

From Solar Energy to Green Mobility

Christos Agrafiotis

Institute of Solar Research
DLR/ Deutsches Zentrum für Luft- und Raumfahrt/
German Aerospace Center
Linder Höhe, 51147 Köln, Germany



Introduction

- Concentrating Solar Systems and Solar Thermal Power Plants (STPPs)
- From solar receivers to receivers/reactors.
- Solar fuels synthesis chemistries.
- Solar fuels technologies: current developments and state-of-the-art.
- Commonalities in materials requirements and reactor concepts among solar energy conversion, storage and transformation-related processes
- R&D needs and outlook.



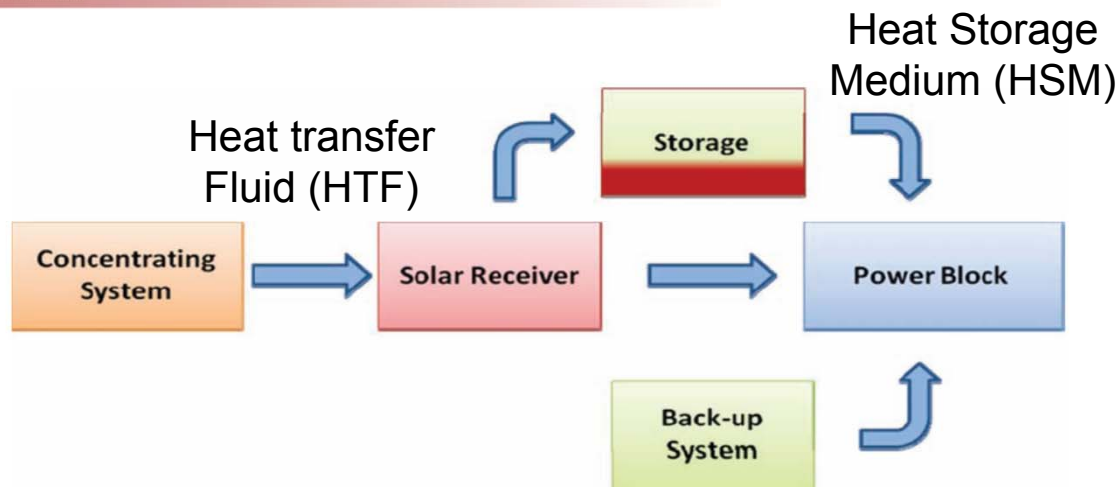
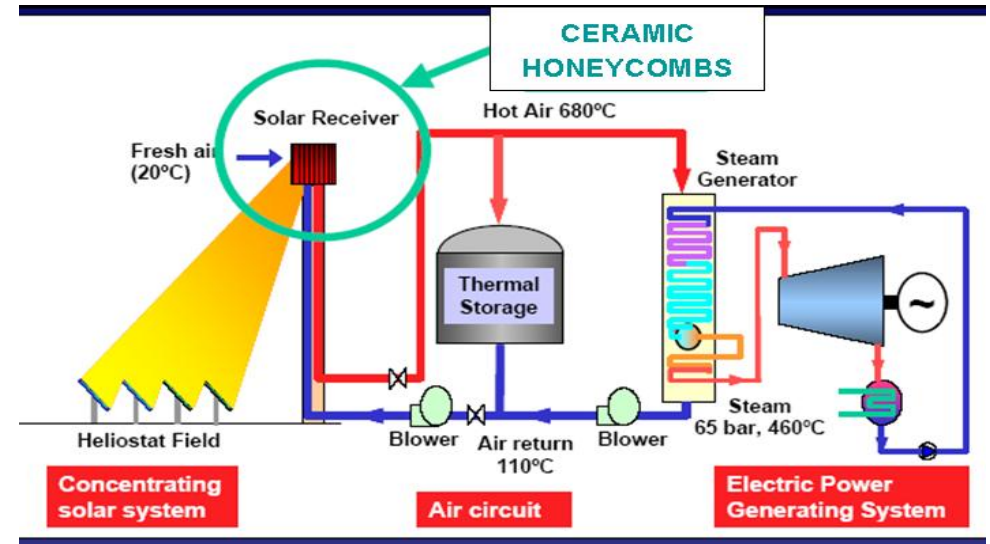
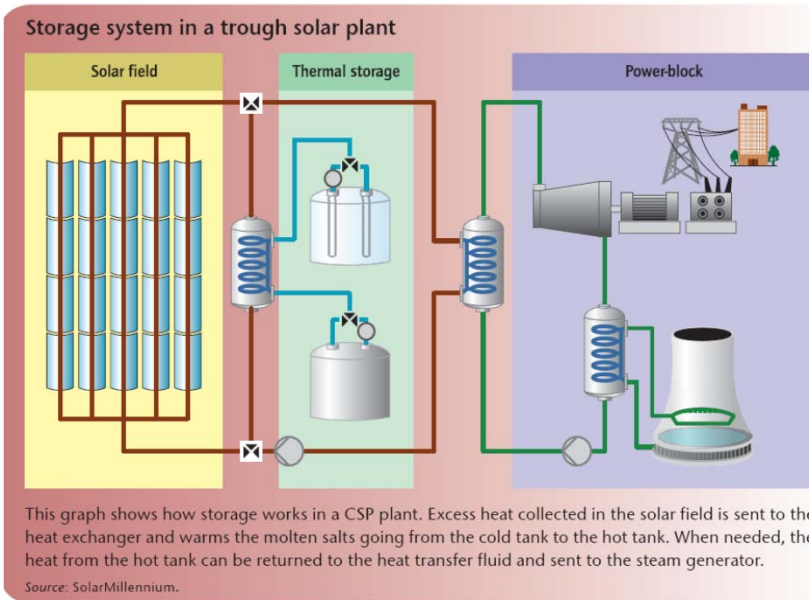
Concentrated Solar Power (CSP) systems

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
 - ...



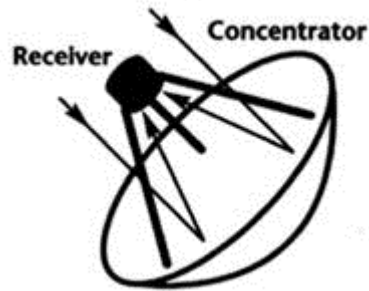
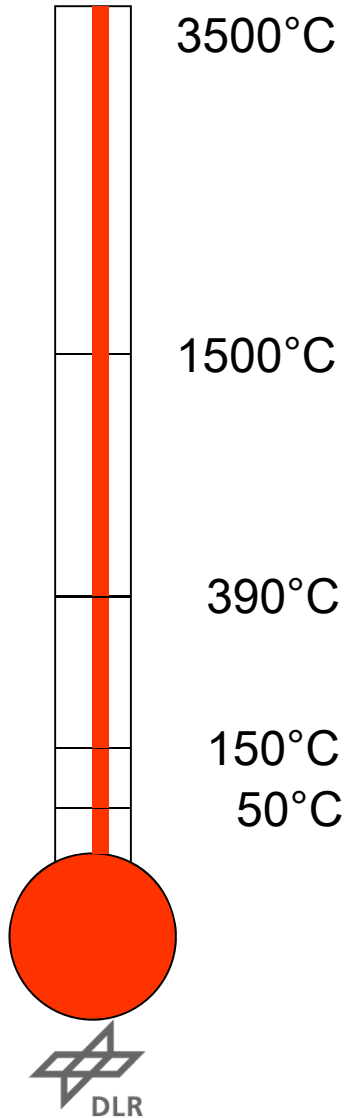
Solar Thermal Power Plants



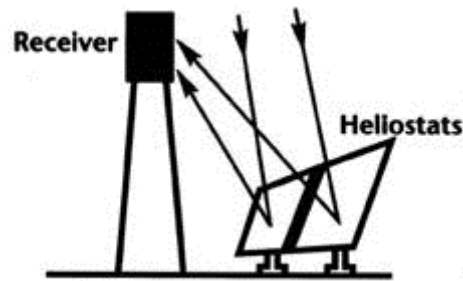
Heat transfer fluid:
thermal oil, air, steam,
molten salt.



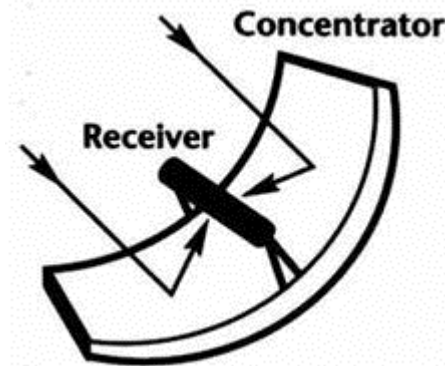
Temperature Levels of CSP Technologies



Paraboloid:
“Dish”



Solar Tower
(Central Receiver System)

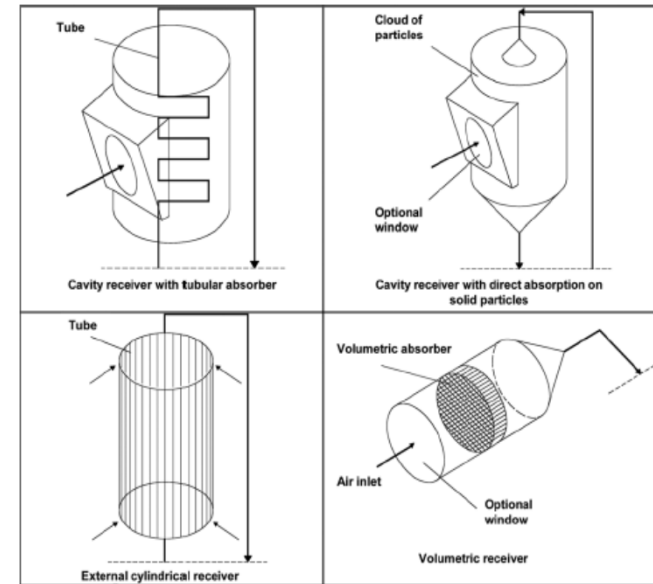


Parabolic Trough /
Linear Fresnel

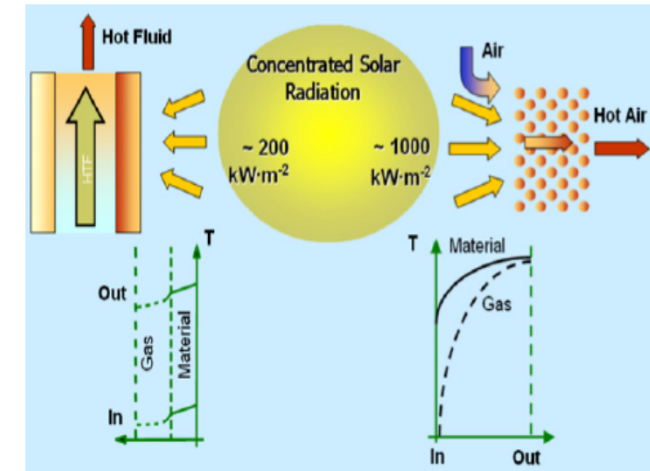


Solar receivers- From solar electricity to solar chemicals

- 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.



Energy densities of fuels

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

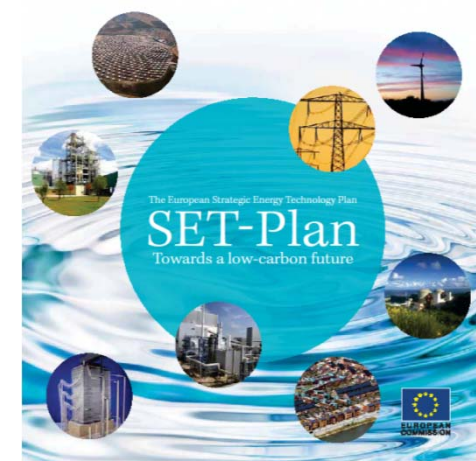
“Solar fuel”: any chemical compound that can react with oxygen to release energy, and was initially formed, at least partly, using energy from solar radiation.

Technology	Energy density (kJ/kg)
Hydrogen	142,000
Gasoline	45,000
Coal	24,000
Sulfur	12,500
Cobalt oxide redox-cycle	850
Lithium-ion battery	580
Molten salt (phase change)	230
Molten salt (sensible)	155
Elevated water dam (100 m)	1

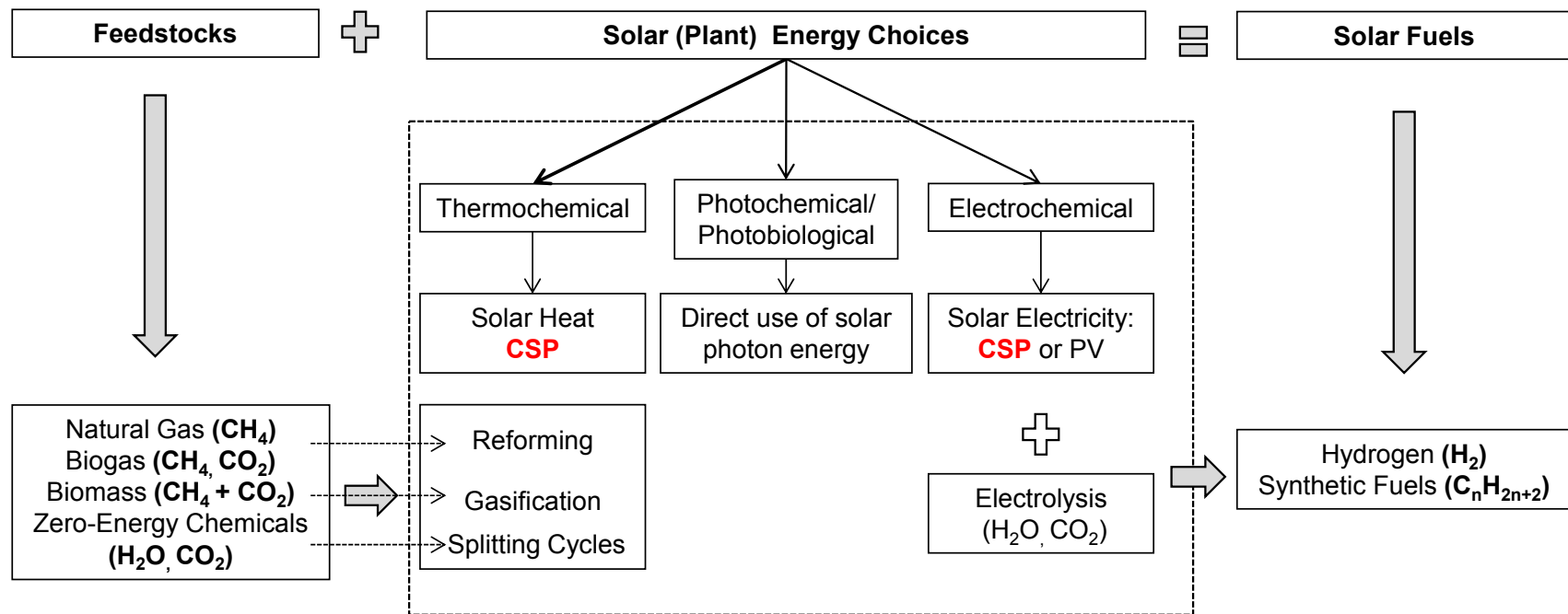


Political Drivers: Examples – EU Sustainable Energy Technology Plan (SET-Plan 2007) G7 Goals (2015)

- **Goals of the EU until 2020 (20/20/20)**
 - **20%** higher energy efficiency
 - **20%** less GHG emission
 - **20%** renewable energy
- **Goal of the EU until 2050:**
 - **80%** less CO₂ emissions than in 1990
- **G7 Goals, Elmau, Germany**
 - **100%** Decarbonisation until 2100
 - **100 bln \$/year** for climate actions in developing countries, large share by industrial investment



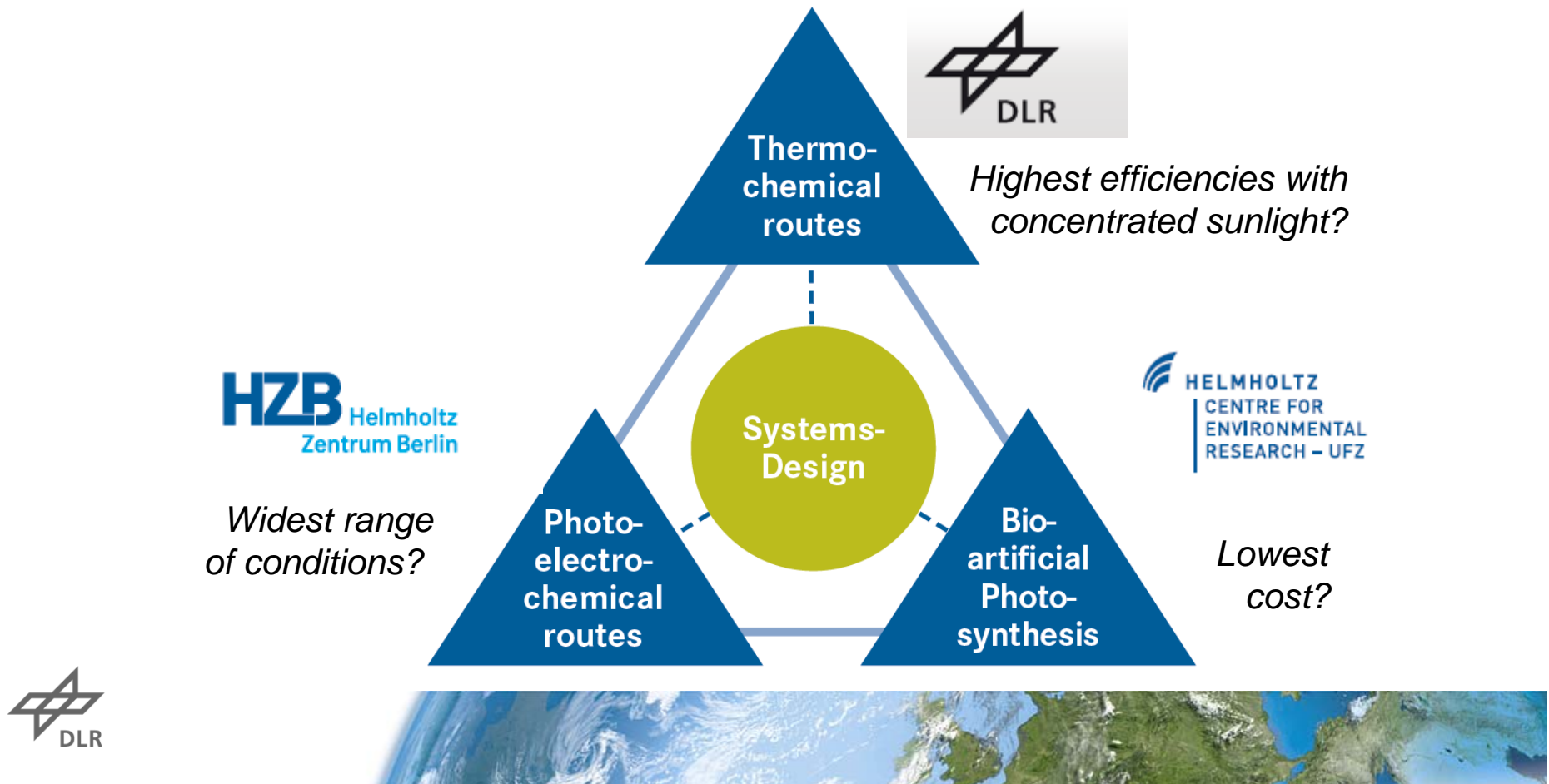
Partial listing of various feedstocks and solar energy variances for solar liquid hydrocarbon fuels production



Strategy and Approach on Solar Fuels in Germany

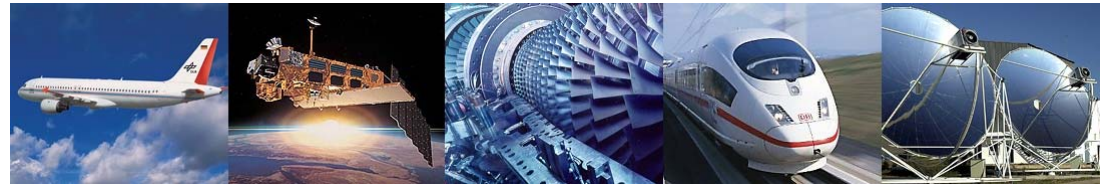
Goal in the Helmholtz Association

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



DLR German Aerospace Center

- Research Institution
- Space Agency
- Project Management Agency

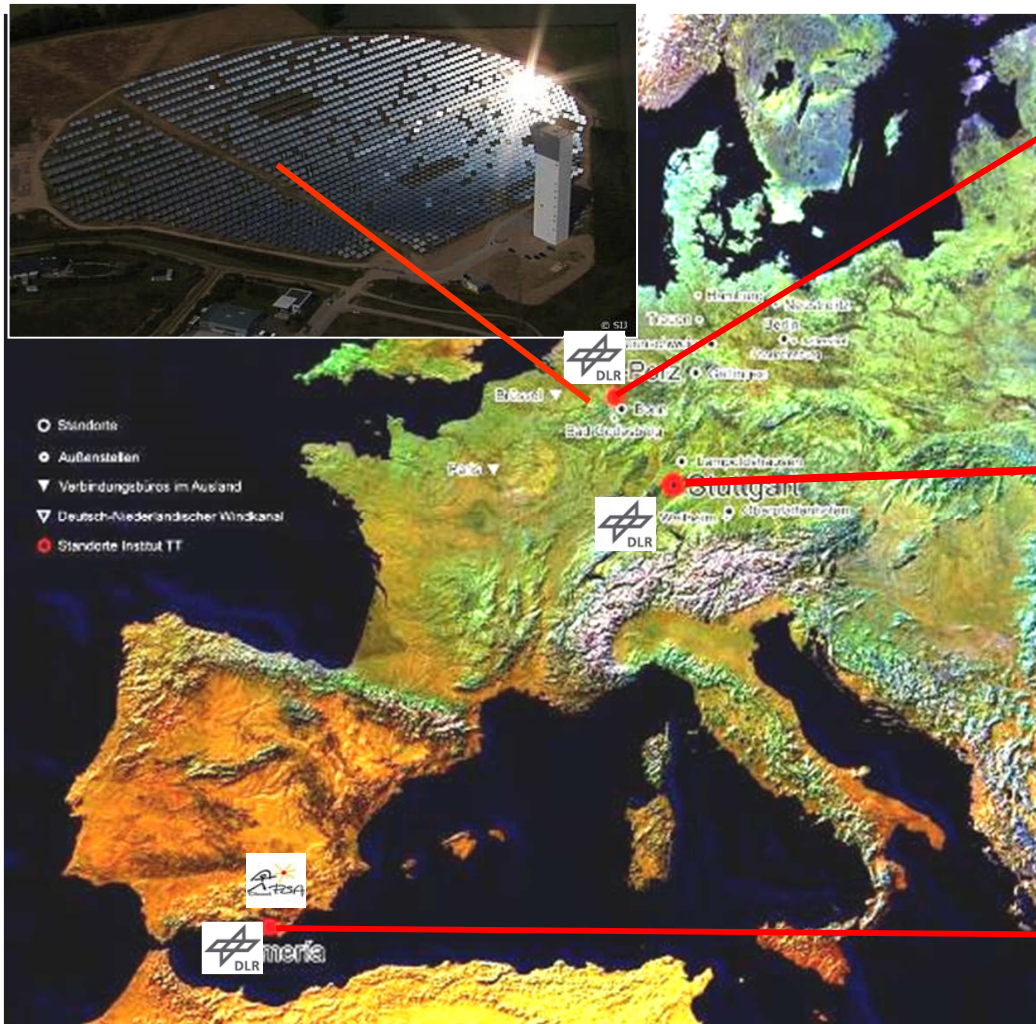


>8000 employees across
32 institutes and facilities at
■ 16 sites.

Offices in Brussels, Paris,
Tokyo and Washington, Almería.



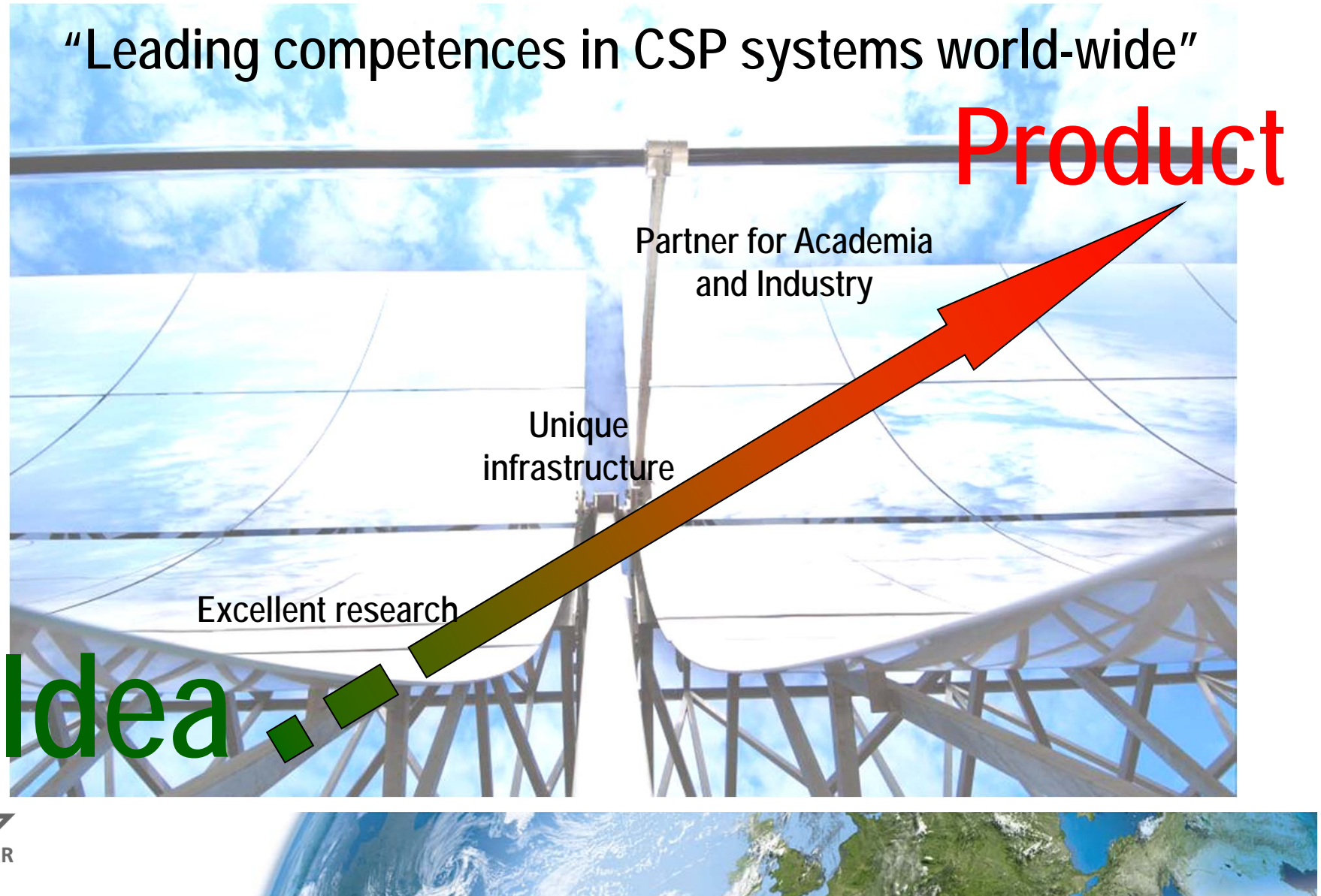
DLR Institute of Solar Research



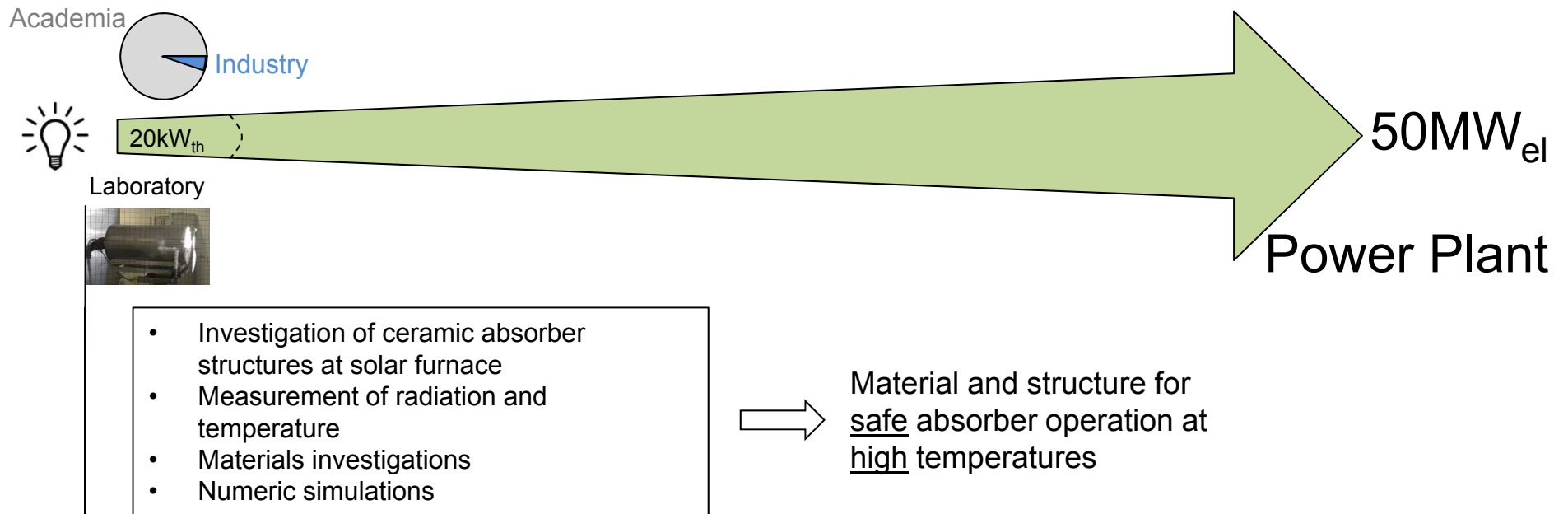
160 staff, 20 M€/a, 4 sites



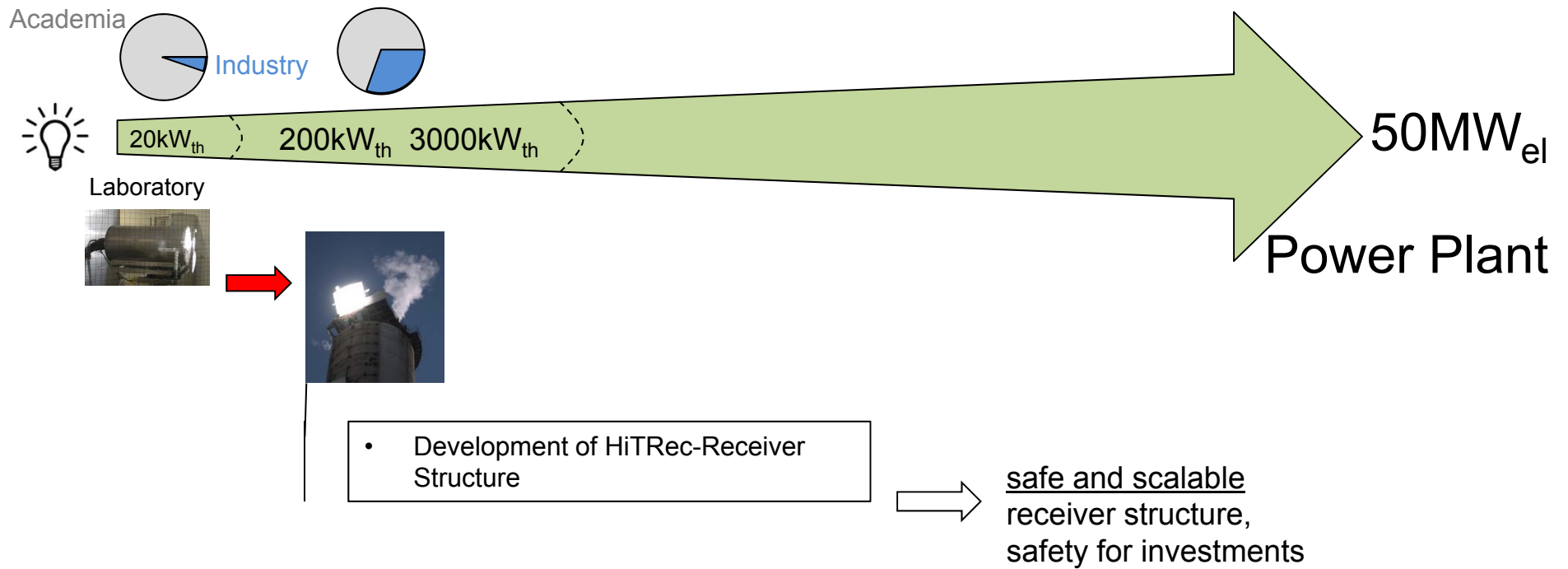
DLR Philosophy of the Institute of Solar Research



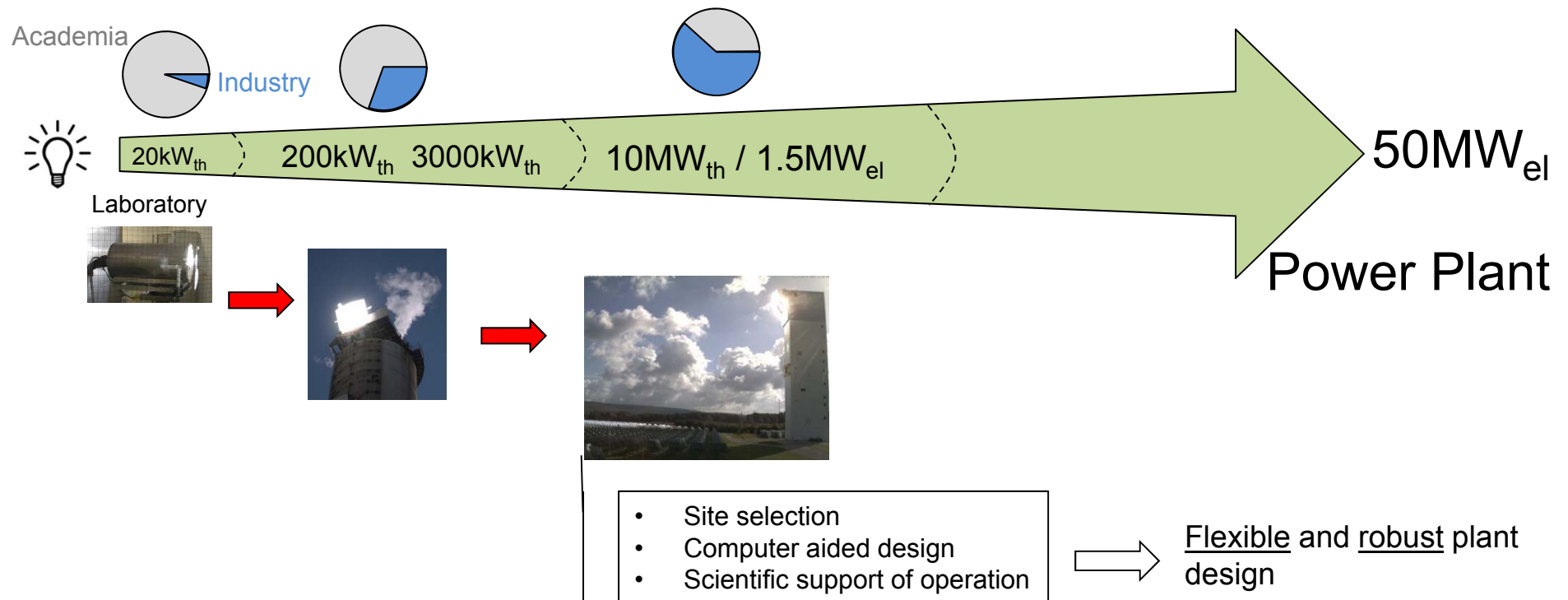
From fundamentals to commercial viability



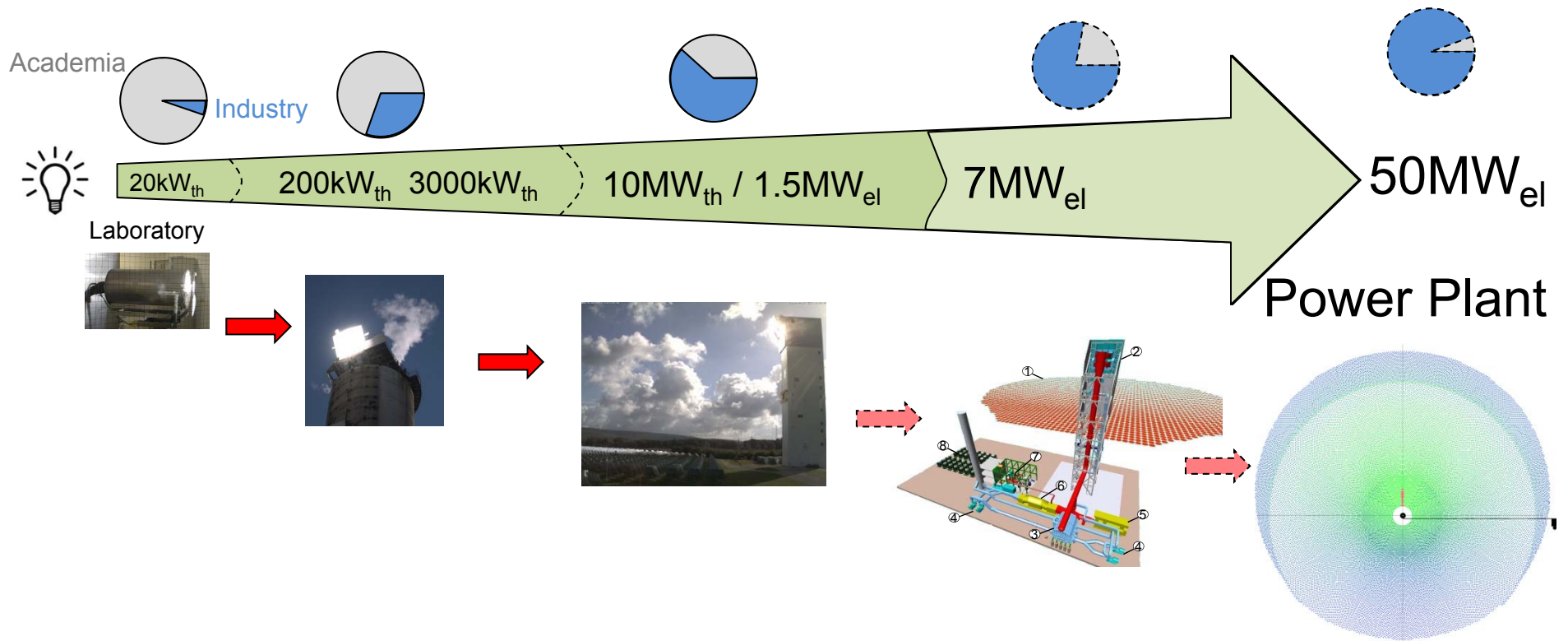
From fundamentals to commercial viability



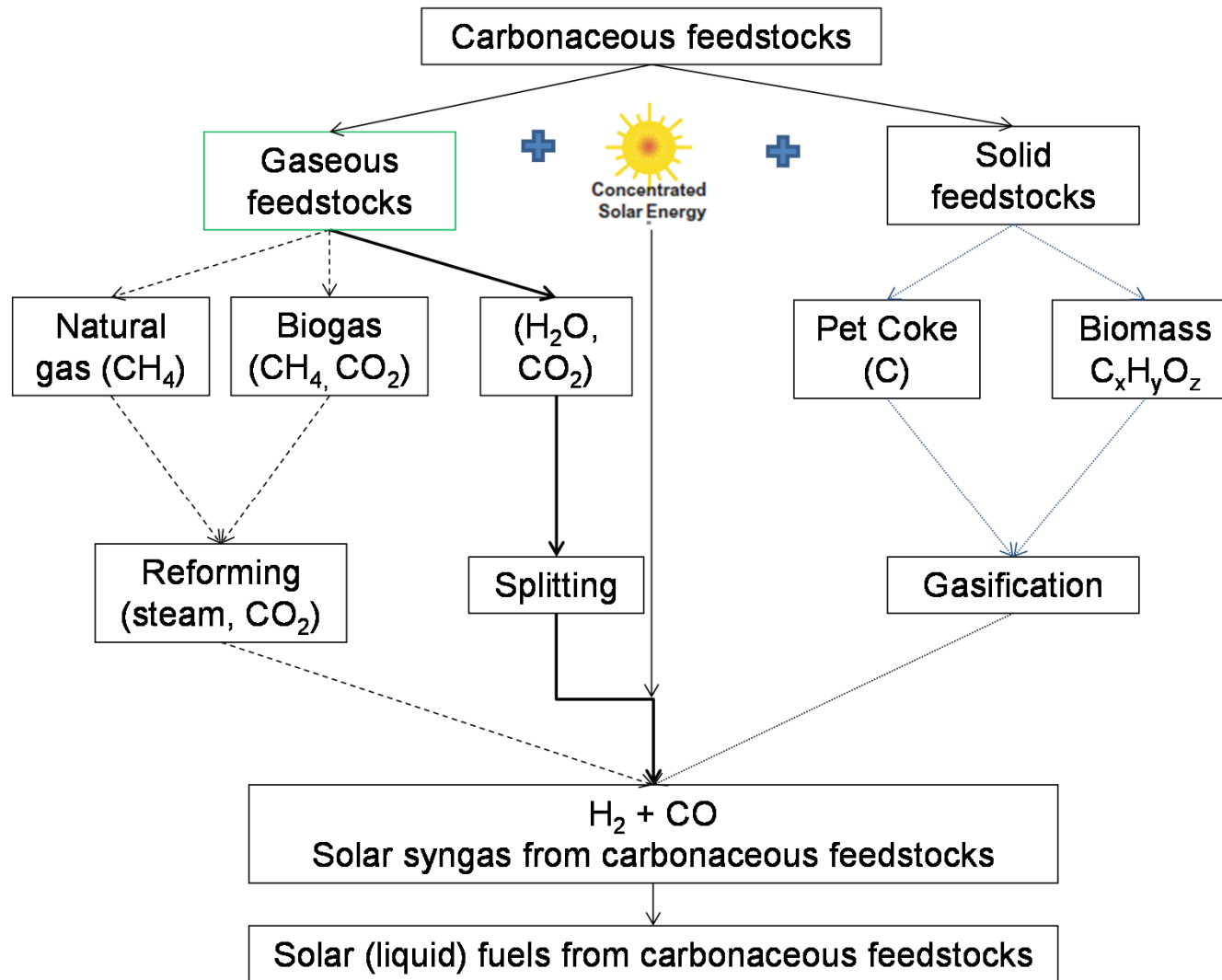
From fundamentals to commercial viability



From fundamentals to commercial viability

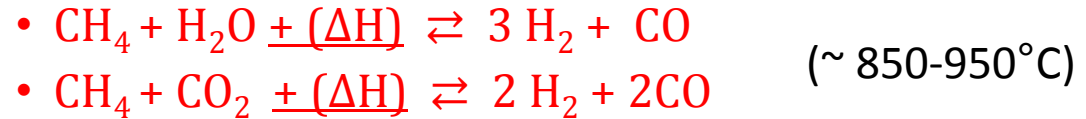


CSP-aided routes for the production of “solar syngas”

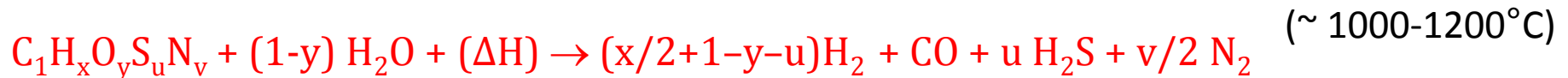


Solar (Fuels) Chemistry

Solar Steam/dry methane Reforming (SMR/DMR)



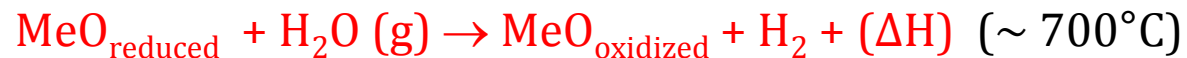
Solar Gasification



Solar Redox processes / Thermochemical (water splitting) cycles

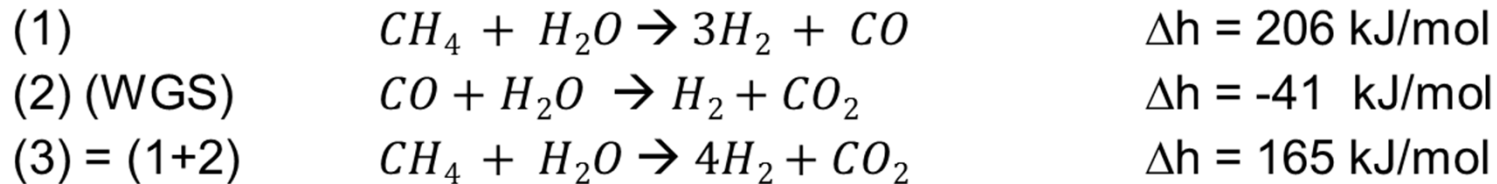
“Net” reactions: $\text{H}_2\text{O} + (\Delta H) \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$

Sulfur-based

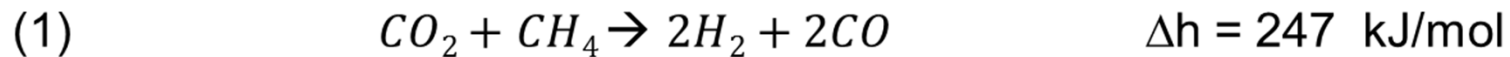


Steam and CO₂-Reforming of Natural Gas Reactions

Steam Reforming:



Dry (CO₂) Reforming:



- Reforming Product is Syngas – Mixture of H₂ 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 CO₂/H₂O 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 H₂ & O₂ production from H₂O
- Why a series of reactions ? The indirect H₂O splitting is necessary since thermolysis is feasible at impractical temperature ranges (>2200°C).

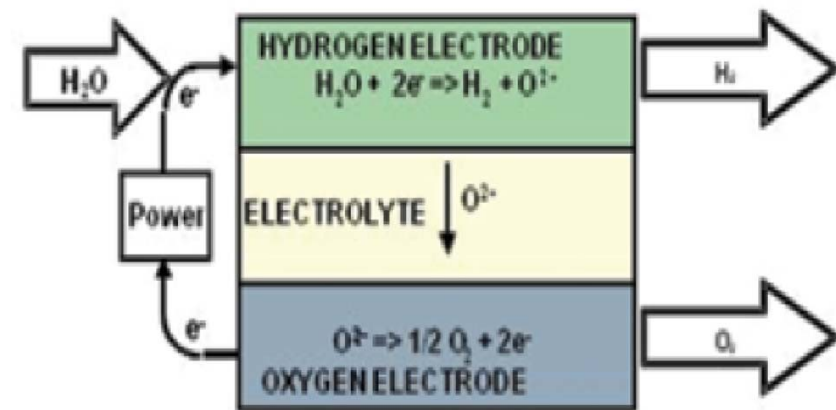
1st Step: Thermal reduction (Regeneration)



2nd Step: H₂O / CO₂ Splitting WS /CDS



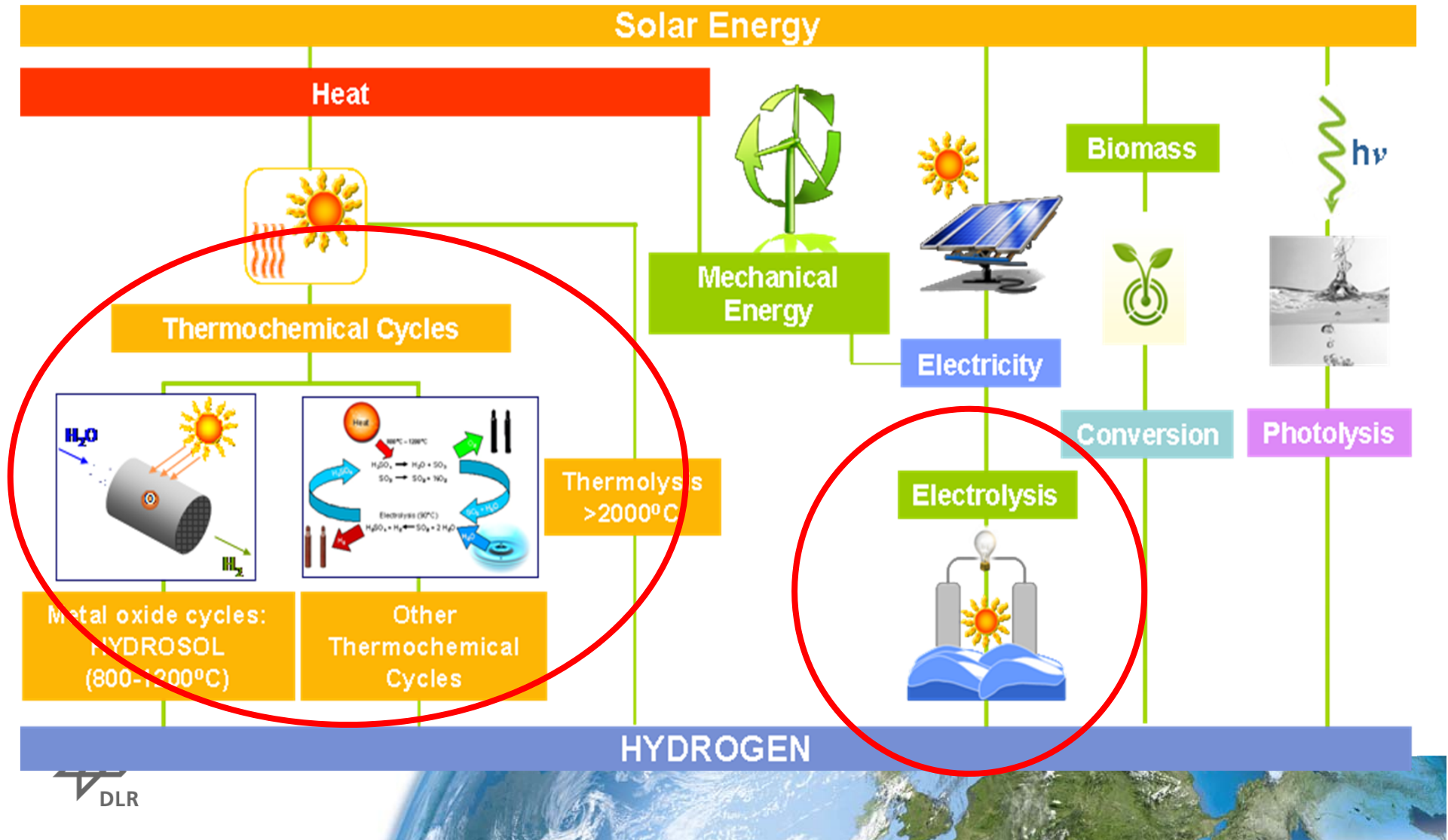
Net effect: Solar Q → Solar Fuels



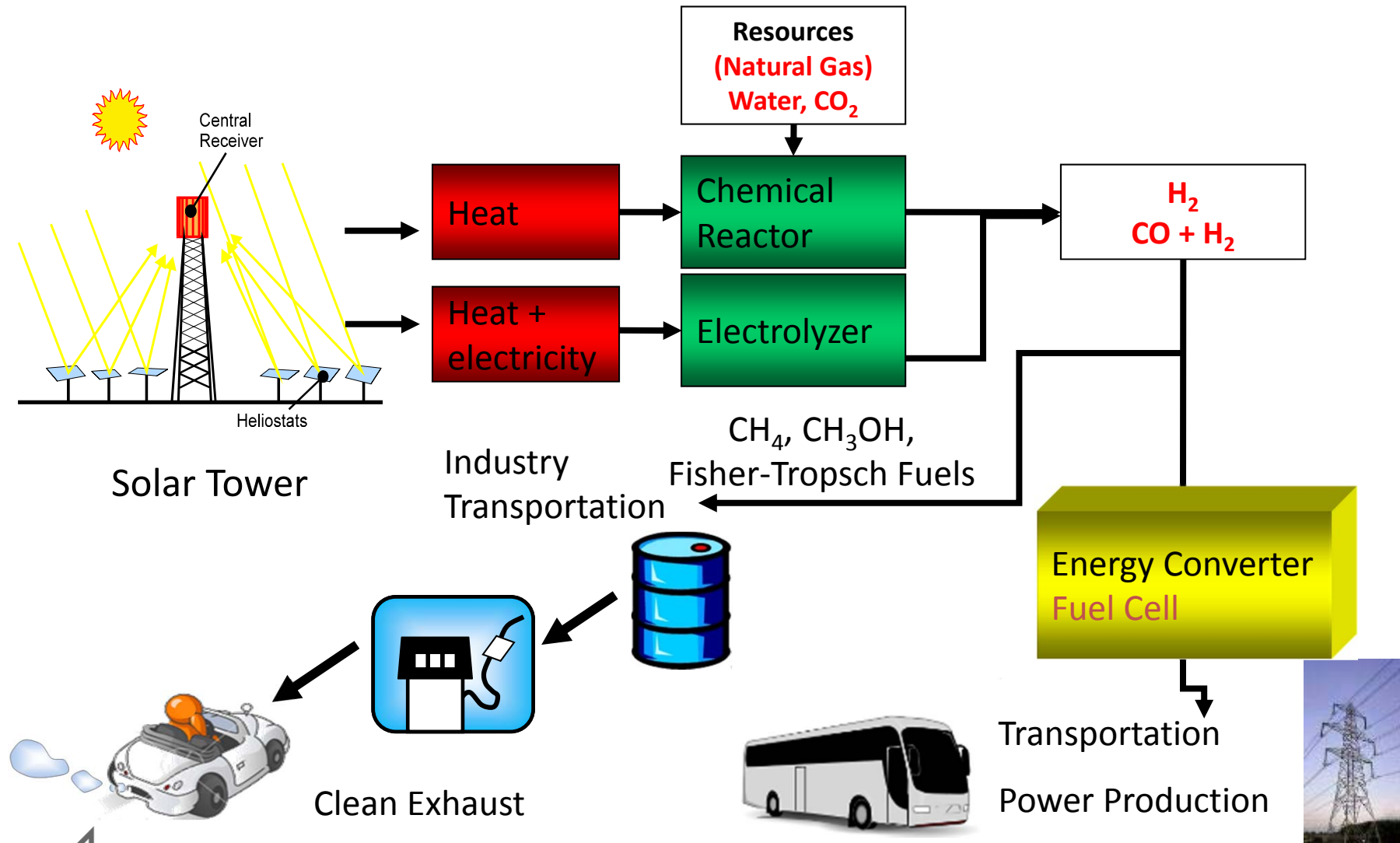
SOEC



Solar Hydrogen



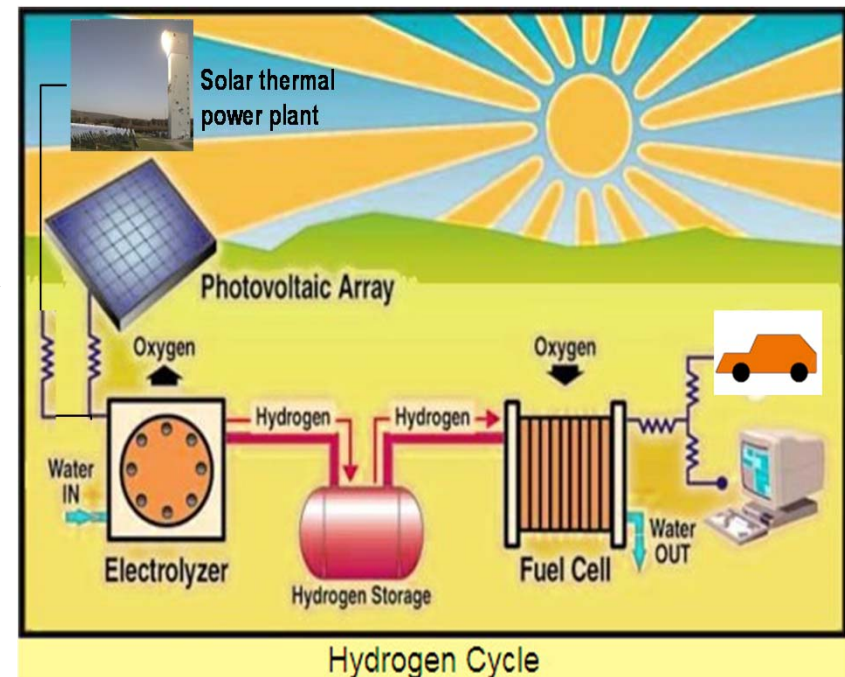
Principle of the solar thermal fuel production



Solar Hydrogen supply : Power to Gas/Liquid Technologies

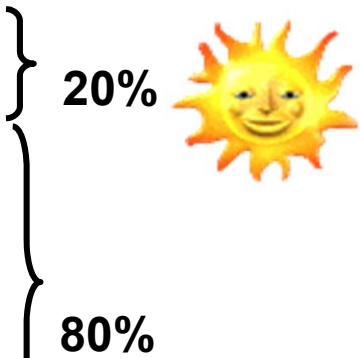
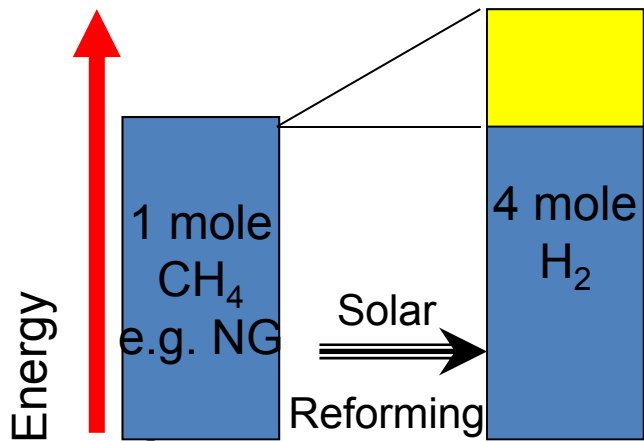
Current such “benchmark” technology: solar-aided electrolysis with electricity supplied from PV or CSP sources.

- **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 CO₂ 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 CO₂ and to synthetic gasoline, Diesel or kerosene.



From “Reforming”

to “Solar Reforming”

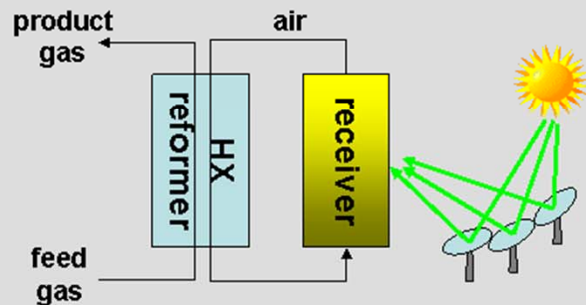


Heliostat field



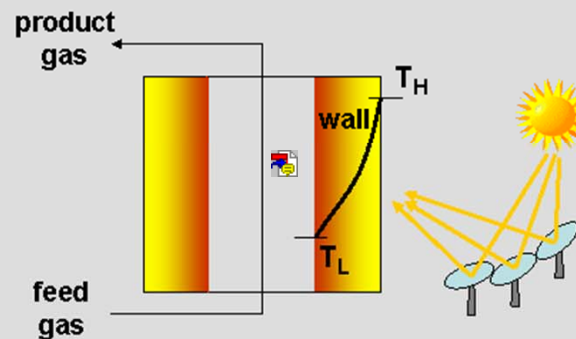
Solar Methane Reforming– Reformer (heating) Technologies

a) decoupled/allothermal



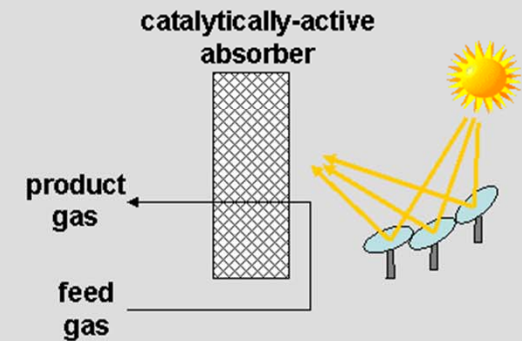
- Reformer heated externally (700 to 850°C)
- Optional heat storage (up to 24/7)
- E.g. **ASTERIX** project

b) indirect (tube reactor)



- Irradiated reformer tubes (up to 850°C), temperature gradient
- Approx. 70 % Reformer-h
- Development: Australia, Japan; Research in Germany and Israel

c) Integrated, direct, volumetric



Source: DLR

- 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



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

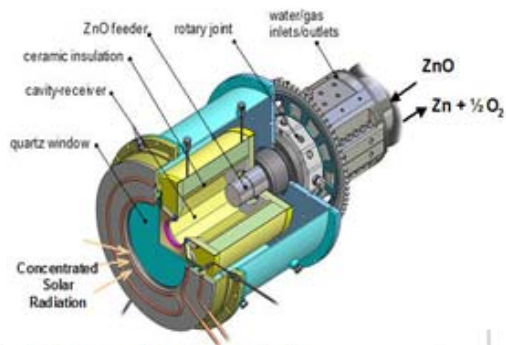
- Employs **fossil fuel (CH₄)** as reactant.
- Solid catalyst: Ni-based catalysts supported on CaAl₆O₁₀ or MgAl₂O₄; noble metals (Ru, Rh, Pd, Pt); Fe, Co.
- Temperature range: **700-850°C**.
- Gaseous reactants can be fed **continuously**.
- Employs **CO₂ as a reactant**; i.e. can “reuse/valorize” atmospheric CO₂.
- Solid redox-pair materials: ferrites (NiFe₂O₄, CoFe₂O₄), CeO₂-ZrO₂, perovskites (La_{1-x}Sr_xMn_yAl_{1-y}O_{3-δ}).
- 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

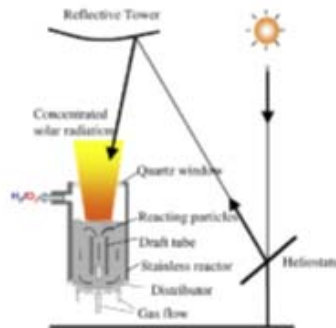
- “Structured” reactors.
- Solar heating: direct or indirect.
- Structured & non-structured (particle) reactors.
- Solar heating: only direct (required Ts too high for indirect heating).



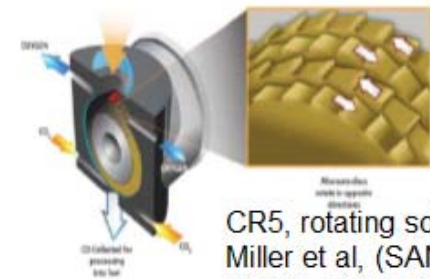
Solar receiver/reactor types (particles vs. porous solids; moving vs. non-moving parts)



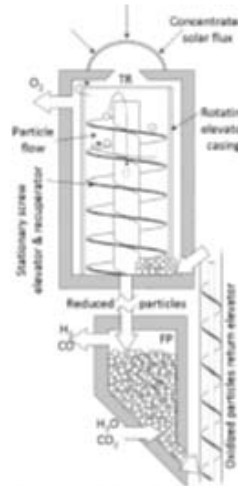
Rotating cavity (powder)
Loutzenhiser et al (ETH),
Materials, 2010.



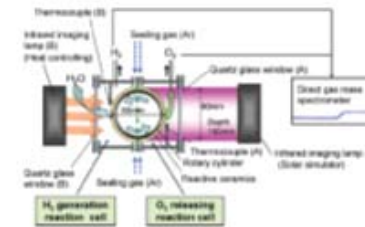
Spouted (powder) bed,
Gokon et al (Niigata Univ.),
IntJHEN, 2011.



CR5, rotating solid disks
Miller et al, (SANDIA) :
PSEC, ASME 2006.



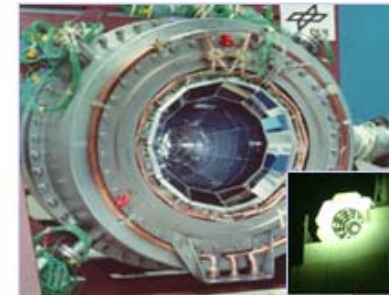
Moving powder bed
Ermanoski et al, (SANDIA),
JSolEnergyEng 2013.



Rotating solid drum
Kaneko et al, (Tokyo Univ.),
EnFuels 2007.



Ceramic honeycombs
SOLAIR receiver (DLR),
2004.



Ceramic foams
SOLREF reactor
(DLR), 2004.



Receiver/reactor technology evolution at DLR

From Materials to Processes

Materials

Components

Systems

TGA



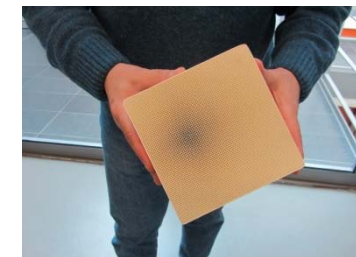
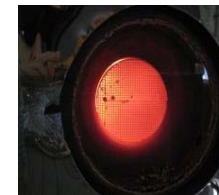
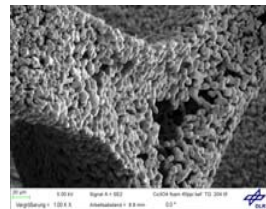
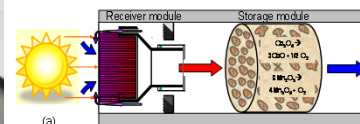
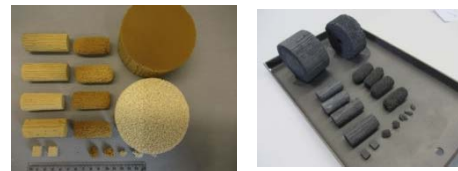
Lab-scale furnace



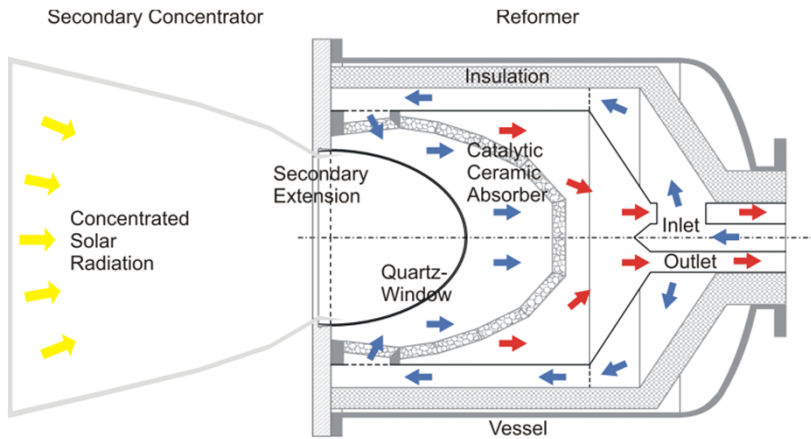
Solar receivers



Solar tower



Directly heated volumetric receiver/reformers: SOLASYS, SOLREF



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



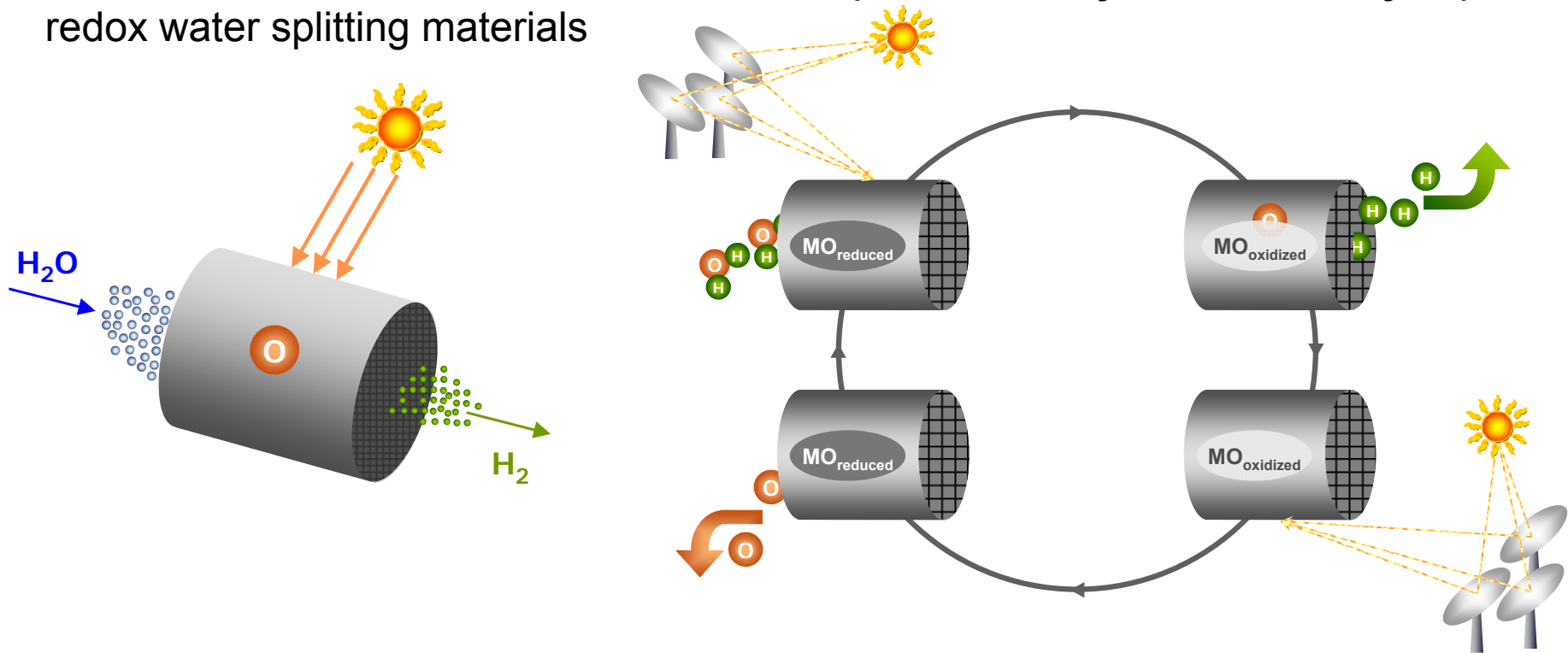
Directly heated volumetric receiver/reformers: SOLASYS, SOLREF

- 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)



H₂ production via CSP-water splitting

The HYDROSOL technology: Monolithic honeycombs capable to absorb concentrated solar irradiation **coated with (or eventually made entirely of) redox water splitting materials**



1st Step: H₂O Splitting (WS)

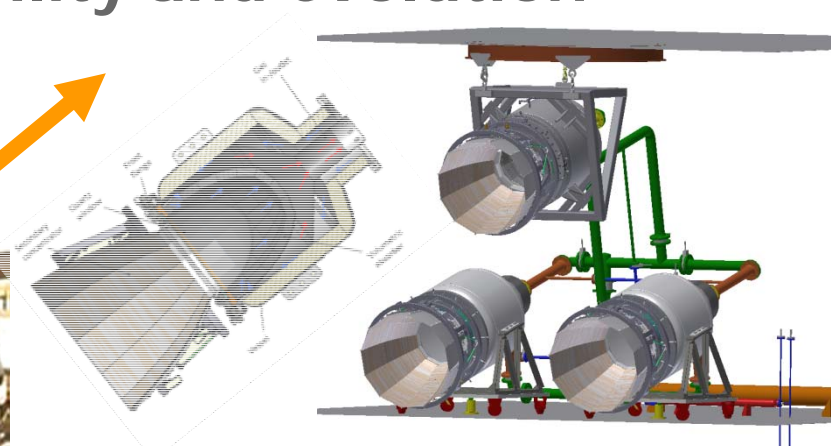


2nd Step: Thermal Reduction (TR/Regeneration)

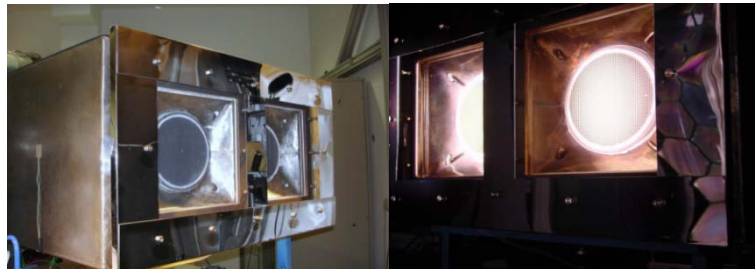


HYDROSOL Technology: Continuous (dual chamber) Solar Receiver/ Reactor scalability and evolution

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).

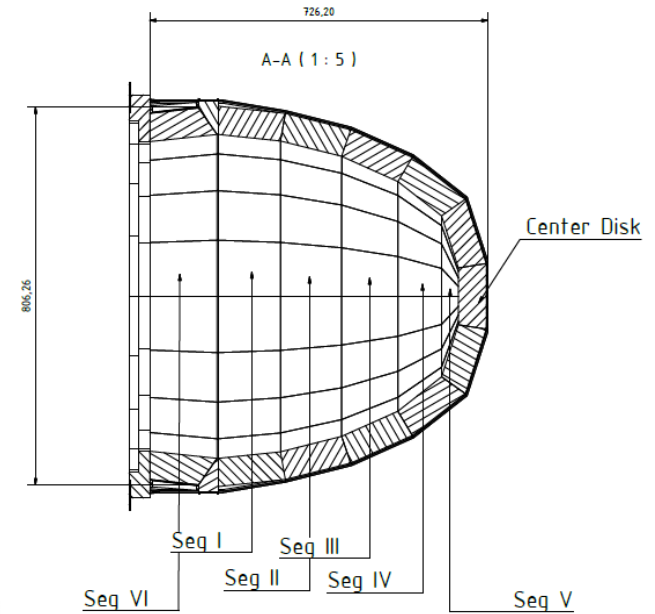
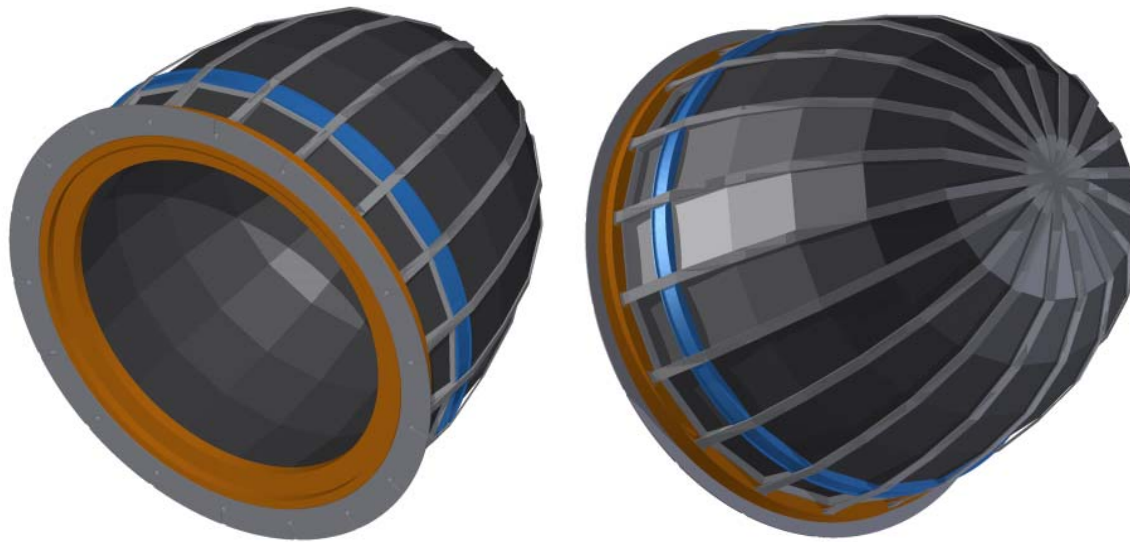


2002: 0.5 kW, DLR, Cologne, (Agrafiotis et al, Solar Energy, 2005).



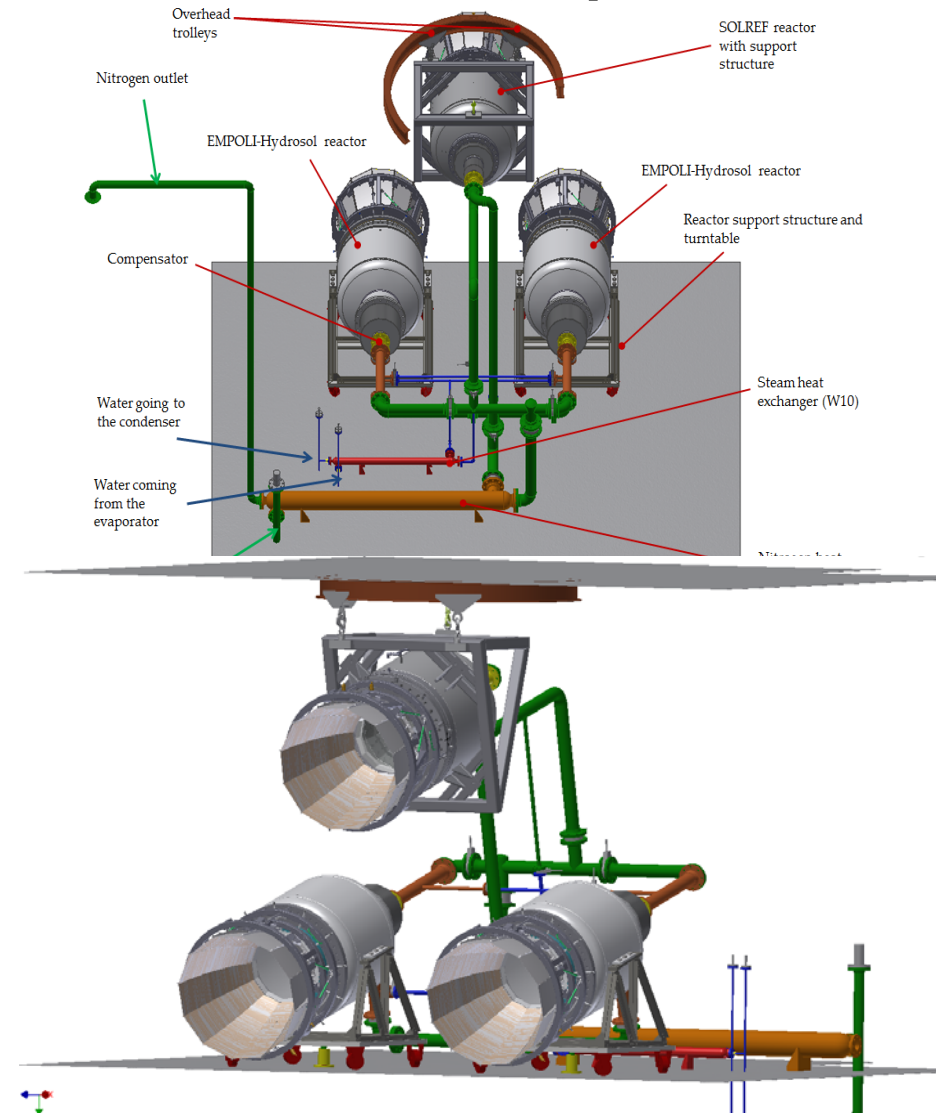
Further scale-up: “Convergence” of reactor concepts

- “Domed” reactor chamber.
- Assembled of individual foam pieces.
- WS/CDS: “**Redox-oxide-made**” foams (from NiFe_2O_4 and $\text{CeO}_2\text{-ZrO}_2$); interchangeable with catalyst-coated ones (SMR).



Hydrosol Plant - Design for CRS tower PSA, Spain

- European FCH-JU project
- Partners: APTL (GR), DLR (DE), HELPE (GR), CIEMAT (ES), HYGear (NL)
- 750 kW_{th} demonstration of thermochemical water splitting
- Location: Plataforma Solar de Almería, Spain, 2017
- Reactor set-up on the CRS tower
- 3 Reactors: two work on regeneration step while the third on water splitting (T = 1400-1100°C).
- Storage tanks and PSA on the ground.



CeO₂-made foam reactor (ETH)

energy&fuels

Article
pubs.acs.org/EF

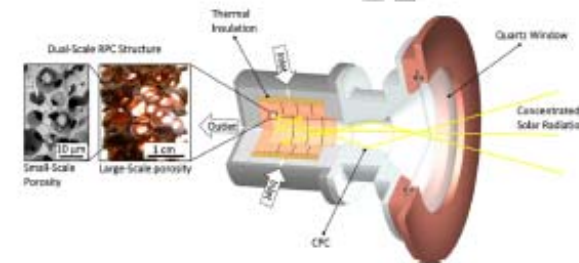
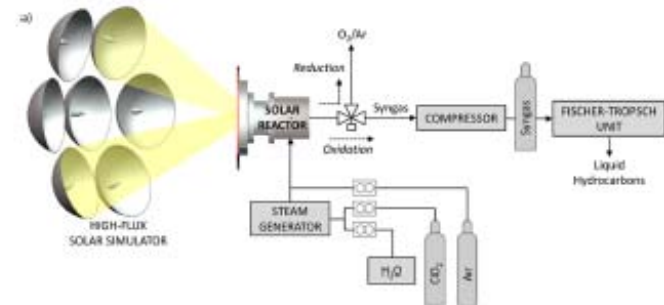
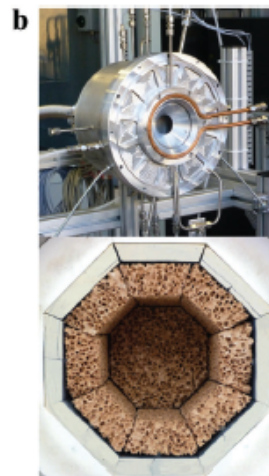
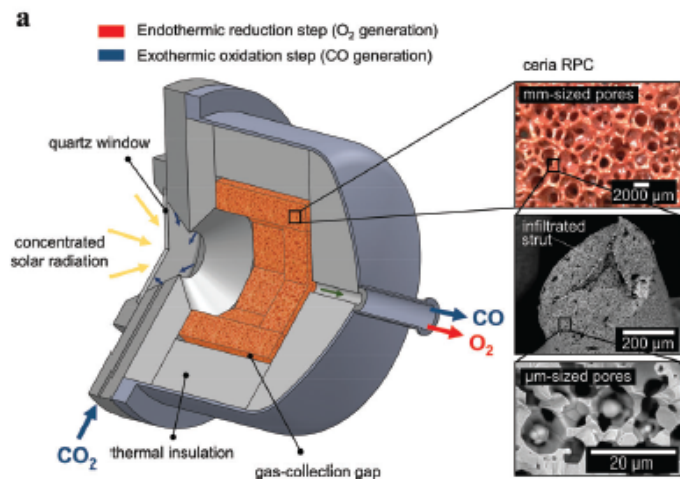
Demonstration of the Entire Production Chain to Renewable Kerosene via Solar Thermochemical Splitting of H₂O and CO₂

Daniel Marxer,[†] Philipp Furler,[†] Jonathan Scheffe,[†] Hans Geerlings,[‡] Christoph Falter,[§] Valentin Batteiger,[§] Andreas Sizmann,[§] and Aldo Steinfeld*[†]

[†]Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland

[‡]Shell Global Solutions International B.V., 1031 HW Amsterdam, The Netherlands

[§]Bauhaus Luftfahrt e.V., 80807 München, Germany



D.A. Marxer, P. Furler, J.R. Scheffe, H. Geerlings, C. Falter, V. Batteiger, A. Sizmann, A. Steinfeld, Demonstration of the entire production chain to renewable kerosene via solar-thermochemical splitting of H₂O and CO₂, *Energy & Fuels*, (2015).

D. Marxer, P. Furler, M. Takacs, A. Steinfeld, Solar thermochemical splitting of CO₂ into separate streams of CO and O₂ with high selectivity, stability, conversion, and efficiency, *Energ. Environ. Sci.*, 10 (2017) 1142-1149.

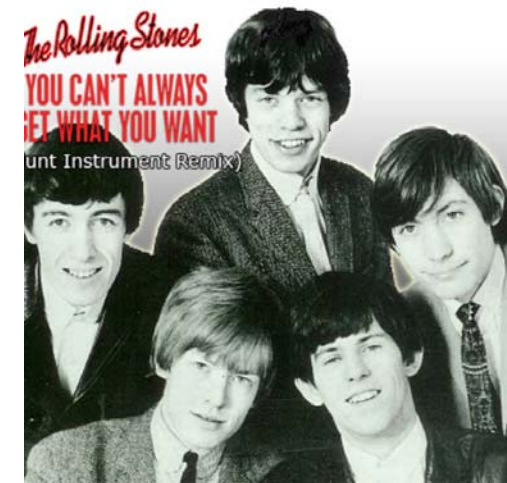


Criteria for the selection of processes of solar thermal hydrogen production

- 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.
- H₂ production costs must be acceptable.
- Reference: H₂ from electrolysis by „solar electricity“

“...You can't always get what you want,
but if you try, sometimes you just might find,
you get what you need...”.....

The Rolling Stones, 1969.



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**, that can comfortably generate solar thermal fluxes in the MW capacity.
- 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 CO₂**. However, **further research efforts are needed for the achievement of these targets in practice**.
- The two main research tasks are the improvement of solar interfaces and **integrated heat recovery** schemes in the one hand and solving the main materials-related issues and **providing the right functional materials at reasonable costs** in the other hand.
- 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.



Summary and Outlook:

- **Solar reforming:** directly heated reformers can reach **higher operating temperatures**, thus **higher fuel conversion**. Their limitations largely centre on the **need for a transparent quartz window** to allow concentrated solar radiation into the receiver whilst at the same time providing a **gas seal for the reacting gases and products** that in most cases are under pressure.
- Indirectly irradiated reformers **eliminate the window need** at the expense of having less efficient heat transfer - by conduction - through the walls of an opaque absorber. While not able to reach as high operating temperatures, **do not have the size limitations** associated with directly heated reformers.
- In this perspective, perhaps “technically simpler” concepts like, for instance, the tubular indirectly-heated (“**allothermal**”) **reformers** might be more attractive for large-scale implementation and demonstration of the technology.
- **CSP systems as electricity providers, can supply** - alternatively to photovoltaics/ PVs - **the renewable electricity for electrolysis of steam or steam/CO₂ mixtures** towards hydrogen/syngas production.
- **(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.



Thank you for your attention!

