



**DIFFER**

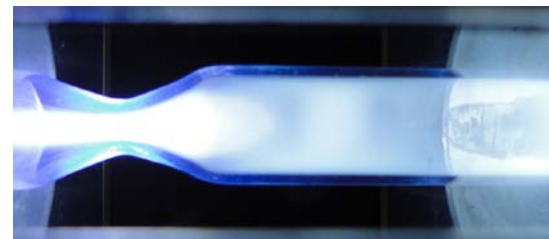
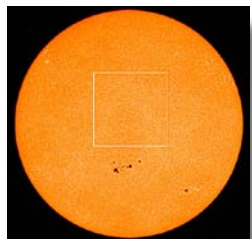
Dutch Institute for  
Fundamental Energy Research

Solar PV 2050 Power Lab -1  
Utrecht 17 maart 2014

# Energy storage in CO<sub>2</sub> neutral fuels: a plasma perspective

**Richard van de Sanden**

**Dutch Institute for Fundamental Energy Research &  
Eindhoven University of Technology, Department of Applied Physics,  
P.O.Box 1207, 3430 BE Nieuwegein, The Netherlands**



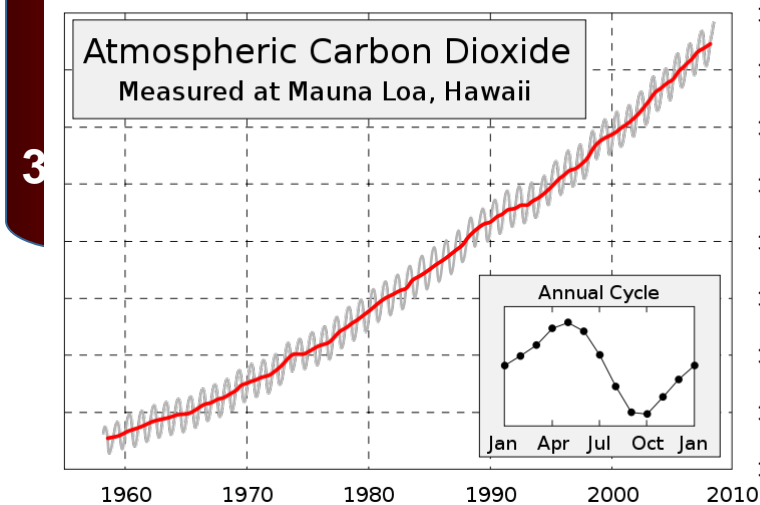


# Energy for the 21<sup>st</sup> century



- Increasing world population and higher standard of living
- In 2100: energy demand 4x higher
- **Strong increase of CO<sub>2</sub> levels**
- Small contribution renewable: >4%
- Strong increase sustainable necessary

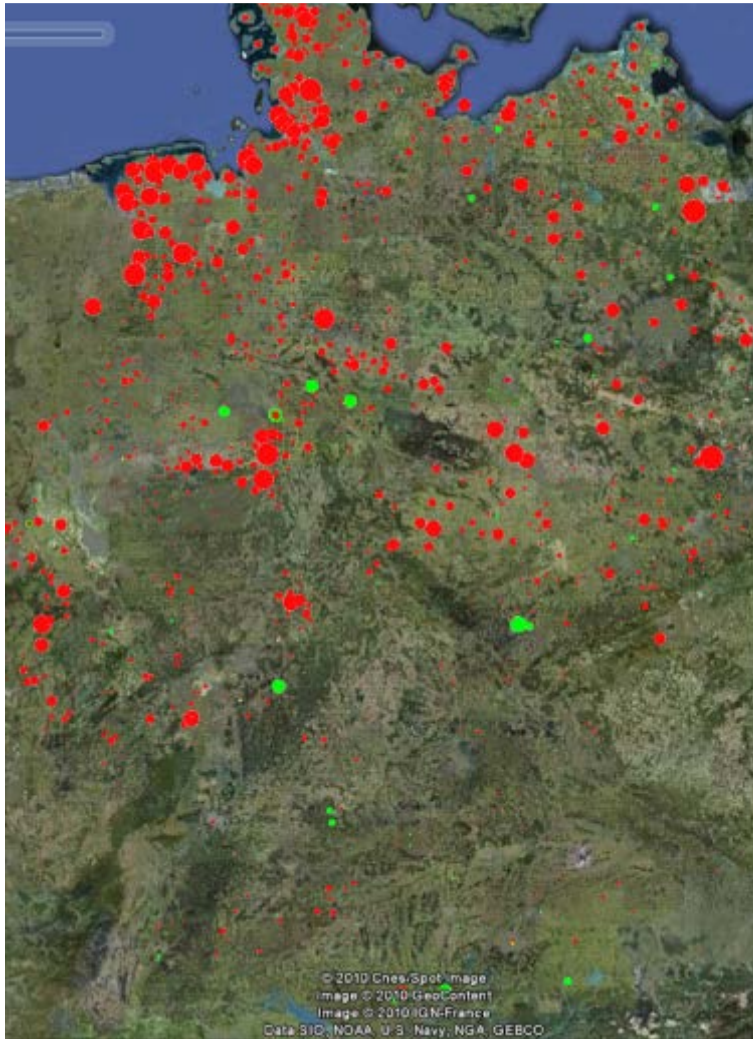
Thermal  
0,11%



Urgency of a renewable energy infrastructure is climate change and CO<sub>2</sub> mitigation;  
**Not** the availability of fossil fuels

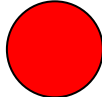
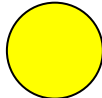
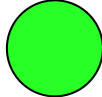


# Renewable energy in Germany



Total capacity of renewables  
*(End 2000)*

~ 30,000 installations

-  *Wind energy*
-  *PV*
-  *Biomass*

*The circle diameter is proportional  
to the electrical capacity*

Sources: 50HertzT, TenneT, Amprion, TransnetBW, Elia group



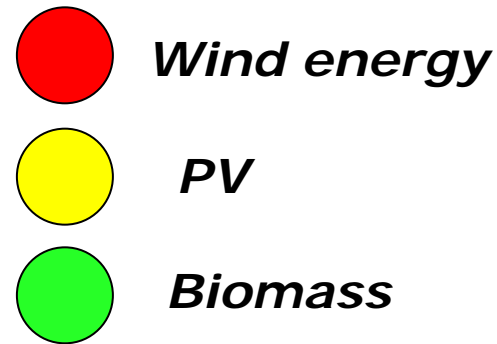


# Renewable energy in Germany



Total capacity of renewables  
*(End 2005)*

~ 221,000 installations



*The circle diameter is proportional  
to the electrical capacity*

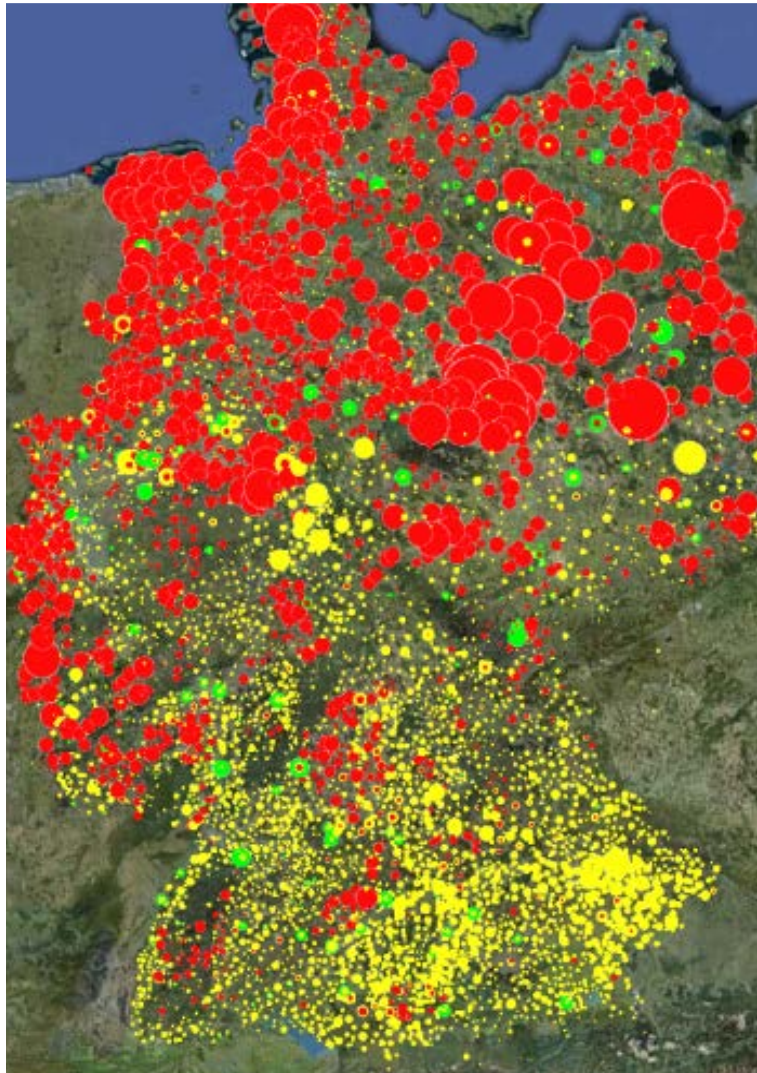
Sources: 50HertzT, TenneT, Amprion, TransnetBW, Elia group

Courtesy Daniel Dobbeni (Elia group)



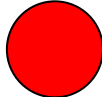
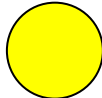
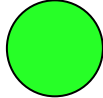


# Renewable energy in Germany



Total capacity of renewables  
*(End 2010)*

~ 750,000 installations

-  *Wind energy*
-  *PV*
-  *Biomass*

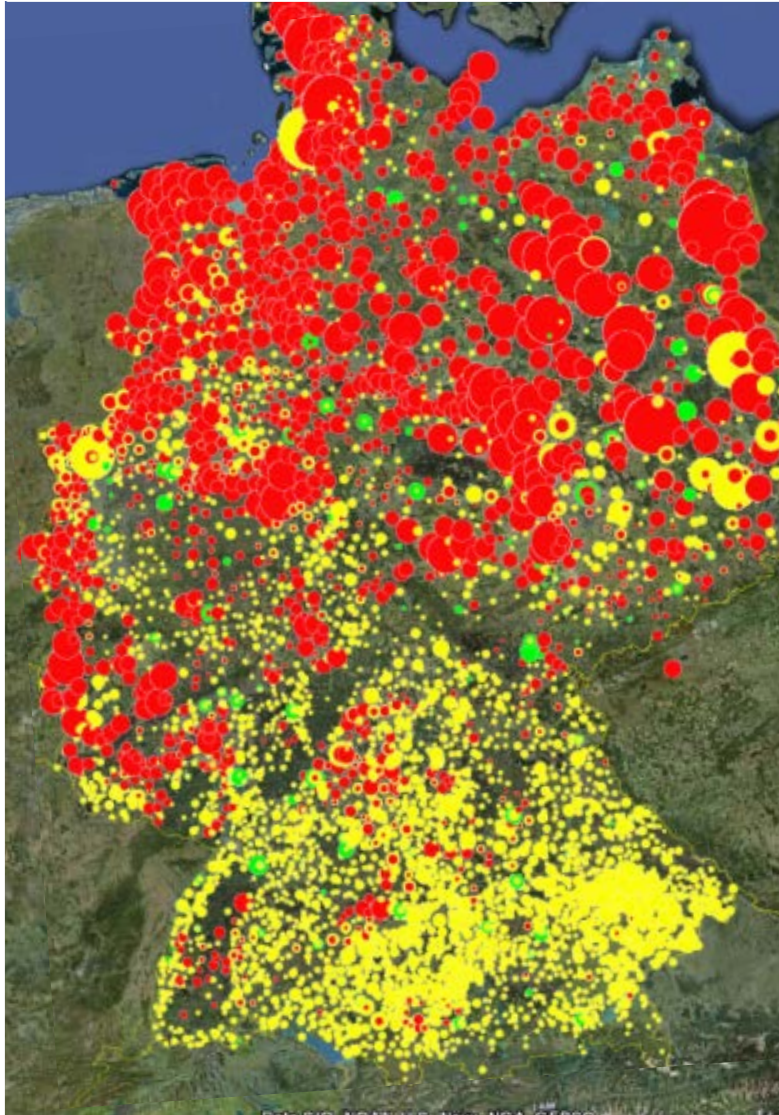
*The circle diameter is proportional  
to the electrical capacity*

Sources: 50HertzT, TenneT, Amprion, TransnetBW, Elia group

Courtesy Daniel Dobbeni (Elia group)

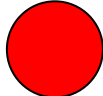
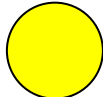
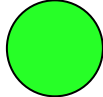


# Renewable energy in Germany



Total capacity of renewables  
*(End 2012)*

~ 1,300,000 installations

-  *Wind energy*
-  *PV*
-  *Biomass*

*The circle diameter is proportional  
to the electrical capacity*

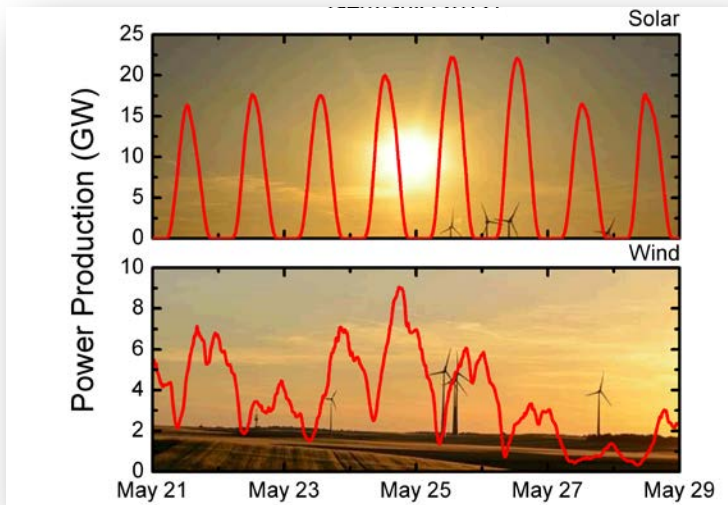
Sources: 50HertzT, TenneT, Amprion, TransnetBW, Elia group

Courtesy Daniel Dobbeni (Elia group)



# However.....

German solar and wind energy

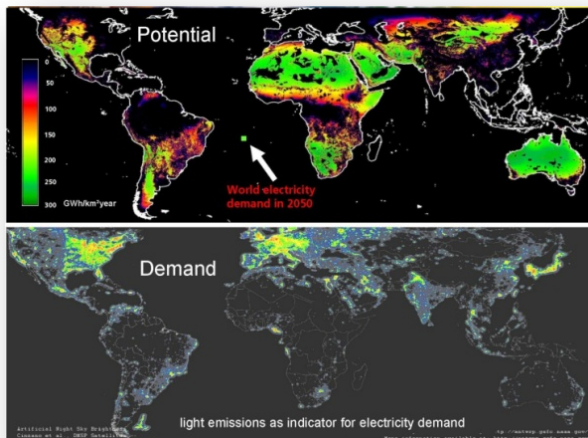


Sustainable power generation is **booming** but it is **inhomogeneous** and **intermittent**

with **time-scales** ranging from minutes to months

most **renewables** generate **electricity**

**Transport fuels** remain **necessary**



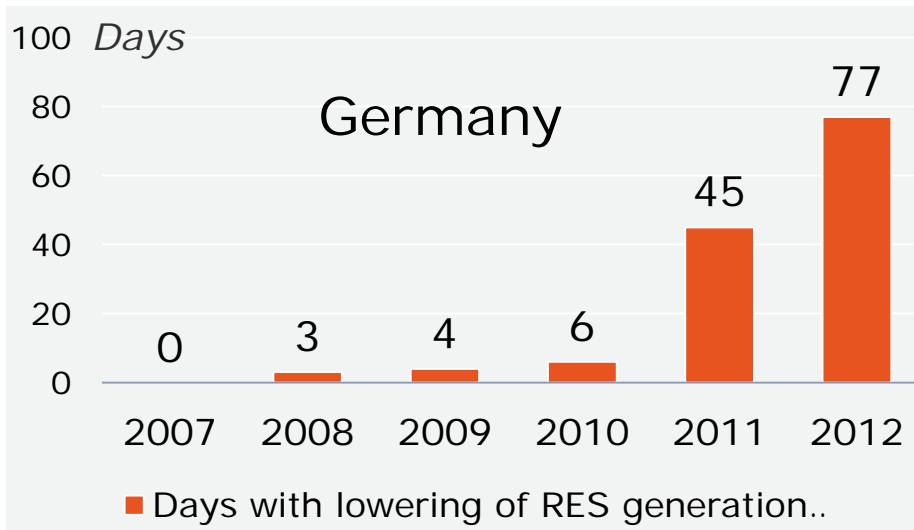
**Mismatch between supply and demand**

**Lack of system approach**



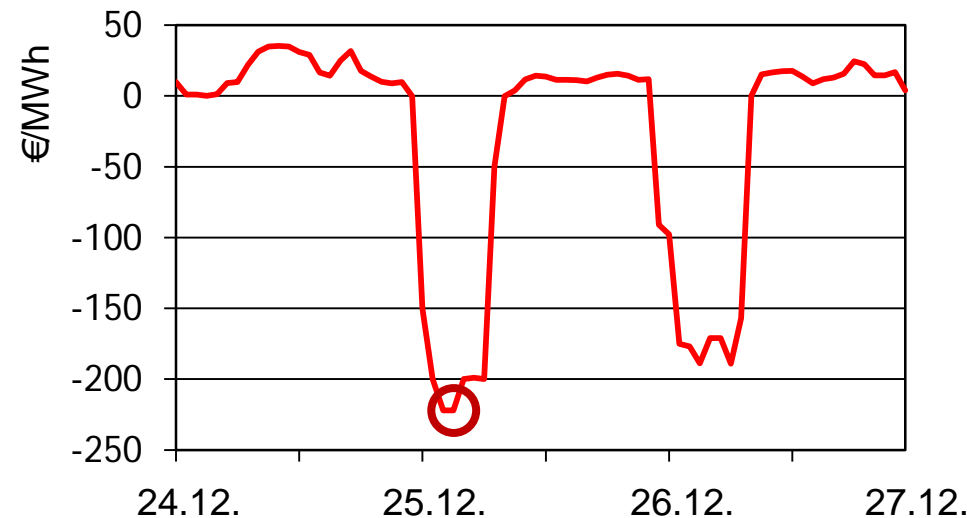


# Large scale deployment of RES



Not only Germany: Spain lost 90 M€ due to wind power curtailment

## 24th to 26th December 2012



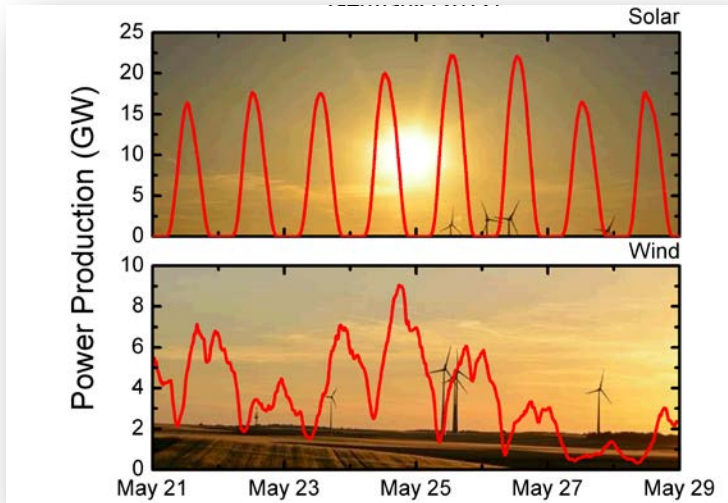
Min. market price: - 221,99 €/MWh

19 (out of 72) hrs with negative prices



# However.....

German solar and wind energy

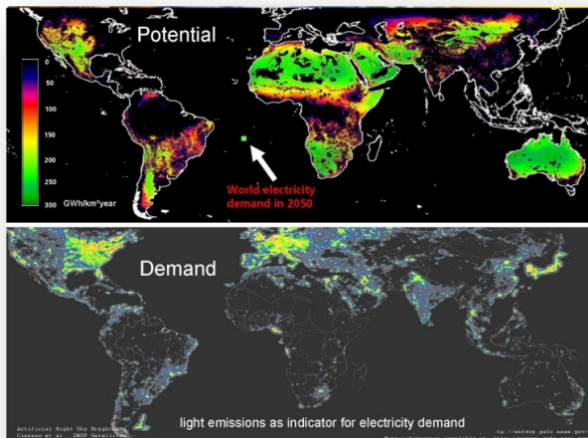


Sustainable power generation is **booming** but it is **inhomogeneous** and **intermittent**

with **time-scales** ranging from minutes to months

most **renewables** generate **electricity**

Transport fuels remain **necessary**



# Solution:

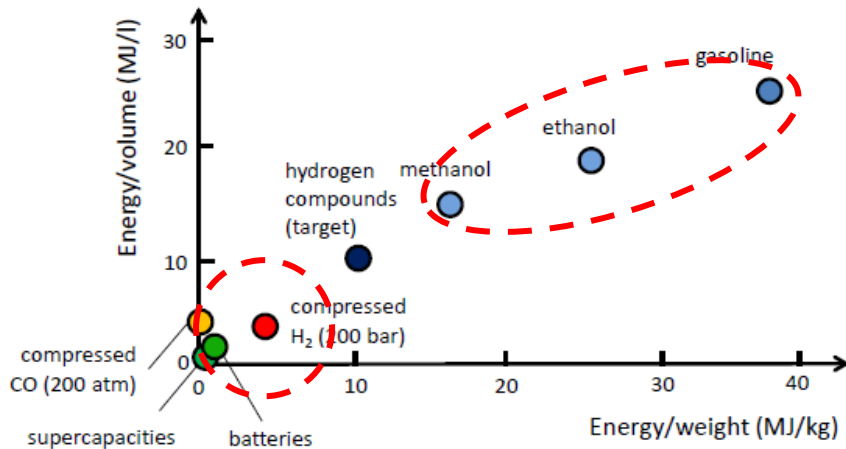
# Energy storage



# RES infrastructure - storage needed

## Storing energy:

- mechanical
- electrical
- electro-chemical
- chemical



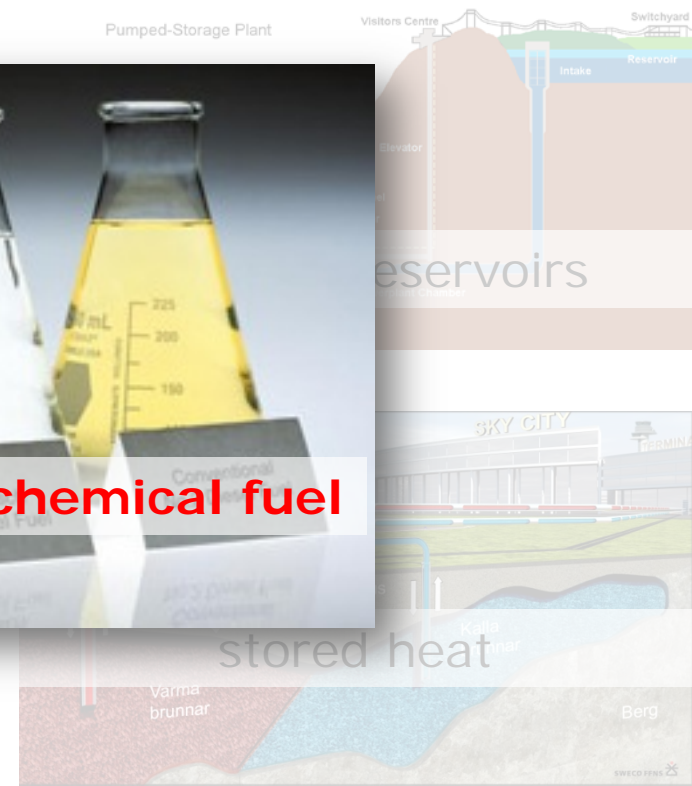
chemical



Artificial chemical fuel



batteries



reservoirs

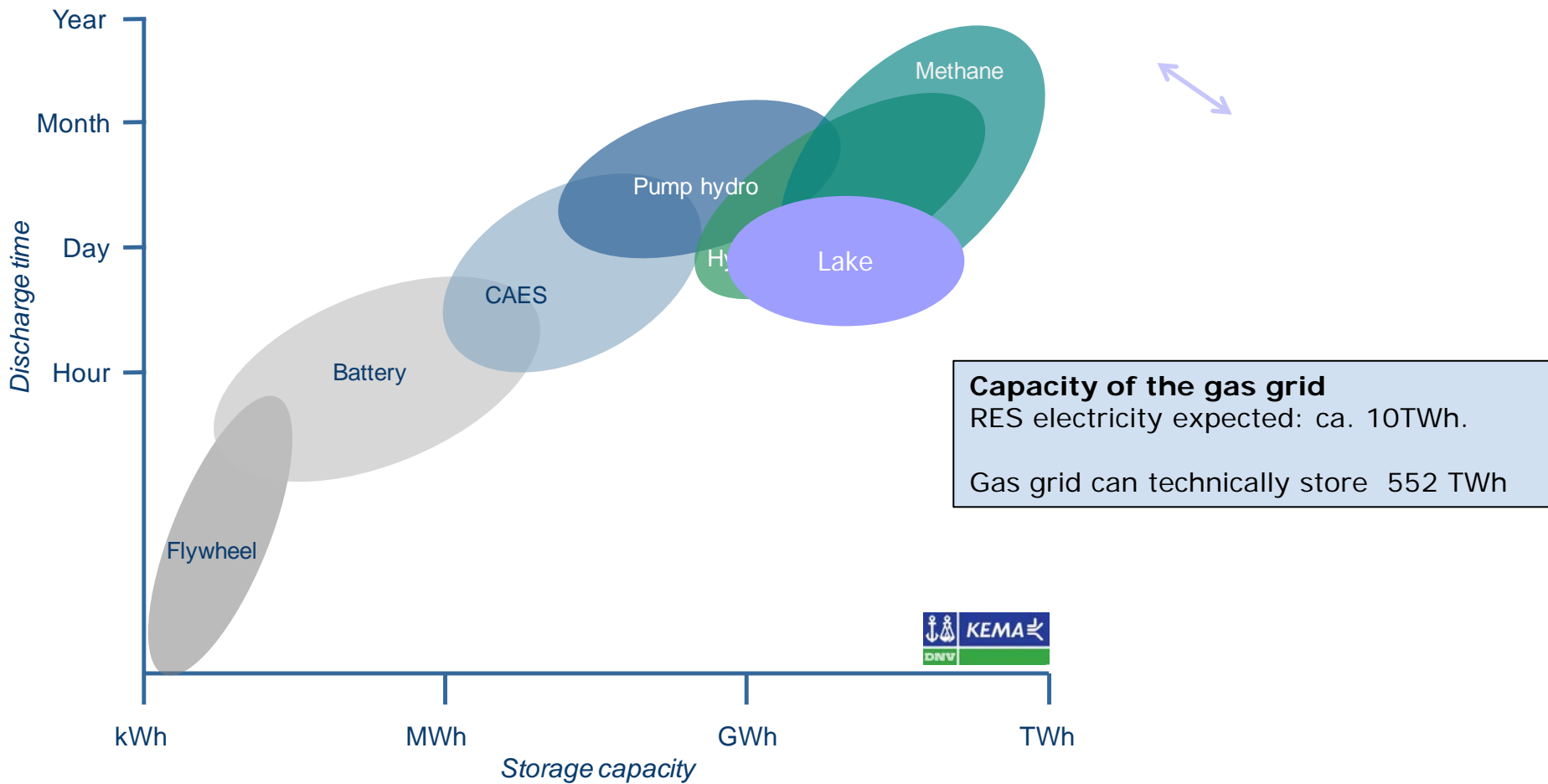
stored heat

Berg



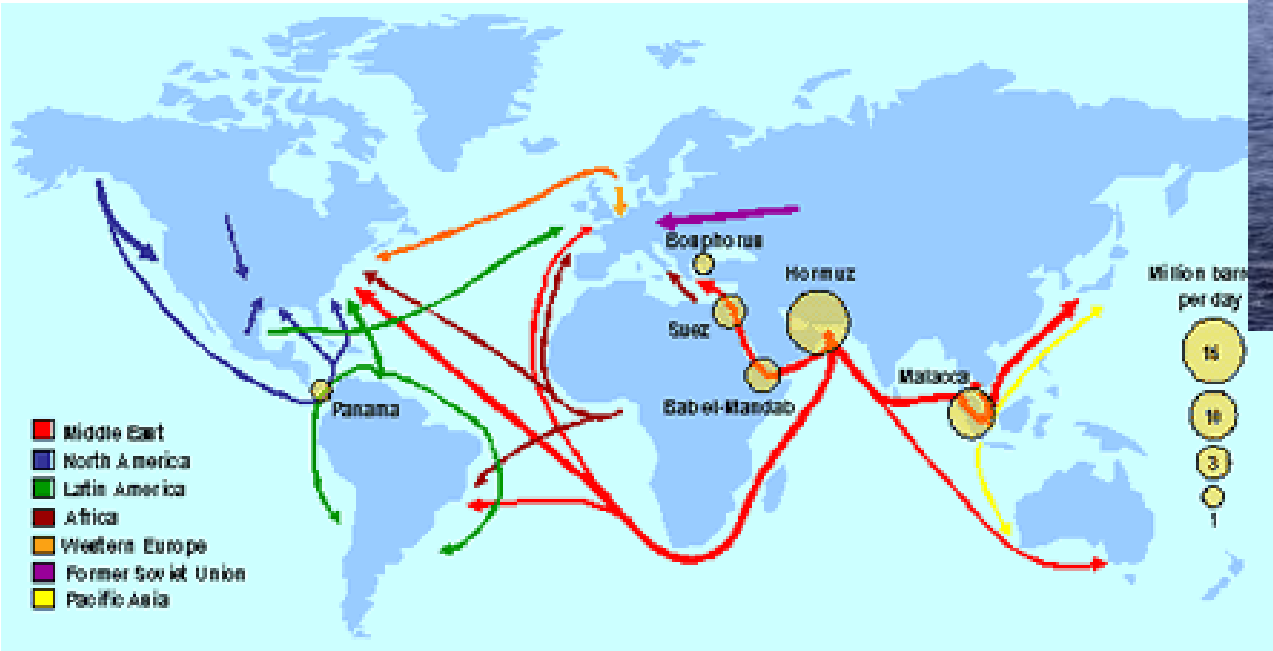


# Options to store energy





# Storing and Transport of Energy



Presently: 85% of the global energy is transported by fuels\*

Global energy infrastructure is based up on transporting liquids

\*Energy transport by gas is cheaper than by electricity per kWh (factor 2-20)



# Vision: CO<sub>2</sub> neutral energy infrastructure

- Large potential to contribute to a CO<sub>2</sub> neutral energy infrastructure
- Storage and transport of sustainable energy in chemical bonds (hydrocarbons): solution close to present infrastructure; mobility and stationary
- Large efforts world wide on Solar Fuels:



Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons

Catalysis Today 148 (2009) 191–205

Somnath C. Roy,<sup>1</sup> Oomma Department of Electrical Engineering, and contributed equally to this work.



Contents lists available at ScienceDirect

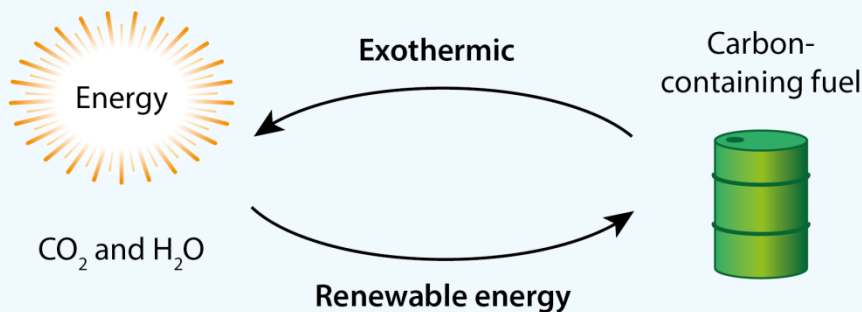
Catalysis Today

journal homepage: [www.elsevier.com/locate/catto](http://www.elsevier.com/locate/catto)

RE



## CO<sub>2</sub>-neutral fuels



Hydrocarbon fuels are most important source due to their ready availability, and high energy density (gasoline). In the United States hydrocarbon fuels (petroleum, natural gas, and coal) provided more than

Opportu

Gabriele Ce

\* Dipartimento di CI

\* CAPE (INSTM Lab

THE JOURNAL OF  
PHYSICAL CHEMISTRY  
Letters

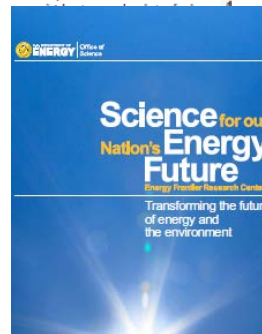
The Emerging Technology of Solar Fuels



**Solar energy conversion**

George W. Crabtree and Nathan S. Lewis

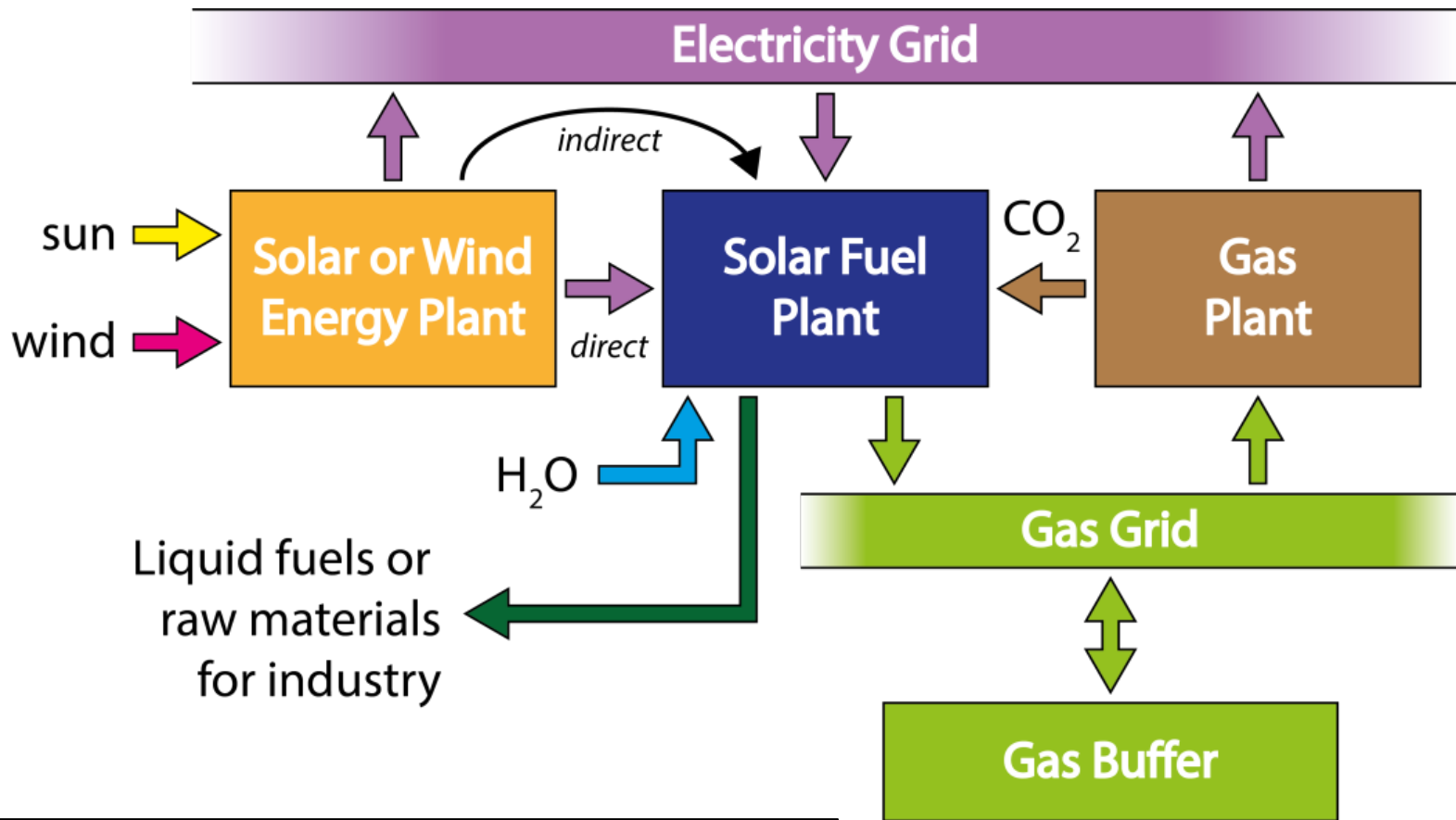
If solar energy is to become a practical alternative to fossil fuels, we must convert photons into electricity, fuel, and heat. The need for better conversion force behind many recent developments in biology, materials, and especially







# Vision: CO<sub>2</sub> neutral energy infrastructure

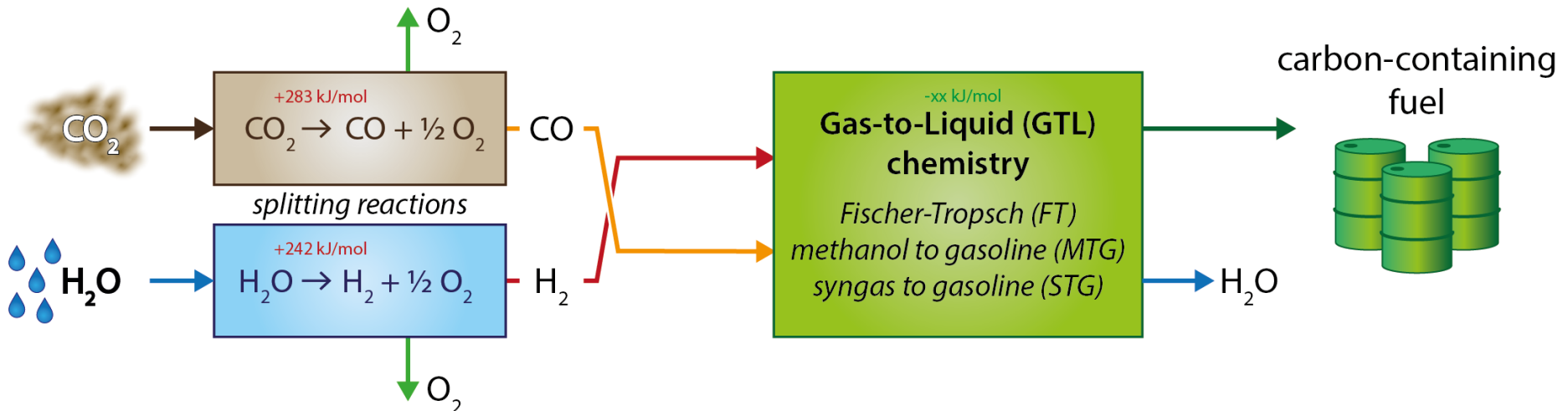


This vision includes CO<sub>2</sub> capture and re-use by means of direct air capture (DAC) or capture at point sources



# Full chain of solar (=CO<sub>2</sub> neutral) fuels

renewable energy

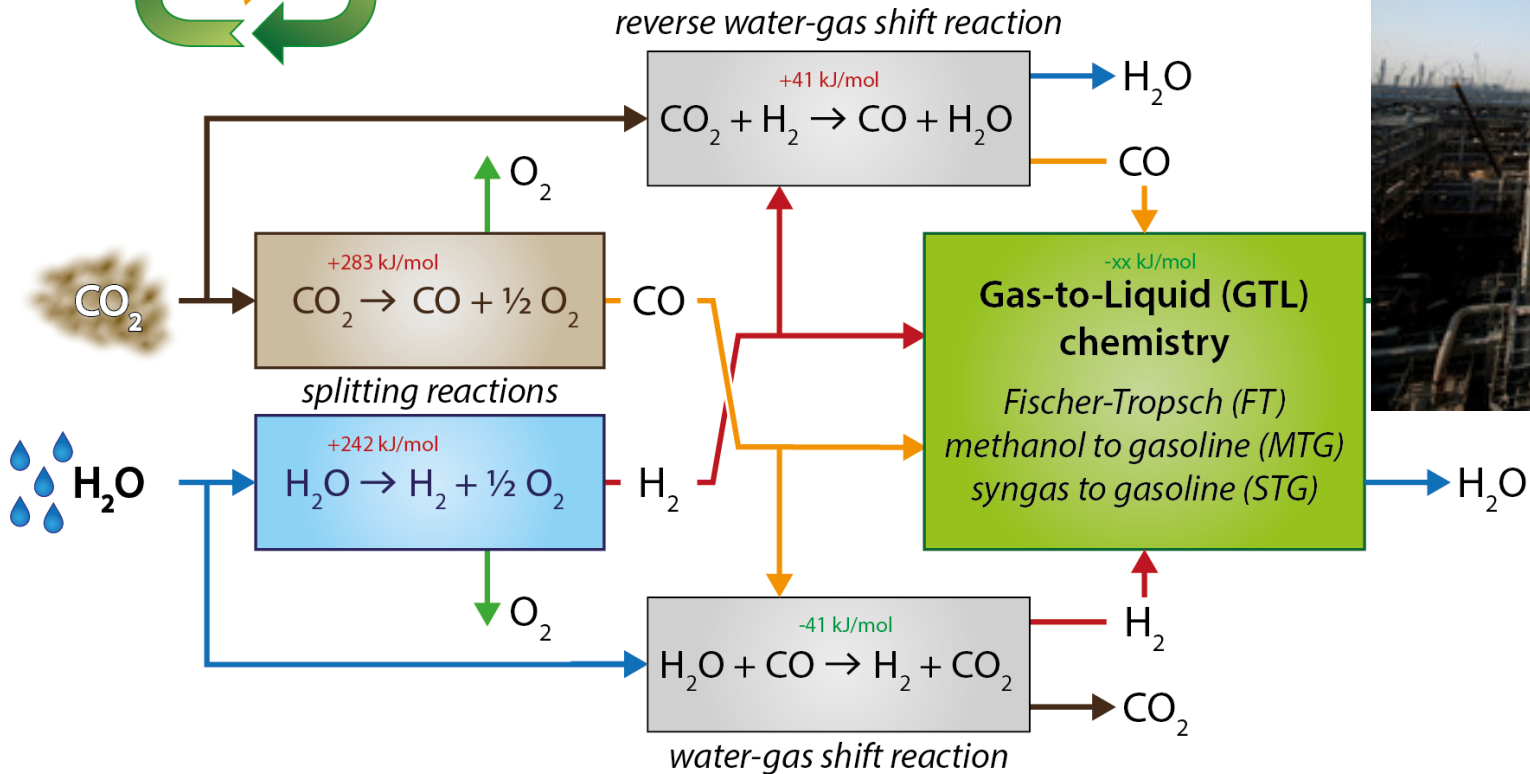


reaction enthalpies calculated for gaseous products at standard conditions



# Full chain of solar (=CO<sub>2</sub> neutral) fuels

renewable energy



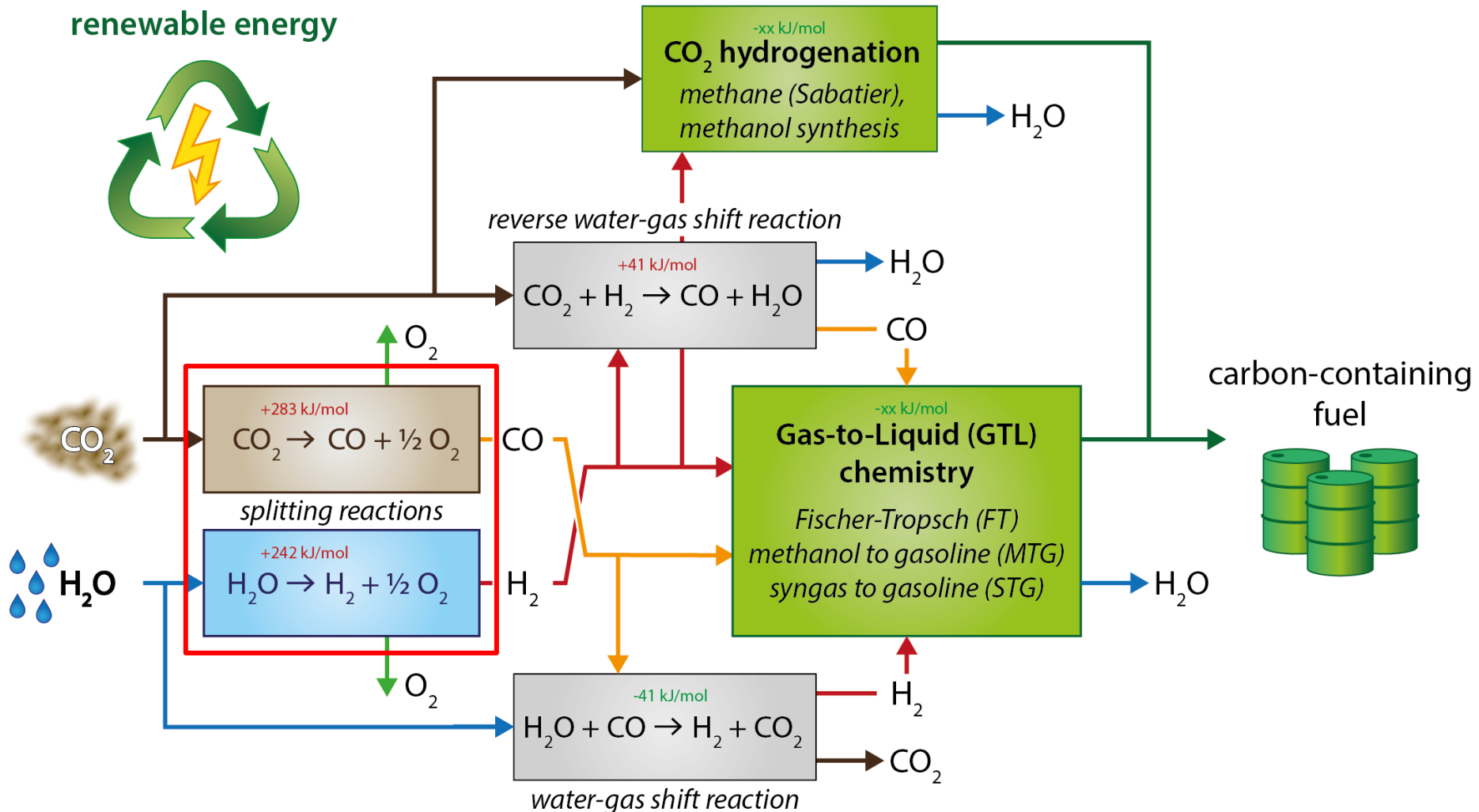
Shell Qatari plant (2009)

reaction enthalpies calculated for gaseous products at standard conditions



# Full chain of solar (=CO<sub>2</sub> neutral) fuels

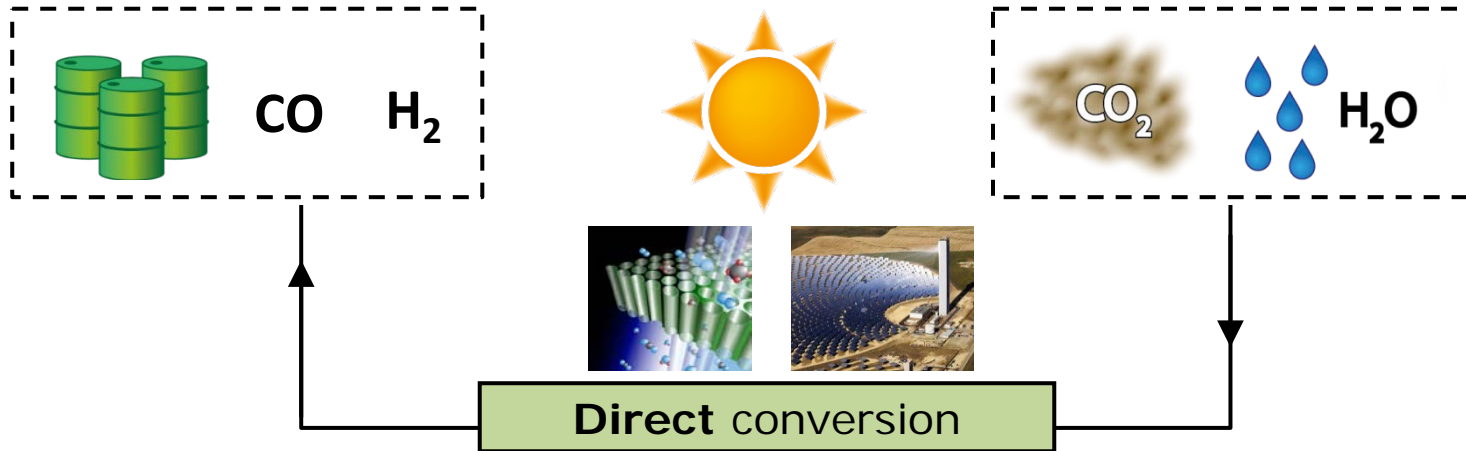
renewable energy



R&D mainly in energy and cost efficient splitting of CO<sub>2</sub> and H<sub>2</sub>O



# Concept of artificial chemical fuels



Photocatalytic:  $< 0.2-6 \%$

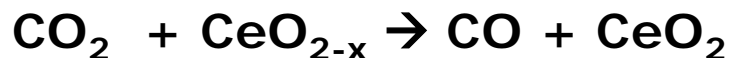
Solar thermal:  $5-7 \%$



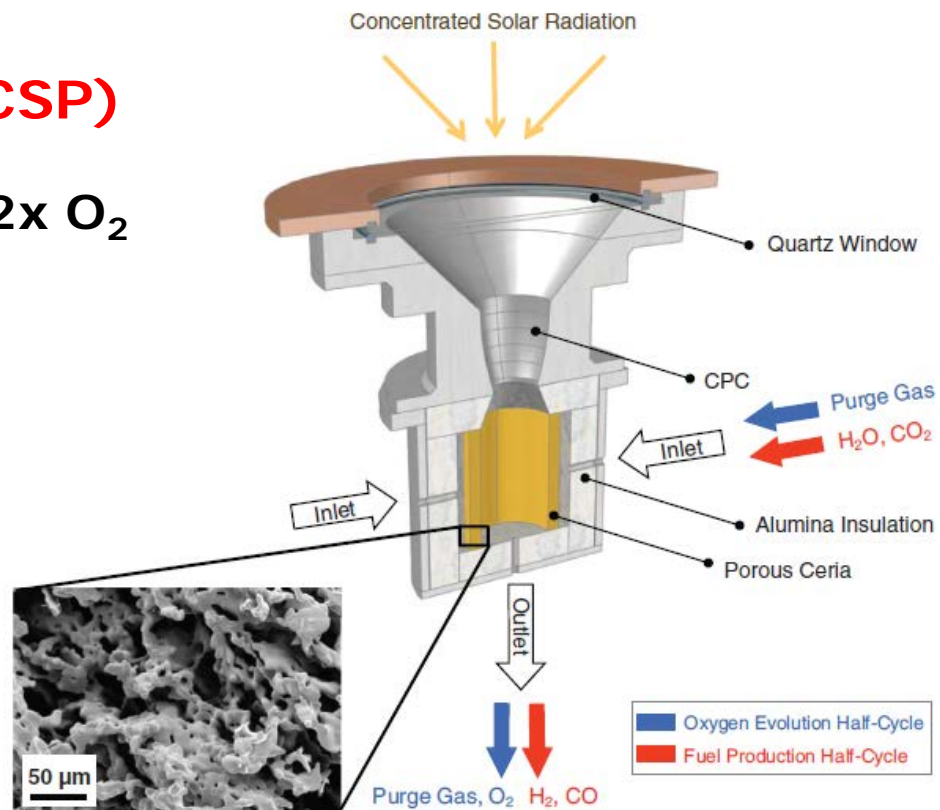


# Thermochemical using CSP (direct)

## Concentrated solar power (CSP)



Or based on ZnO, Fe<sub>3</sub>O<sub>4</sub>



**Cyclic, solar to CO efficiency: 5-7%**

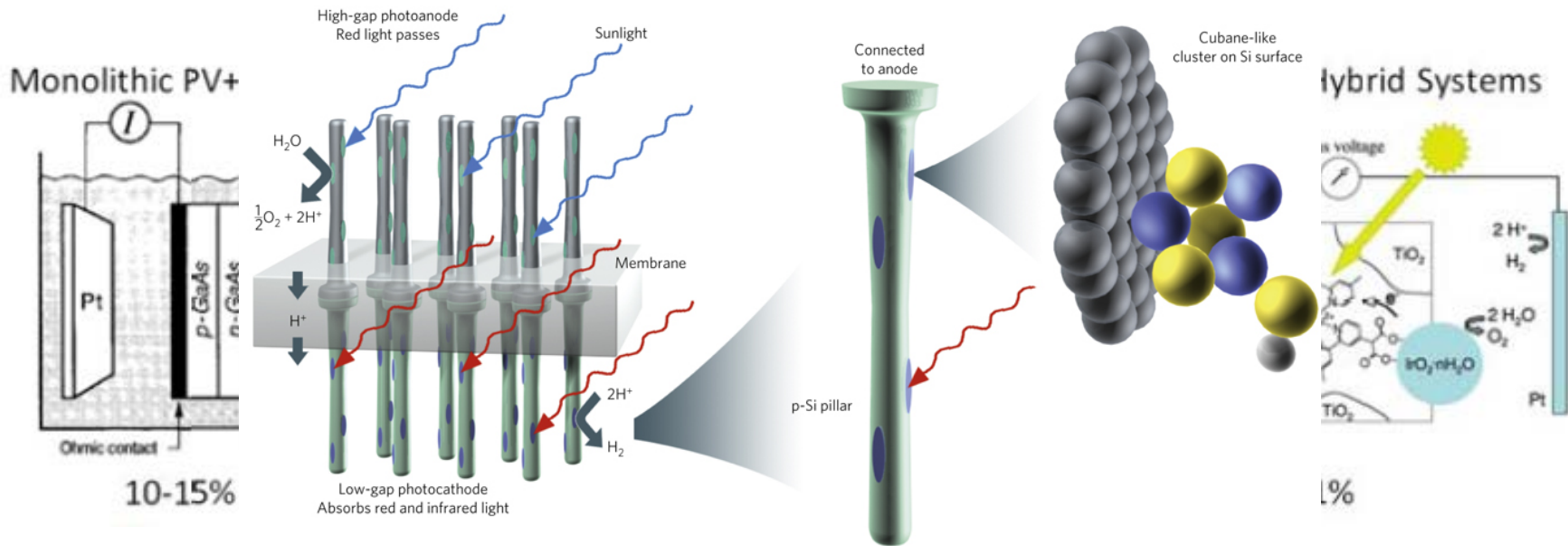
Nanostructuring of robust materials + catalysis under harse conditions essential



# Direct photocatalytic conversion of H<sub>2</sub>O

## The challenge

Which approach is most promising ?



Nano engineering/structuring of materials and catalysis essential

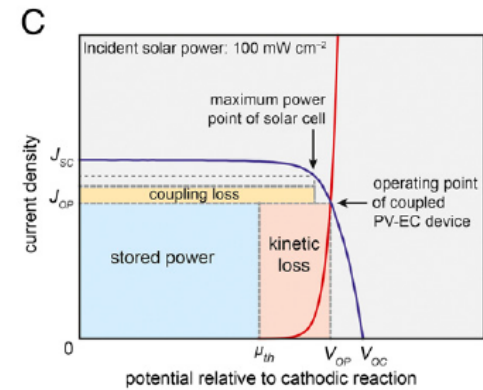
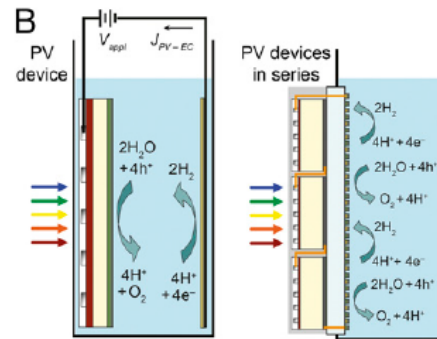
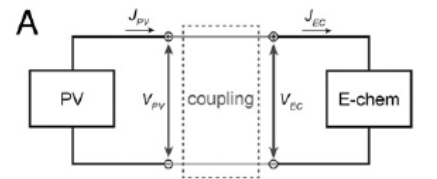
But also photon management: plasmonics, etc.



# Direct photocatalytic conversion of H<sub>2</sub>O

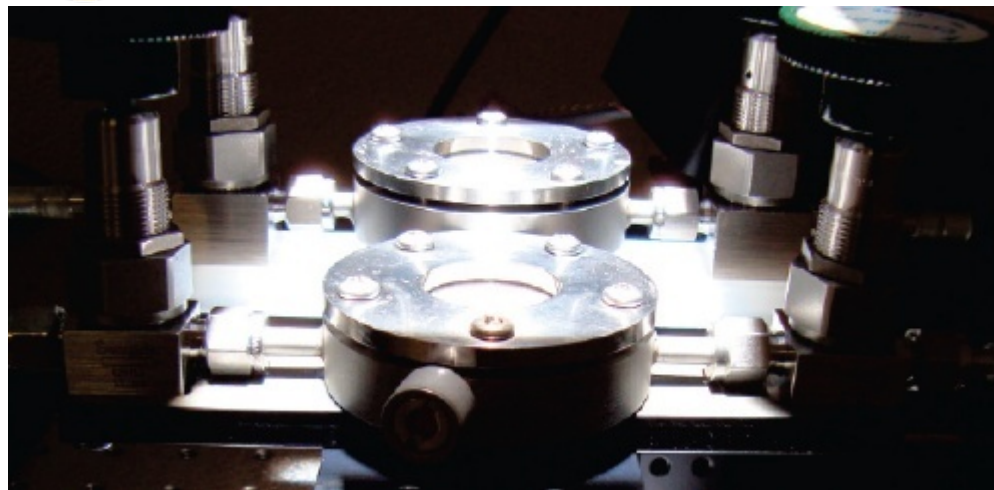
## The challenge

Which approach is most promising ?



Basically a (tandem) solar cell with earth abundant catalyst

# What about the direct photocatalytic conversion of CO<sub>2</sub> ?

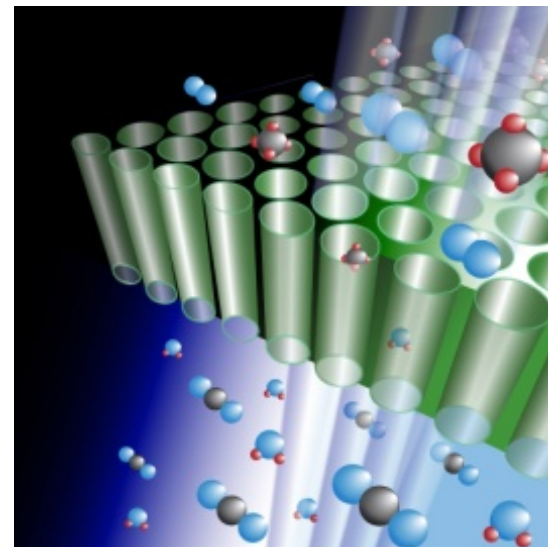


## The challenge

To tailor the catalyst to optimally use the solar spectrum for activating the catalyst

$$\eta = 0.0148\%$$

Nano engineering/structuring of abundant materials and discovery novel efficient catalysts essential (bio-inspired?)



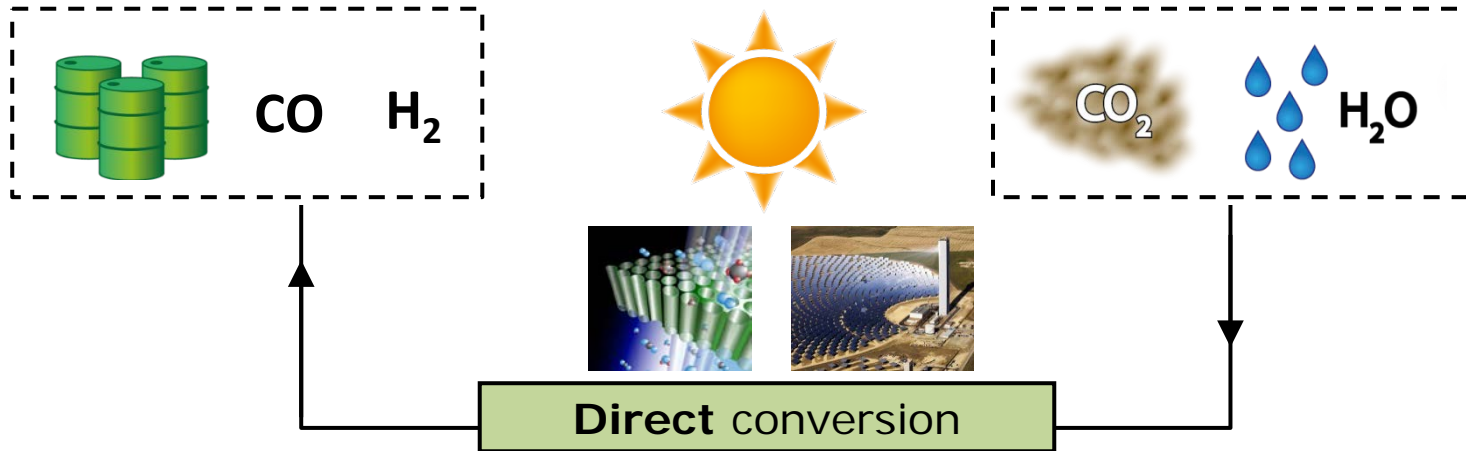
TiO tubes with Cu catalyst







# Concept of artificial chemical fuels

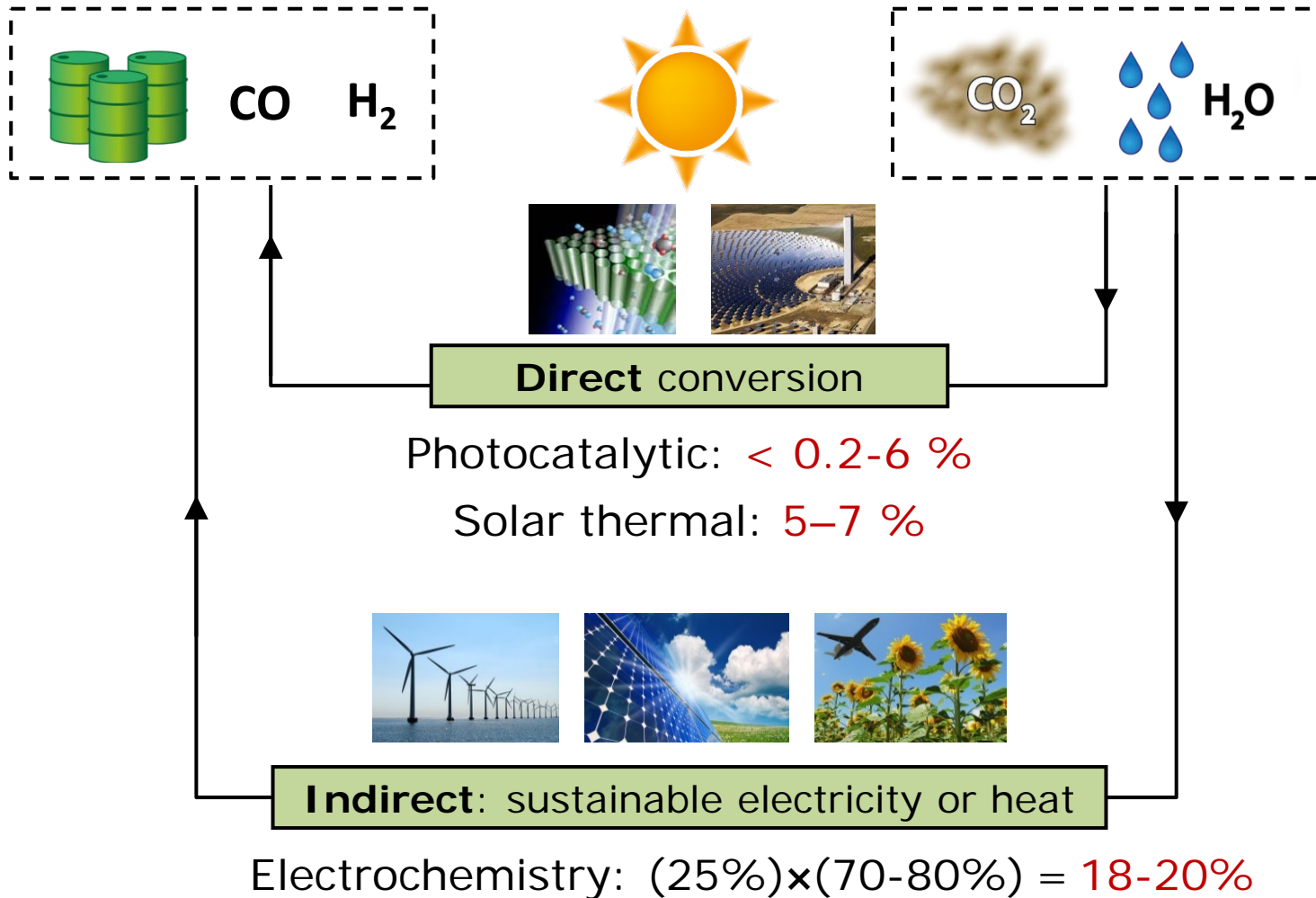


Photocatalytic: < 0.2-6 %

Solar thermal: 5-7 %



# Concept of artificial chemical fuels

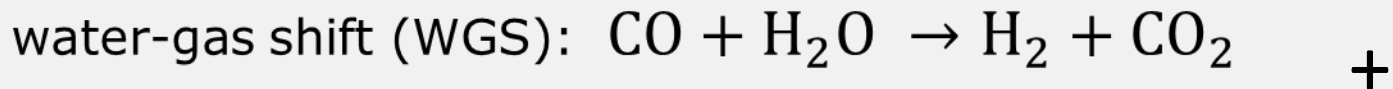
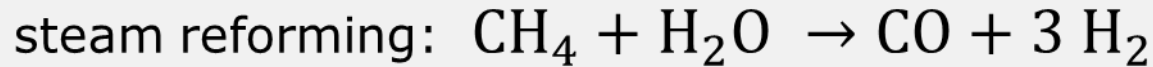
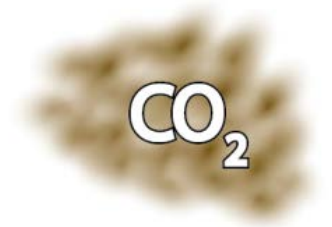




# Benchmark for H<sub>2</sub> production

## Steam reforming

- + Industrialized process: < 1 € / kg H<sub>2</sub>
- Long term issue: **fossil fuel based**
- Prominent short term issue: **CO<sub>2</sub> footprint**
  - CO<sub>2</sub> emission price: 3-4 € / 1000 kg

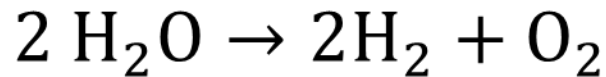




# H<sub>2</sub> production without CO<sub>2</sub> footprint

CO<sub>2</sub>-neutral process (driven by sustainable energy)

→ **State-of-the-art water electrolysis**

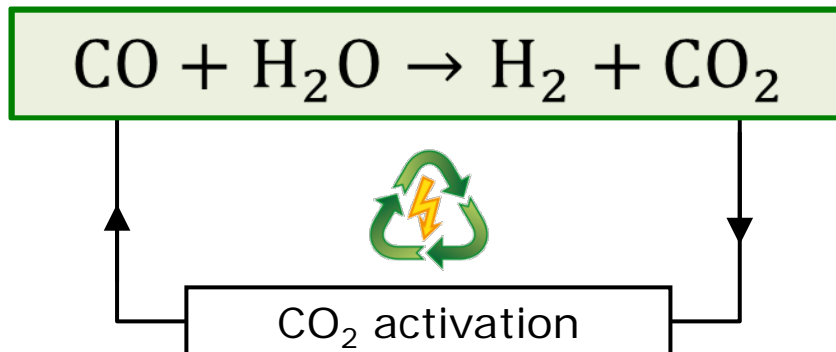


6-10 € / kg H<sub>2</sub>

→ **Control chemistry: no CO<sub>2</sub> production (Hüls arc process)**



→ **CO activation and WGS**



## Power-to-Chemistry®

An alternative route to clean hydrogen from electrical power

Power-to-Chemistry® combines elements of Power-to-Gas (i.e. hydrogen generation from electrical power) and Demand Side Management (i.e. flexible power consumption). Base technology is the synthesis of acetylene and possibly other base chemicals from short-chain hydrocarbons such as methane in a plasma arc. The synthesis is strongly endothermic and the energy is provided mainly by electrical power. The

mainly naphtha-based synthesis routes became economically superior. Worldwide, only one plant is still in operation (at the Chemical Site Marl, North Rhine-Westphalia).

The potential of the acetylene technology in the context of future energy systems mainly results from two facts. Firstly, the hydrogen yield is high. It corresponds to up to 5 MWh per 1 MWh of the power to be adjusted



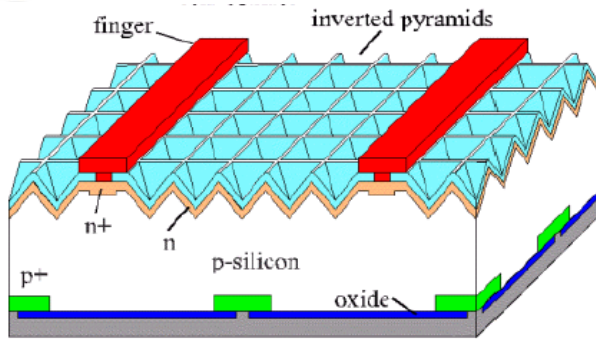
New concept: Material use of fossil carbon (from natural gas) for chemicals and of hydrogen as clean energy carrier for various applications (e.g. mobility)



Intermezzo



# Watersplitting using PV & electrolyser



Efficiency >> 20 %

sustainable energy



Advantage: separate optimization possible

Current bottleneck: **use of scarce materials (a.o. Pt)**

\*H<sub>2</sub> generation from steam reformation <1€/kg





# EASA/EERA report on Electrical Energy Storage

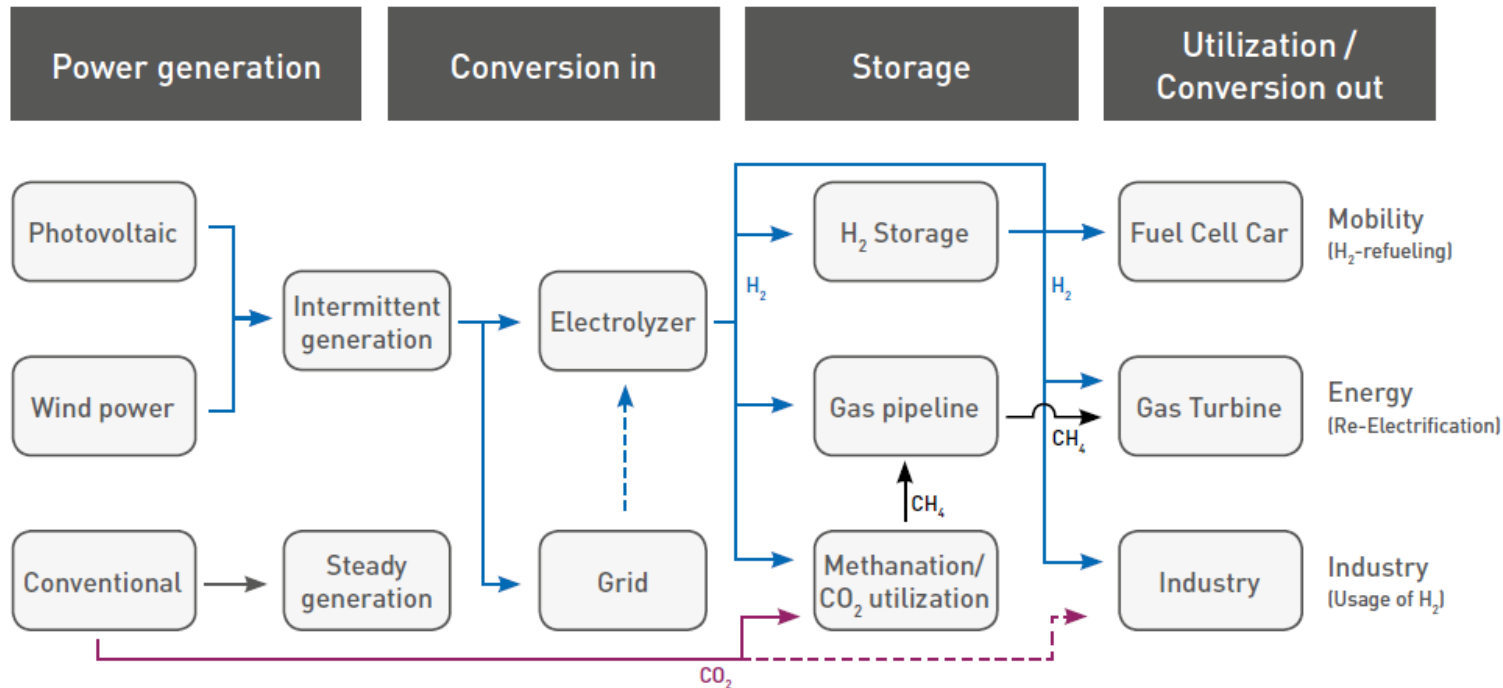
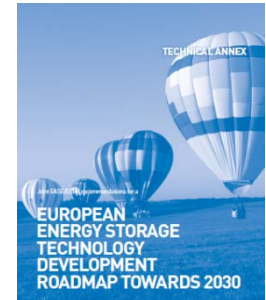
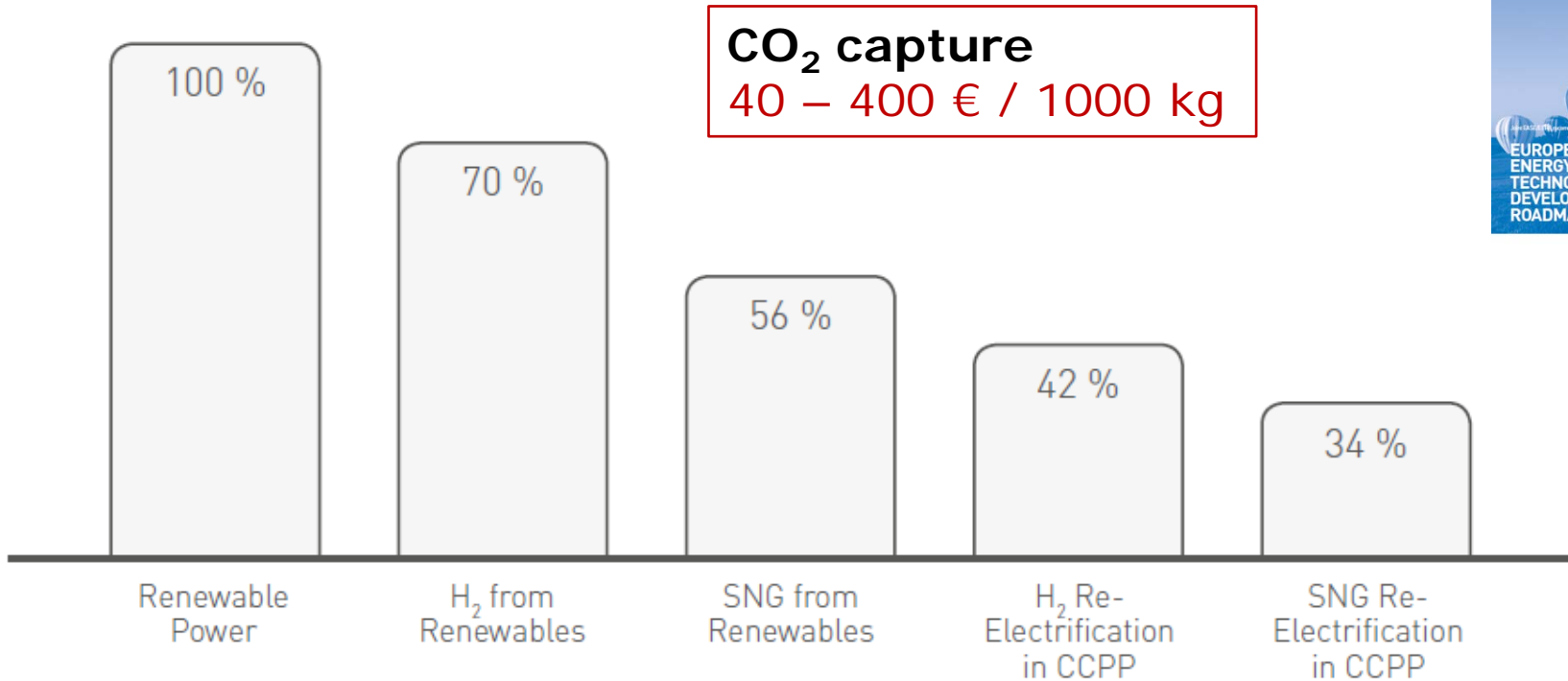


FIGURE 1 - Schematic of chemical storage pathways

For the chemical storage route:  
important role for H<sub>2</sub> and CH<sub>4</sub>



# EASE/EERA report on Electrical Energy Storage



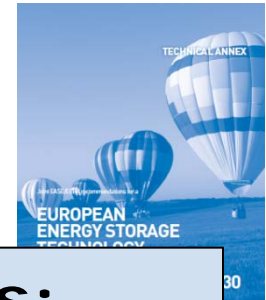
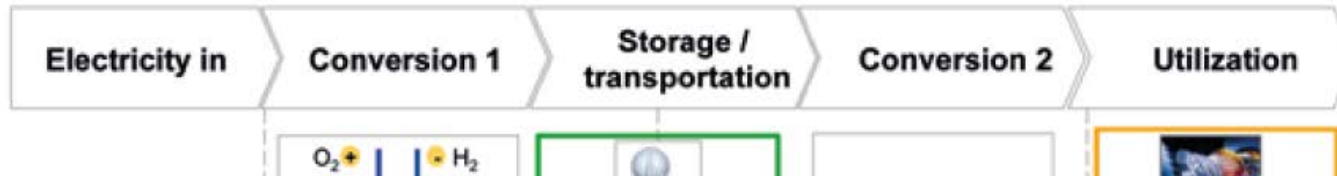
**FIGURE 2 - Efficiency of hydrogen based chemical electricity**

Note: most costly step is H<sub>2</sub> generation NOT CO<sub>2</sub> capture!





# EASE/EERA report on Electrical Energy Storage



**R&D concentrates on main challenges:  
on high efficiency electrolyser, using earth  
abundant cost effective materials (scalability)**



VIEWPOINT

pubs.acs.org

## Efficient Production of Solar Fuel Using Existing Large Scale Production Technologies

Wim Haije<sup>\*,†,‡</sup> and Hans Geerlings<sup>†,§</sup>

<sup>†</sup>Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

<sup>‡</sup>Energy research Centre of The Netherlands, PO BOX 1, 1755 ZG, Petten, The Netherlands

<sup>§</sup>Shell Global Solutions International B.V., Grasweg 31, 1031 HW Amsterdam, The Netherlands

**Topsector Energy:**

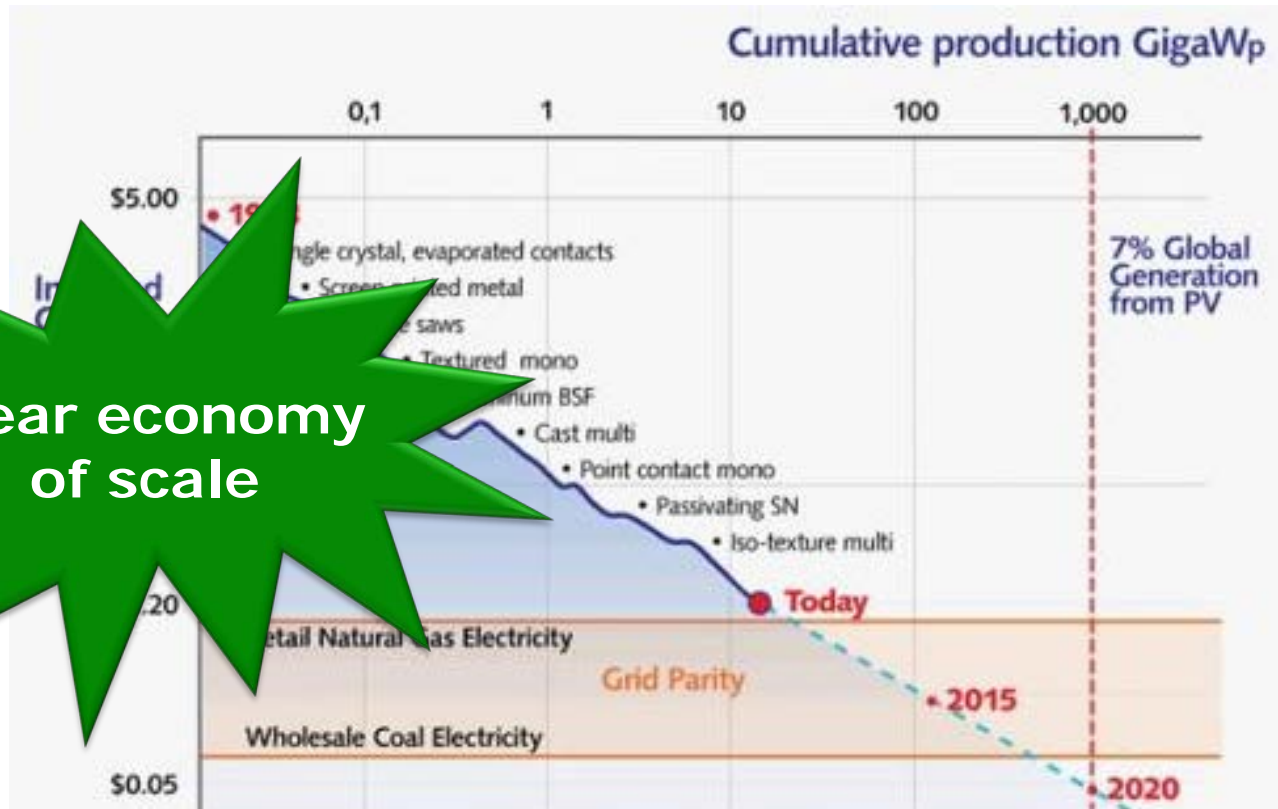
**Power to gas  
(P2G) scheme**

**R&D needed!**



# Solar power generation: Economy of scale

**Price-experience curve of silicon PV modules**  
*(combined effects of research innovation, experience and scale)*

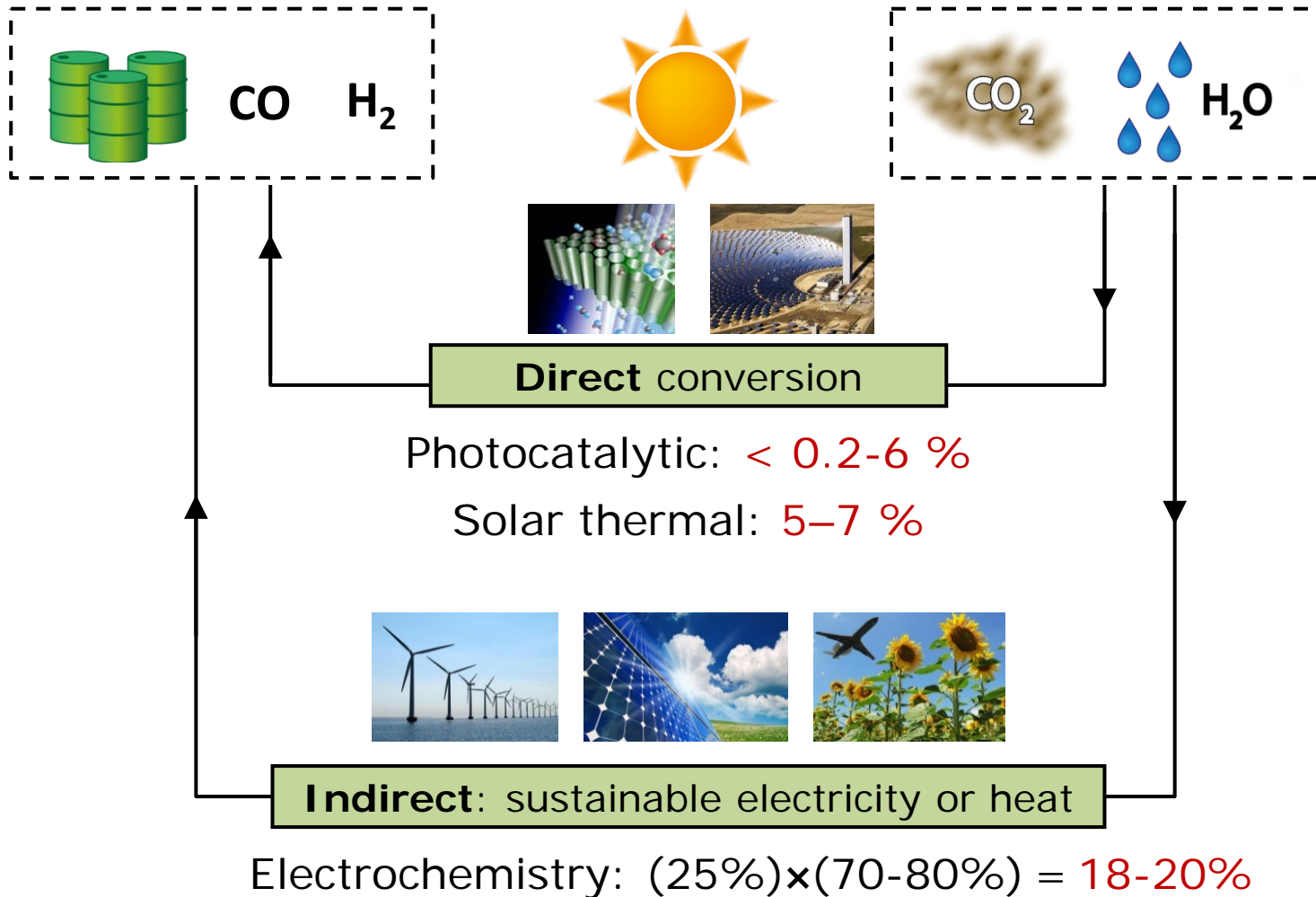


**Clear economy of scale**

For electrolysers we need a > 10 cost reduction: research, innovation, experience and scale essential



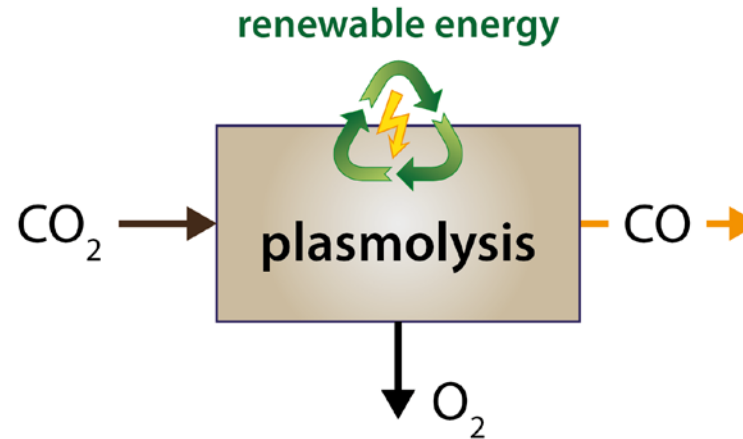
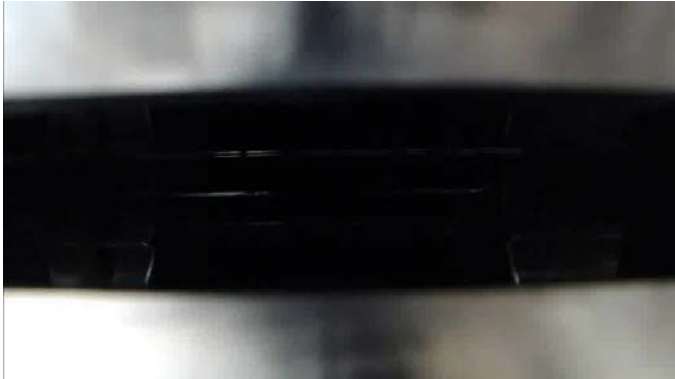
# Concept of artificial chemical fuels



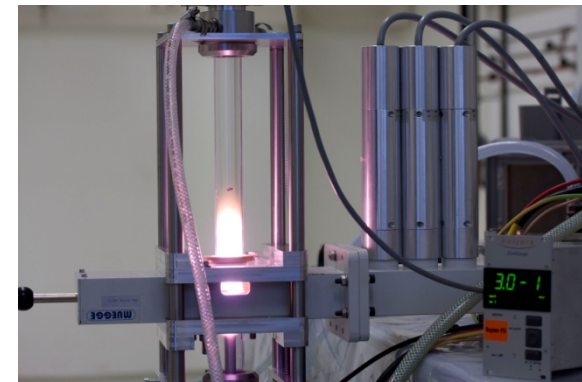
Activation of  $\text{CO}_2$  difficult: plasma might provide pathway



# Hydrogen generation using plasmolysis



- Generate a plasma in  $\text{CO}_2$
- No use of scarce materials
- Higher power density, smaller footprint
- On demand capability
- $\text{H}_2$  generation using WGS reaction



$\text{CO}_2$  plasma set up  
@ DIFFER



# CO<sub>2</sub> dissociation by plasma activation

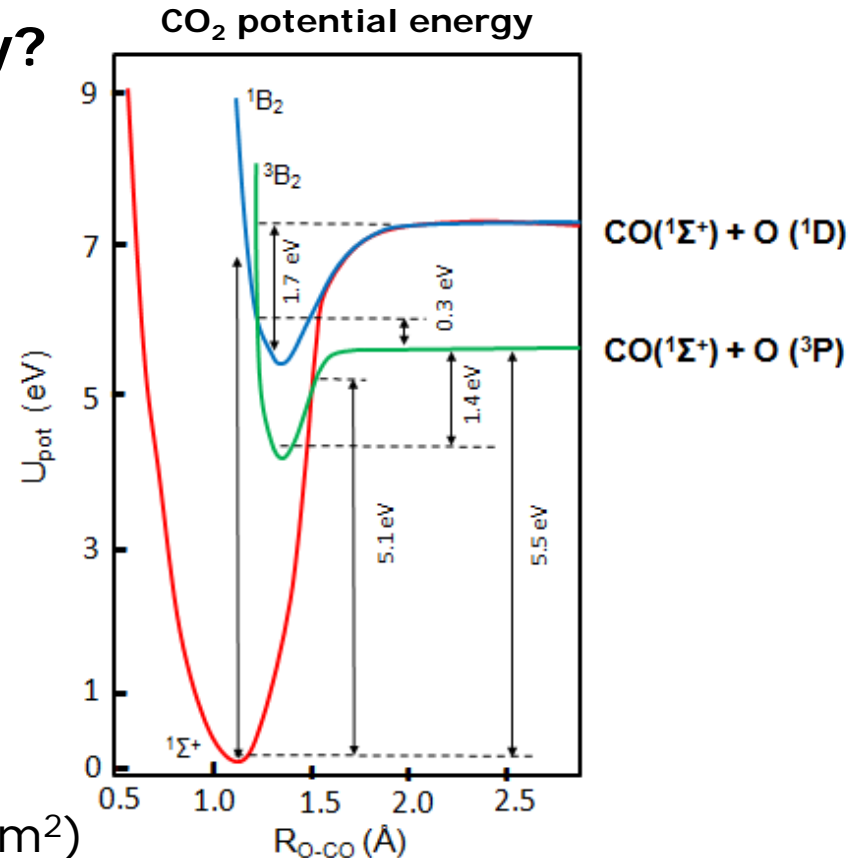
## Can it be done energy efficiently?

Plasma processing energy expensive:

- Creating electron-ion pair > 30 eV
- Dissociation energy CO<sub>2</sub> > 5.5 eV

## YES if:

- Vibrational excitation CO<sub>2</sub> by slow electrons (1 eV) creating out-of-equilibrium  $T_{\text{vib}} > T_{\text{gas}}$
- Low degree of ionisation ( $10^{-5}$ )
- Low reduced electric field ( $\sim 10^{-16}$  Vcm<sup>2</sup>)

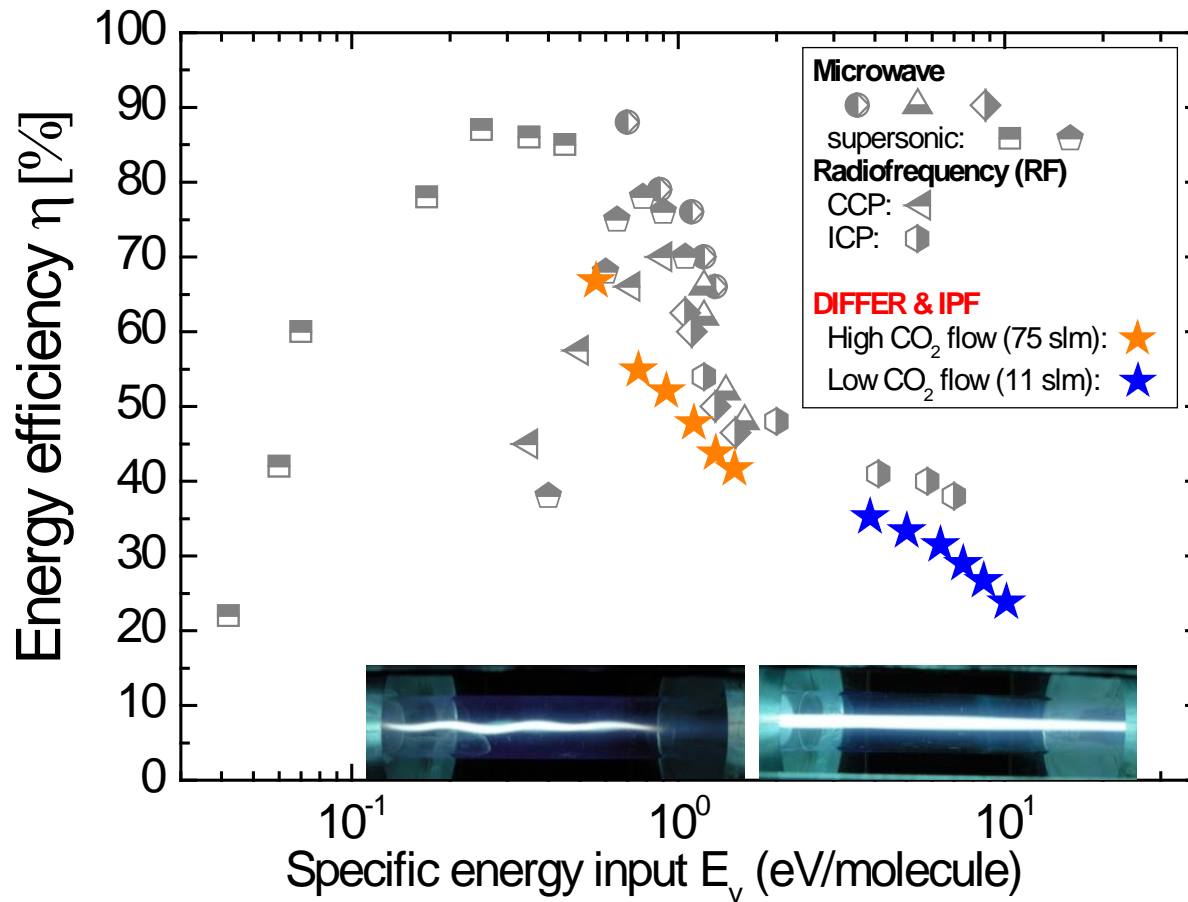


**energy efficient dissociation** possible through **vibrational excitation CO<sub>2</sub>** in asymmetric stretch mode





# Reported results on energy efficiency

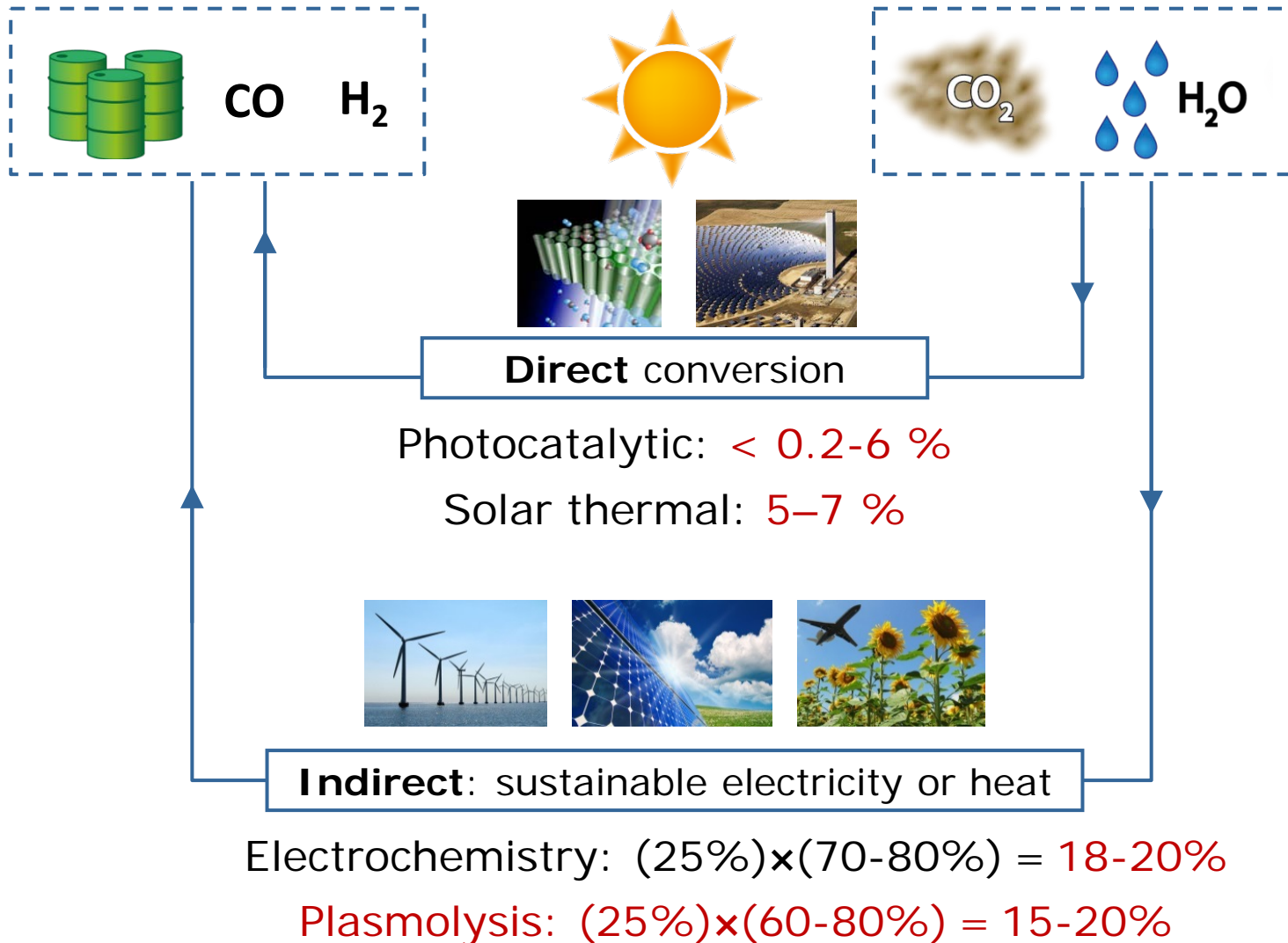


$$\eta = \Delta H / E_{CO}$$

Literature reports > 50% energy efficiency of CO<sub>2</sub> dissociation !



# Concept of artificial chemical fuels





# Conclusions

- Storage of sustainable energy in chemical fuels one of the approaches to provide a stable energy supply and liquid transport fuels: use of **earth abundant** materials essential because of the scale
- Especially **power-to-gas** is being deployed due to negative prices RES; **more R&D** is necessary to get **cost and energy efficient P2G** schemes; *there is not **one solution**, we need most probably a mix*
- ***Innovations are necessary, new materials** for membranes and catalysts, plasma might provide solutions if energy efficiency is proven*
- Several issues need to be addressed **overall**: CO<sub>2</sub> conversion efficiency, **efficiency** of the **gas separation**, **supply** of CO<sub>2</sub>, etc....



# TV uitzending Labyrint "CO<sub>2</sub>"

Uitzending Gemist  Zoek

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**Labyrint**  
CO2

Uitgezonden zo 24 nov 2013, 19:55 Omroep **VPRO · NTR**

Aantal x bekeken 4.587 Genre **Informatief · Wetenschap**

CO2, ofwel kooldioxide, we willen er niet teveel van uitstoten. Maar de auto aan de kant laten staan, daartoe zijn we ook niet bereid. Wat als we die CO2 zouden omzetten in brandstof? Nog rendabel ook!

Deel

Pop-out Beeld vergroten

<http://www.uitzendinggemist.nl/afleveringen/1380791>