Solar Fuels

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Overview

- European Perspectives: 2020
    - Reasons for solar fuel production, connection to Fuel Cells
- Concentrating Solar Systems
- Solar Fuels short and long term applications
    - Processes
    - Projects and existing pilot plants
- Summary and Outlook

European Perspectives

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Political view: SET-Plan (2007) European Strategic Plan for Energy Technology

- **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 CO_2 emissions than in 1990
- Actions in the field of energy efficiency, codes and standards, funding mechanisms, and the charging of carbon emissions necessary
- Significant research effort for the development of a new generation of CO_2 emission free energy technologies, like
  - Offshore-Wind
  - **Solar**
  - 2nd generation Biomass

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

European Commission

New Energy World IG
fuel cells & hydrogen for sustainability

N.ERGHY

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- Private – Public – Partnership
  - European Commission
  - Industry – Represented by NEW-IG (more than 60 companies)
  - Research – Represented by N.ERGHY (more than 60 research organizations)
- Budget 940 M€
  - 50% EC : 50% Industry + Research
- Contains all Fuel Cell and Hydrogen Research within the European Research Framework Programme 7 since 2008
- Annual Calls for proposals until 2013
- Presently preparation of the JU 2.0 (2014 – 2020)

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

European Commission

New Energy World IG
fuel cells & hydrogen for sustainability

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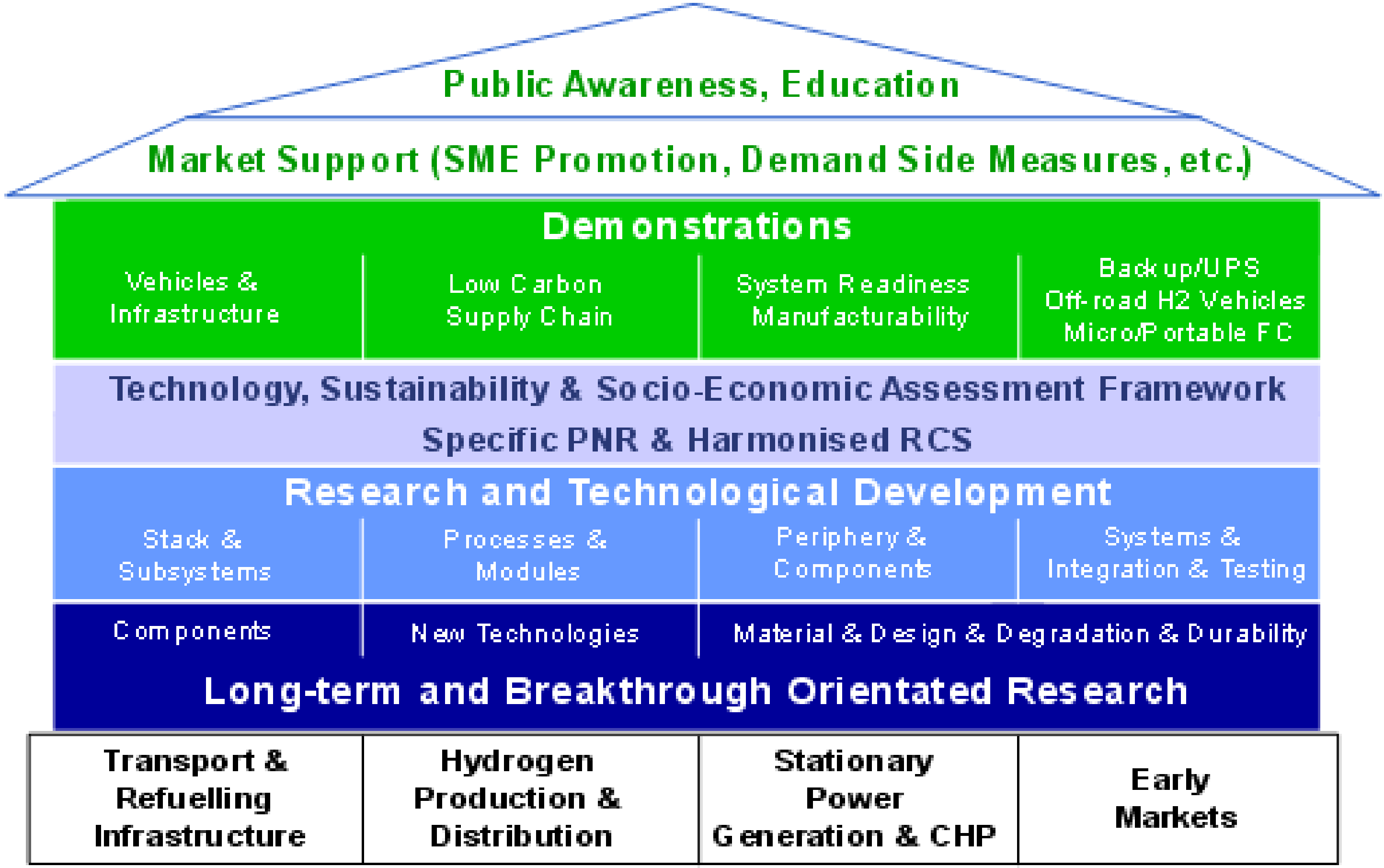
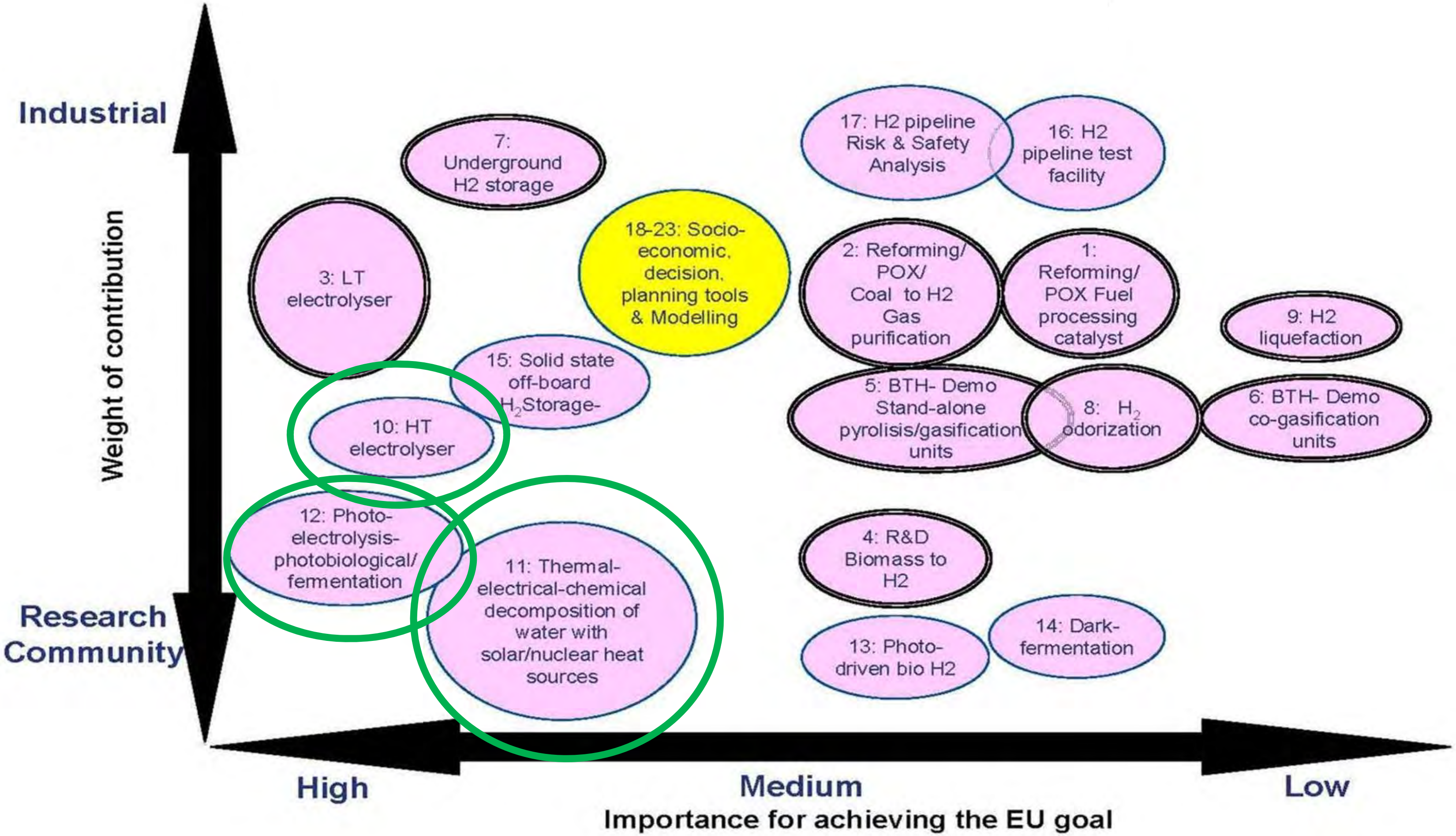


Production-, Storage- and Infrastructure topics of the European Hydrogen and Fuel Cell JTI



Hydrogen production & distribution (including energy storage) *2020 Objectives*

- **Portfolio of cost-competitive, energy efficient and sustainable hydrogen production, storage and distribution processes,**
  - Europe: largest hydrogen pipeline network in the world
  - More than 100 000 bulk and cylinder deliveries per year all over Europe
- **50% of hydrogen used for energy applications produced from renewable sources or from near zero-CO_2-emission sources.**
  - **The mature production technologies include:**
  - **Reforming technologies** (and gas purification) based on **bio-fuels** as well as **conventional fuels**
  - Cost-efficient **low-temperature electrolyzers** adapted for the large-scale use of carbon free electricity
  - **Biomass-to-hydrogen** (BTH) thermal conversion

Studies Published (www.fch-ju.eu)

Long-term and breakthrough oriented research

- Improving efficiencies of technologies for water splitting
  - **High temperature electrolyzers**
  - **Thermo-chemical processes based on solar**, nuclear or waste heat
  - Low-temperature, low-cost biological hydrogen (e.g. enzymes for fermentation) and **photo-electrochemical processes**
  - High capacity and **flexible electrolysis-systems** essential for hydrogen production for the EU wide increasing share of fluctuating renewable energies such as wind or solar

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Hydrogen Storage and Distribution

- Establishment of a safe, efficient and reliable hydrogen distribution and refueling infrastructure.
- Progress has been made in providing options for high volume and safe hydrogen storage such as
  - underground storage capacities
  - liquefaction
- Stepping-stone for long-term research on improved hydrogen storage based on solid and liquid materials for increased efficiency and storage capability.
- For hydrogen distribution, the sector will strive to achieve a delivery cost to weight ratio that can compete with existing fossil fuel solutions

European FCH Technology Objectives until 2020

Transport	Contribution of 500,000 Fuel Cell Electric vehicles (FCEVs) and 1,000+ hydrogen refueling stations towards the transition of the transport sector towards electric drives
Energy conversion	Contributing to the transformation of the European energy mix by producing 50% of H_2 used for these applications from renewables energies or from zero-CO_2 emission sources
Energy storage	Contributing to the integration of intermittent renewable energies (wind, solar) by applying hydrogen storage capacity up to 500 MWh as part of a grid scalable storage
Early Markets	Contributing to the demonstration of cost-efficient solutions with clean and sustainable FCH technologies for material handling vehicles, back-up power and portable power applications
Heat & Power generation	Contributing to the transformation of the energy sector by providing heat and power to more than 50,000 households using stationary fuel cell systems

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Estimated Ressources needed until 2020

- The total estimated financial need for reaching the hydrogen production, storage and distribution objectives is €1806 million.
- Almost 50% of this amount is needed for R&D (€330 million) and demonstration projects (€492 million).
- This has to be covered in the continuation of the FCH-JU under the next Framework Programme the HORIZON 2020

- Financial effort to support market introduction is estimated at €984 million covering
  - deployment of distributed production (€498 million),
  - centralized production and underground storage (€390 million)
  - carbon capture technologies for hydrogen production (€96 million)

Source: New-IG, 2011

Solar Fuels

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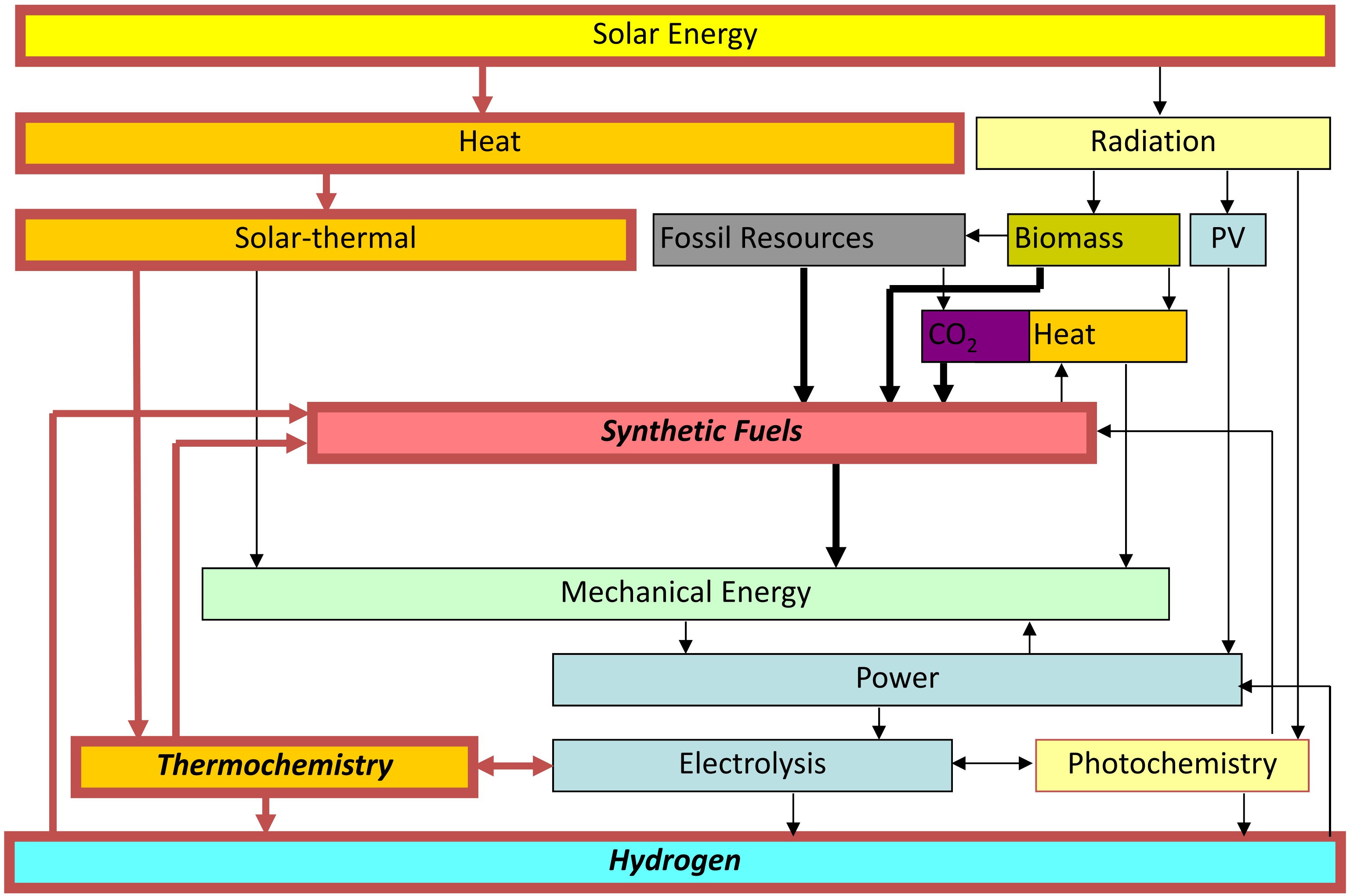
Solar Chemistry instead of Solar Power

- Solar Thermochemistry is efficient because energy conversion steps are reduced!
  - Example: Hydrogen production: $H_2O \rightarrow H_2 + ½\, O_2$
  - Solarchemical: 2 conversions
    - Solar radiation – heat – Chemical reaction
  - Via solar power: 4 conversions
    - Solar radiation – heat – mechanical energy – electrical energy – chemical reaction
- Solar photo-chemistry uses the light directly without any conversion. Photo-chemistry is economical if the reaction needs a large amount of photons
  - Example: Production of Caprolactam an intermediate for Nylon

    Annual production > 200,000 t (by artificial light)

Energy Routes



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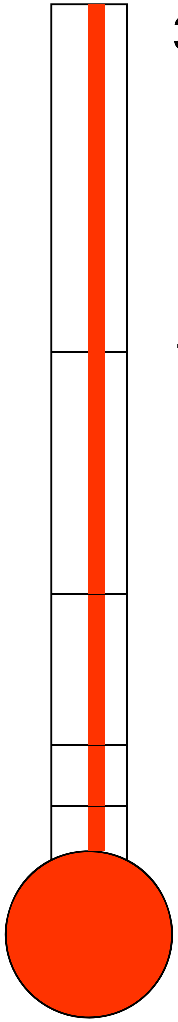
Temperature Levels of CSP Technologies



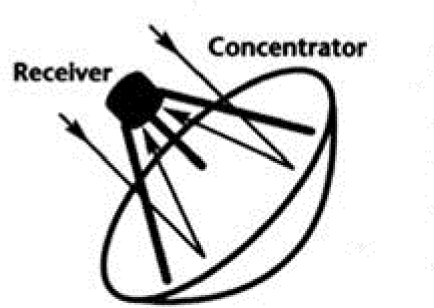
3500°C

1500°C

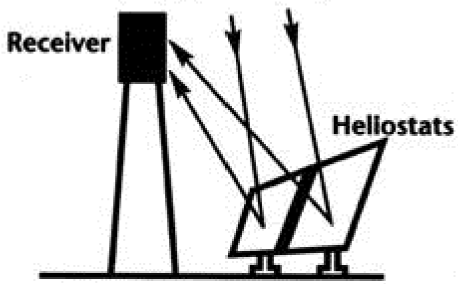
390°C

150°C

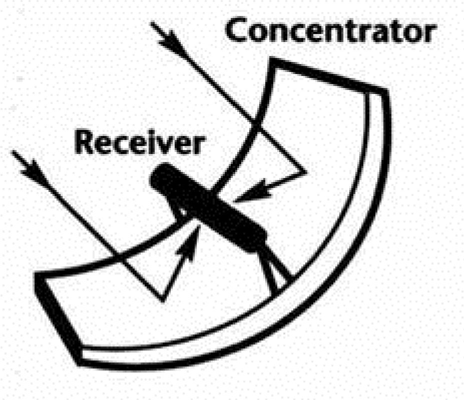
50°C



Paraboloid:
„Dish“

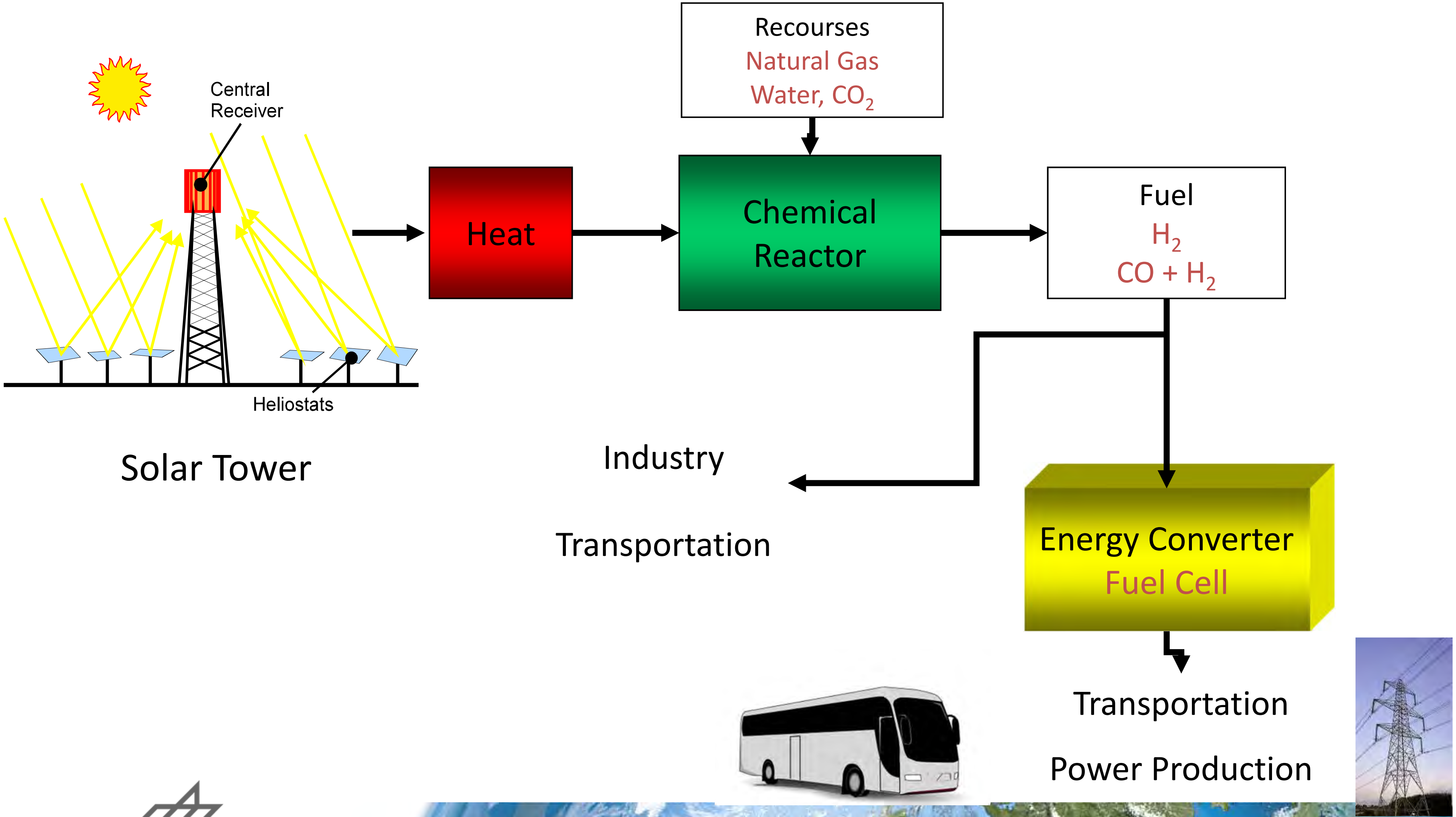


Solar Tower
(Central Receiver
System)



Parabolic Trough /
Linear Fresnel

Principle of the solar thermal fuel production



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Solar Towers, “Central Receiver Systems”





-PS10, PSA CESA-1, Torresol, Spain
-Solar-Two, Daggett, USA
-Solarturm Jülich, Germany

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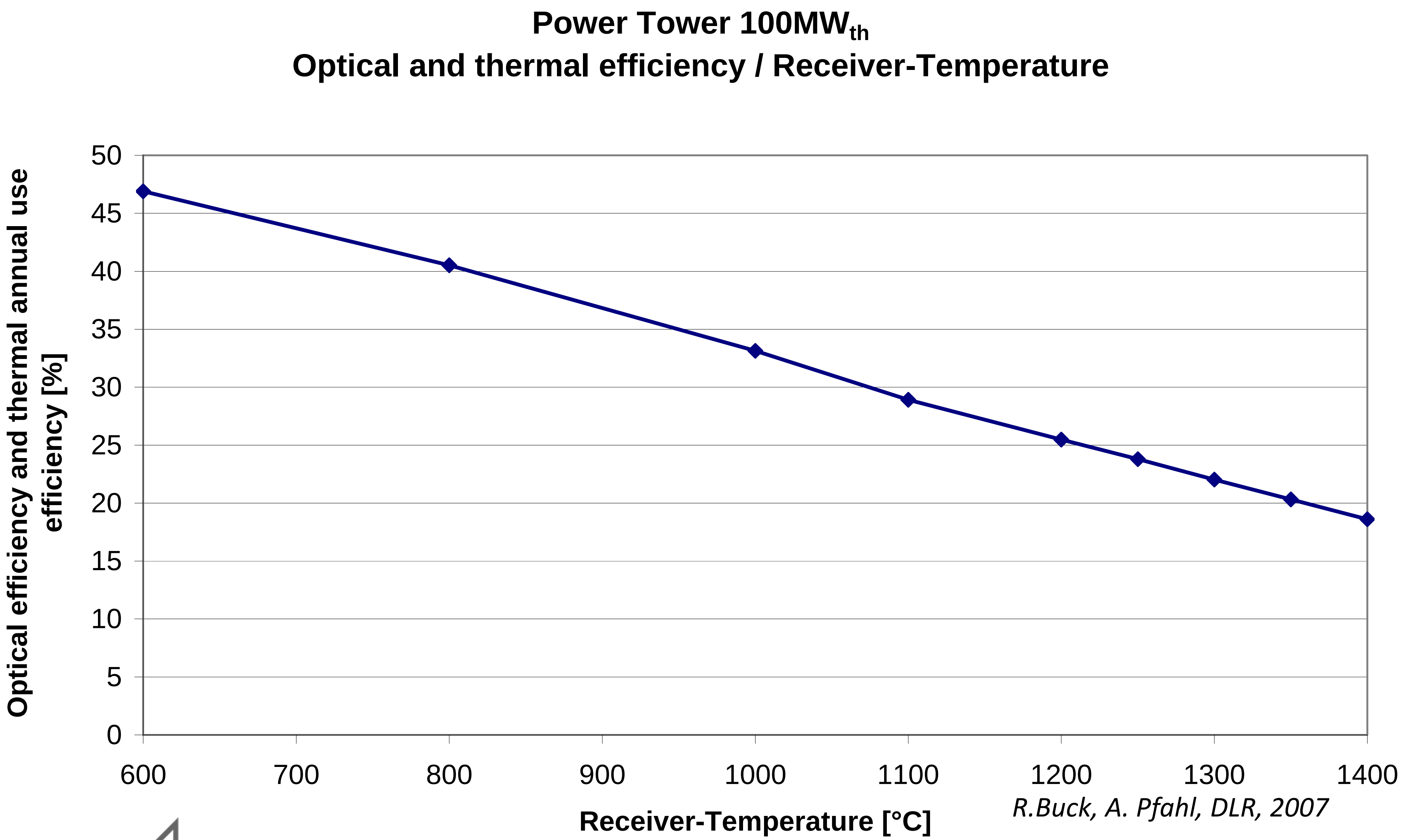
Annual Efficiency of Solar Power Towers



R.Buck, A. Pfahl, DLR, 2007

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Solar Tower Jülich

Receiver 22.7m²

(Intratec, Saint-Gobain)

Tower 60m

(Züblin)

2150 Heliostats á 8.2 m²

(SHP/AUSRA)

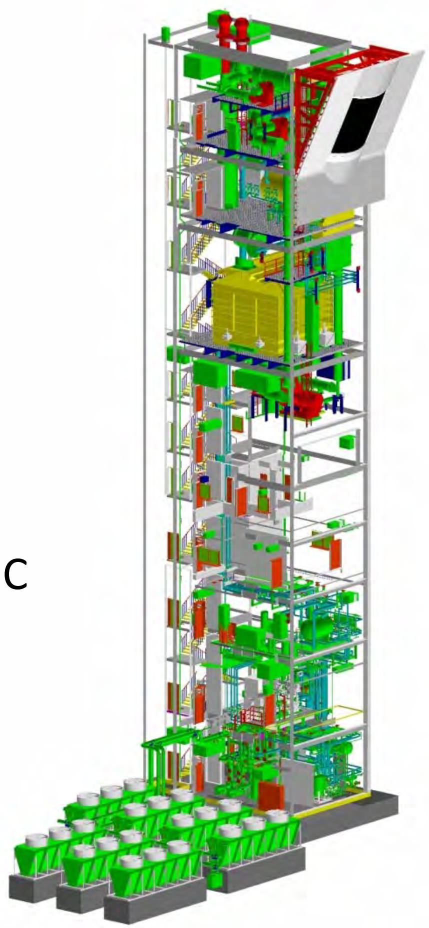
Vessel 9t/h, 30 bar/500°C

(VKK-Standardkessel)

Thermal storage 1h

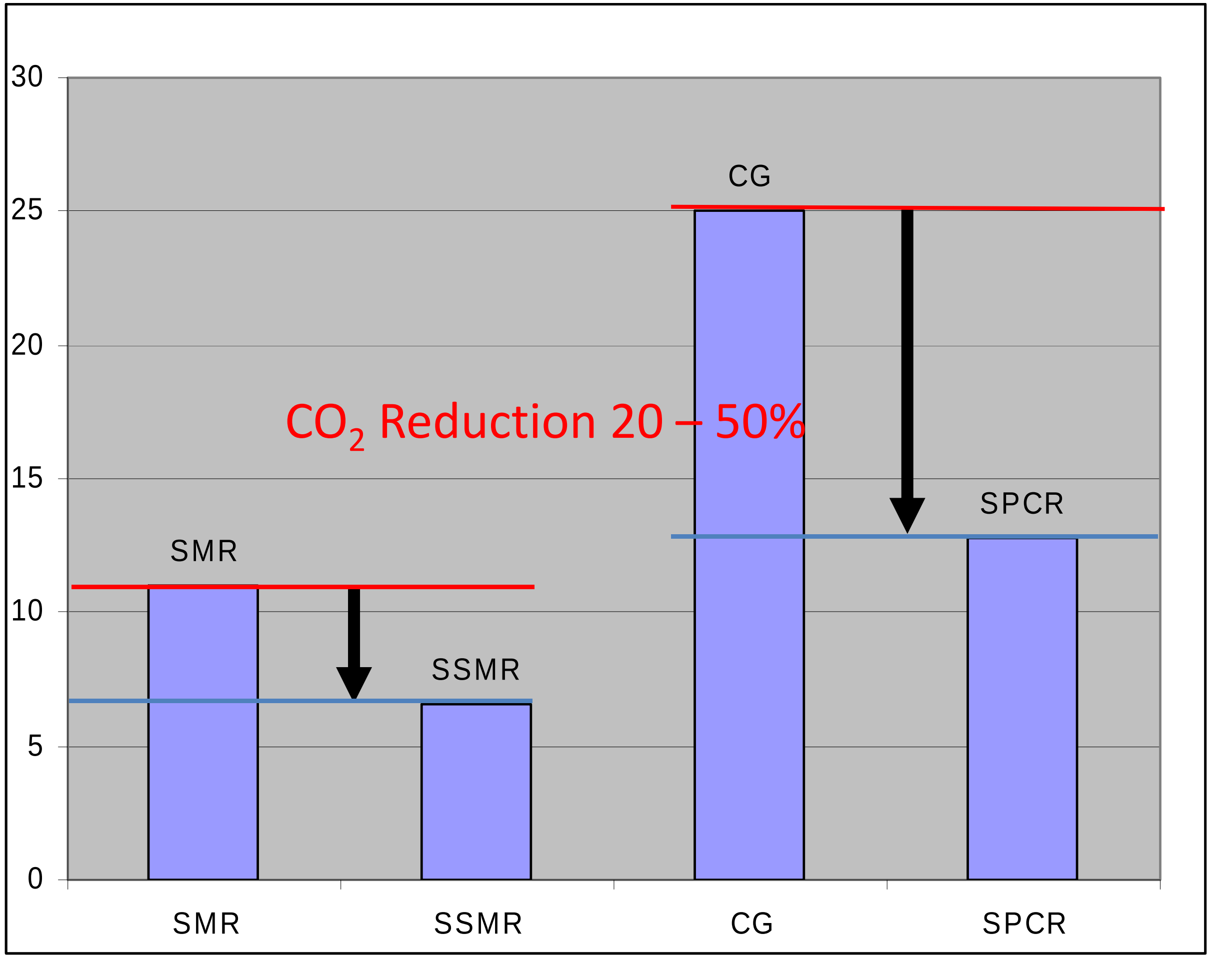
Turbine 1.5 MWe

(KKK-Siemens)



Short-term CO_2-Reduction: Solar Reforming

CO_2 Reduction by solar heating of state of the art processes like steam methane reforming and coal gasification



Steam and CO_2-Reforming of Natural Gas

Steam reforming: $H_2O + CH_4 \rightarrow 3\ H_2 + 1\ CO$

CO_2 Reforming: $CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$

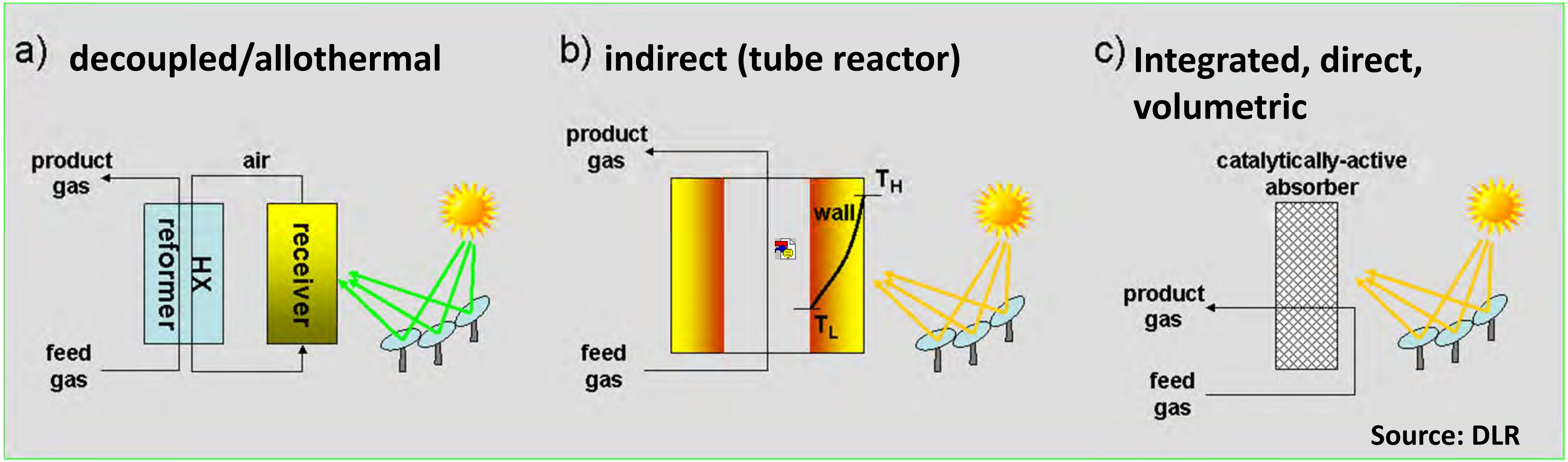
Reforming of mixtures of CO_2/H_2O is possible and common

Use of CO_2 for methanol production:

e.g. $2H_2 + CO \rightarrow CH_3COH$ (Methanol)

Both technologies can be driven by solar energy as shown in the projects: CAESAR, ASTERIX, SOLASYS, SOLREF…

Solar Methane Reforming – 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: CSIRO, Australia and in Japan; Research in Germany and Israel

Australian solar gas plant in preparation

Catalytic active direct irradiated absorber

Approx. 90 % Reformer-h

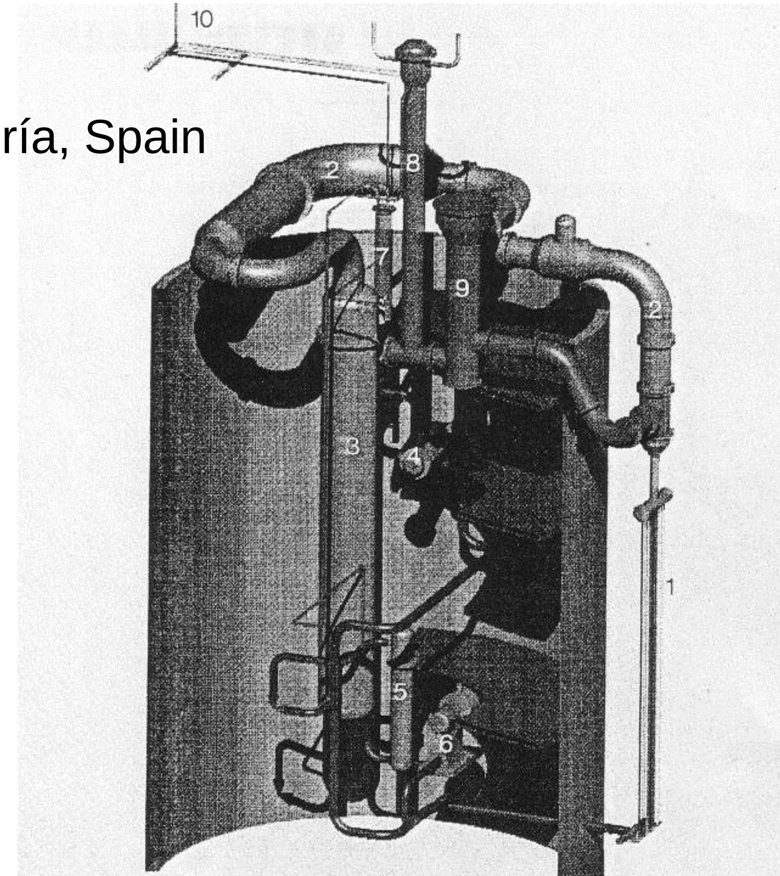
High solar flux, works only by direct solar radiation

DLR coordinated projects: Solasys, Solref; Research in Israel, Japan

Project Asterix: Allothermal Steam Reforming of Methan

- DLR, Steinmüller, CIEMAT
- 180 kW plant at the Plataforma Solar de Almería, Spain (1990)
- Convective heated tube cracker as reformer
- Tubula

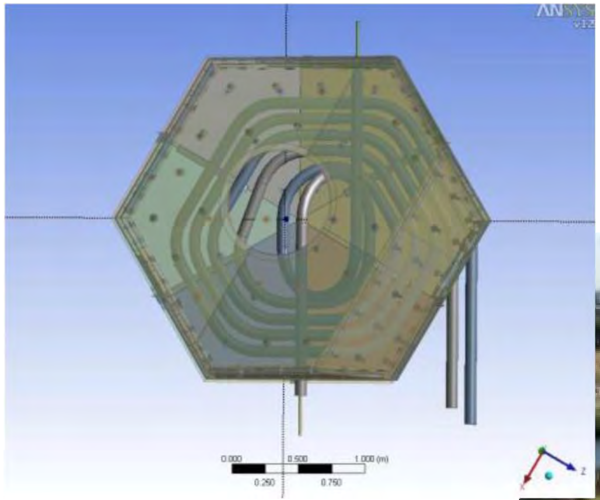
CESA-1, PSA, Spain. The solar radiation is collected by a field of heliostats and redirected to a tower, where different platforms allow the tests of various receiver technologies.

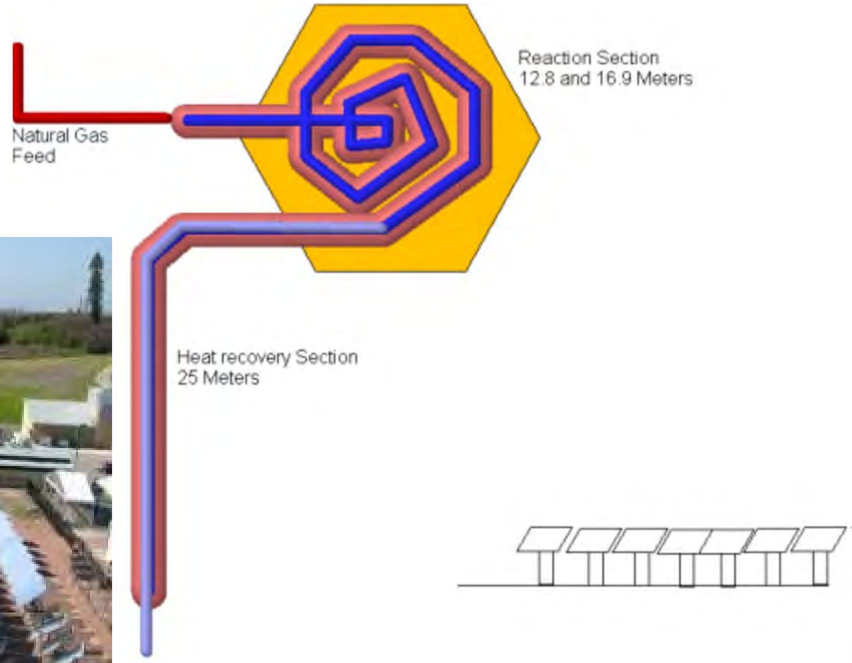


1 = Receiver, 2 = Heißgasleitungen, 3 = Rekuperator, 4 = Elektrischer Heizer, 5 = Kühler, 6 = Kompressor, 7 = Kühler E-106/7, 8 = Reformer V-101 mit Wärmeübertragern E-102/3/4, 9 = Elektrischer Heizer E-105, 10 = Fackel Z-102.

Pilot Scale Solar Chemical Reactors - SolarGas

Experimental set-up of the 200 kW SolarGas reactor





Top view of DCORE reactor (right) layout of entire integrated reformer and HRU

Source: R. McNaughton et al., CSIRO, Australia

Direct heated volumetric receivers: SOLASYS, SOLREF (EU FP4, FP6)

- 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)

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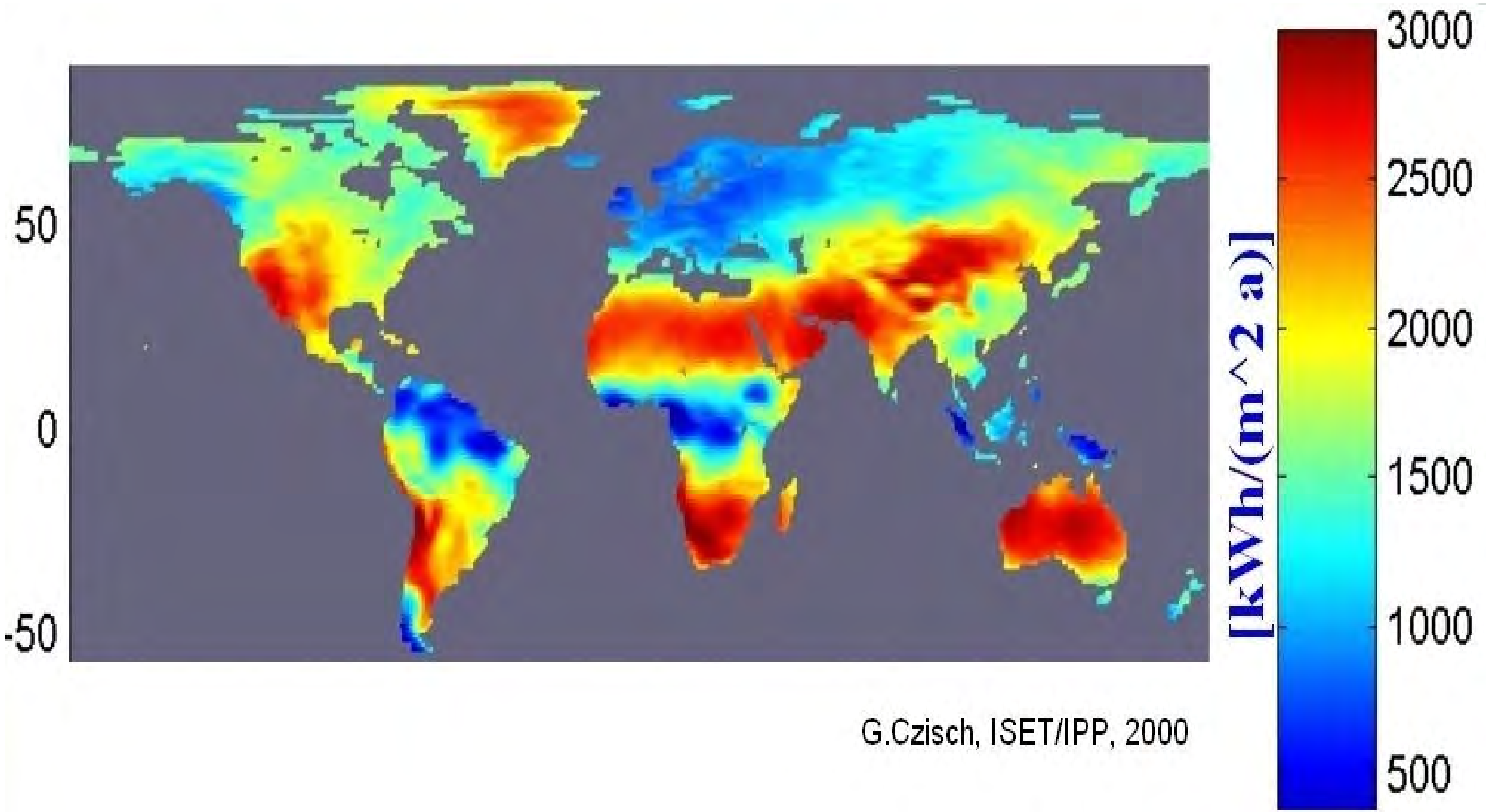
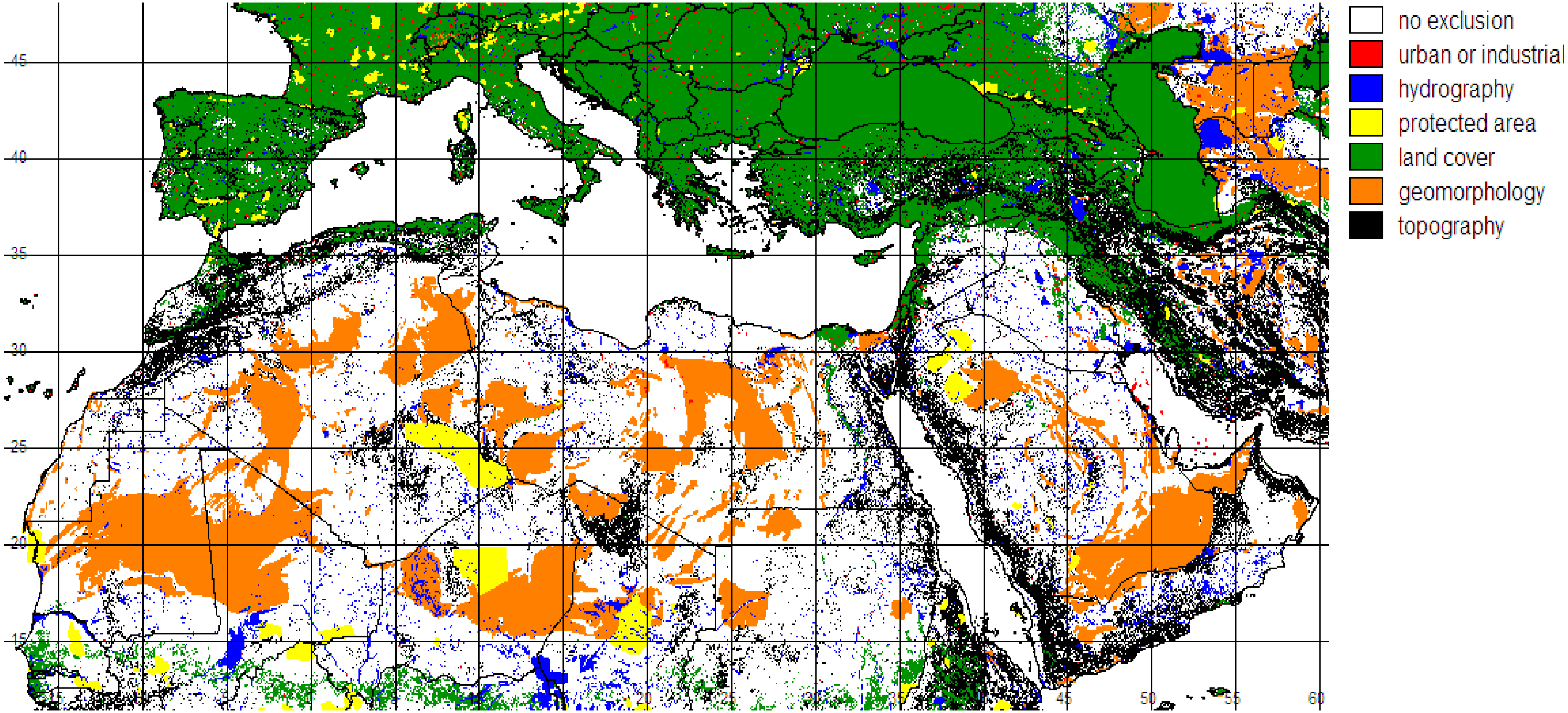
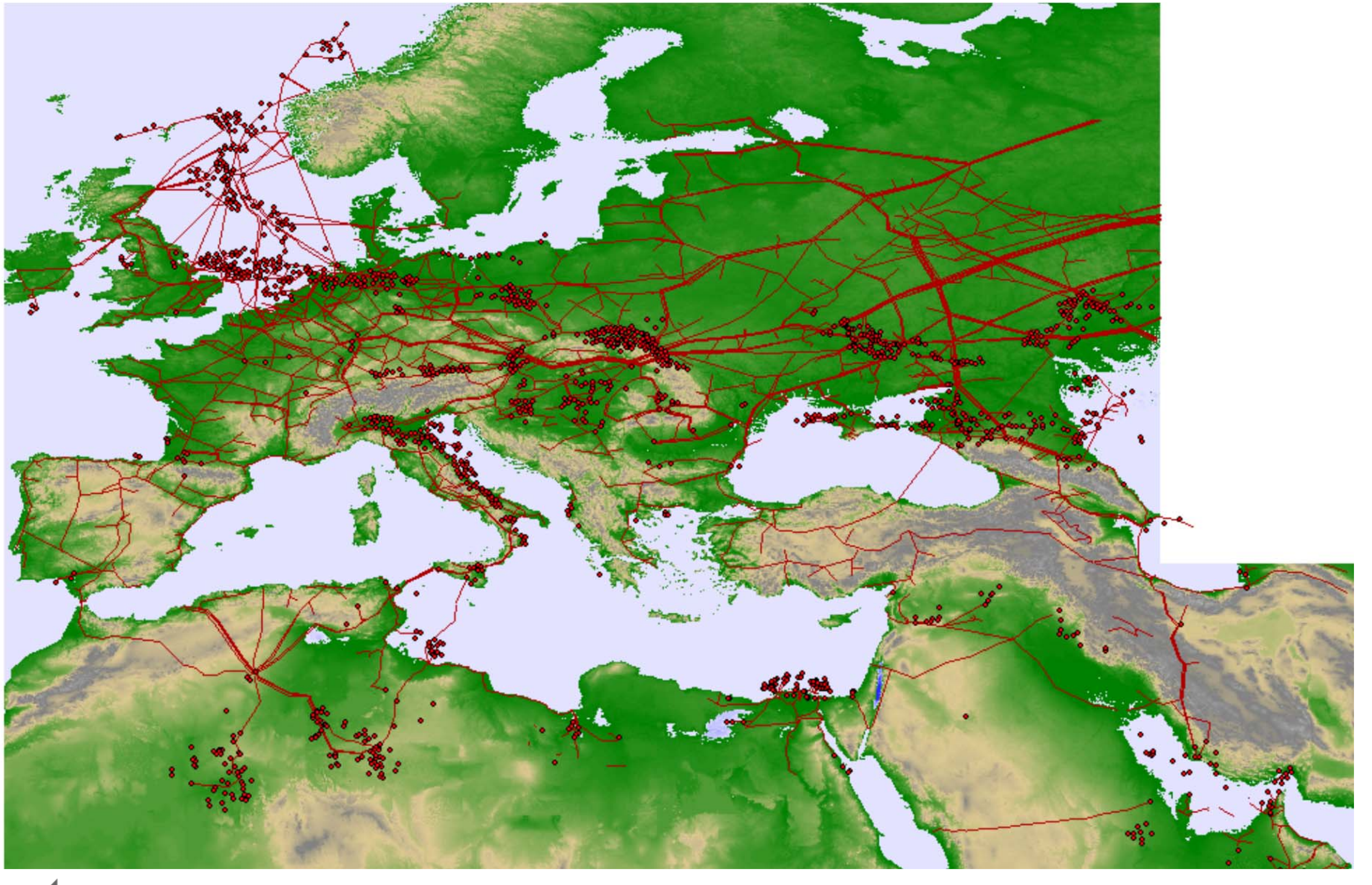
Potential Solar sites



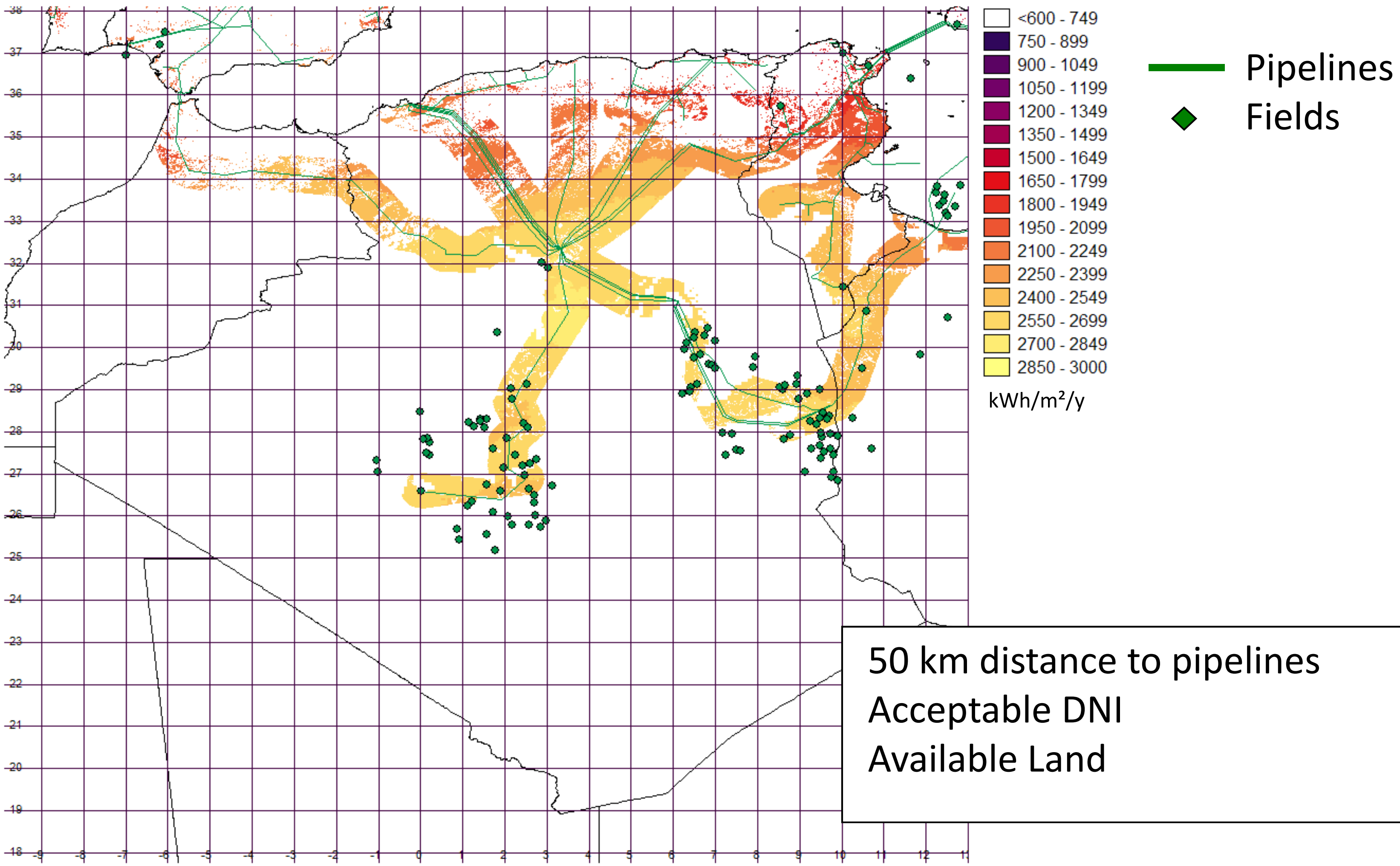
Suitable locations for CSP in Northern Africa



Natural Gas Pipeline Grid and Natural Gas Fields



Suitable locations for solar reforming - Example Algeria and Tunisia



50 km distance to pipelines
Acceptable DNI
Available Land

Long-term: Water splitting processes

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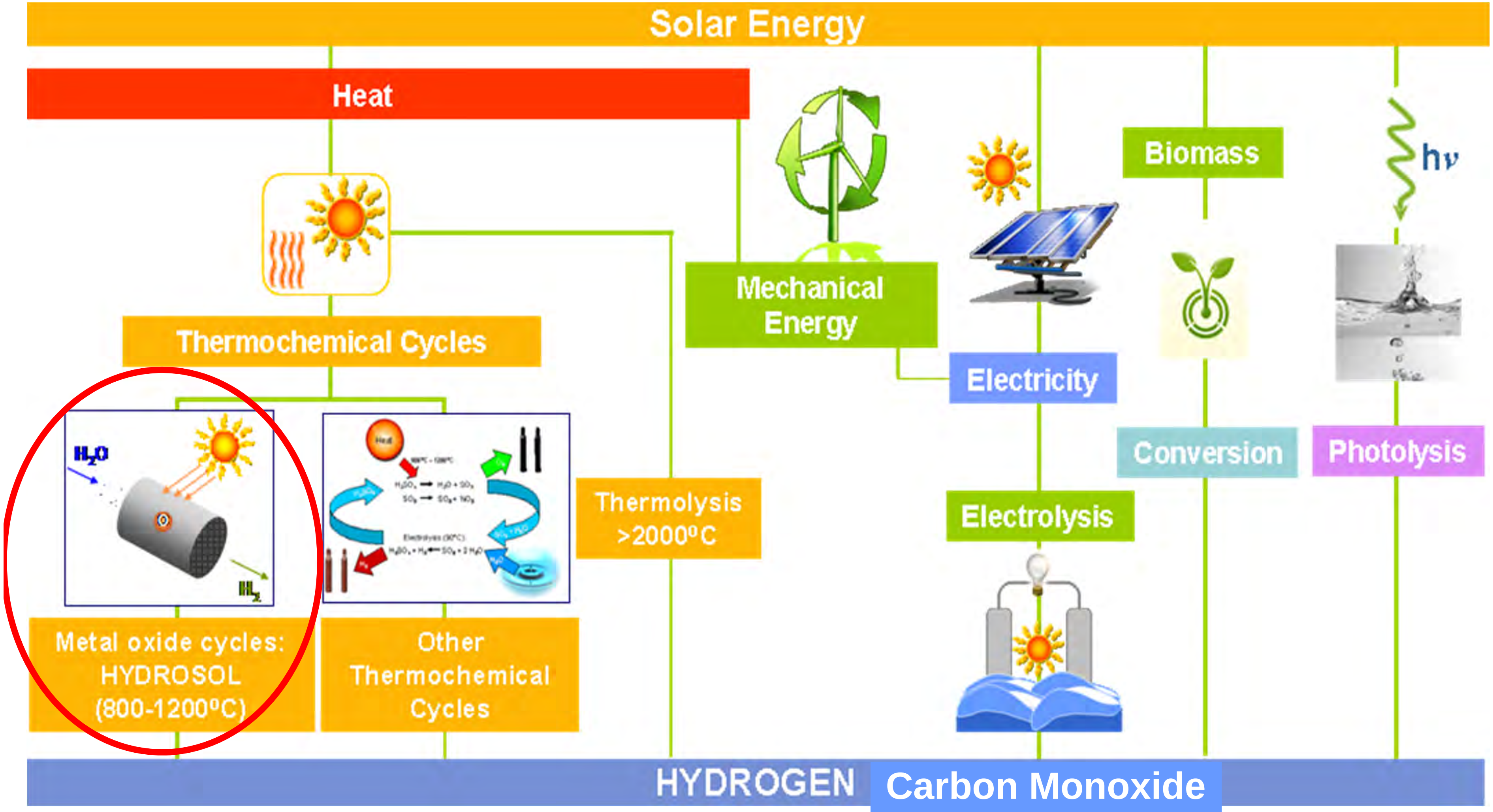
Solar Pathways from Water or CO_2 to Fuels



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Promising and well researched Thermochemical Cycles

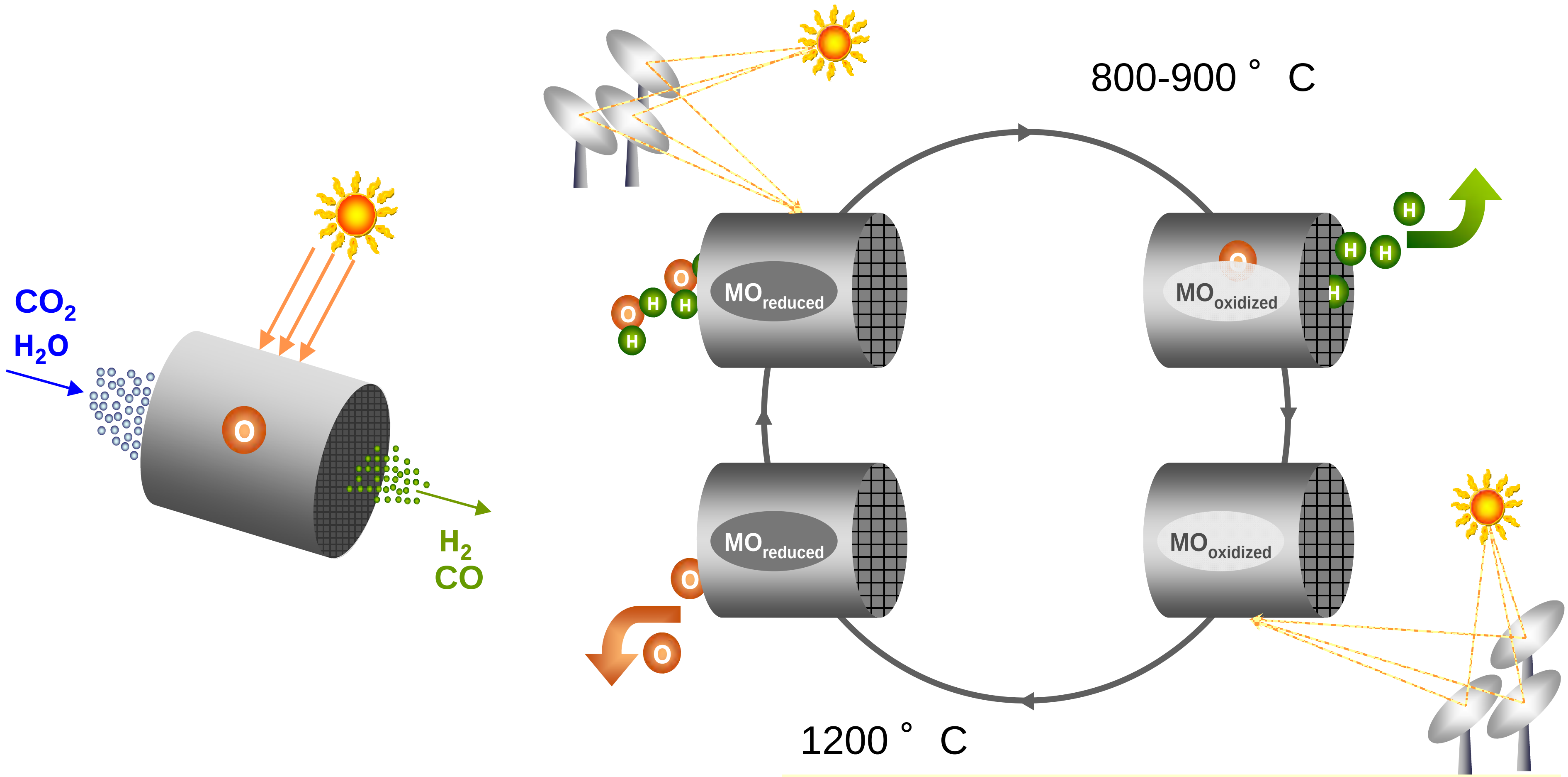
	Steps	Maximum Temperature (°C)	LHV Efficiency (%)
Sulphur Cycles			
Hybrid Sulphur (Westinghouse, ISPRA Mark 11)	2	900 (1150 without catalyst)	43
Sulphur Iodine (General Atomics, ISPRA Mark 16)	3	900 (1150 without catalyst)	38
Volatile Metal Oxide Cycles			
Zinc/Zinc Oxide	2	1800	45
Hybrid Cadmium		1600	42
Non-volatile Metal Oxide Cycles			
Iron Oxide	2	2200	42
Cerium Oxide	2	2000	68
Ferrites	2	1100 – 1800	43
Low-Temperature Cycles			
Hybrid Copper Chlorine	4	530	39

Efficiency comparison for solar hydrogen production from water (SANDIA, 2008)*

Process	T [°C]	Solar plant	Solar-receiver + power [MWth]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H_2
Elctrolysis (+solar-thermal power)	NA	Actual Solar tower	Molten Salt 700	30%	57%	83%	14%
High temperature steam electrolysis	850	Future Solar tower	Particle 700	45%	57%	76,2%	20%
Hybrid Sulfur-process	850	Future Solar tower	Particle 700	51%	57%	76%	22%
Hybrid Copper Chlorine-process	600	Future Solar tower	Molten Salt 700	49%	57%	83%	23%
Nickel Manganese Ferrit Process	1800	Future Solar dish	Rotating Disc < 1	52%	77%	62%	25%

**G.J. Kolb, R.B. Diver SAND 2008-1900*

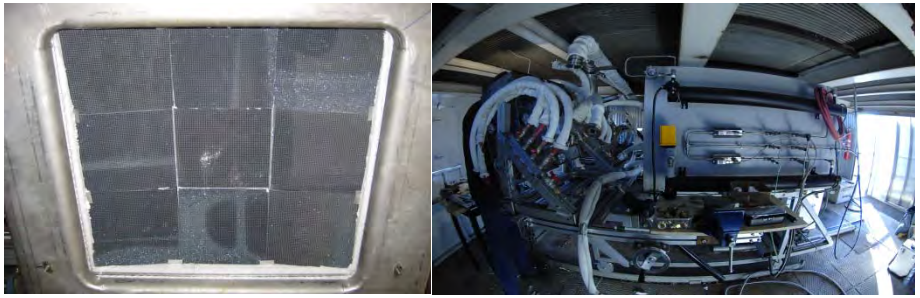
Fuel Production from H_2O and CO_2 by Solar Radiation



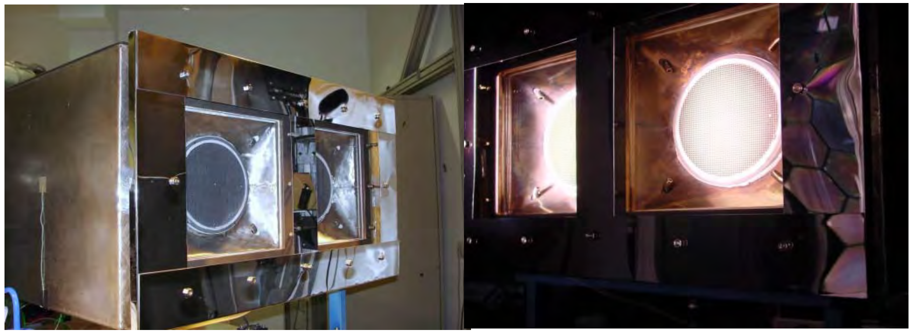
DLR: Roeb, Müller-Steinhagen, *Science*, Aug. 2010

HYDROSOL technology scale-up

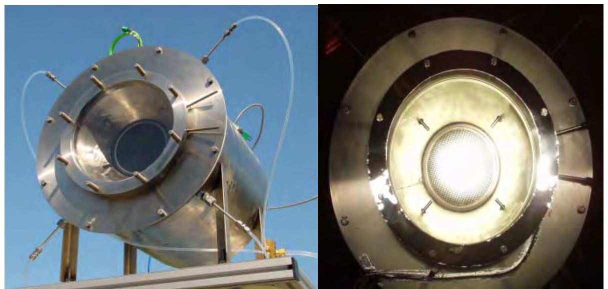
PSA solar tower



2008:
Pilot reactor (100 kW)



2005:
Continuous H_2 production



2004:
First solar thermochemical
H_2 production

DLR solar furnace

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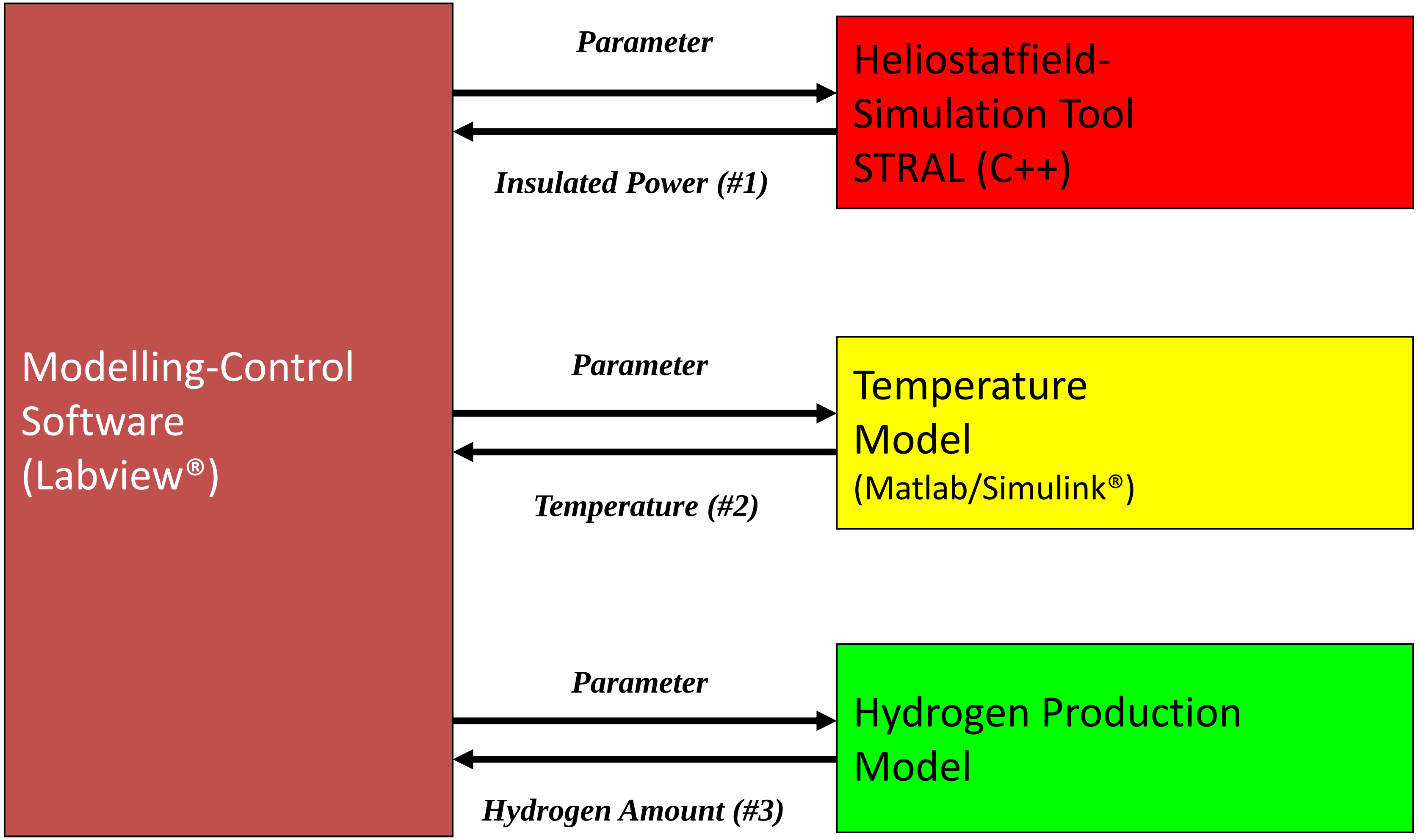
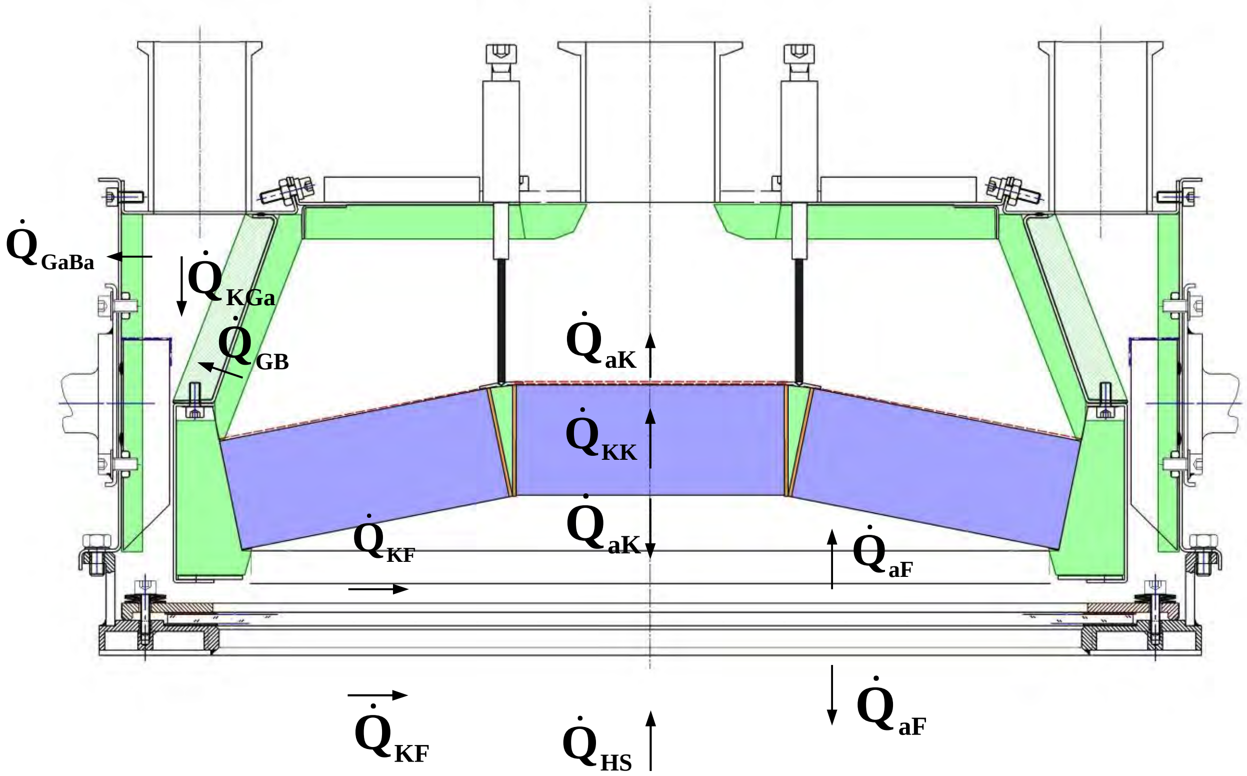
Modelling of the pilot plant - Overview Modelling:



Modelling – Temperature model:

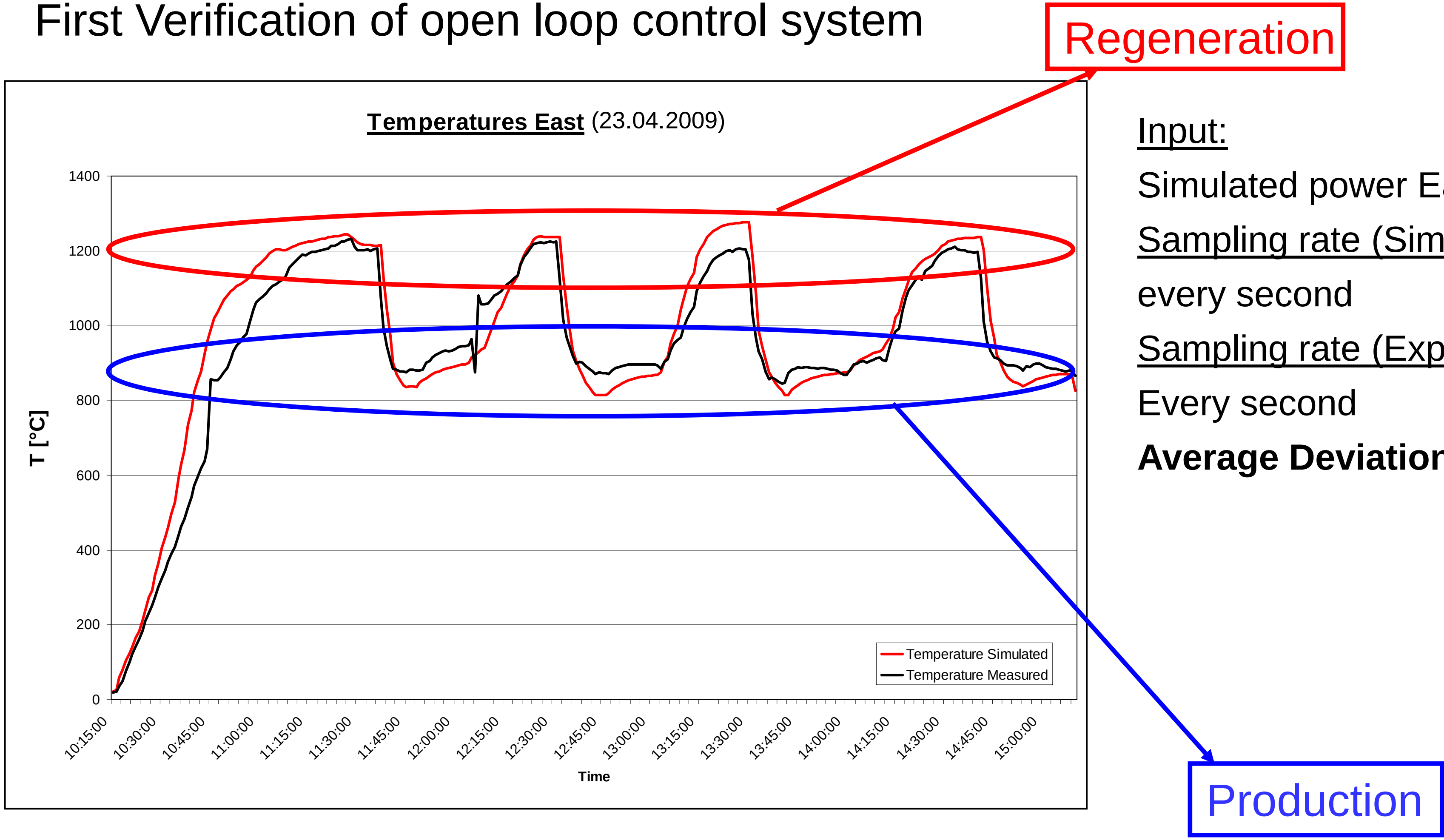
Collecting formulas of the **heat flows** (simplified balance!)



Heat flows: heat radiation, heat conduction and convection

Modelling – Temperature model:

First Verification of open loop control system



Input:

Simulated power East

Sampling rate (Sim.):

every second

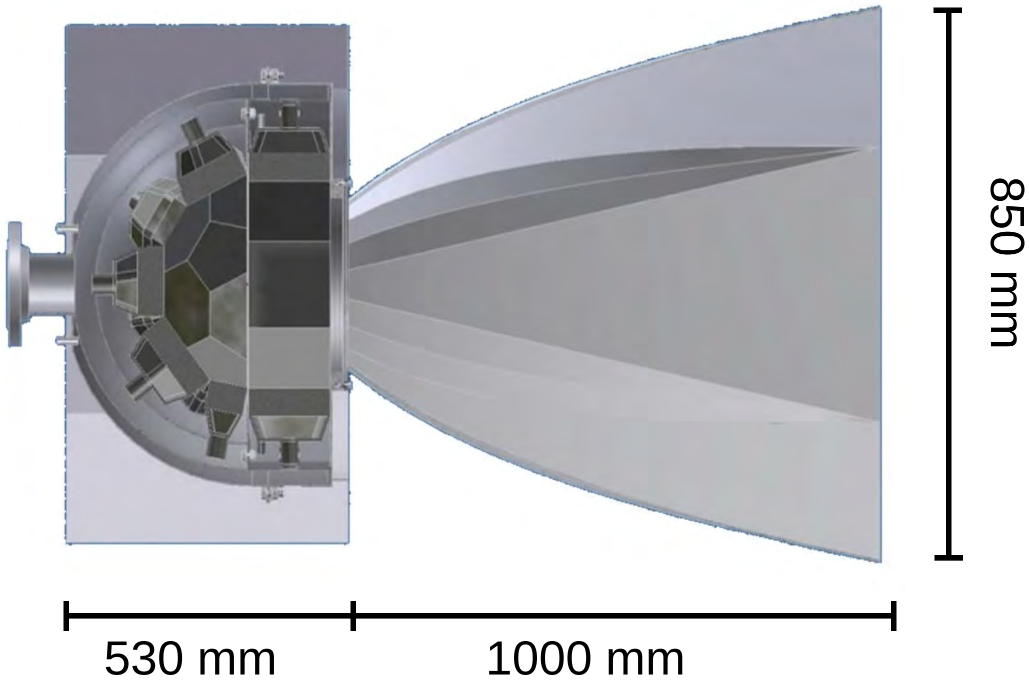
Sampling rate (Exp.):

Every second

Average Deviation: 6.5%

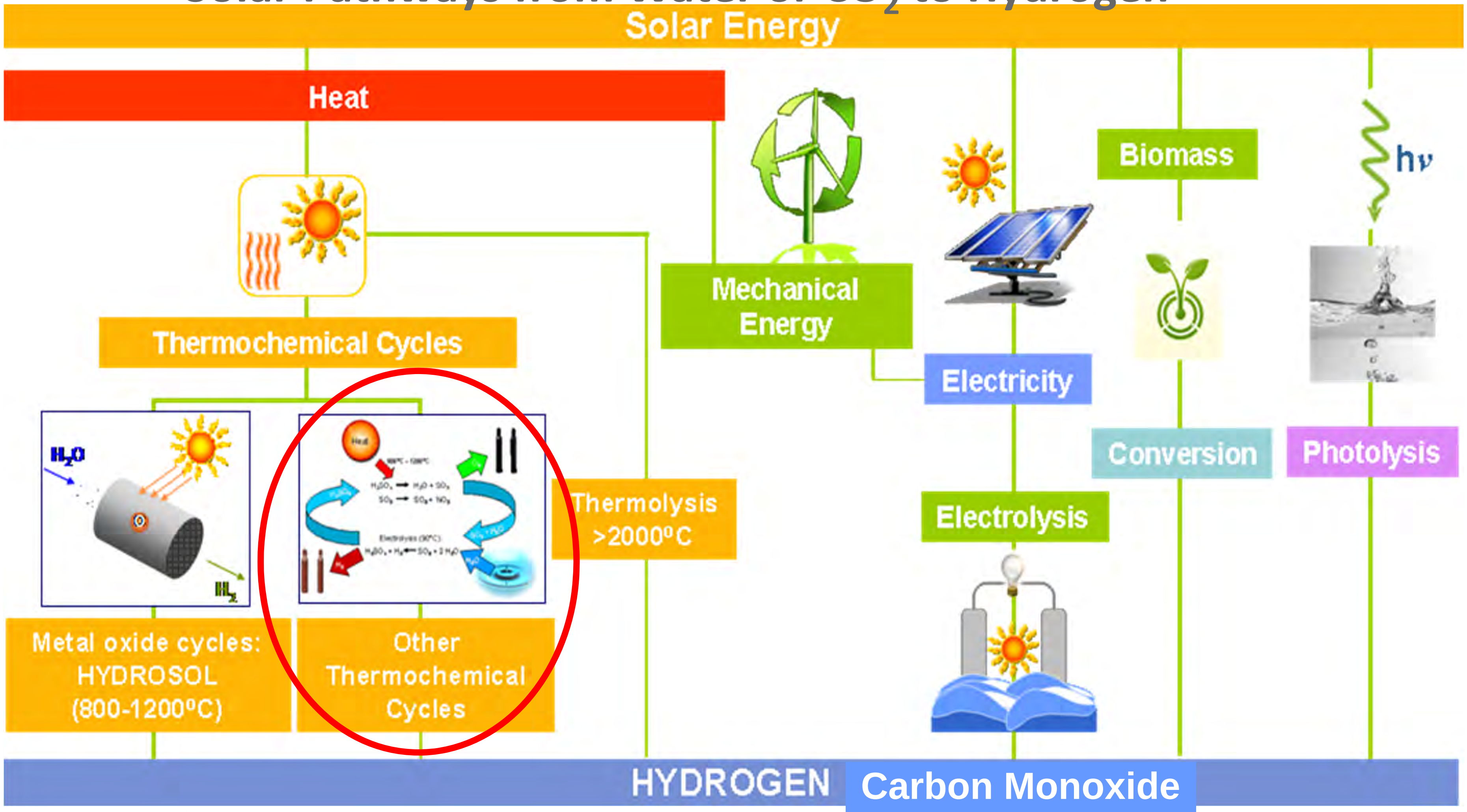
1 MW Pilot Plant Designs

Installation on DLR‘s Solar Tower Jülich (Artistic View)



Compact 1 MW Receiver Design

Solar Pathways from Water or CO_2 to Hydrogen



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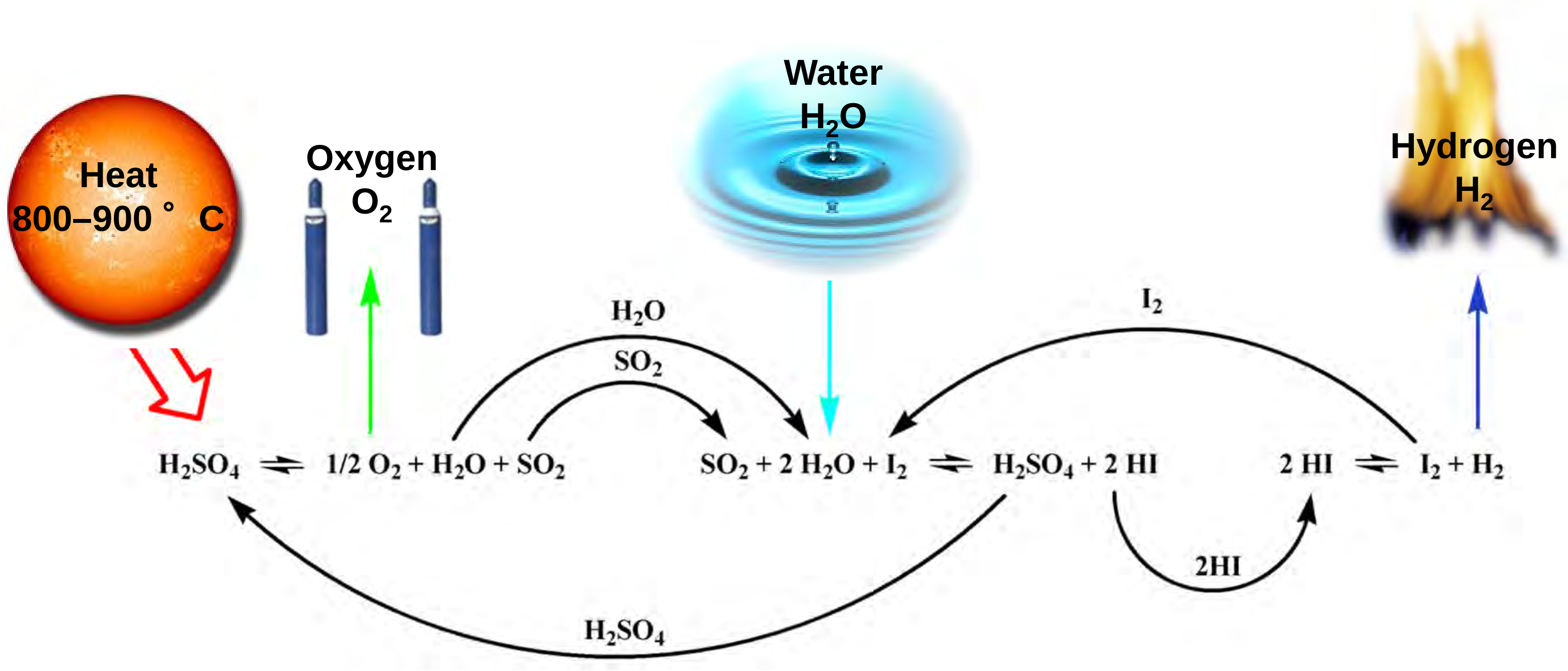
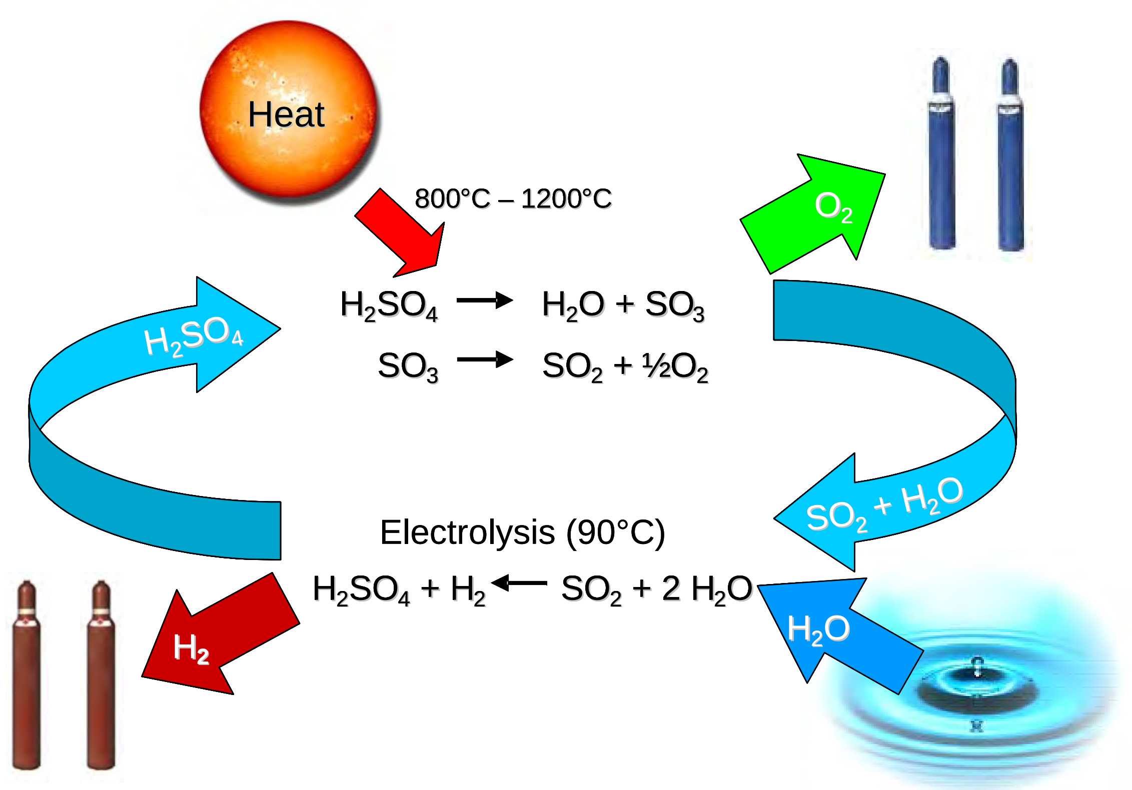
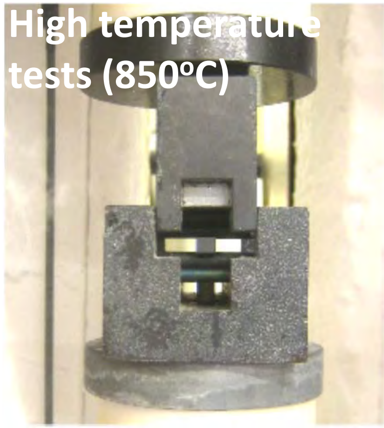
Sulphur-Iodine Process

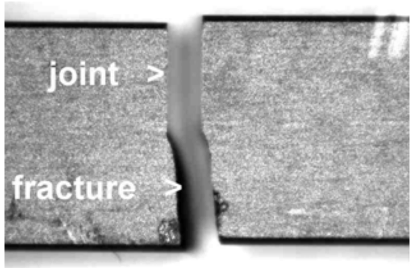


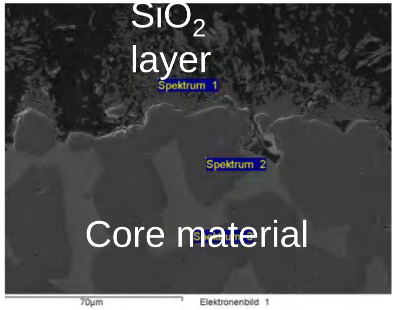
Hybrid Sulphur Cycle



Stability of construction materials







- Performance of long-term corrosion campaigns (SO_2, SO_3 rich, boiling H_2SO_4) and post-exposure mechanical testing and inspection
- mainstream materials SiC-based as well as brazed samples
- SiC based materials retained suitable for the intended application since they are not affected significantly by the SO2-rich, SO3-rich and boiling sulphuric acid exposures.

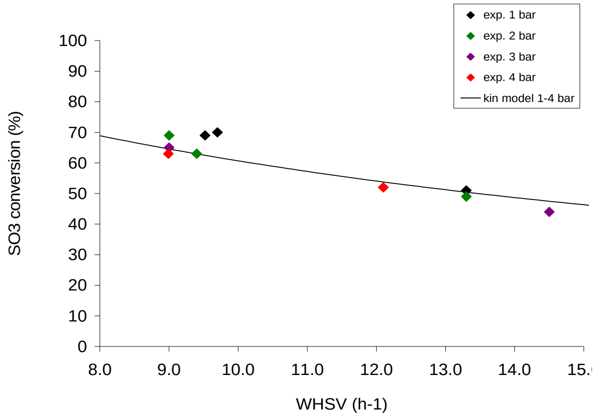
Advanced catalysts and coatings for H_2SO_4 decomposition

– ‘In-house’ synthesized materials (metal oxide based) with high catalytic activity in terms of SO_2 production from H_2SO_4:

– Coating of active materials in small- & large-scale SiSiC monoliths or fragments

– Satisfying stability of samples coated with ‘in-house’ materials under ‘long-term’ operation

– Derivation of an empirical kinetic model



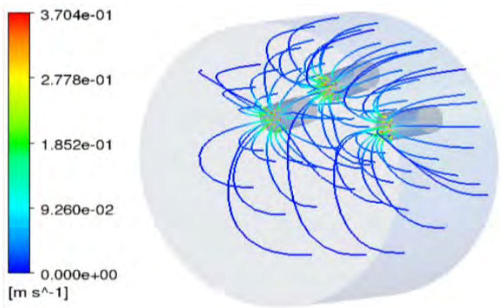
– Evaluation of the employed materials chemical stability

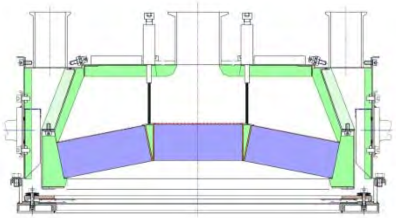
– Extraction of an SO_3 dissociation mechanism

– CrFe oxide identified as the most suitable catalyst

Karagianakis et al, IJHE 2011/2012; Giaconia et al, IJHE 2011

Solar reactor as H_2SO_4 decomposer

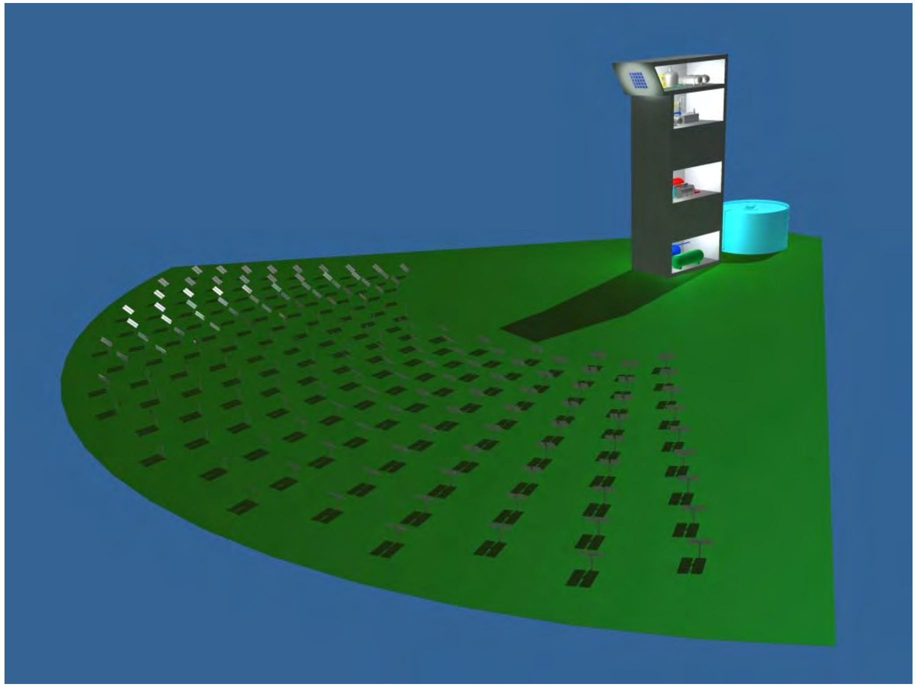


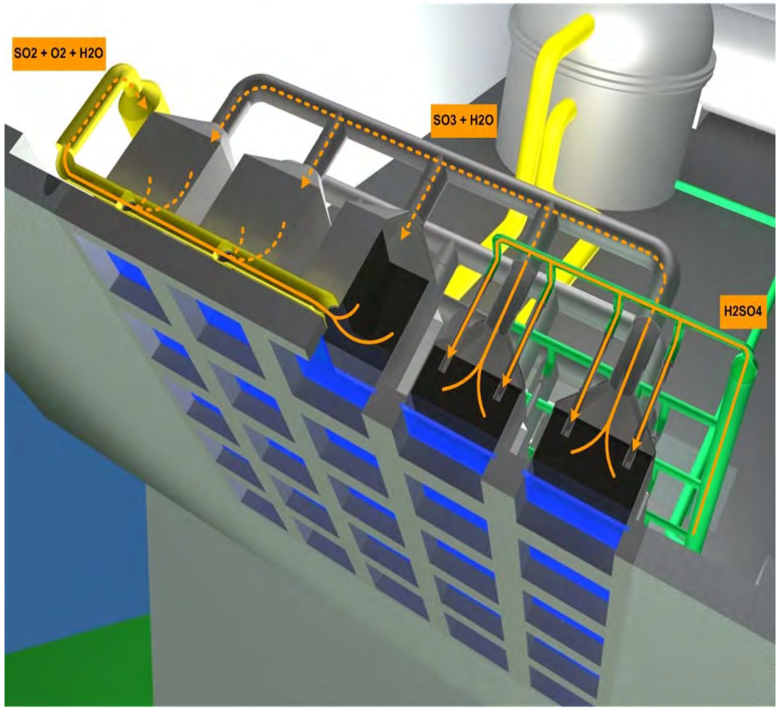


- Development and operation of a scalable prototype
  - FEM analysis
  - trouble-free operational > 200 h
  - conversions > 80 %
  - reactor efficiency > 25 %
- Continuum model of foam vaporiser
  - Computer tomography
- Modelling of SO_3 decomposition
  - Validation with experimental data
- Control procedure for scale-up solar tower system

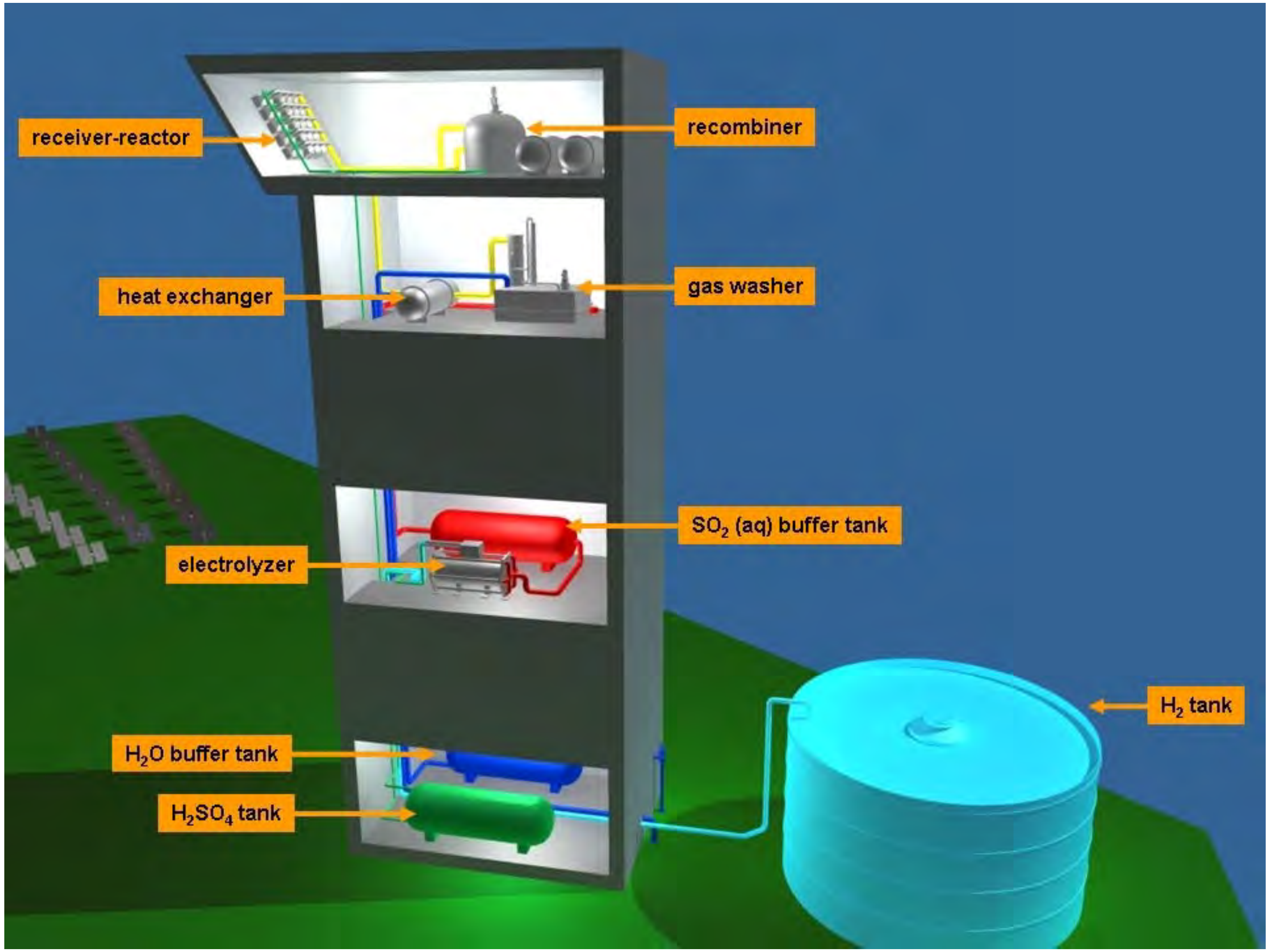
Thomey et al, IJHE 2012
Noglik et al, IJER 2010
Haussener et al, ASME-JHT 2009

Scale-up of the solar HyS process

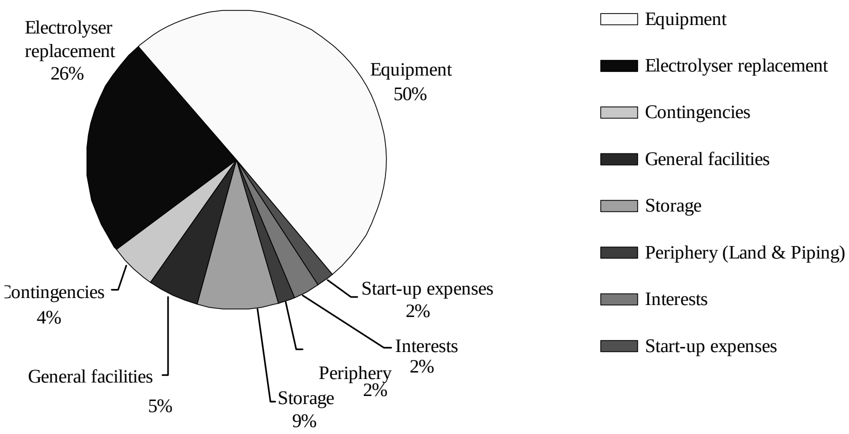




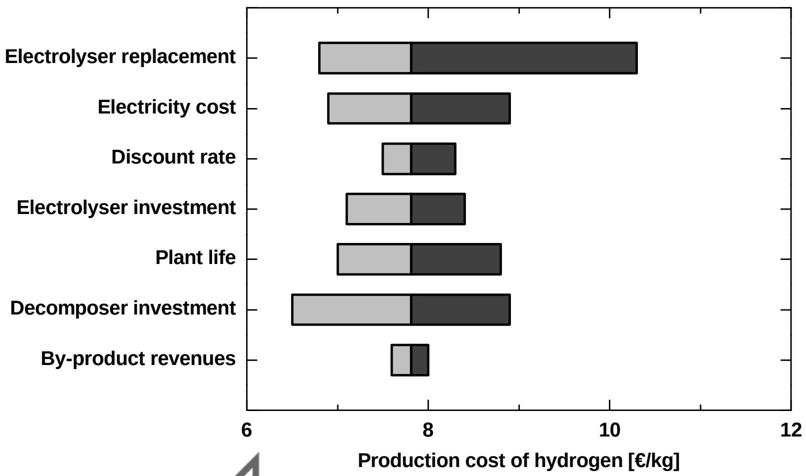
Implementation into a Solar Tower



Techno-economics

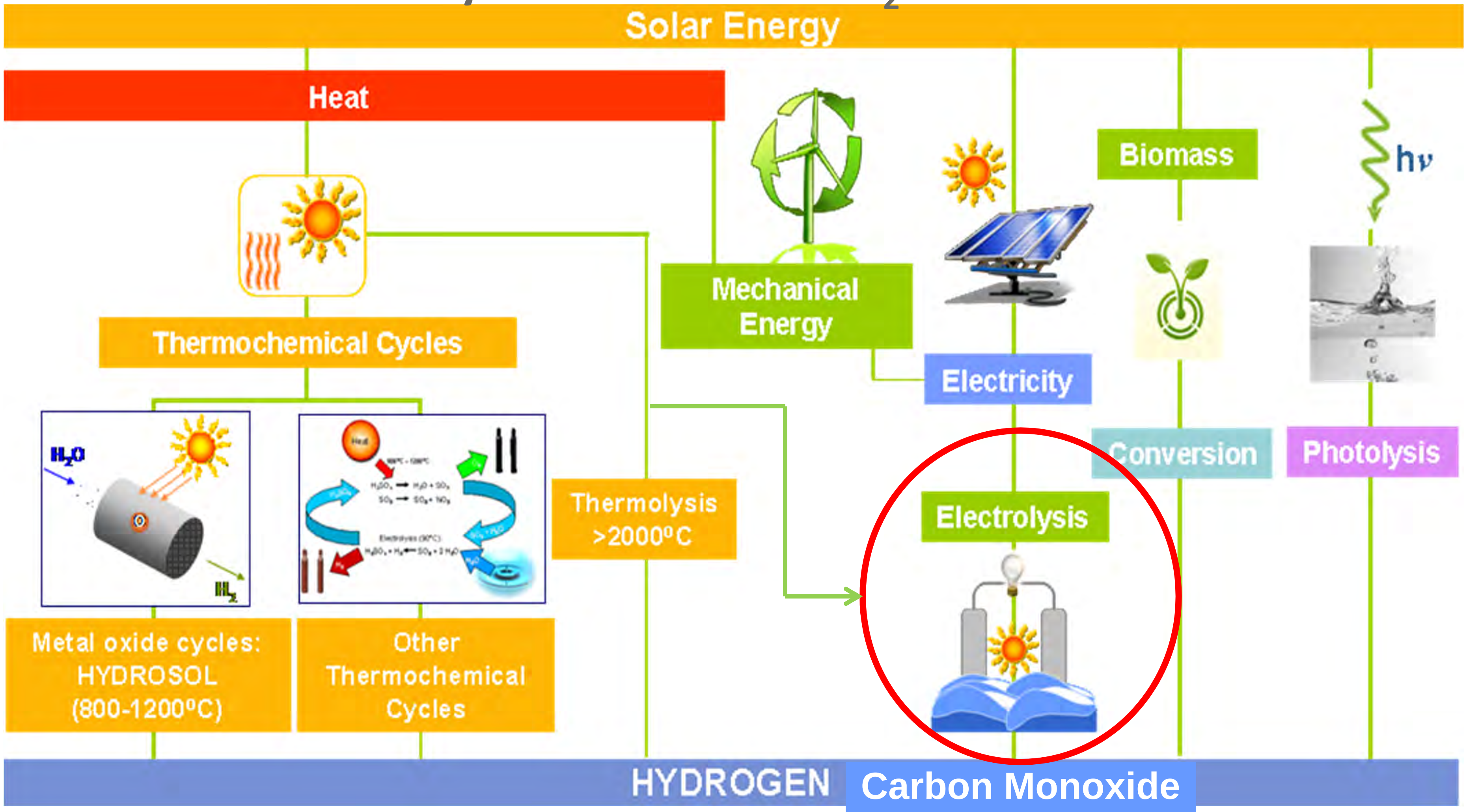


Lebros et et al, IJHE 2010



- Flowsheet for solar HyS process refined and completed
- All Components including the solar field were sized for a nuclear HyS and SI process and a solar HyS process
- Investment, O&M cost, production cost were analysed
  $\rightarrow$ 6-7 €/kg(H_2) for HyS
  $\rightarrow$ scenarios lead to 3.5 €/kg(H_2)
- 50 MW solar tower plant for hydrogen production by HyS cycle defined and depicted
- Thorough safety analysis was carried out for respective nuclear and solar power plants

Solar Pathways from Water or CO_2 to Fuels



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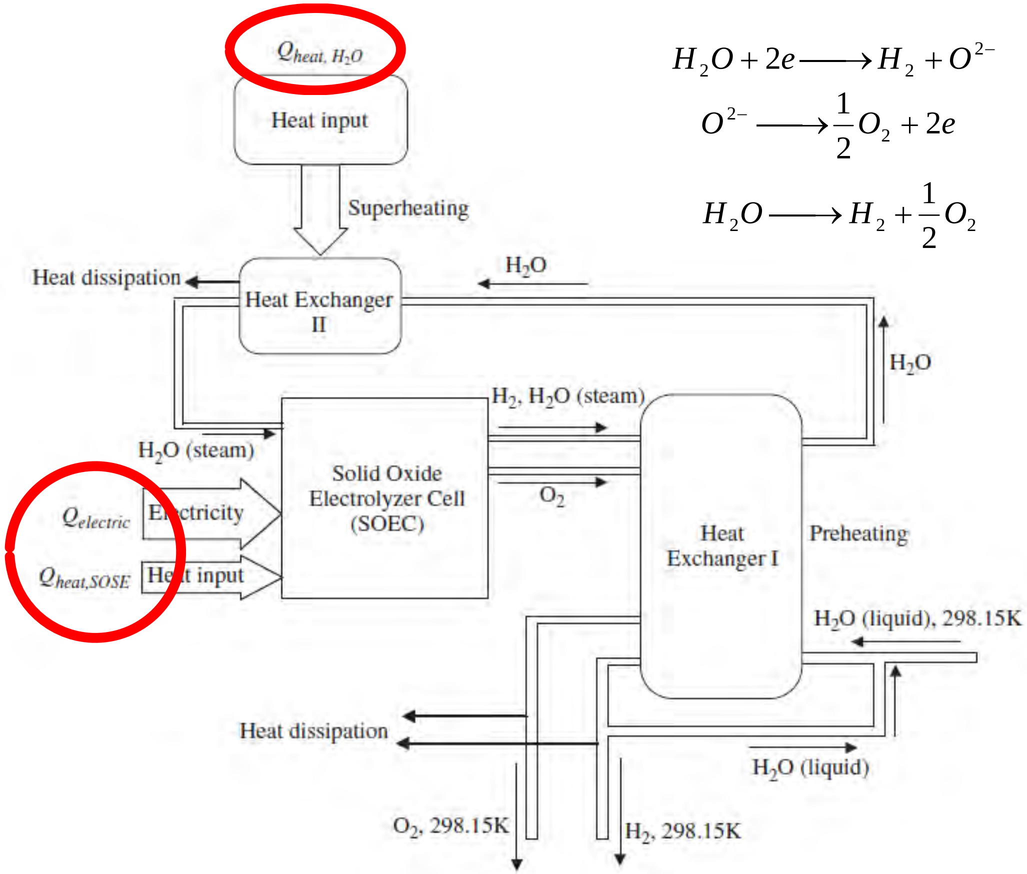
High temperature electrolysis process

- Temperature in the range of 600°C to 900°C are required to drive the electrolyser.
- Electricity and heat are supplied to the electrolyser to drive the electro-chemicals reactions.
- The waste heat from the H_2 and O_2 gas streams existing the cell is used to evaporate water.
- The H_2O stream is further heated by the second Heat exchanger to raise the temperature of the electrolyser.



$$H_2O + 2e \longrightarrow H_2 + O^{2-}$$

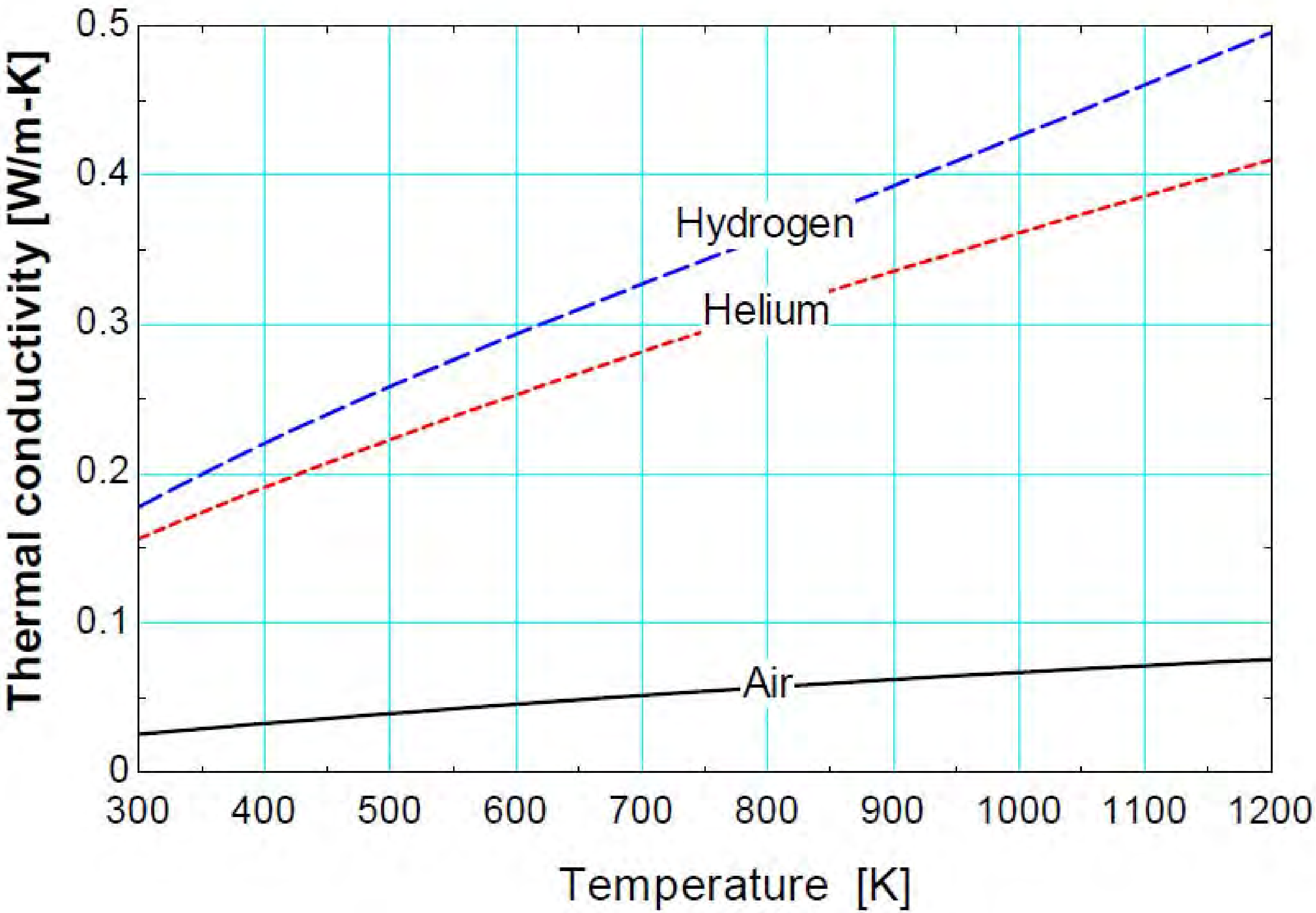
$$O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e$$

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

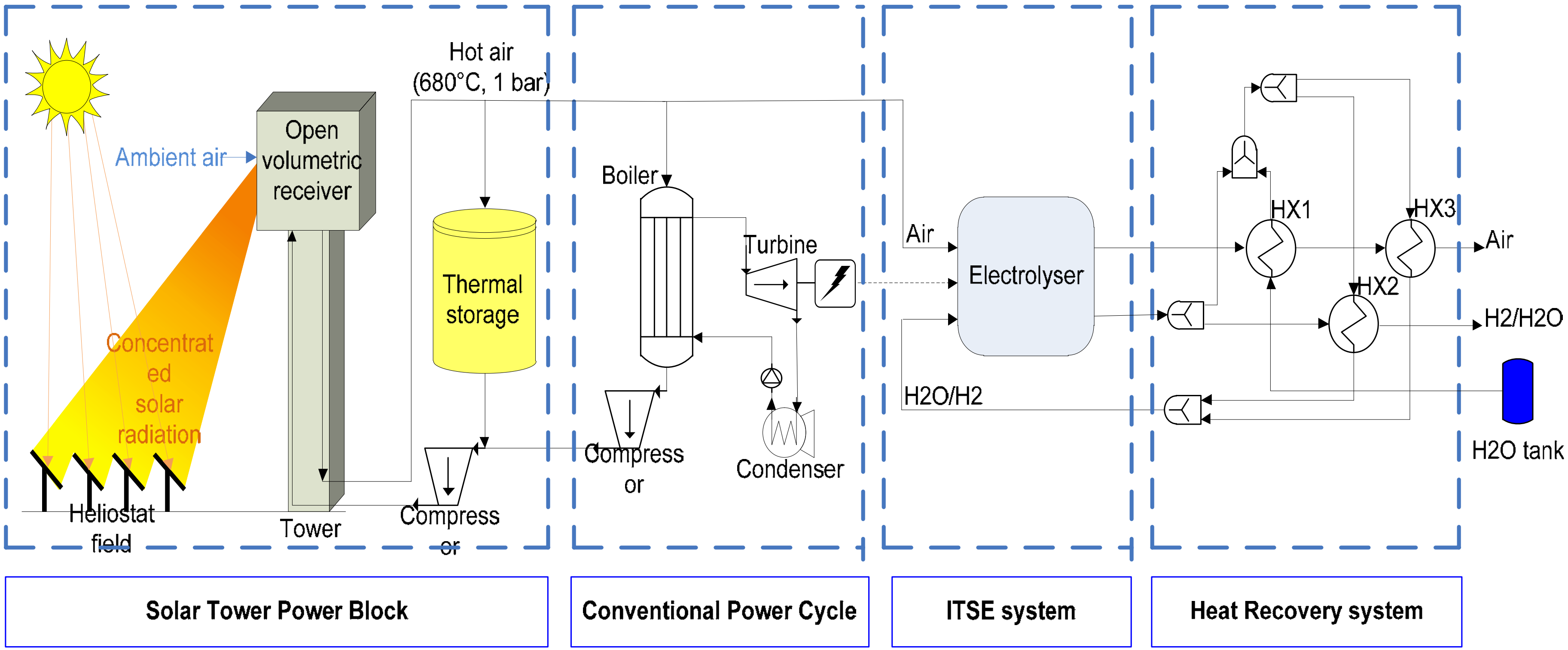
Economic analysis

- Key parameters of the hydrogen production cost with the a concentrating solar installation coupled to a high temperature electrolyzer:
  - Efficiency of the plant
    - Efficiency of the solar installation
    - Electricity consumption of the electrolyzer
  - Site of the plant (annual solar irradiation, availability of water, connection to the electricity and gas grit
  - Investment
  - Lifetime of the plant

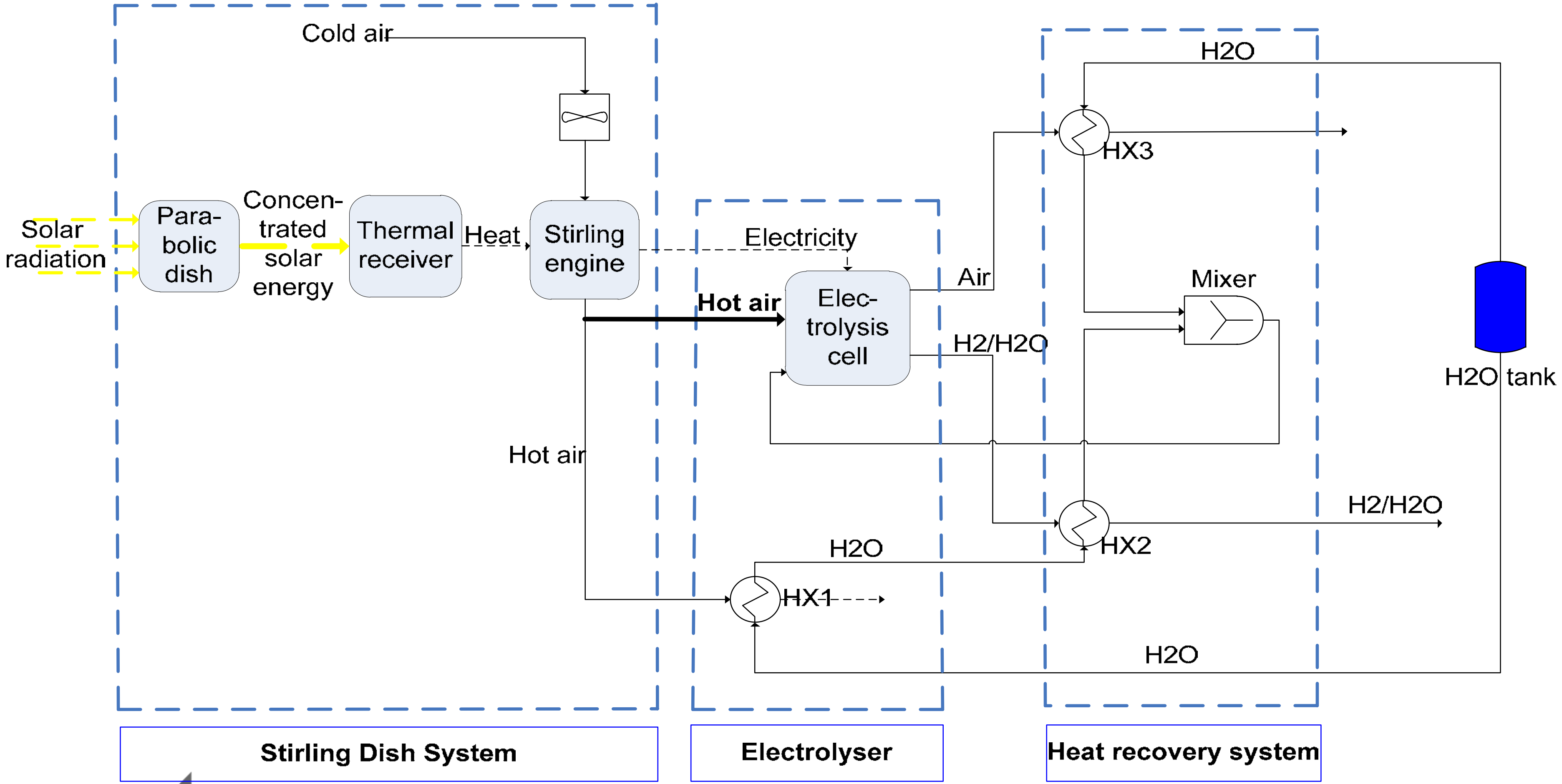
Thermal conductivity of working fluids



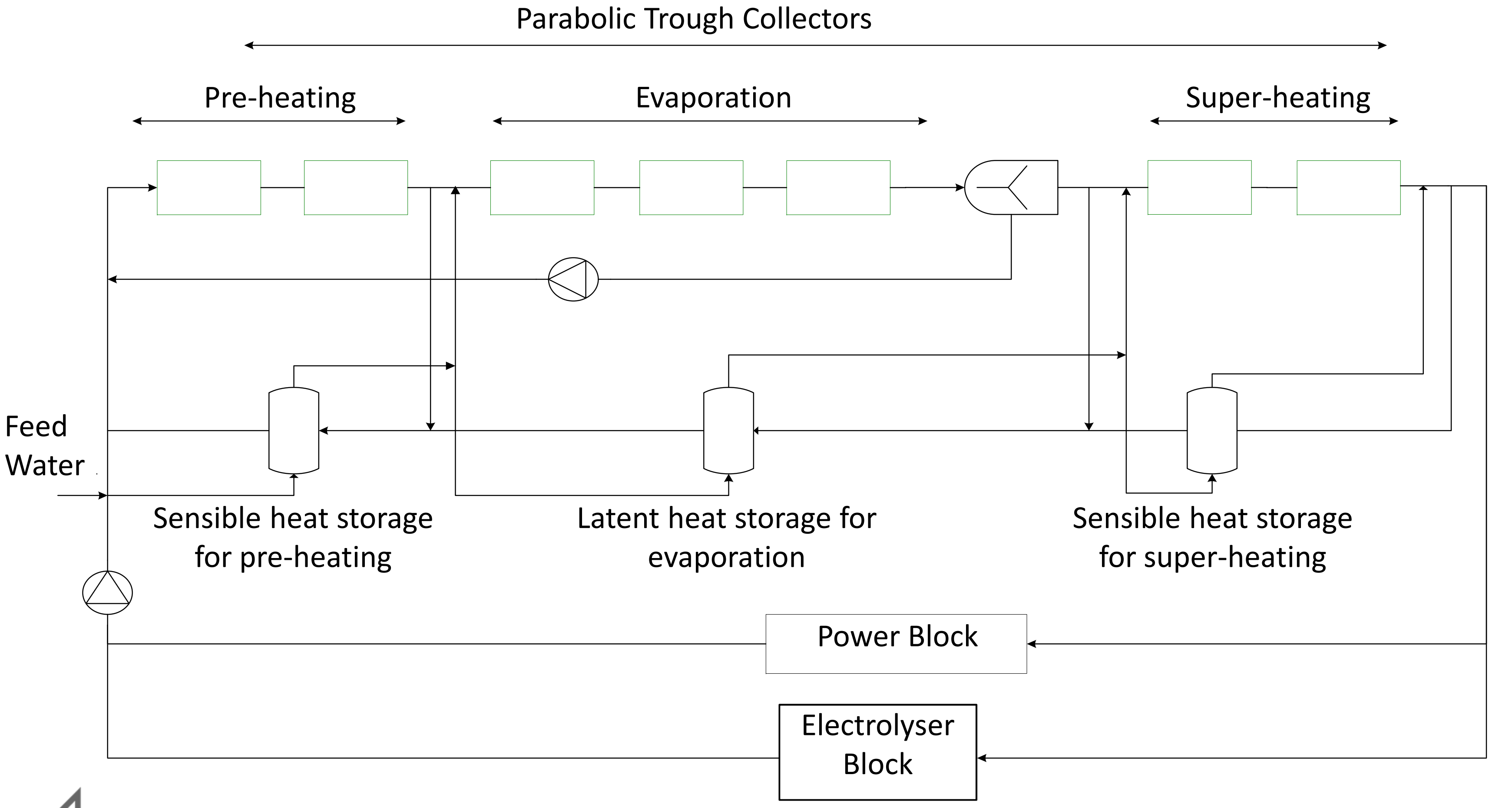
Flow diagram of the coupling of the solar power tower with the electrolyzer



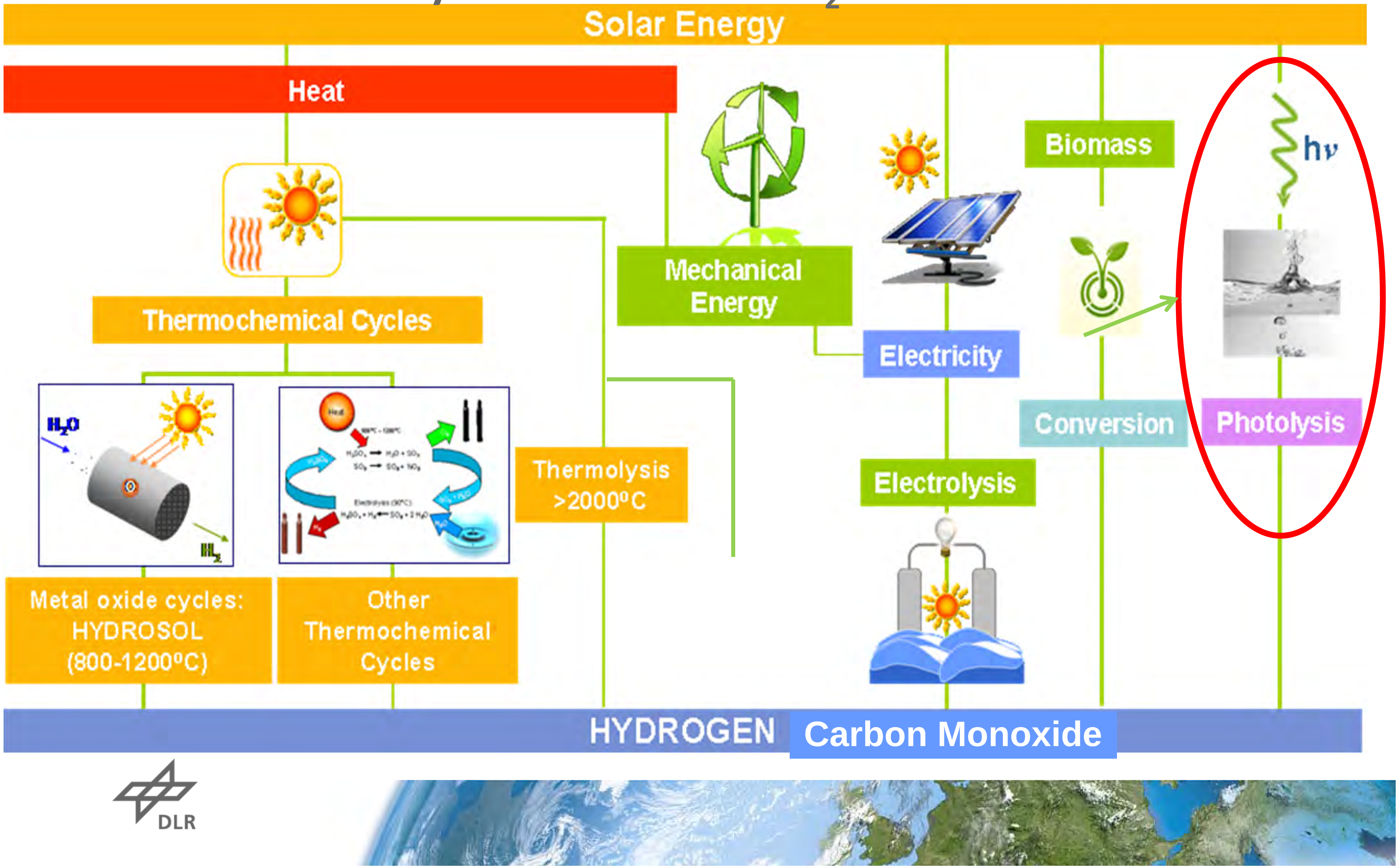
Flow diagram of the coupling of the parabolic dish to the electrolyzer



Flow Diagram of the coupling of the parabolic trough to the electrolyzer

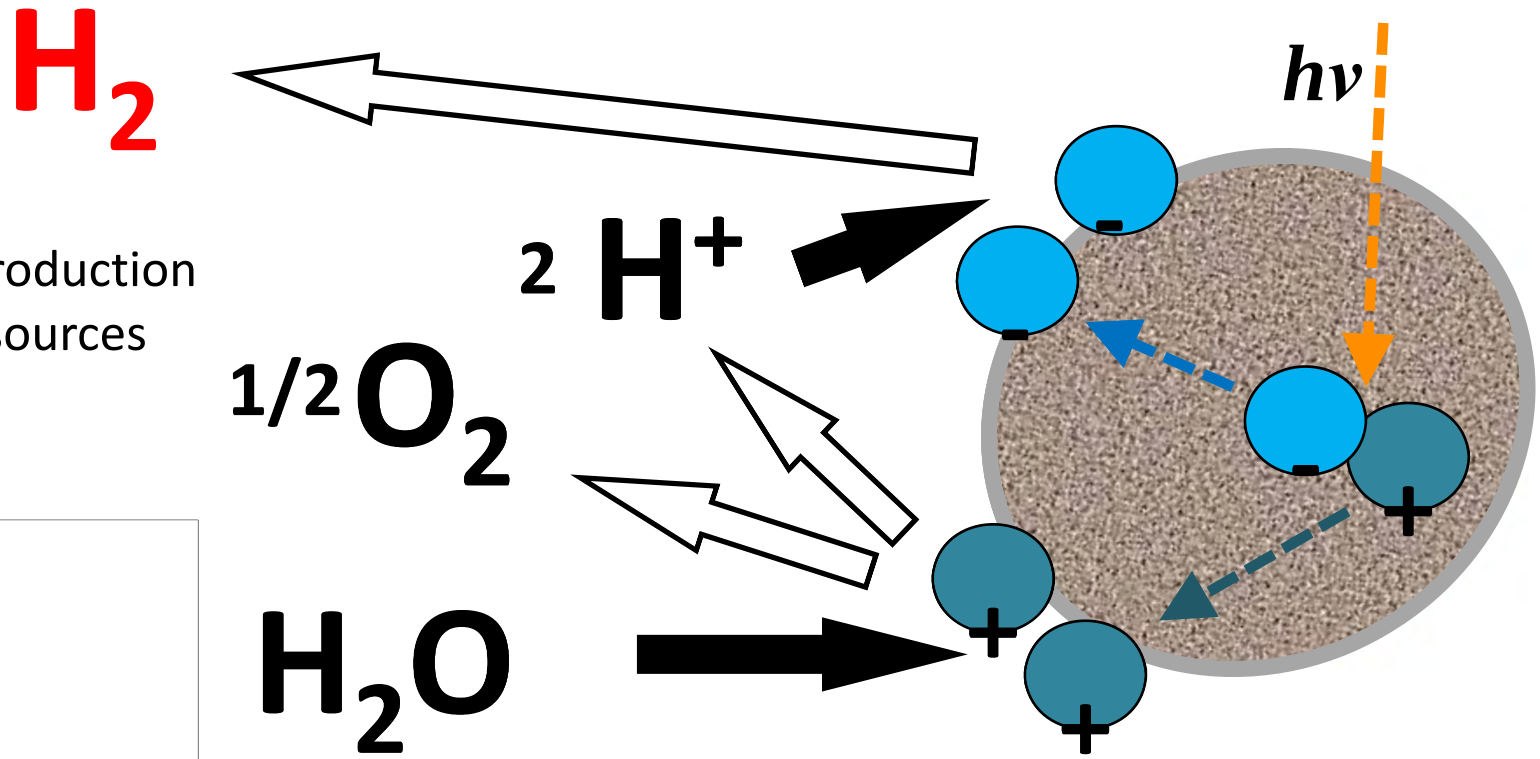


Solar Pathways from Water or CO_2 to Fuels



Chemistry

Photocatalytic Water Splitting



- CO_2-free production
- abundant sources

Engineering:
Choice of a Concentrator Concept

$C \approx 20$
Risks
Oblong focus
Complexity / size

Concentrator

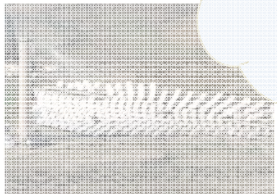
Reflector

~~Refractor~~

Parabolic Trough

Analyzed by ray tracing!

Central Receiver System



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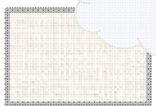
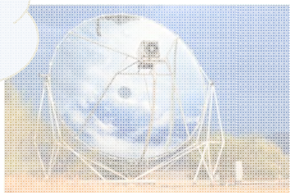
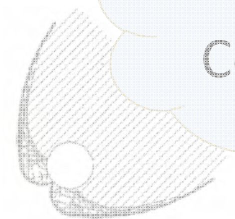


Parabolic Dish

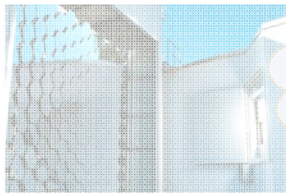


Linear Fresnel Collector

Compound Parabolic Concentrator



Solar Furnace



Conclusion and Outlook

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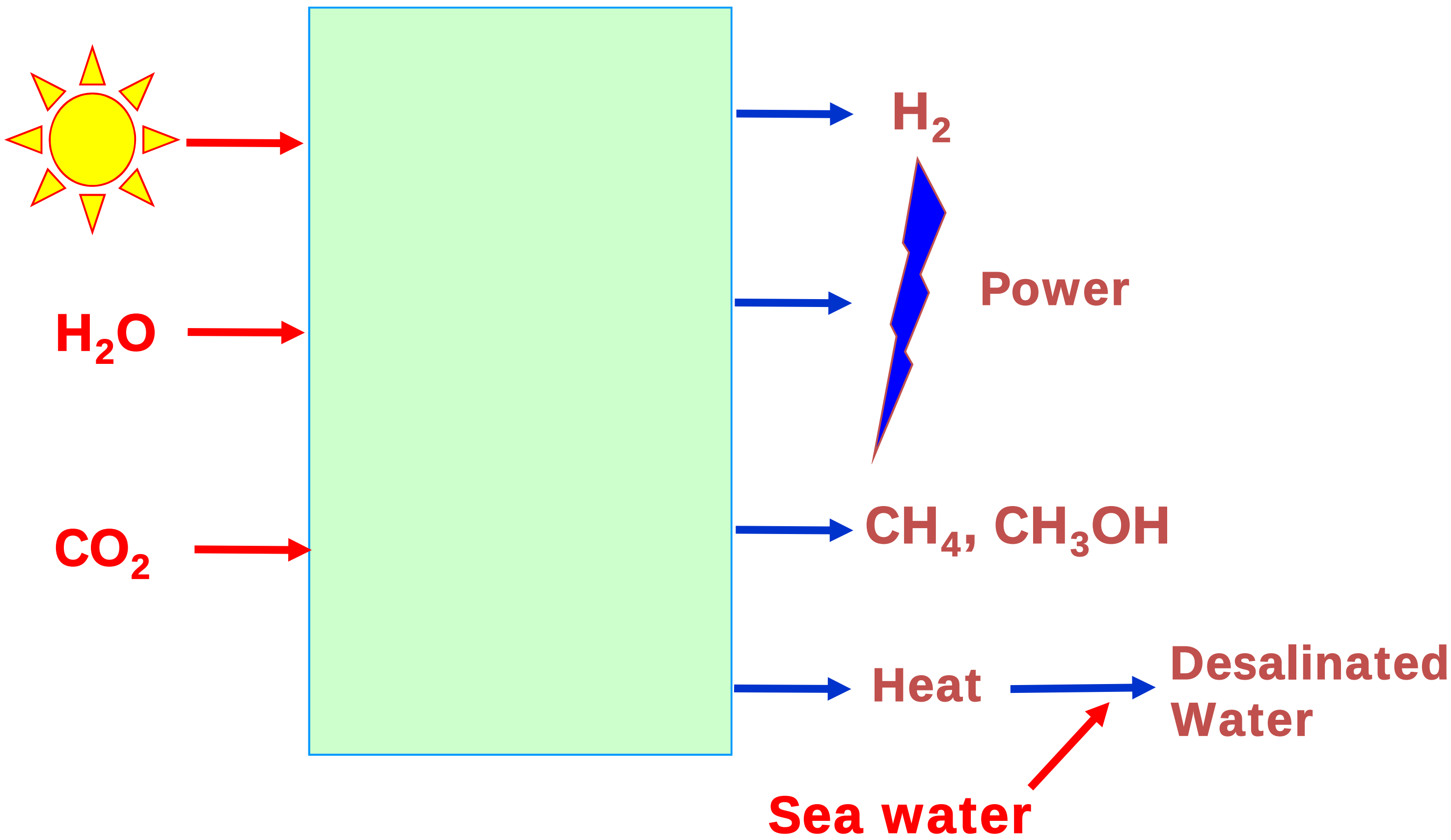
Future Concentrated Solar Plants – more than power!

Production of solar fuels (renewable H_2 and CH_4 / CH_3OH), Recycling of CO_2, Power Production and Water Desalination (H_2O)



Acknowledgement

- Thanks to all agencies funding the development of solar fuel technologies, especially the European Commission and to all industrial partners involved.

- Thanks to all colleagues and partners who provided various contributions to this work.

DLR Fuel Cell Aircraft ANTARES

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Thank you very much for your attention!