Solar fuels production via high-temperature processes

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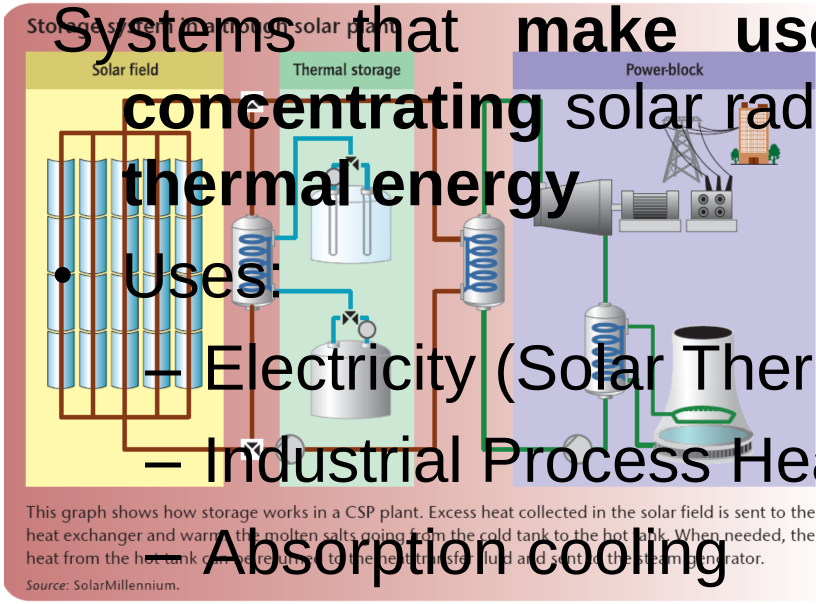
Introduction

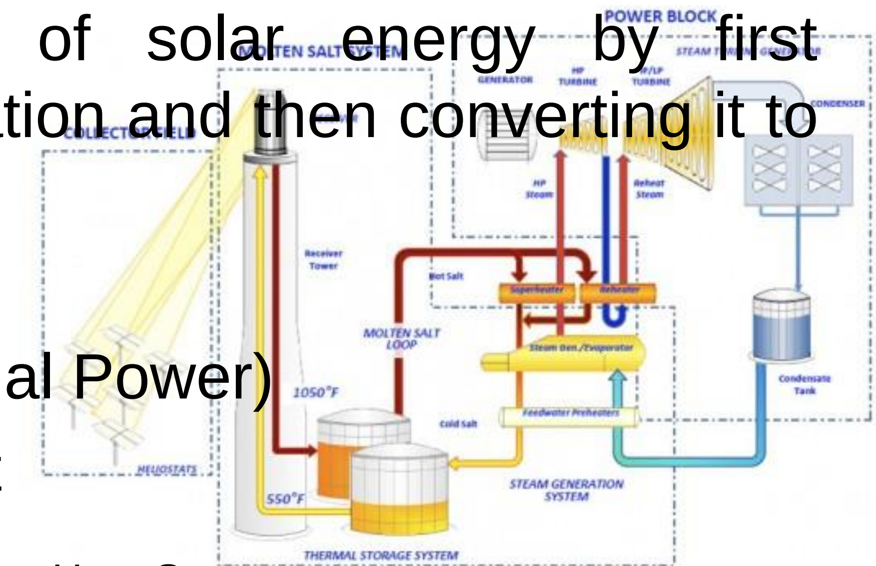
- Concentrating Solar Systems
- Solar Thermal Power Plants (STPPs): from receivers to receivers/reactors.
- Solar fuels synthesis chemistries.
- Solar fuels technologies pursued at DLR, current developments and state-of-the-art.
- R&D needs and outlook.

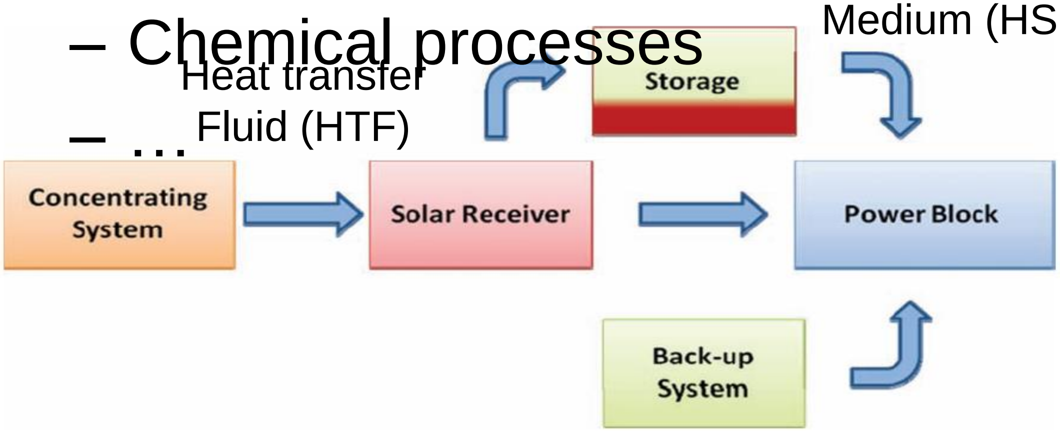
Solar Thermal Power Plants

Systems that **make use** of solar energy by first **concentrating** solar radiation and then converting it to **thermal energy**

- Uses:
  - Electricity (Solar Thermal Power)
  - Industrial Process Heat
  - Absorption cooling
  - Chemical processes
  - …

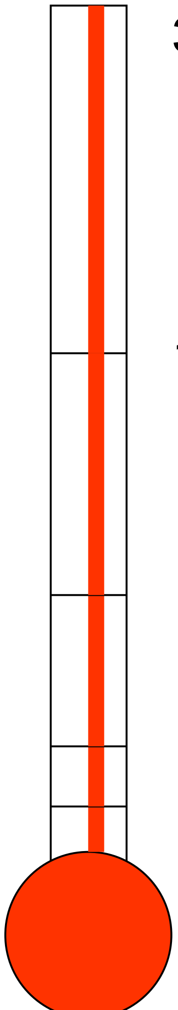






- Heat transfer fluid: thermal oil, air, steam, molten salt.

Temperature Levels of CSP Technologies



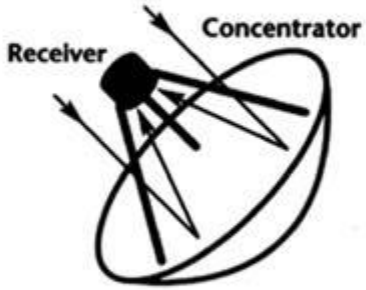
3500°C

1500°C

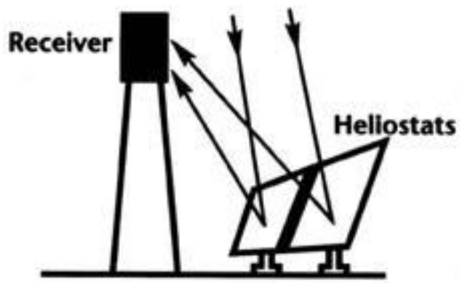
390°C

150°C

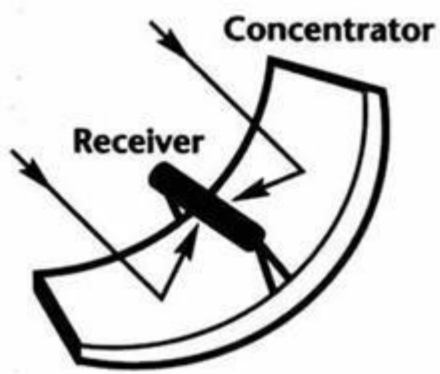
50°C



Paraboloid:
“Dish”



Solar Tower
(Central Receiver System)

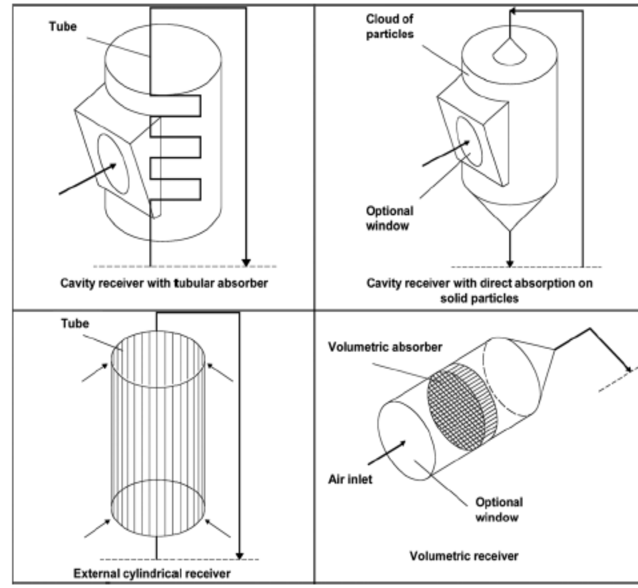


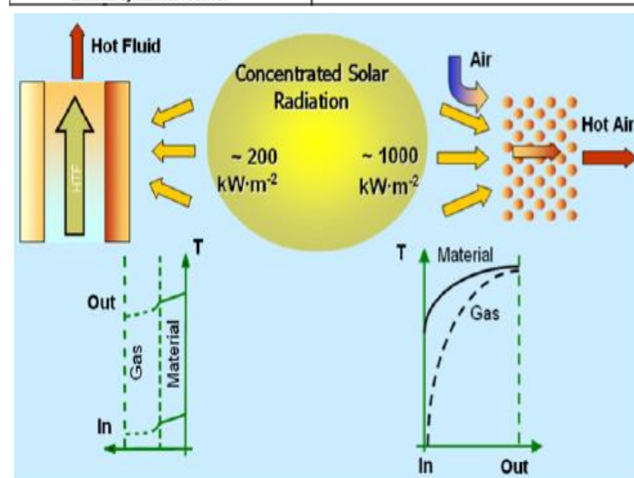
Parabolic Trough /
Linear Fresnel

Solar receivers- From solar electricity to solar chemicals

- In direct analogy with “conventional” catalytic applications, solar receivers can employ proper functional materials capable of performing/ catalyzing a variety of high-temperature chemical reactions and thus be “transformed” to solar receiver/reactors where (endothermic) chemical reactions can take place.

- In this way absorbed radiation is converted from thermal to chemical form, storing solar energy in the chemical bonds of the reaction products (e.g. Hydrogen) rather than as thermal energy in a working fluid.





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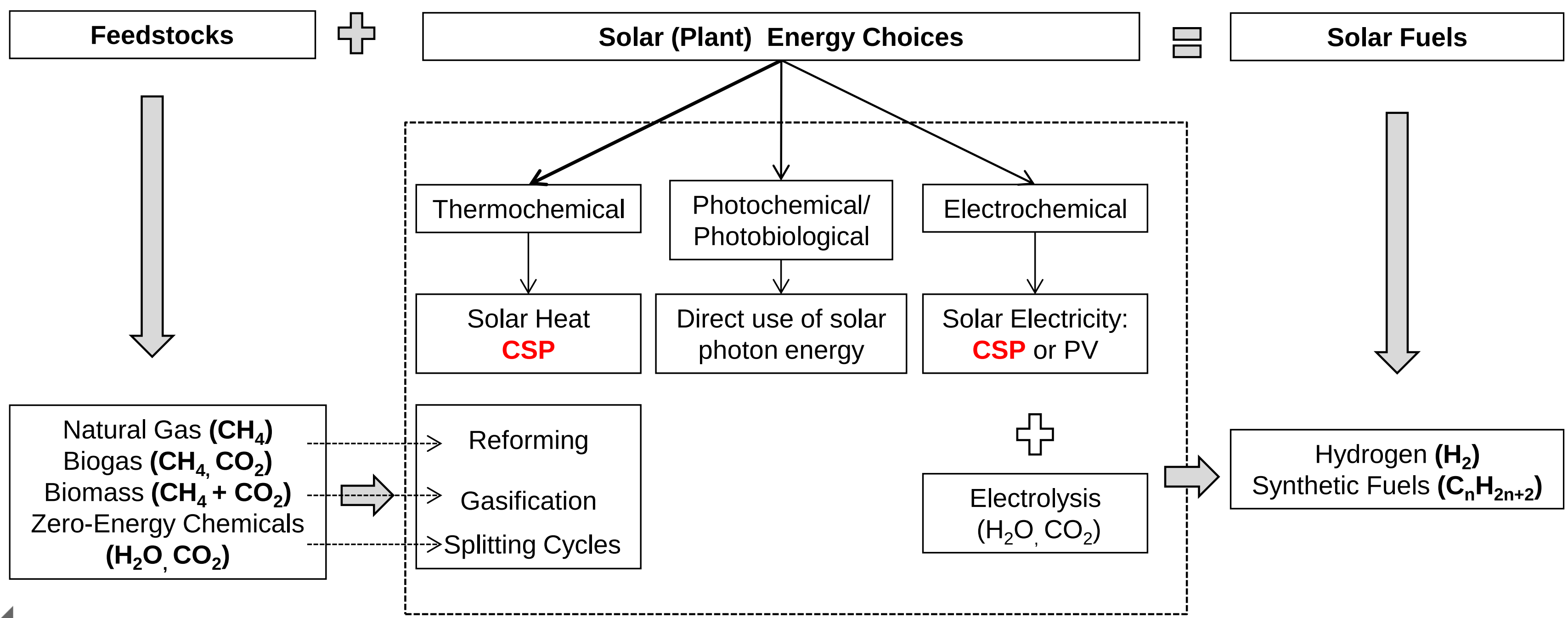
Partial listing of various feedstocks and solar energy variances for solar liquid hydrocarbon fuels production

Fuel: any chemical compound that stores energy, which can be released by being oxidised to provide heat.

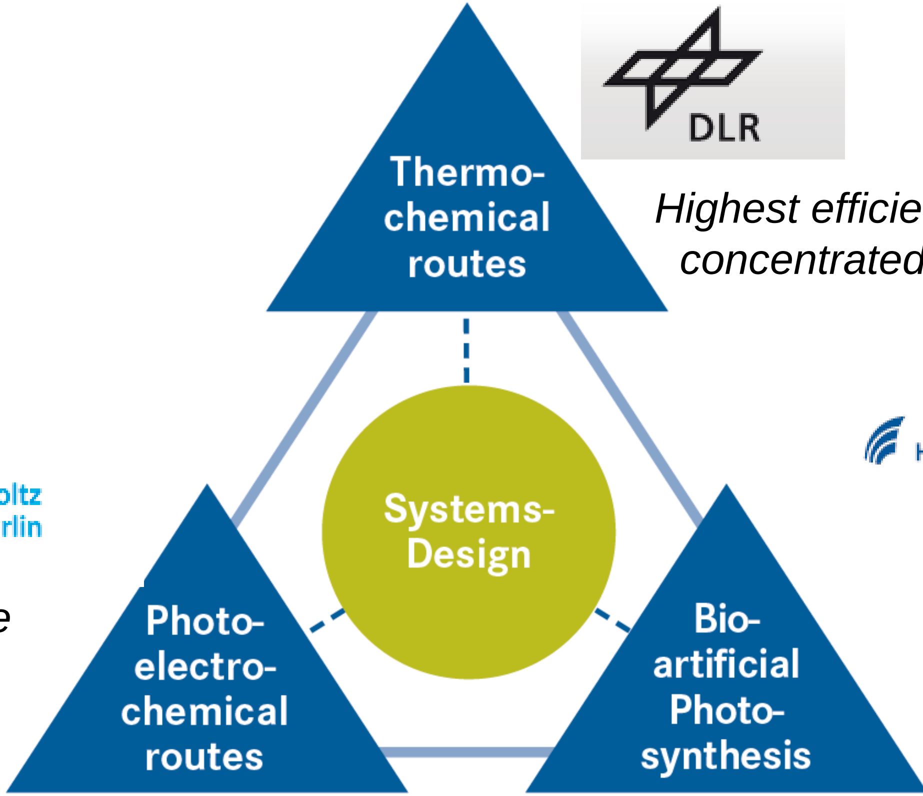
“Solar fuel”: any chemical compound that can react with oxygen to release energy, and was initially formed, at least partly, using energy from solar radiation.



Strategy and Approach on Solar Fuels in Germany

Goal in the Helmholtz Association

To demonstrate stand-alone, viable systems for the emission-free production of chemical fuels – especially **Hydrogen** - with sunlight



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Highest efficiencies with concentrated sunlight?

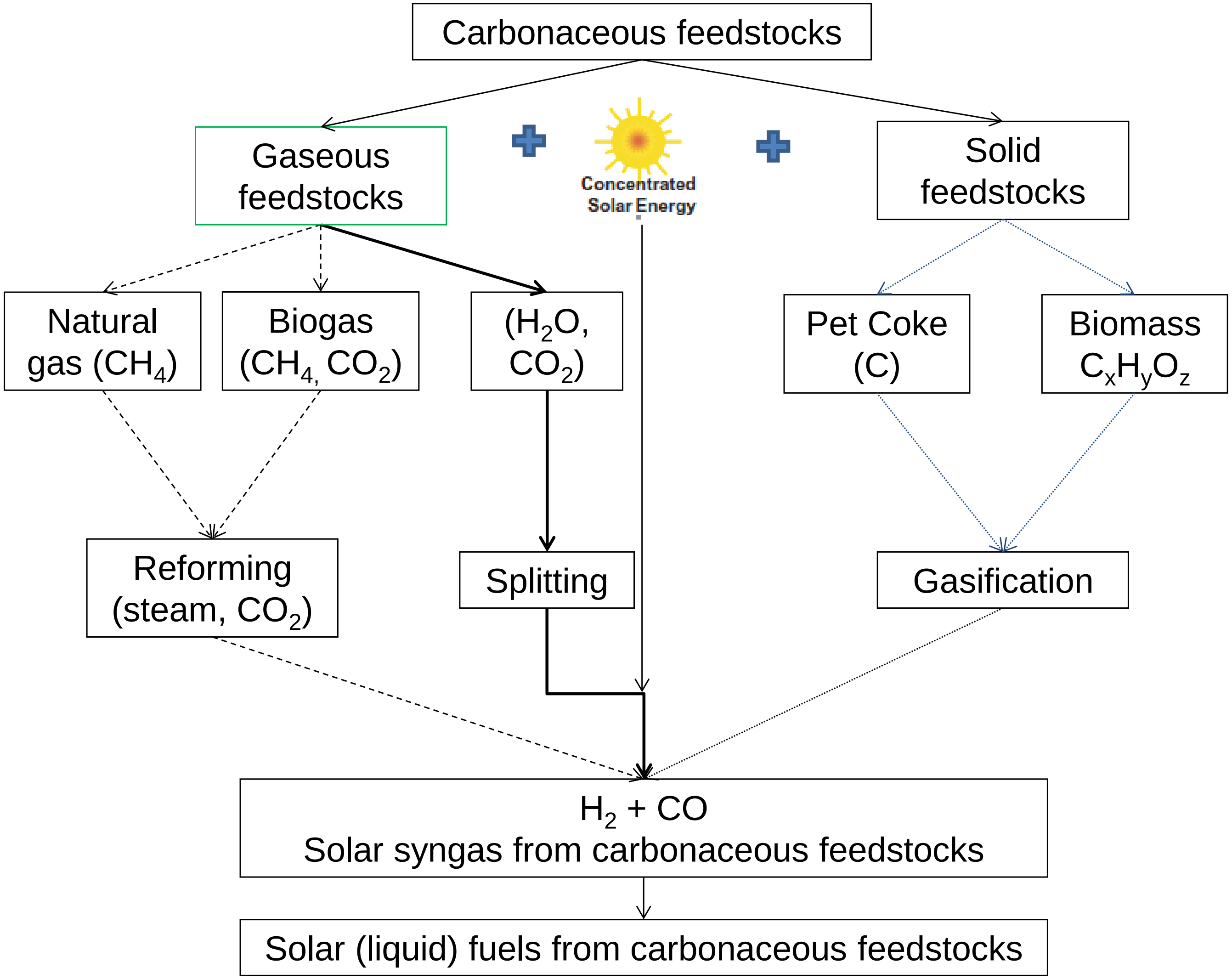
HZB Helmholtz Zentrum Berlin

Widest range of conditions?

HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

Lowest cost?

CSP-aided routes for the production of “solar syngas”



Solar (Fuels) Chemistry

Solar Steam/dry methane Reforming (SMR/DMR)

- $CH_4 + H_2O + (\Delta H) \rightleftarrows 3\,H_2 + CO$
- $CH_4 + CO_2 + (\Delta H) \rightleftarrows 2\,H_2 + 2CO$

(~ 850-950°C)

Solar Gasification

$$C_1H_xO_yS_uN_v + (1\text{-}y)\,H_2O + (\Delta H) \rightarrow (x/2+1-y-u)H_2 + CO + u\,H_2S + v/2\,N_2$$

(~ 1000-1200°C)

Solar Redox processes / Thermochemical (water splitting) cycles

“Net” reactions: $H_2O + (\Delta H) \rightarrow H_2 + ½\,O_2$

Sulfur-based

$H_2SO_4 \rightarrow SO_3 + H_2O$ (~ 400°C)

$SO_3 + (\Delta H) \leftrightarrow SO_2 + ½\,O_2$ (~ 850-950°C)

$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ (80-120°C, electrolysis)

Redox-oxides based

$MeO_{oxidized} + (\Delta H) \rightarrow MeO_{reduced} + ½\,O_2$ (~ 1100-1450°C)

$MeO_{reduced} + H_2O\,(g) \rightarrow MeO_{oxidized} + H_2 + (\Delta H)$ (~ 700°C)

Steam and CO_2-Reforming of Natural Gas Reactions

Steam Reforming:

(1)	$CH_4 + H_2O \rightarrow 3H_2 + CO$	Δh = 206 kJ/mol
(2) (WGS)	$CO + H_2O \rightarrow H_2 + CO_2$	Δh = -41 kJ/mol
(3) = (1+2)	$CH_4 + H_2O \rightarrow 4H_2 + CO_2$	Δh = 165 kJ/mol

Dry (CO_2) Reforming:

(1)	$CO_2 + CH_4 \rightarrow 2H_2 + 2CO$	Δh = 247 kJ/mol

- Reforming Product is Syngas – Mixture of H_2 and CO
- Highly endothermic → Favoured by high temperatures; > 700 °C in industrial processes
- Increase in number of moles → Favoured by low pressures
- Reforming of mixtures of CO_2/H_2O is possible
- Use of syngas for methanol production: e.g. $2H_2 + CO \rightarrow CH_3COH$
- Both technologies can be driven by solar energy

(Water-splitting) Redox-oxide-based Thermochemical Cycles

- Series of chemical reactions with net result being H_2 & O_2 production from H_2O
- Why a series of reactions ? The indirect H_2O splitting is necessary since thermolysis is feasible at impractical temperature ranges (>2200ºC).

1st Step: Thermal reduction (Regeneration) $MO_{ox} + \Delta H \rightarrow MO_{red} + \frac{1}{2} O_2$

2nd Step: H_2O / CO_2 Splitting WS /CDS

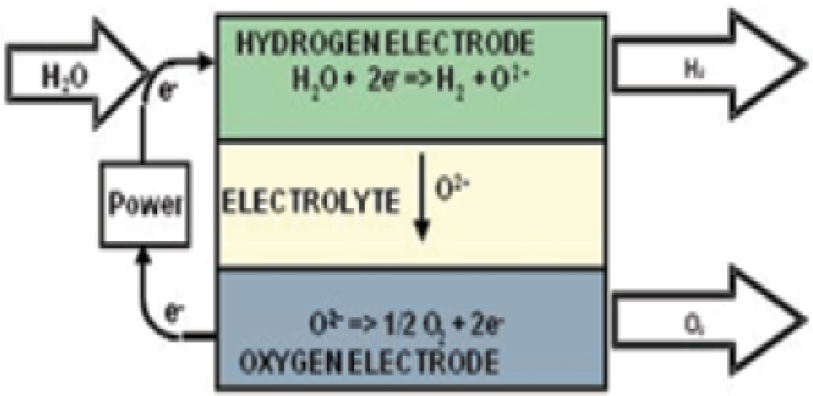
$H_2O + MO_{red} \rightarrow MO_{ox} + H_2 + (\Delta H)$

$CO_2 + MO_{red} \rightarrow MO_{ox} + CO + (\Delta H)$

Net reaction: $H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Net reaction: $CO_2 \rightarrow CO + \frac{1}{2} O_2$

Net effect: Solar Q → Solar Fuels



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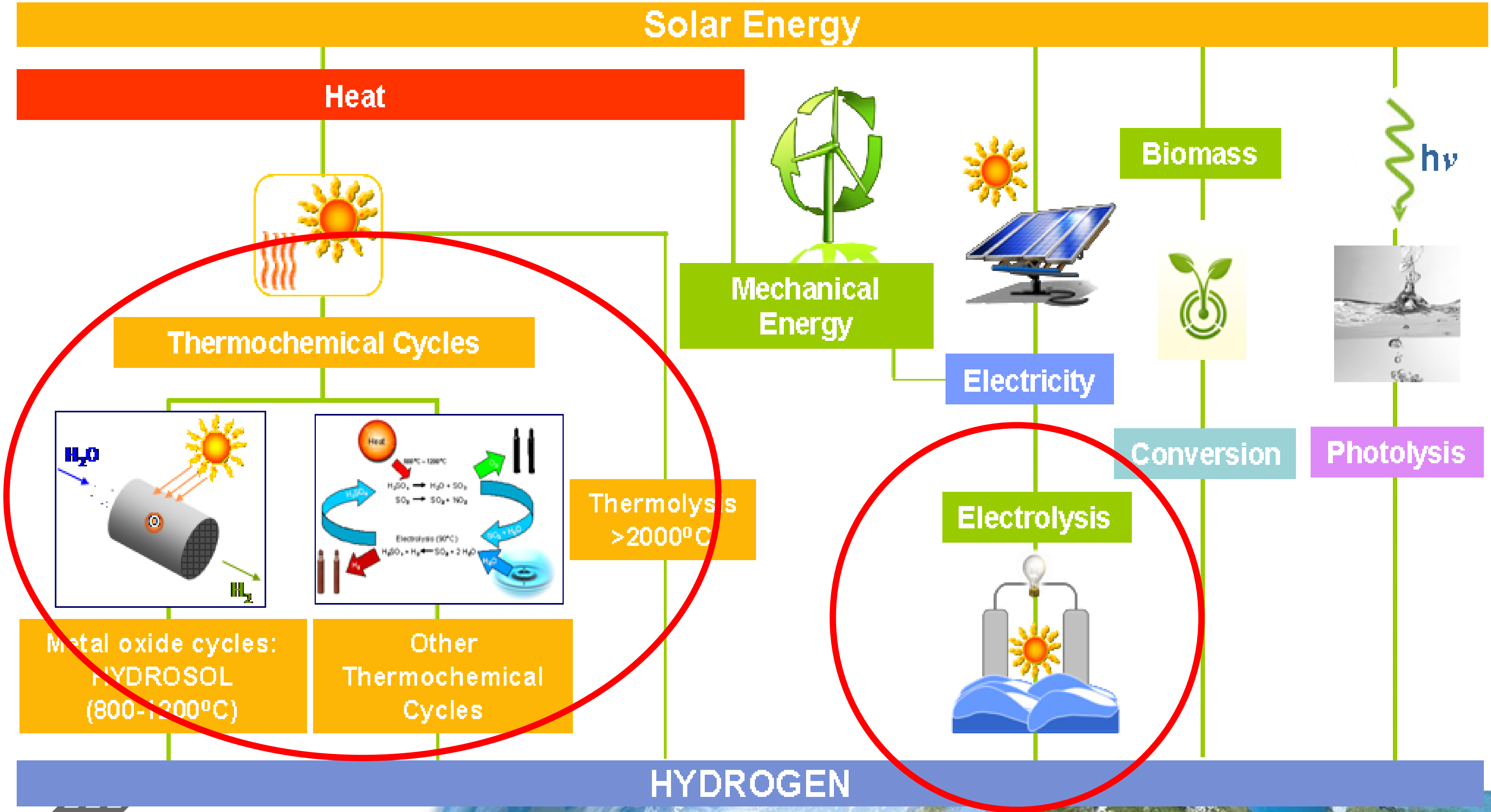
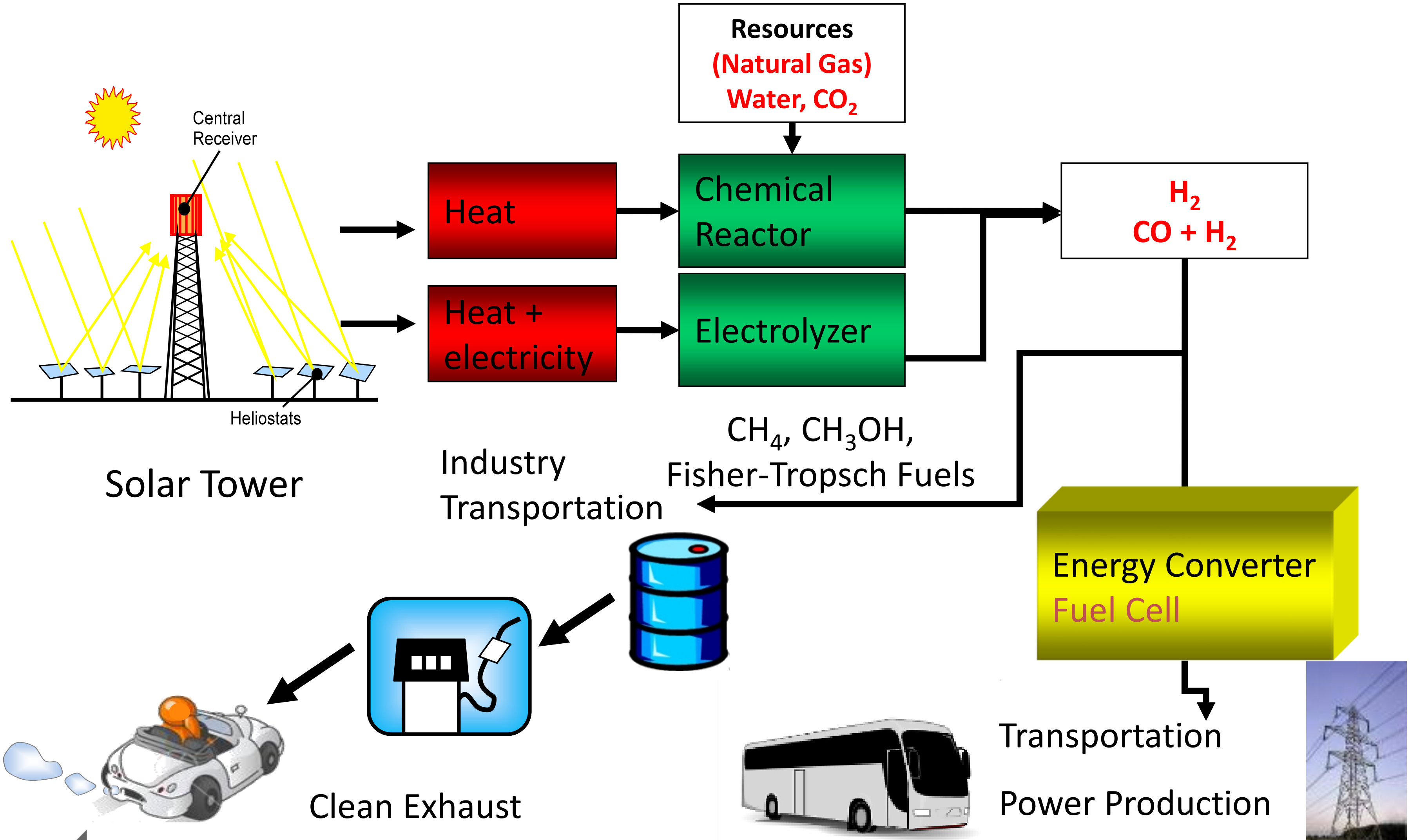
Solar Hydrogen



Principle of the solar thermal fuel production



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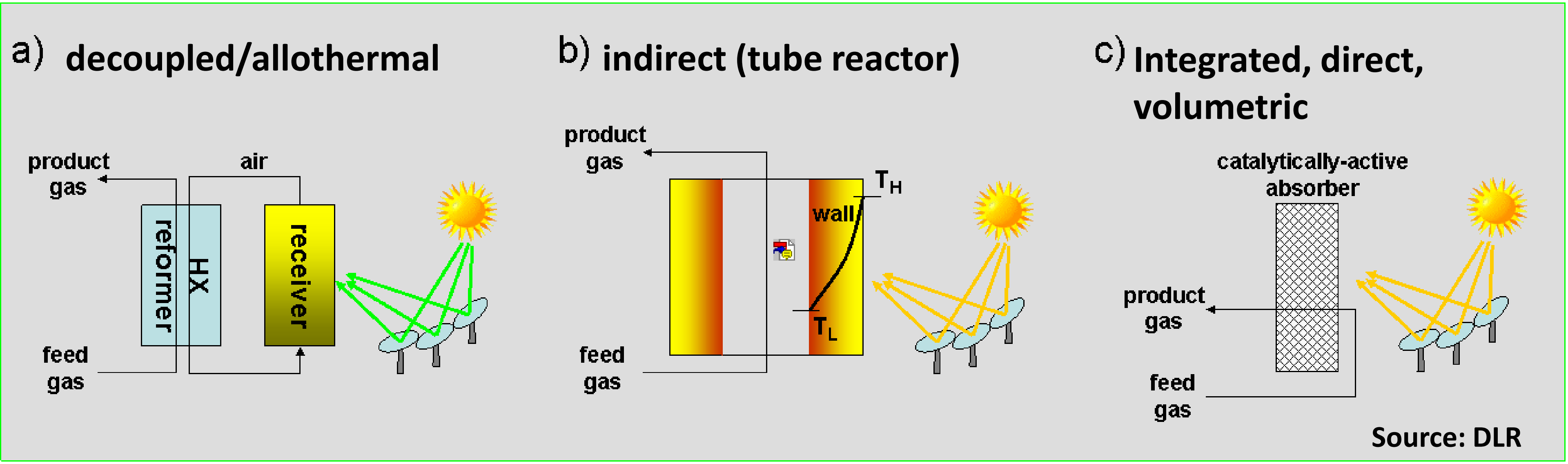
Solar Methane Reforming– Reformer (heating) Technologies



- Reformer heated externally (700 to 850°C)
- Optional heat storage (up to 24/7)
- E.g. **ASTERIX** project

Irradiated reformer tubes (up to 850°C), temperature gradient

Approx. 70 % Reformer-h

Development: Australia, Japan; Research in Germany and Israel

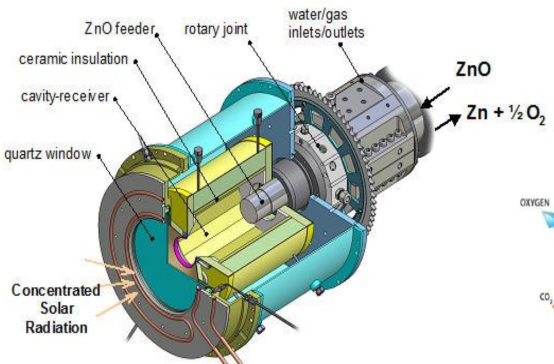
Catalytic active direct irradiated absorber

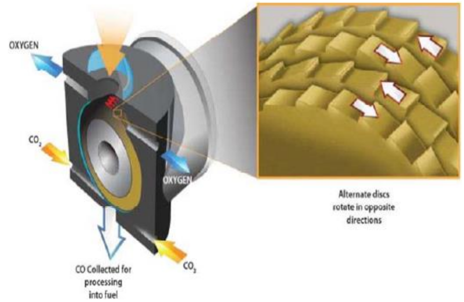
Approx. 90 % Reformer-h

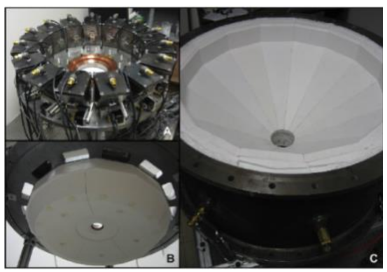
High solar flux, works only by direct solar radiation

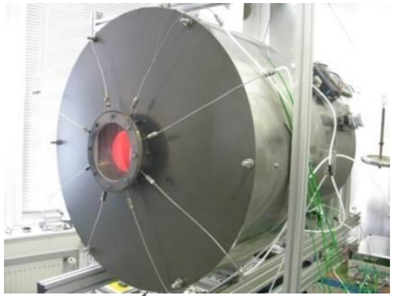
DLR coordinated projects: **SOLASYS, SOLREF**; Research in Israel, Japan

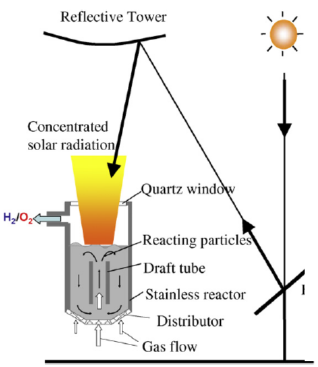
Solar receiver/reactor types (particles vs. porous solids; moving vs. non-moving parts)

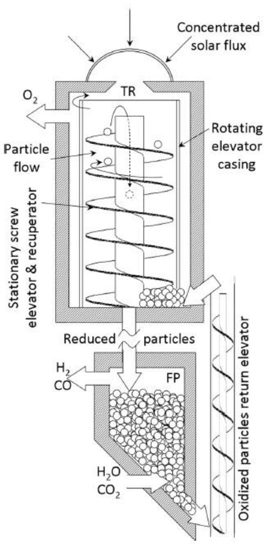


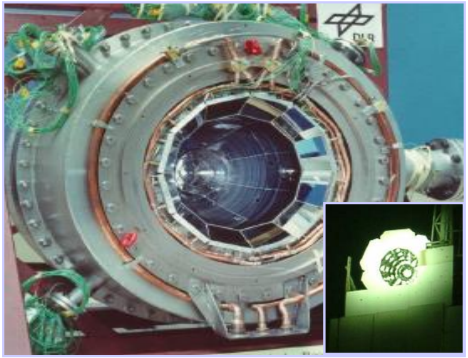


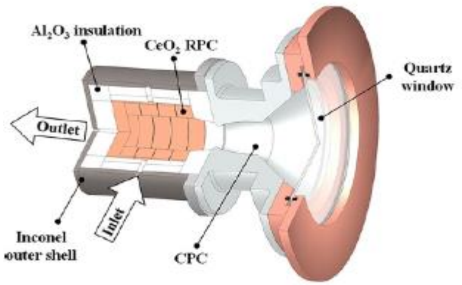












Reforming vs. W/CD redox-oxides-“splitting” Chemistry

- Employs fossil fuel (CH_4) as reactant.
- Solid catalyst: Ni-based catalysts supported on $CaAl_6O_{10}$ or $MgAl_2O_4$; noble metals (Ru, Rh, Pd, Pt); Fe, Co.

- Temperature range: **700-850°C.**
- Gaseous reactants can be fed **continuously.**

- Employs **CO_2 as a reactant**; i.e. can “reuse/valorize” atmospheric CO_2.
- Solid redox–pair materials: ferrites ($NiFe_2O_4$, $CoFe_2O_4$), CeO_2-ZrO_2, perovskites ($La_{1-x}Sr_xMn_yAl_{1-y}O_{3-\delta}$).
- Temperature range: 750-1500°C.
- Solid is not a “catalyst” but a reactant, with non-negligible mass to be heated to the reaction temperature and progressively depleted during reaction, having to be replenished (reactions cannot be carried out continuously).

Reforming vs. W/CD “splitting” solar reactors

- “Structured” reactors.
- Solar heating: direct or indirect.

- Structured & non-structured (particle) reactors.
- Solar heating: only direct (required Ts too high for indirect heating).

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Criteria for the selection of processes of solar thermal hydrogen production

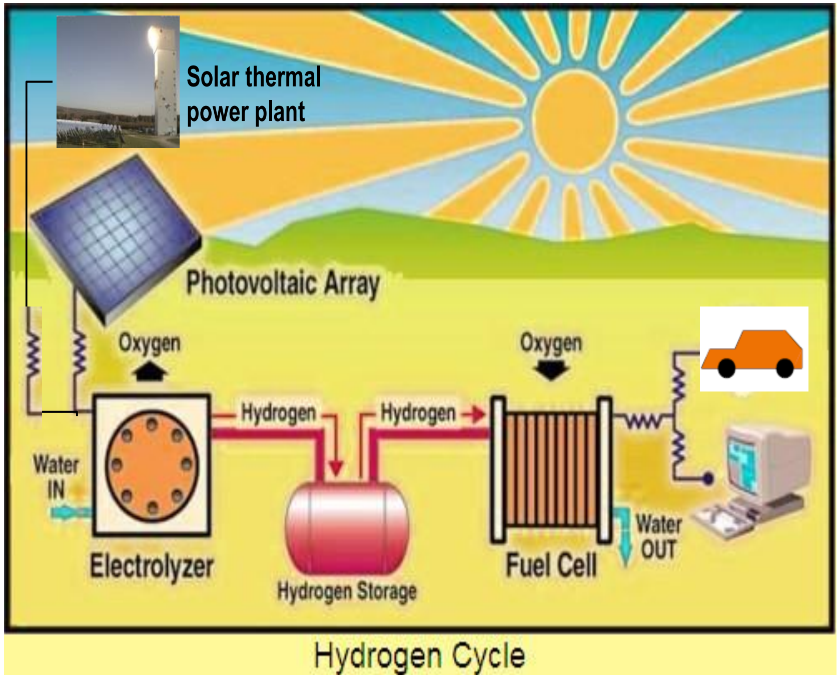
- Operation temperature has to be feasible and practicable
  Optimum Temperature is between 800 and 1600 K.

- Fast reactions are desirable.
- High availability of raw materials.
- High efficiency must be realisable.
- H_2 production costs must be acceptable.
- Reference: H_2 from electrolysis by „solar electricity“

Solar Hydrogen supply : Power to Gas/Liquid Technologies

Current such "benchmark" technology: solar-aided electrolysis with electricity supplied from PV or CSP sources.

- **Power-to-Gas (PtG):** Production of a high-energy density gas via the electrolysis of water. First intermediate product is hydrogen; may be converted to methane via methanation requiring CO_2 feed-in.
- **Power-to-Liquids (PtL):** Production of liquid carbon-based energy carriers from electricity via the electrolysis of water. Hydrogen is the intermediate product;is further converted to synthesis gas by adding CO_2 and to synthetic gasoline, Diesel or kerosene.



Summary and Outlook:

- **CSP-aided large scale production of solar fuels** will require the economies of scale offered by **heliostat fields with central tower receivers.**
- CSP systems as electricity providers, can supply - alternatively to photovoltaics/ PVs - the **renewable electricity for electrolysis of steam or steam/CO_2 mixtures** towards hydrogen/syngas production.
- CSP can be employed as the only energy source for the renewable thermochemical production of hydrogen and/or syngas from **water/carbon dioxide via solar redox processes**. Such a route has in principle the potential to culminate essentially to the **synthesis of liquid hydrocarbon fuels using only renewable/recyclable resources: solar energy, water and captured/recycled CO_2.** However, further research efforts are needed for the achievement of these targets in practice.
- Thus, at least for a transition period, CSP-**aided reforming of methane-containing gaseous feedstocks** with natural gas (NG) being the first choice, can offer a viable route for fossil fuel decarbonization and create a transition path towards a “solar hydrogen- solar fuels” economy.
- **(Co-)Electrolysis shares common features with solar redox processes:** both involve the composition optimization and the development of bulk, porous oxide structures that perform cyclic redox operations for extended periods of time.

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Acknowledgements:

- **To EU:** for funding within several Projects within the 6th and 7th Framework Programmes, the Fuel Cells and Hydrogen Joint Technology Initiative (SOLREF, HYDROSOL Series Projects, and the Marie-Curie Action schemes (ATLAS-MHC Project).

MARIE CURIE ACTIONS

SEVENTH FRAMEWORK PROGRAMME

atlas MHC

Thank you for your attention !

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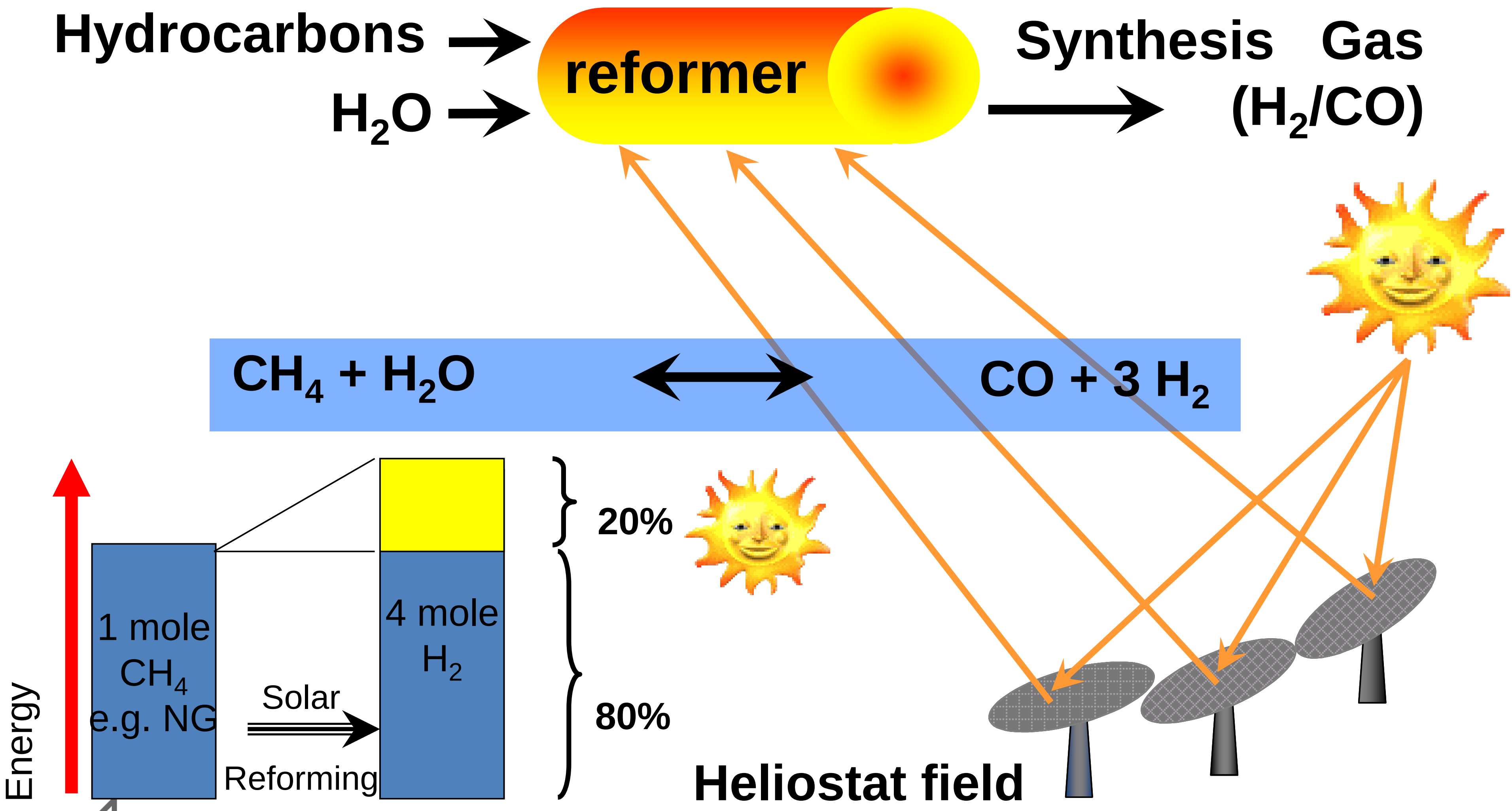
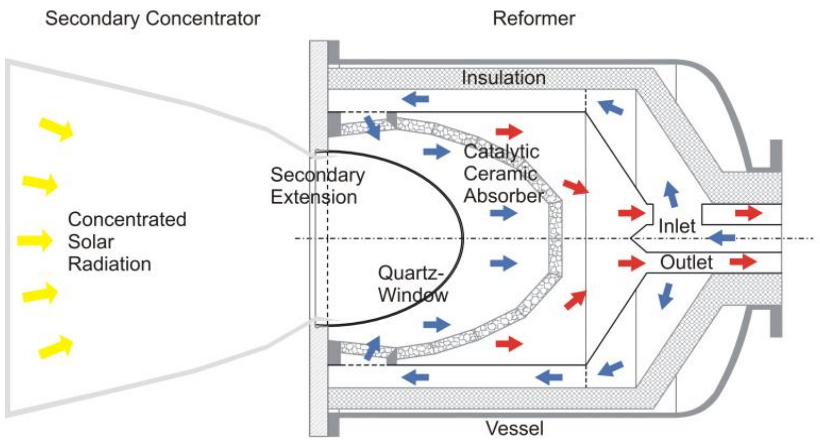
Extra slides

From “Reforming” to “Solar Reforming”



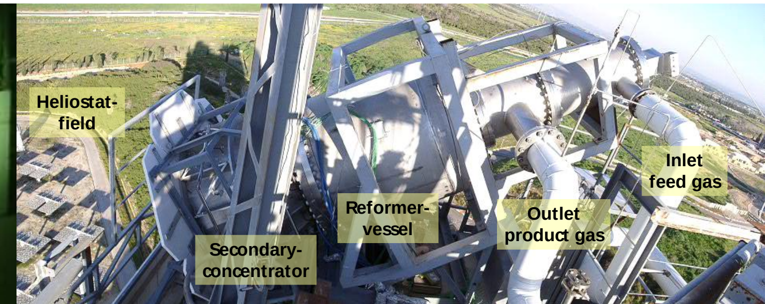
Directly heated volumetric receiver/reformers: SOLASYS, SOLREF



Volumetric Reactor/Receiver realised in EU-project SOLASYS (1998-2002)

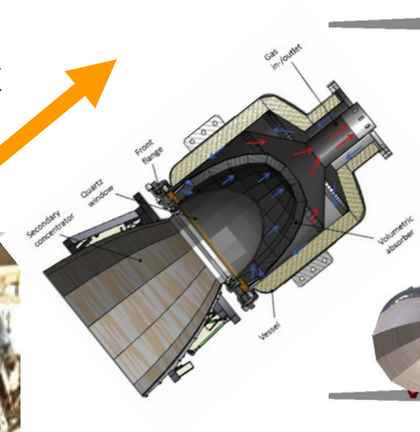
Directly heated volumetric receiver/reformers: SOLASYS, SOLREF

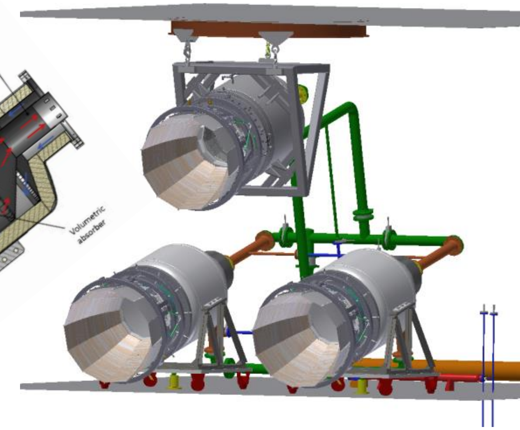
- Pressurised solar receiver,
  - Developed by DLR
  - Tested at the Weizmann Institute of Science, Israel
- Power coupled into the process gas: 220 kW_{th} and 400 kW_{th}
- Reforming temperature: between 765°C and 1000°C
- Pressure: SOLASYS 9 bar, SOLREF 15 bar
- Methane Conversion: max. 78 % (= theor. balance)



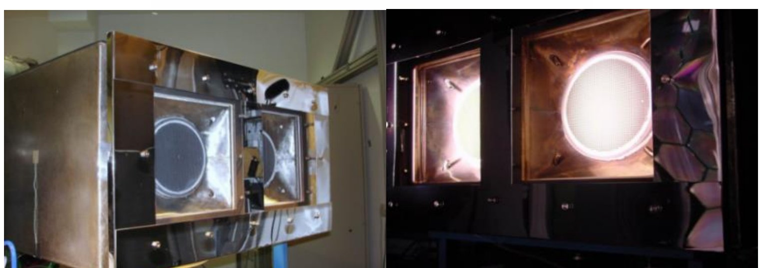
HYDROSOL Technology: Continuous (dual chamber) Solar Receiver/ Reactor scalability and evolution

2017: 750 kW_{th}, Almeria, (Schack et al. Solar Energy, 2016,17).





2008: 100 kW, PSA, Almeria, (Roeb et al, Solar Energy, 2011).

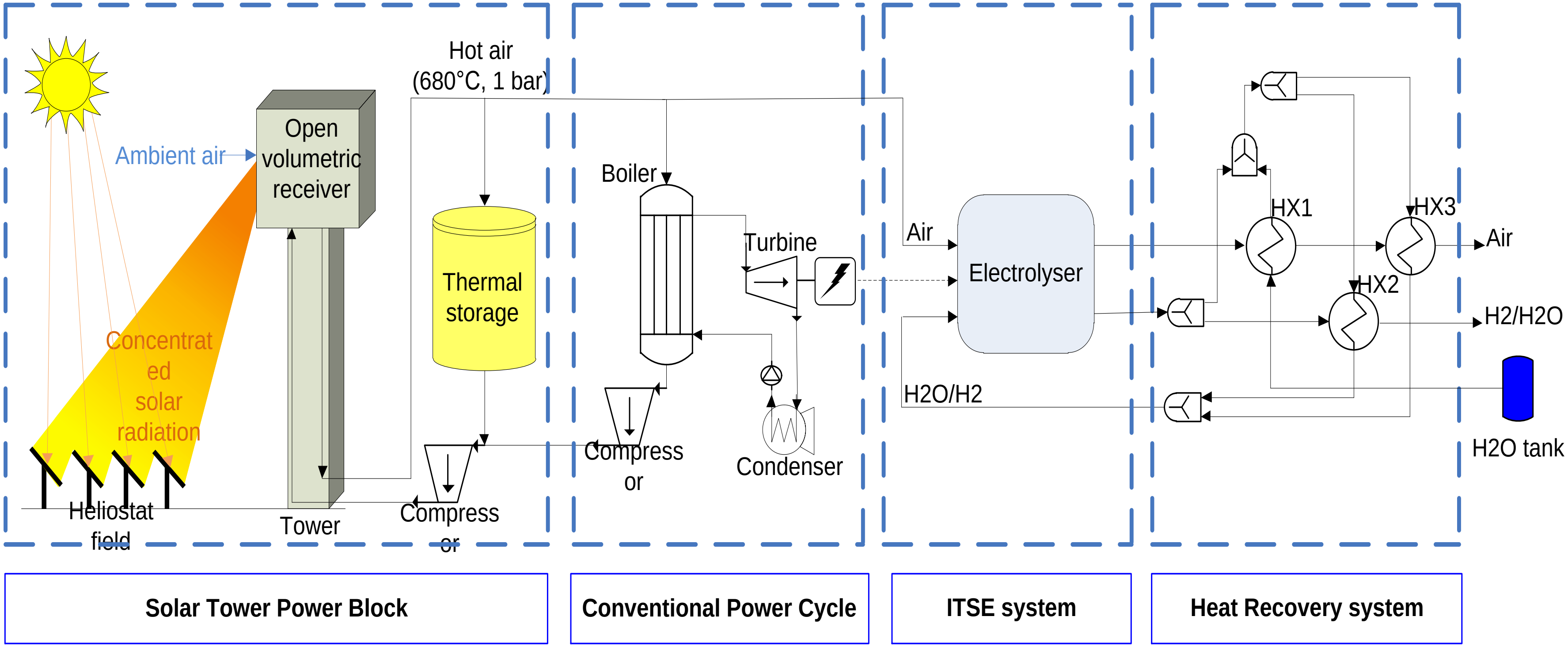


2004: 3 kW, DLR, Cologne, (Roeb et al, WHEC, 2006).

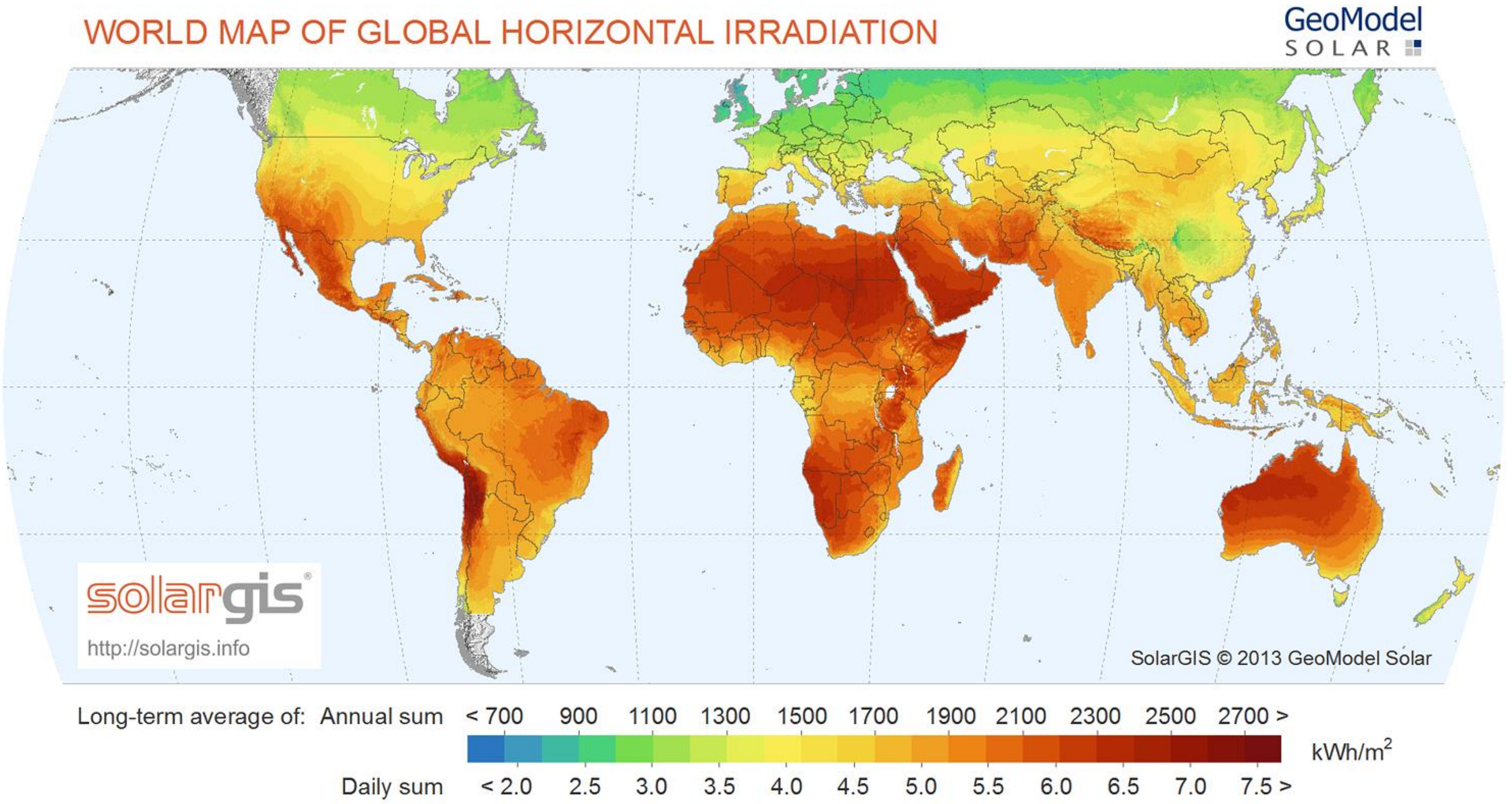
2002: 0.5 kW, DLR, Cologne, (Agrafiotis et al, Solar Energy, 2005).

CSP-electrolysis

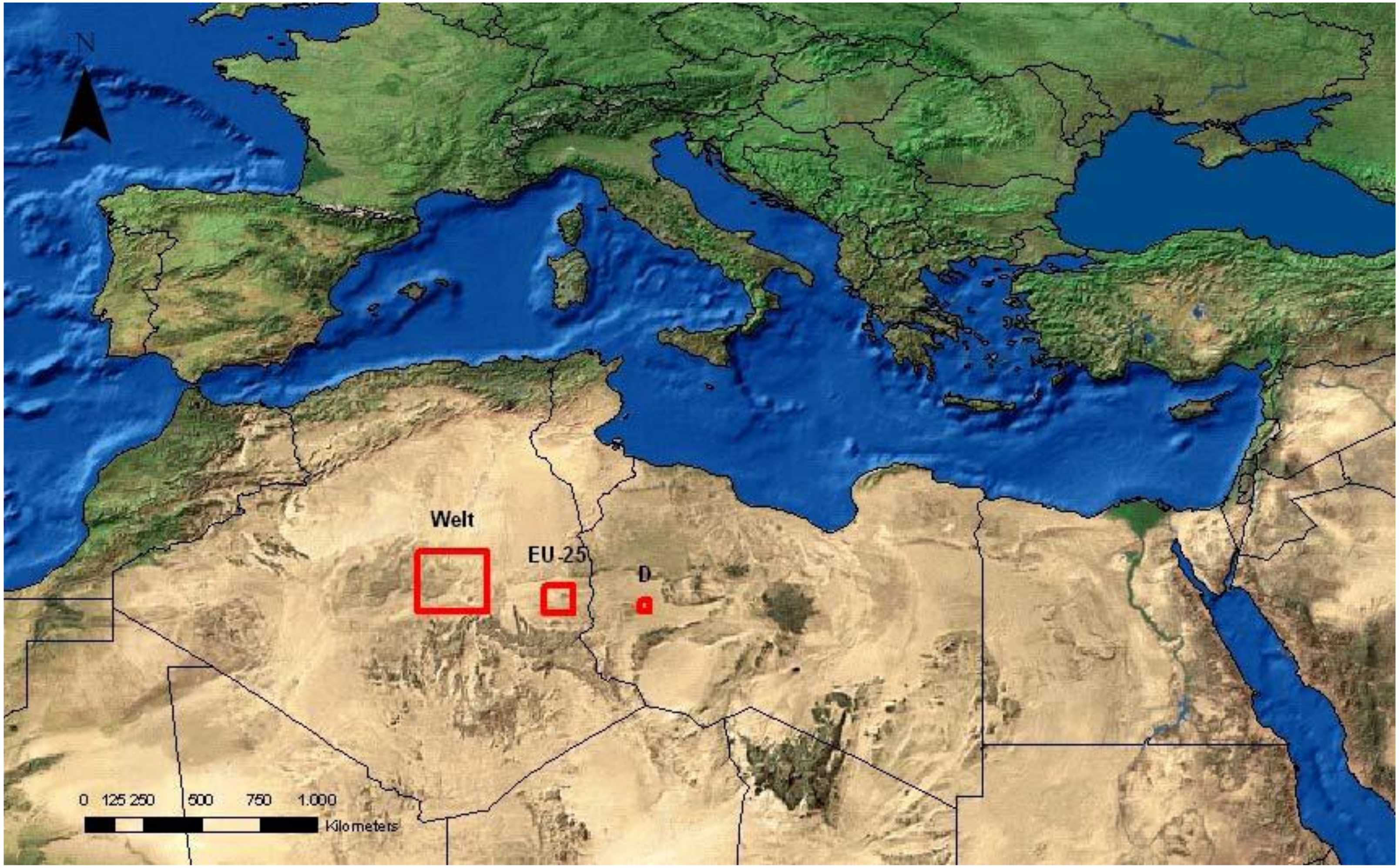
Flow diagram of the coupling of the solar power tower with the electrolyser



Potential of Solar Energy



Potential of Solar Energy



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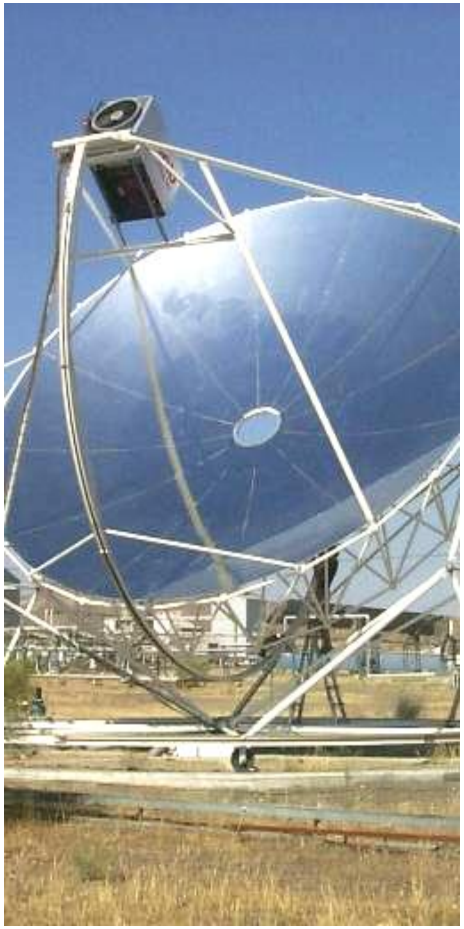
Types of Concentrating Solar Thermal Technologies



Dish-Stirling
650-2250°C

Solar Power Tower
500-2000°C

Parabolic Trough
250-650°C

Linear-Fresnel
250-650°C

(Solar) Chemical Looping Reforming ("Open" TCs)

$CH_4 + MeO_{oxidized} + (\Delta H) \rightarrow CO + H_2 + MeO_{reduced}$ …(1)

$H_2O/CO_2/(N_2+O_2) + MeO_{reduced} \rightarrow H_2/CO/(N_2+\text{less } O_2) + MeO_{oxidized} + (\Delta H)$ …(2)

$CH_4 + H_2O/CO_2/(N_2+O_2) \rightarrow H_2/CO/(N_2+\text{less } O_2) + CO + H_2$ …(3)