane**:
  $CO + 3\ H_2 \rightarrow CH_4 + H_2O$ $\Delta H_{298K} = -206\ kJ \bullet mol^{-1}$ exothermic
- **Methanol**:
  $CO + 2\ H_2 \rightarrow CH_3OH$ $\Delta H_{298K} = -\ 92\ kJ \bullet mol^{-1}$ exothermic
- **Alkanes** (Fischer-Tropsch, n>1):
  $(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$

Commercial process, however development needed in:

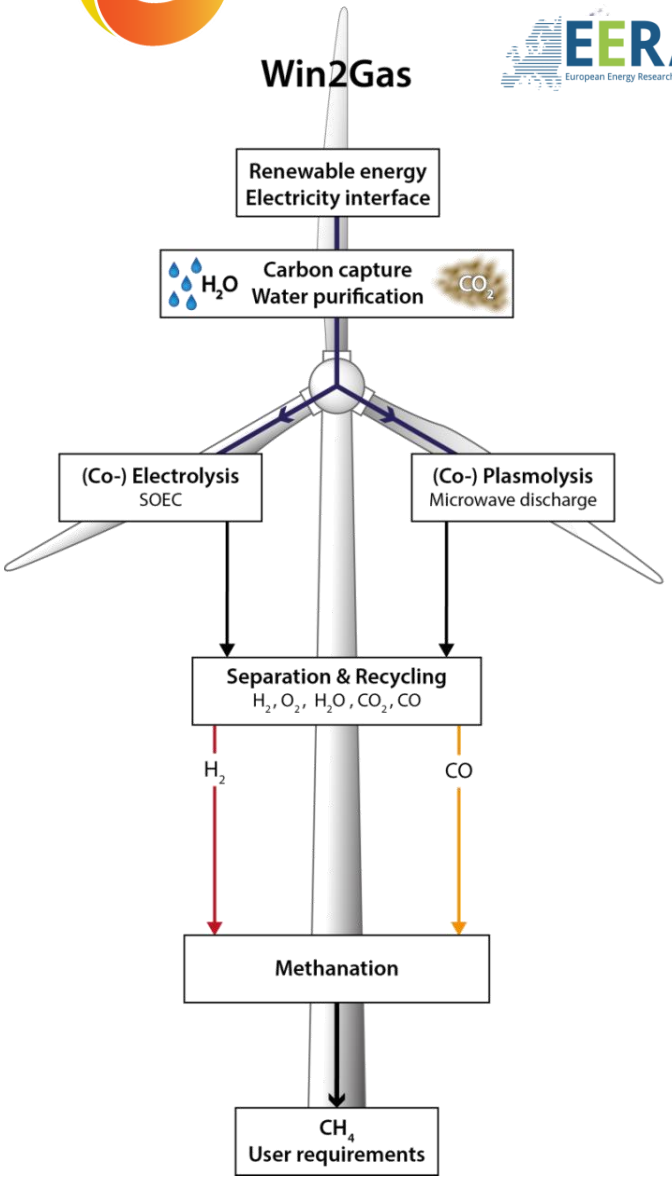
- Integrated system: splitting, separation, processing into fuel
- Main issue catalysts: stability, low temperature/pressure, high selectivity

Catalysis: reactants absorb on catalyst surface, rearrange and combine into product.

CO bond stays intact = methanol, or broken = higher alkane

- Methane: Ni-CeO_2 tandem nano-structured catalyst (T= 150-250 ˚C, p= 10-30 bar)
- Methanol: Cu catalyst on ZrO_2 surface supported by Al_2O_3 (T= 220-275˚C, p= 50-100 bar)
- Fischer-Tropsch: Co, Fe, Ru based catalyst (T= 150-300 ˚C, p= 1-30 bar)

Concept wind to gas energy system



- End-to-end system
  - Input: wind electricity (surplus)
  - Output: feed CH_4 into gas grid (P2G)
- Research challenges individual elements
  - Carbon capture
    - Novel materials for direct air capture
  - Energy efficiency splitting of H_2O and CO_2
    - (Co-)Electrolysis: SOEC
    - Plasmolysis: microwave
  - Separation
  - Methanation
- System integration Wind Energy to Gas
  - Requirements:
    - Rapid response to intermittency (surplus electricity)
    - Scalability to MW (high energy density)
    - Use of abundant materials

End of lecture 1

Thank you for your attention!

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