

Solar Fuels

Overview on the work carried out at the German
Aerospace Center

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 - High Temperature Electrolysis
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German Aerospace Center (DLR)



DLR German Aerospace Center



- Research Institution
- Space Agency
- Project Management Agency



Research Areas

- Aeronautics
- Space Research and Technology
- Transport
- Energy
- Space Administration
- Project Management Agency

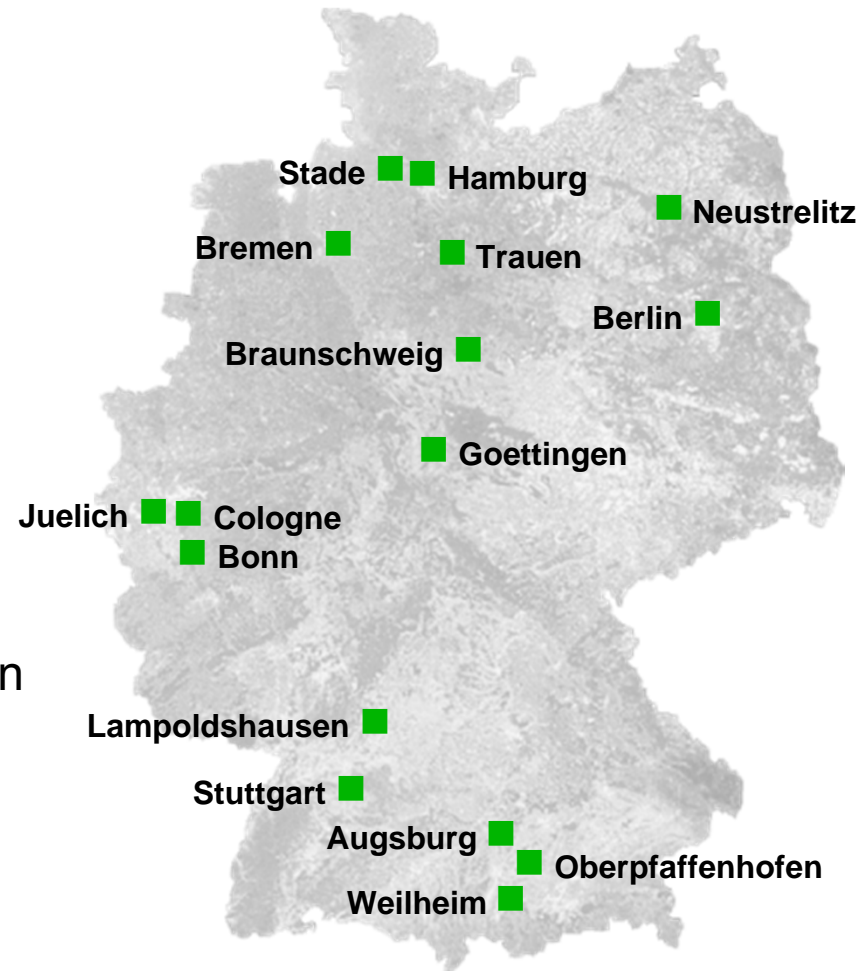


Locations and employees

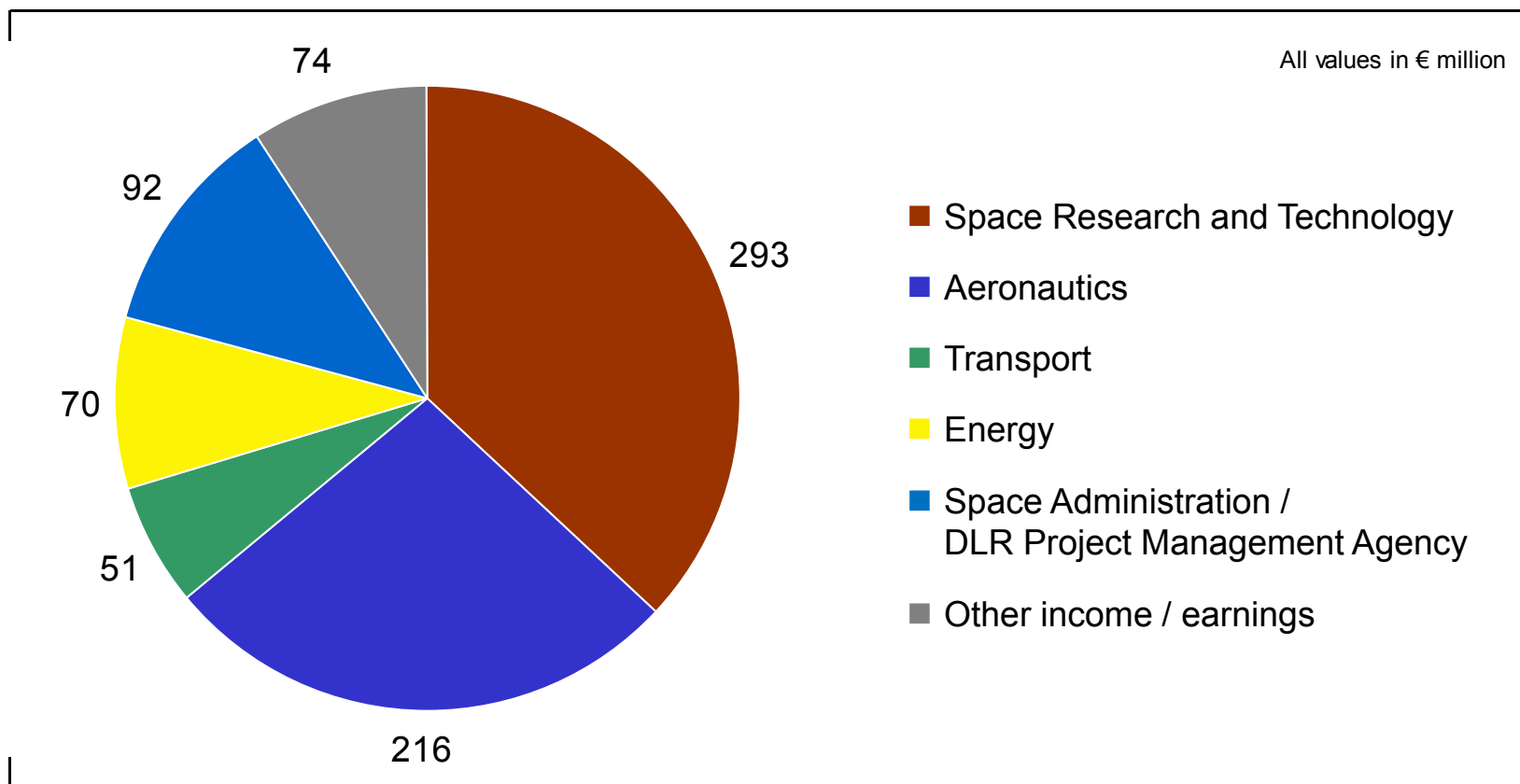
7000 employees across
32 institutes and facilities at
■ 16 sites.

Offices in Brussels,
Paris, Washington, and Almería.

Permanent delegation at the
European Solar Test Centre
Plataforma Solar de Almería, Spain



Total income 2011 – Research, operations and management tasks (excluding trustee funding from the Space Administration / DLR Project Management Agency): **€796 Mio.**



Participation in the Helmholtz Association

- Success in obtaining program-oriented funding
- Added value from support of the Helmholtz Association
- Helping to shape the organisational development process



HelmholtzZentrum münchen



National and International Networking

Customers and partners: Governments and ministries, agencies and organisations, industry and commerce, science and research

World



Europe



Germany



 **Deutsches Zentrum für Luft- und Raumfahrt**



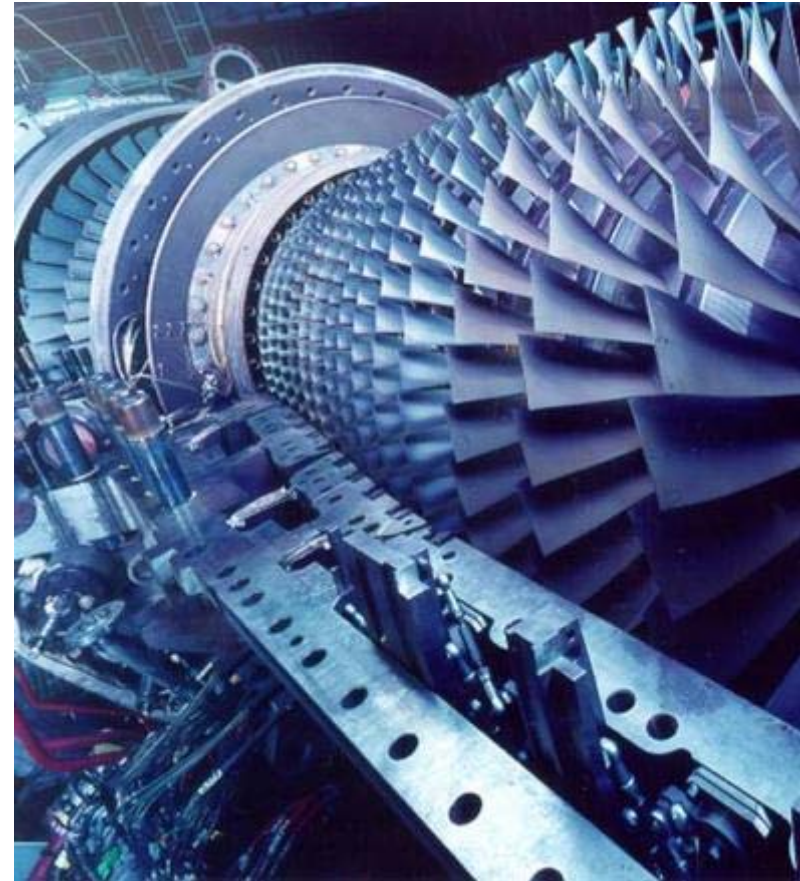
Energy



DLR Energy

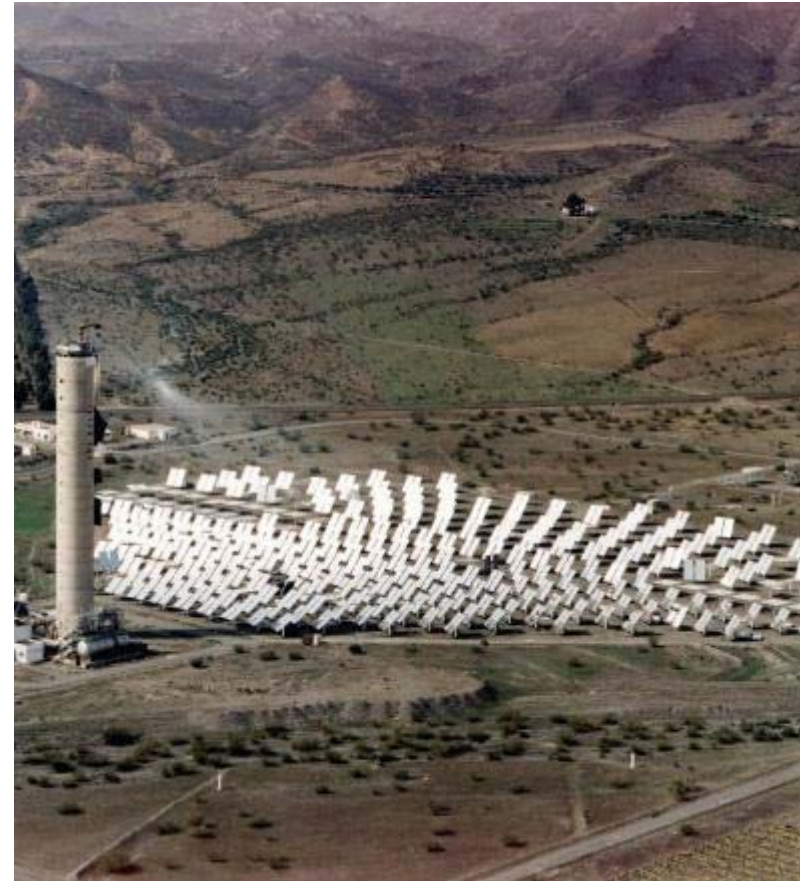
DLR Energy Research concentrates on:

- CO₂ avoidance by efficiency optimisation and renewable energies
- synergies within the DLR
- major research specific themes that are relevant to the energy economy



Energy Program Themes

- Efficient and environmentally compatible fossil-fuel power stations
(turbo machines, combustion chambers, heat exchangers)
- Solar thermal power plant technology, **solar fuels**
- Thermal and **chemical energy storage**
- High and low temperature fuel cells
- Systems analysis and technology assessment



Institute of Solar Research

Department of Solar Chemical Engineering



DLR Institute of Solar Research

Main Topic:

Solar Thermal Power Plants

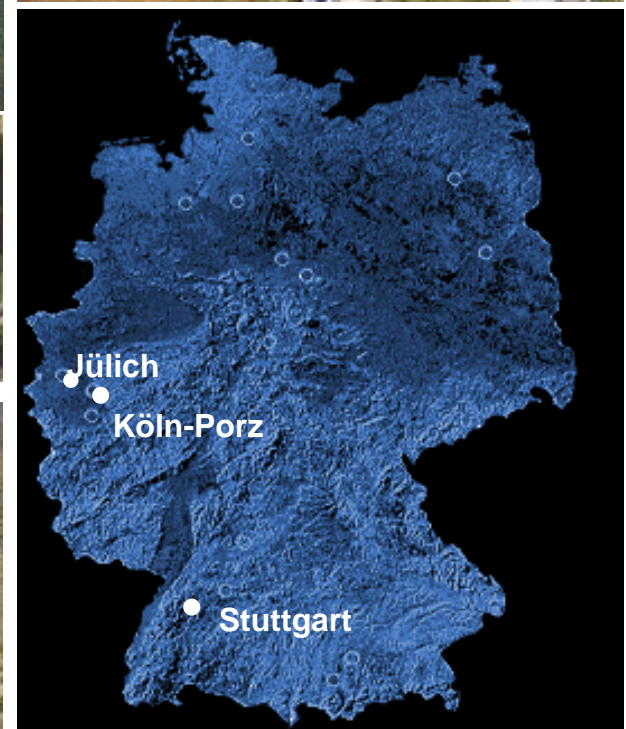
140 Persons

5 Departments, 4 Sites

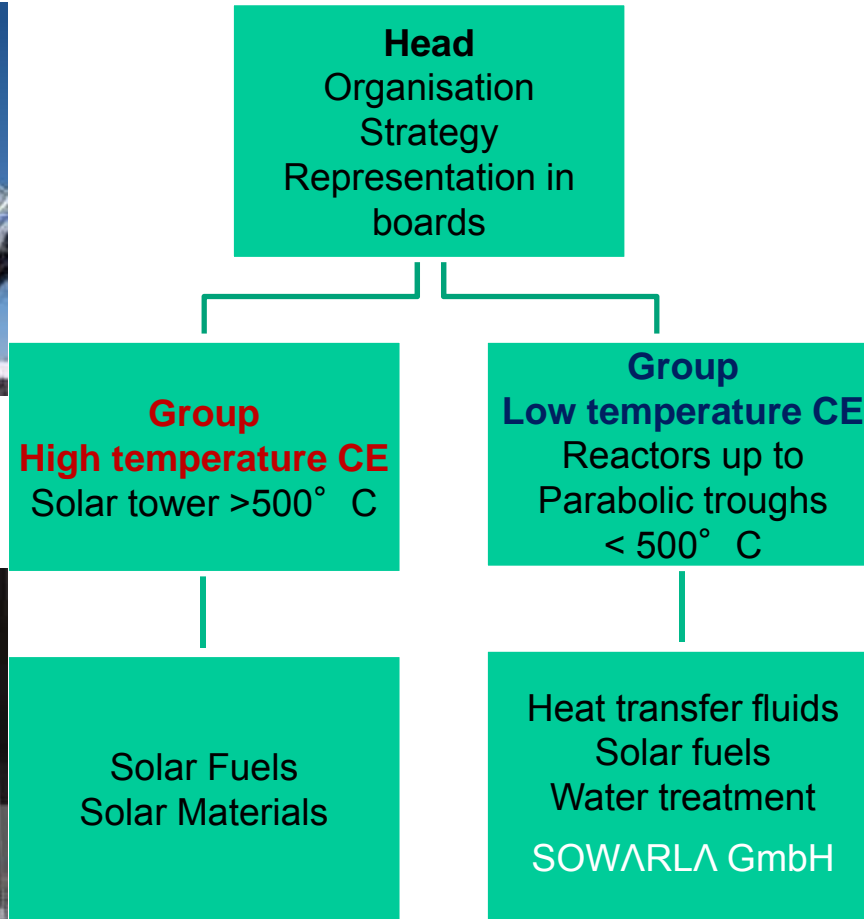
Köln-Porz, Jülich

Stuttgart

**Plataforma Solar de Almería
(Permanent Delegation)
and Office in Almería, Spain**



Department of Solar Chemical Engineering



25 Persons + Students, 65% external funding

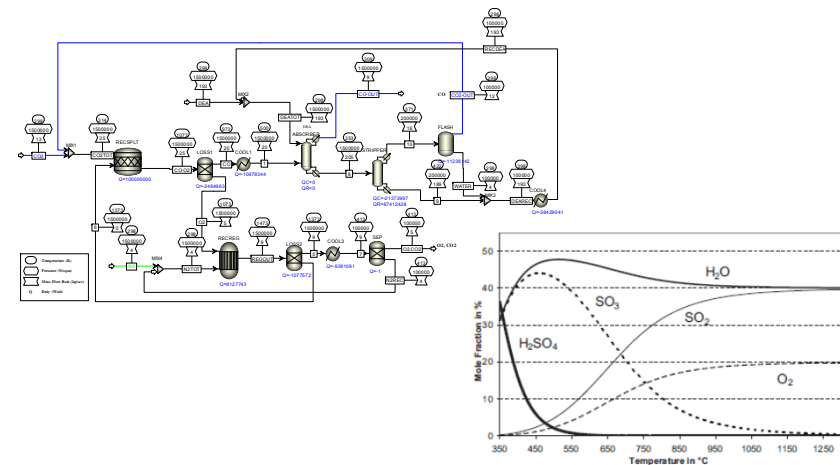
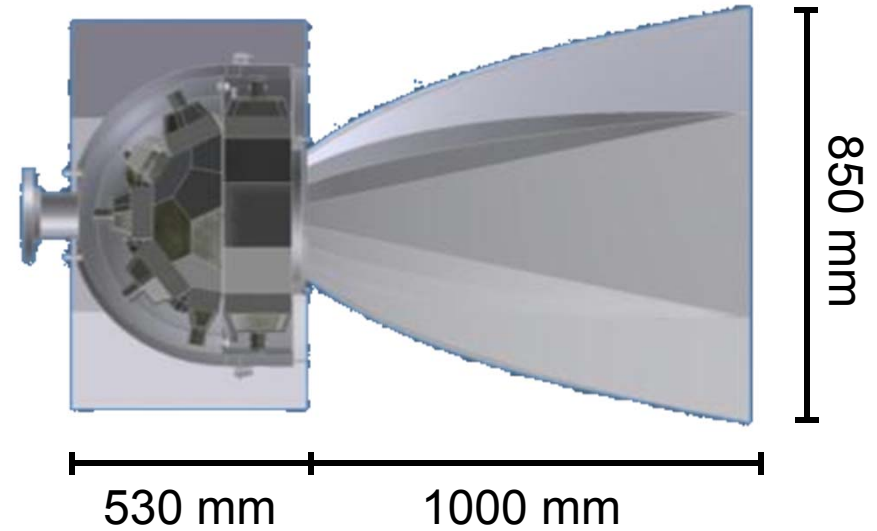


Competences

Development of components and processes

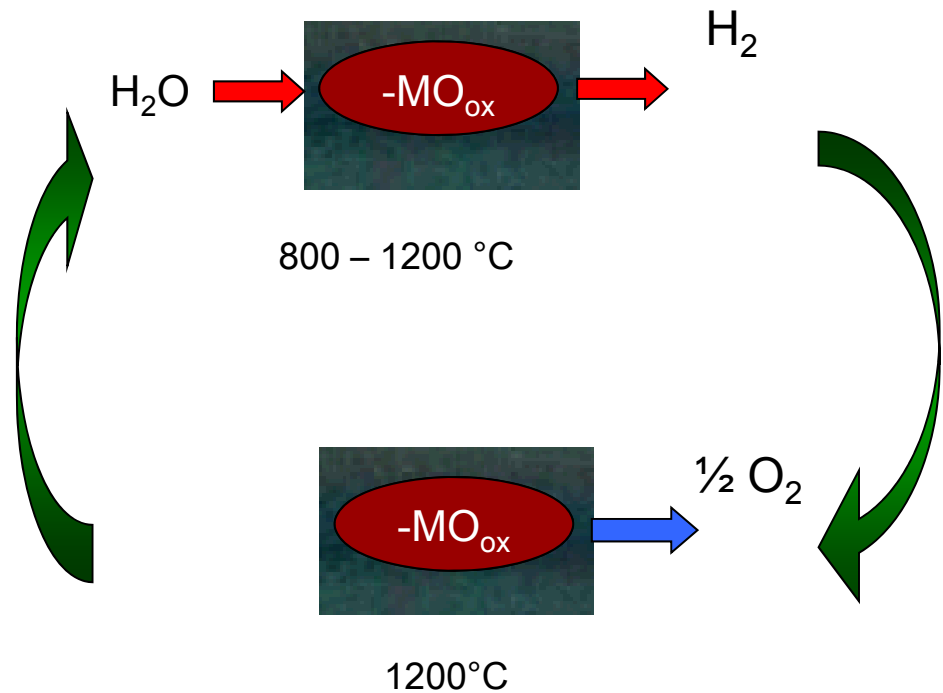
and

scientific, technologic and economic evaluation



Solar Fuels

- > 20 years experience and international cooperation
- Processes
 - Reforming of NG
 - Thermo-chemical cycles
 - Sulfur
 - metal oxides
 - Solar HT electrolysis
 - Cracking of methane
 - Photo-catalysis
- Products
 - H₂, syn-gas, methanol, FT-Synfuels ...



(Roeb, Müller-Steinhagen, Science, Aug. 2010.)

Contact DLR: Dr. Martin Roeb, (martin.roeb@dlr.de Tel.: +49(0)2203 601 2673)

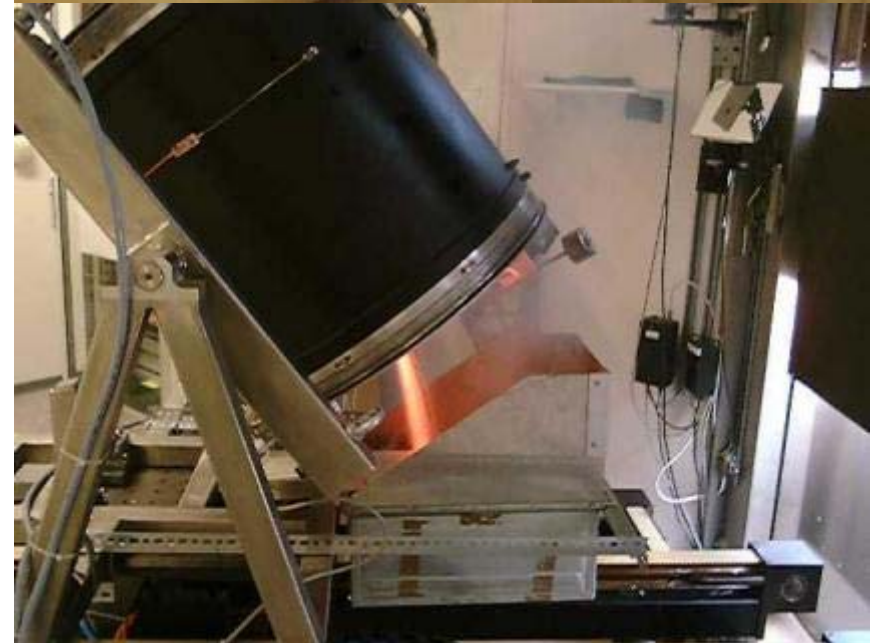


Solar Materials

- High temperature recycling of waste materials (e.g. aluminium, sulfuric acid)
- Development of solar heated reactors – solar heated rotary kilns
- Development and demonstration of production processes

Contact DLR: Dr. Martin Roeb, martin.roeb@dlr.de

Tel.: +49(0)2203 601 2673



Heat Transfer Fluids for CSP

- Accelerated Aging
 - Degradation rates, and kinetics of gas, water, and other degradation products formation
- Physico-chemical parameter at high temperatures
 - Vapor pressure, density, heat capacity, heat conductivity, viscosity, gas solubility
- Interaction with power plant components
 - Hydrogen diffusion, influence of material contacts and impurities on the aging of the heat transfer fluids
- Field tests
 - Authentic and representative samples of heat transfer fluids during power plant operation, inline- / atline- / offline-analysis

Contact DLR: Dr. Christian Jung (christian.jung@dlr.de; Tel. +49 (0) 2203 601 2940)

Photocatalytic Synthesis of Solar Fuels

- Qualification of new photo-catalysts for hydrogen production or the reduction of CO₂
 - Determination of spectral quantum yields by special lamp technologies,
 - Determination of the solar efficiency in our solar test facilities,
 - Evaluation of long term stability, and product quality, optimisation of the produktivity
- Chemical Engineering
 - Development of solar receiver-reactors, design of concentrator technologies, scale-up, and economic evaluation

Contact DLR:

Dr. Christian Jung (christian.jung@dlr.de; Tel. +49 (0) 2203 601 2940)

Photochemical Water Treatment

- Evaluation of solar photochemical processes (VUV to solar)
Actinometry of light sources, degradation tests by photolytic and photo-catalytic processes; water analytics
- Development of photo-reactors
Solar receiver-reactor technology and photo-reactors for innovative light sources
- Development of photo-chemical plants
Plants for water treatment with photo-chemical key steps up to demonstration scale, research on the combination of treatment technology, automation, recycling of photo-catalysts, energetic optimisation

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Solar Fuels - Strategic Basis



HGF

- Presently „Solar Fuels“ is a sub-topic of the Concentrating Solar Power Topic within the Renewable Energy Program of the „HGF Program oriented Funding II“ (PoF II)
 - DLR is the only contributor
 - The sub-topic is only on thermochemical processes
- From 2014 under PoF III there will be a new topic Solar Fuels (one level up!)
 - Contributors will be HZB, FZJ, DLR
 - Sub-topics will be
 - Thermochemical Processes
 - Photoelectrochemical Process
 - Systems Design



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 CO₂ 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 CO₂ emission free energy technologies, like
 - Offshore-Wind
 - **Solar**
 - 2nd generation Biomass



FUEL CELLS AND HYDROGEN

JOINT UNDERTAKING

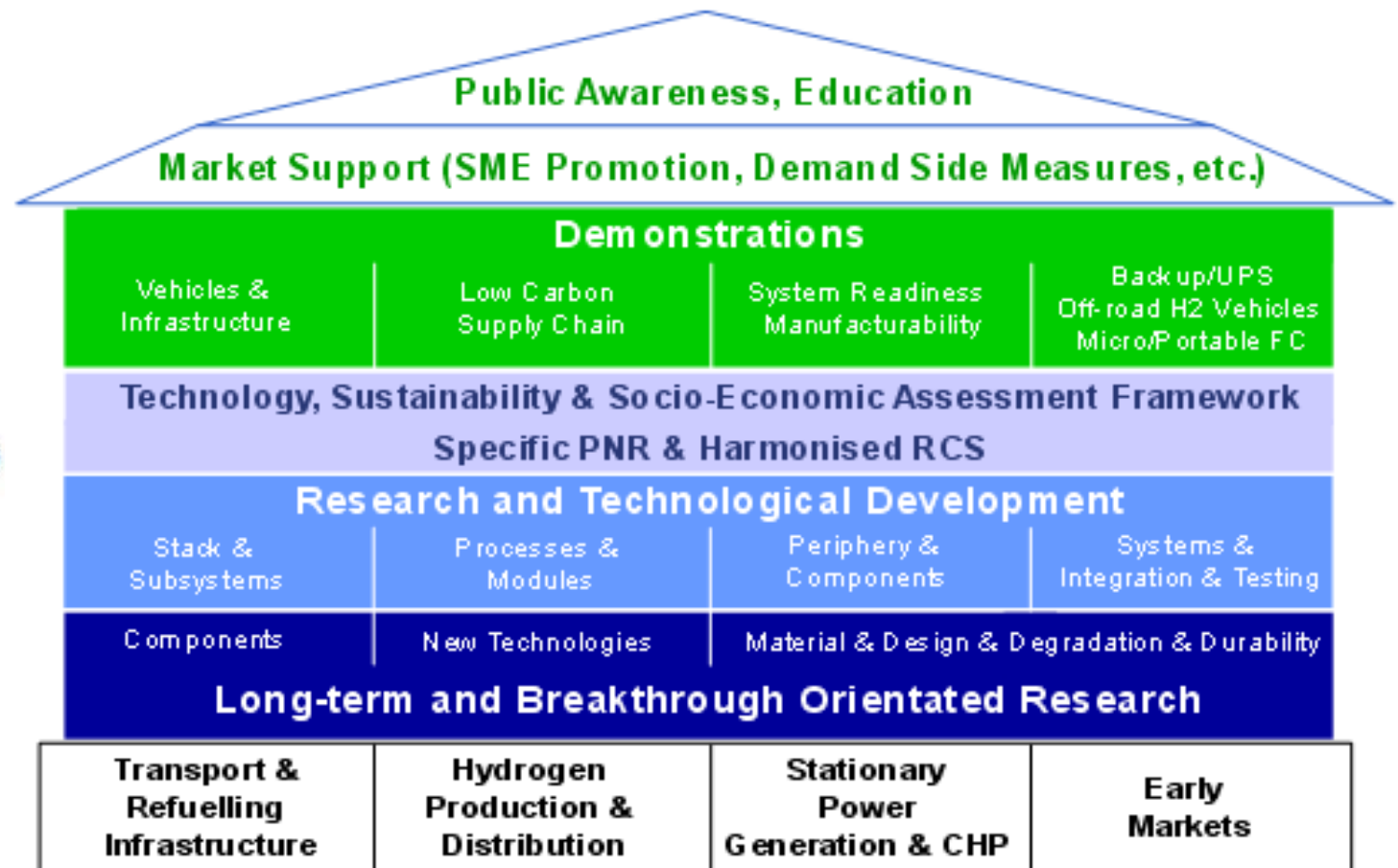


- Private – Public – Partnership
 - European Commission
 - Industry – Represented by NEW-IG (more than 60 companies)
 - Research – Represented by N.ERGHY (more than 60 research organizations)
- Budget 940 M€
 - 50% EC : 50% Industry + Research
- Contains all Fuel Cell and Hydrogen Research within the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

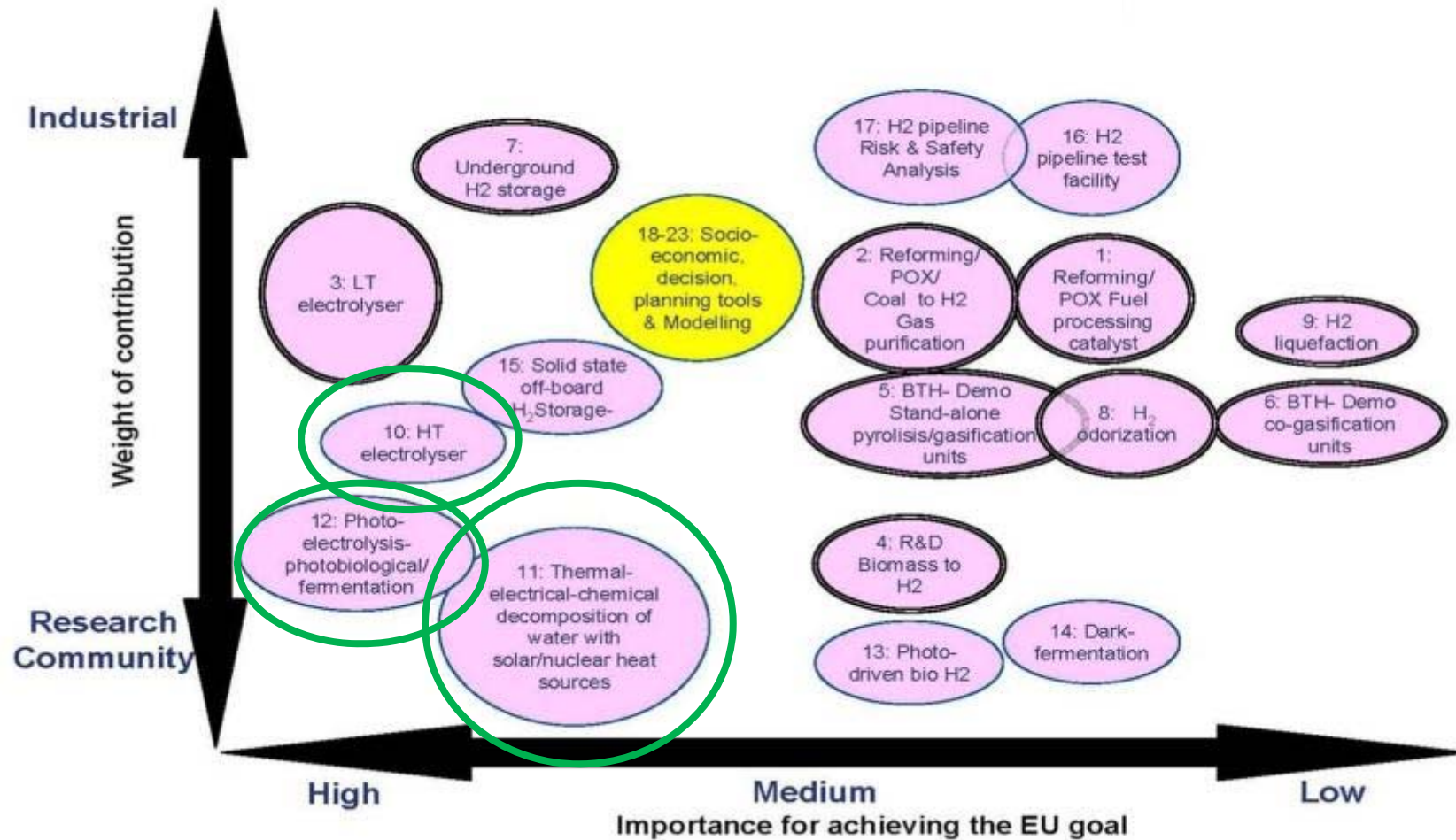


FUEL CELLS AND HYDROGEN

JOINT UNDERTAKING



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



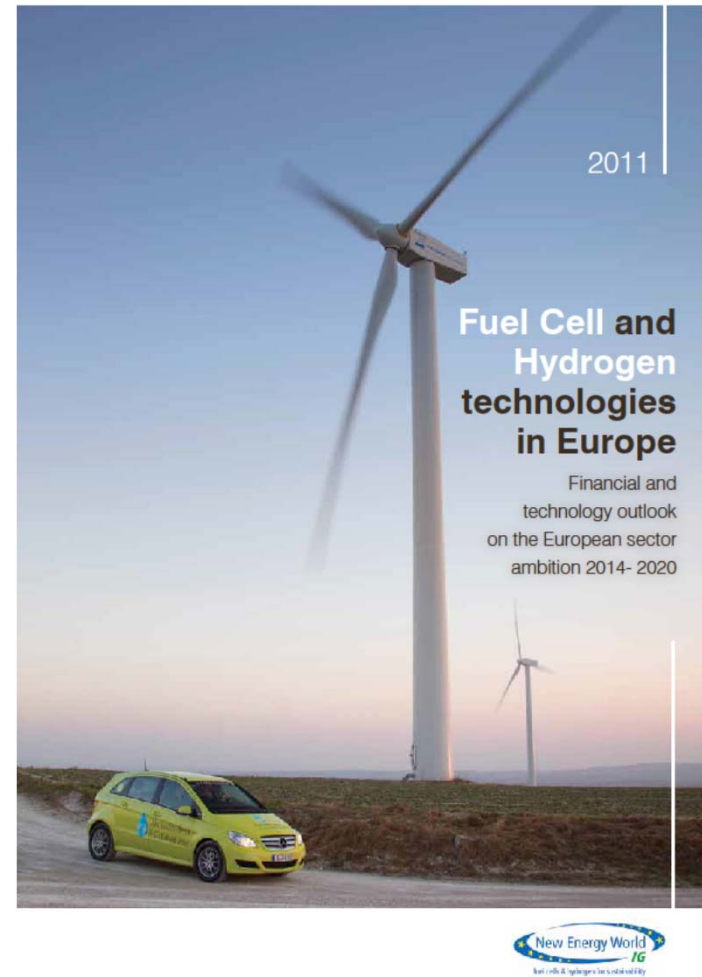
Hydrogen production & distribution (including energy storage) *2020 Objectives*

- **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-CO₂-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)

A portfolio of power-trains for Europe:
a fact-based analysis



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



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 H₂ used for these applications from renewables energies or from zero-CO₂ 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



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



Solar Chemistry - Basics

- Role models
 - photosynthesis - use of photons for photochemistry
 - burning glass – use of heat for thermochemistry
- Principle in chemical reactions:
 - photochemistry \neq thermochemistry
- However in some cases there are synergies in chemical processes, especially if not only one reaction takes place
 - Example: degradation of wastes

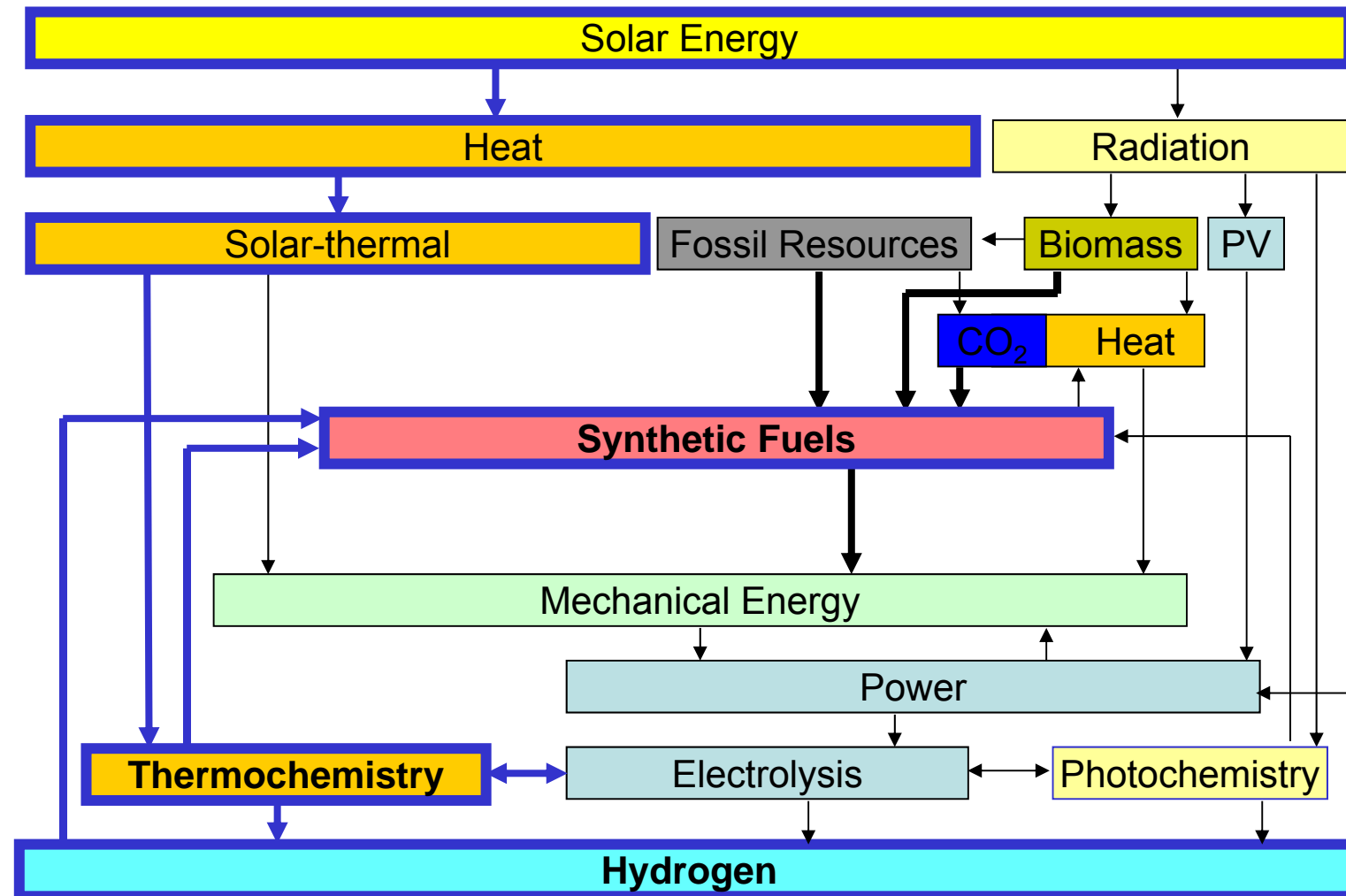


Solar Chemistry instead of Solar Power

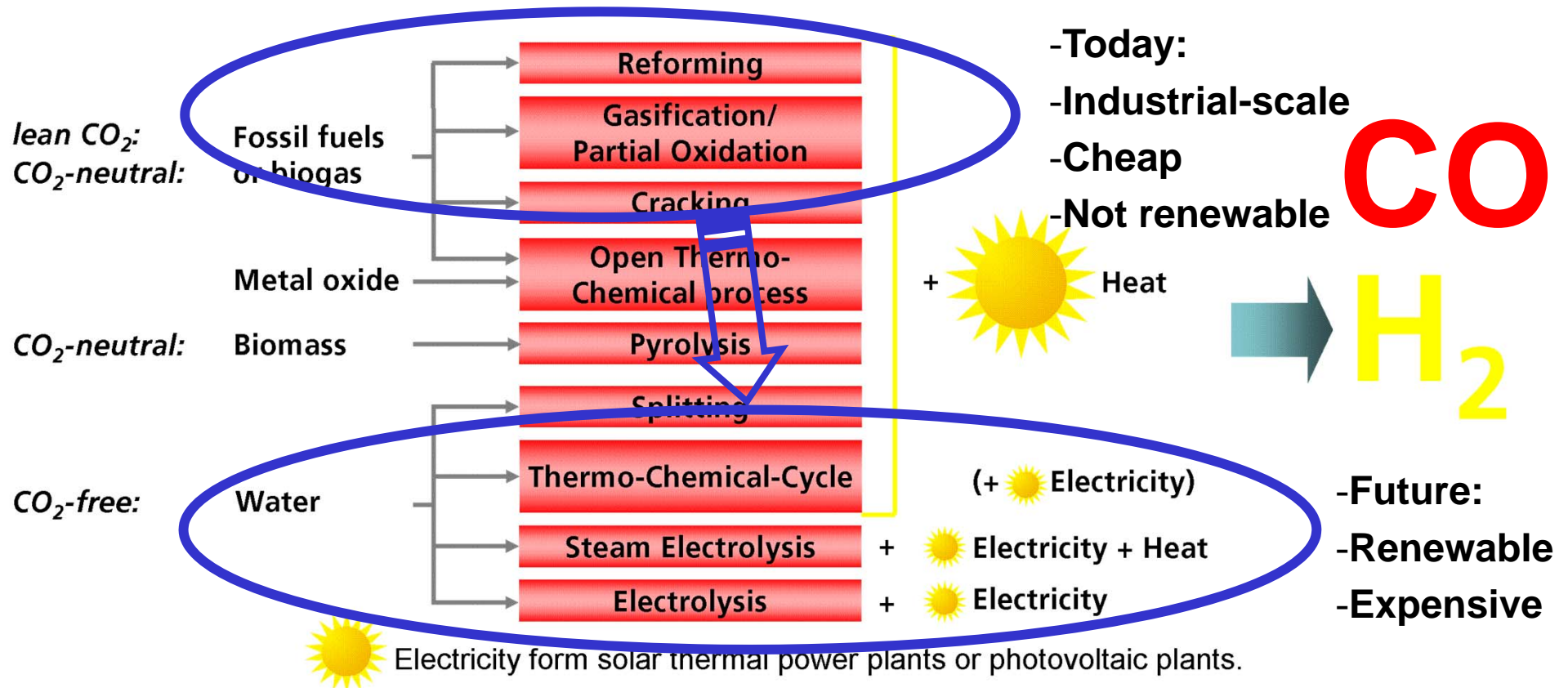
- Solar Thermochemistry is efficient because energy conversion steps are reduced!
 - Example: Hydrogen production: $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
 - **Solarchemical: 2 conversions**
 - Solar radiation – heat – Chemical reaction
 - **Via solar power: 4 conversions**
 - 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)



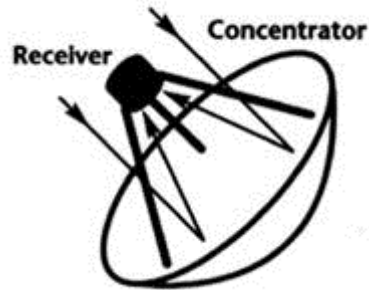
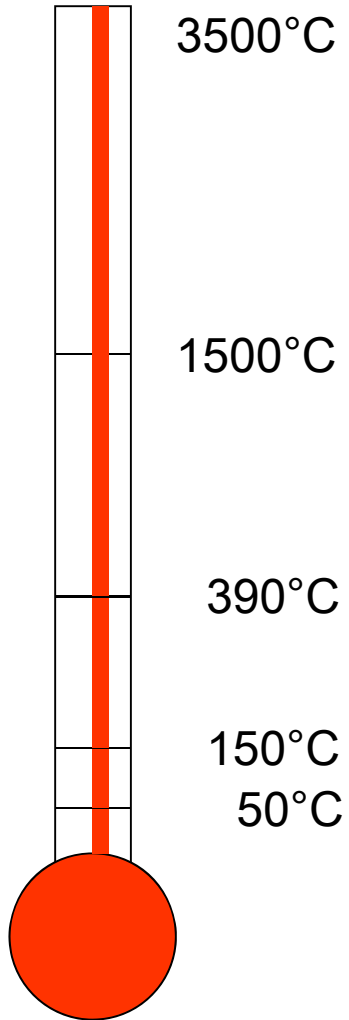
Solar Fuels – Production pathways



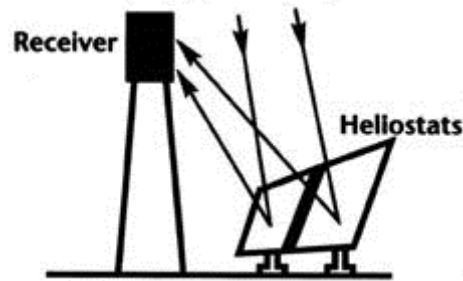
Solar Thermal Processes for Fuel Production



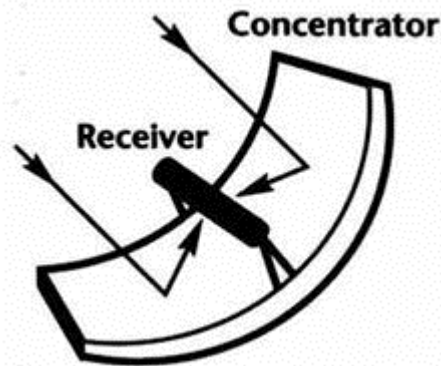
Temperature Levels of CSP Technologies



-Paraboloid:
„Dish“



-Solar Tower
(Central Receiver
System)



-Parabolic Trough /
Linear Fresnel



Solar Towers, “Central Receiver Systems”

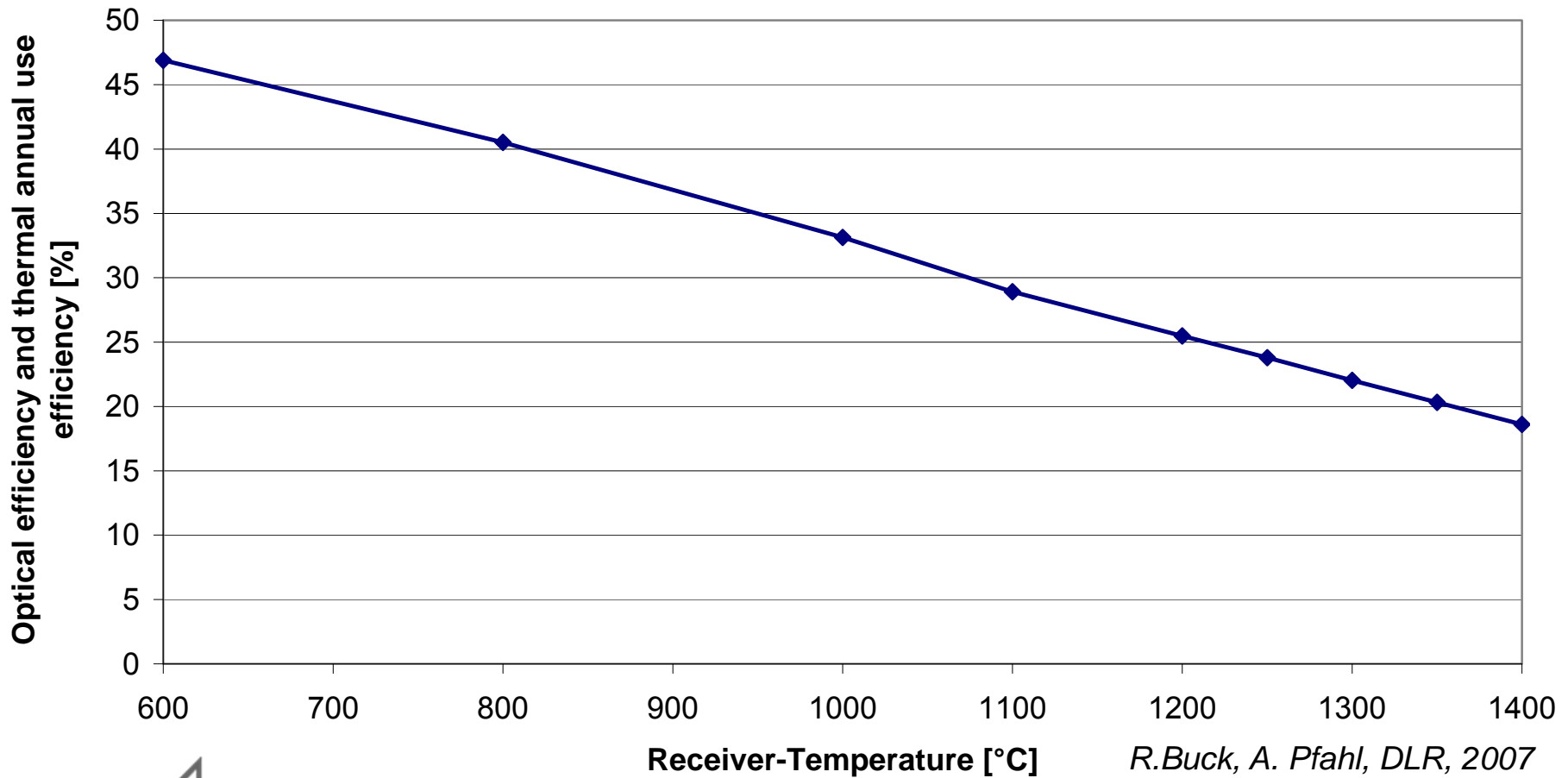


- PS10, PSA CESA-1, Torresol, Spain
- Solar-Two, Daggett, USA
- Solarturm Jülich, Germany



Annual Efficiency of Solar Power Towers

Power Tower 100MW_{th}
Optical and thermal efficiency / Receiver-Temperature



R.Buck, A. Pfahl, DLR, 2007



Solar Tower Jülich

Receiver 22.7m²

(Intratec, Saint-Gobain)

Tower 60m

(Züblin)

2150 Heliostats á 8.2 m²

(SHP/AUSRA)

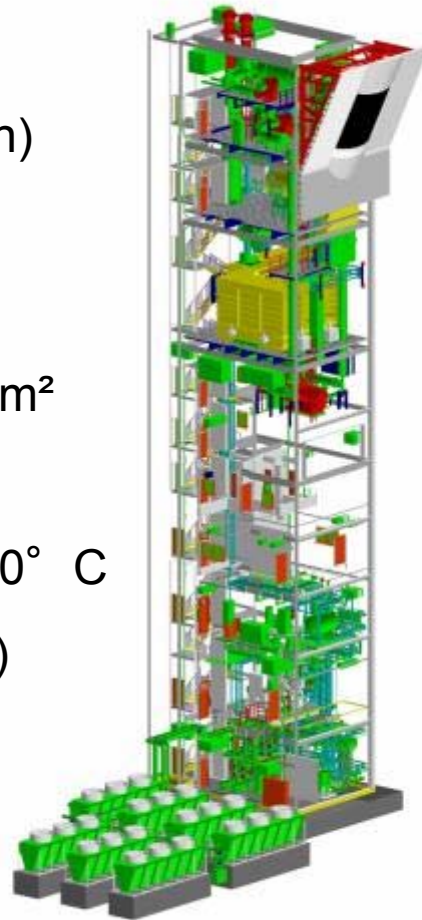
Vessel 9t/h, 30 bar/500° C

(VKK-Standardkessel)

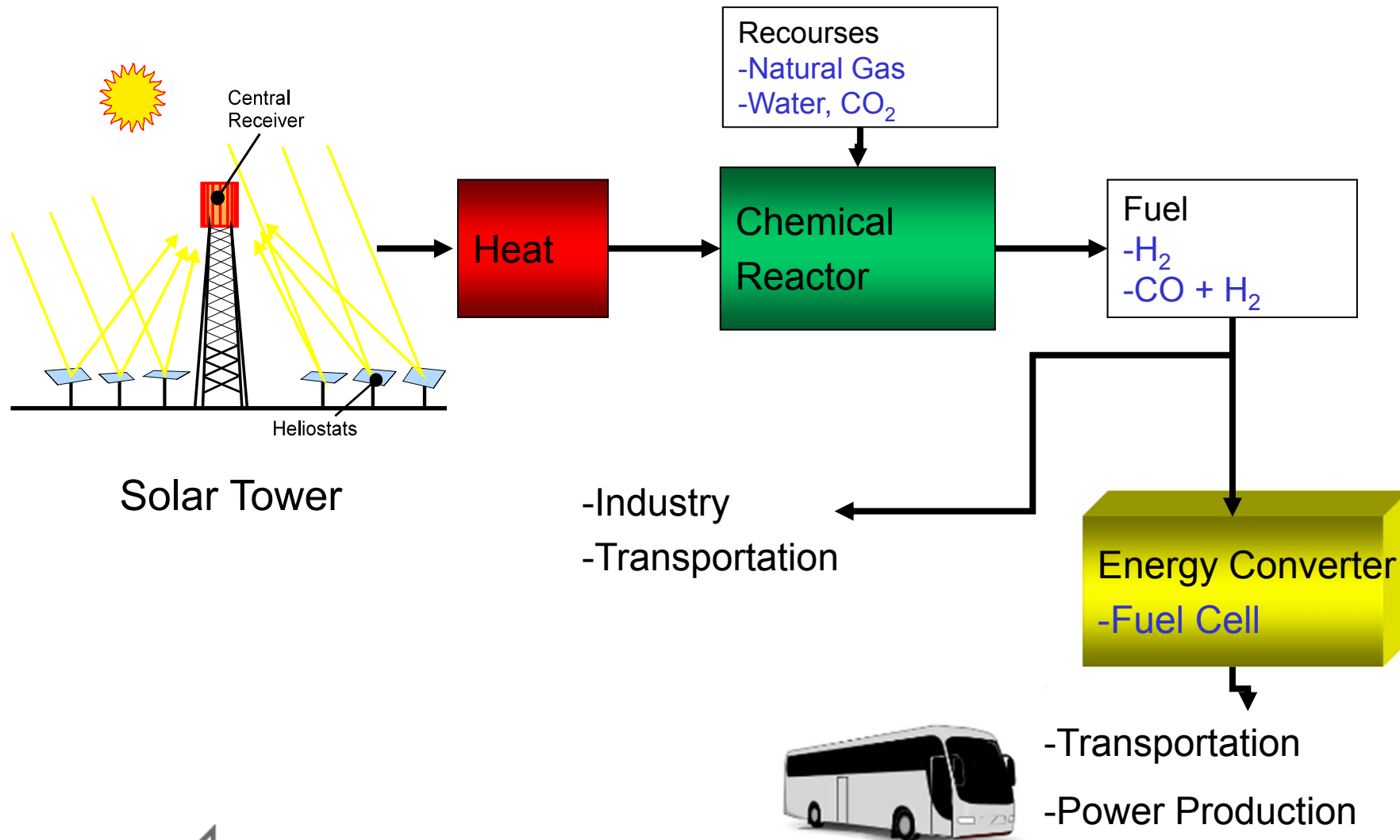
Thermal storage 1h

Turbine 1.5 MWe

(KKK-Siemens)



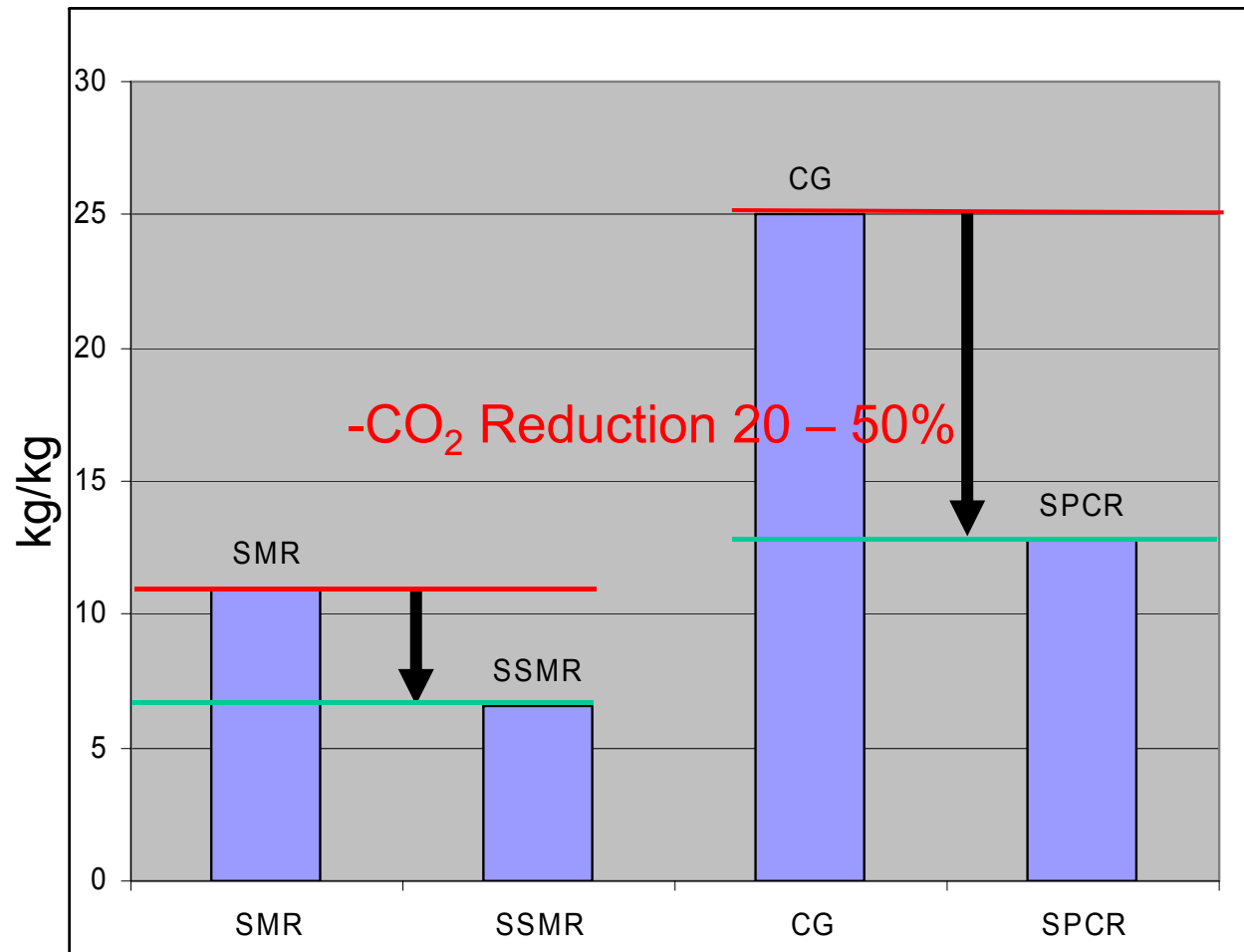
Principle of the solar thermal fuel production



Short-term CO₂-Reduction: Solar Reforming



CO₂ Reduction by solar heating of state of the art processes like steam methane reforming and coal gasification



Steam and CO₂-Reforming of Natural Gas

Steam reforming: $\text{H}_2\text{O} + \text{CH}_4 \rightarrow 3 \text{H}_2 + 1 \text{CO}$

CO₂ Reforming: $\text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{H}_2 + 2 \text{CO}$

Reforming of mixtures of CO₂/H₂O is possible and common

Use of CO₂ for methanol production:

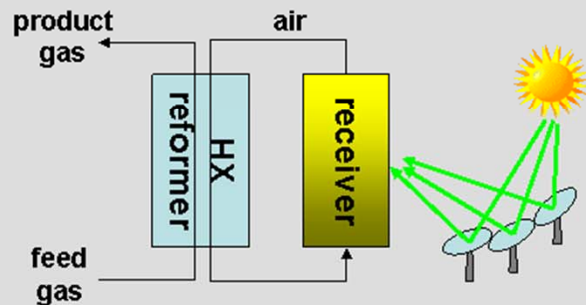
e.g. $2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{COH}$ (Methanol)

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



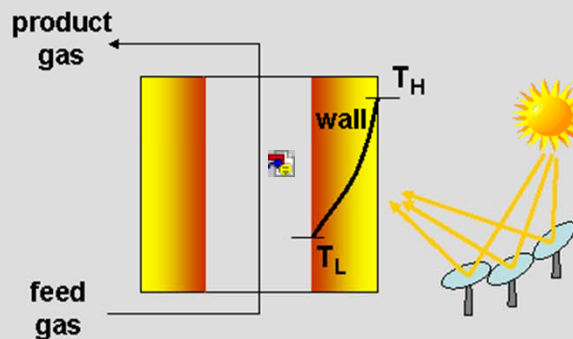
Solar Methane Reforming – Technologies

a) decoupled/allothermal



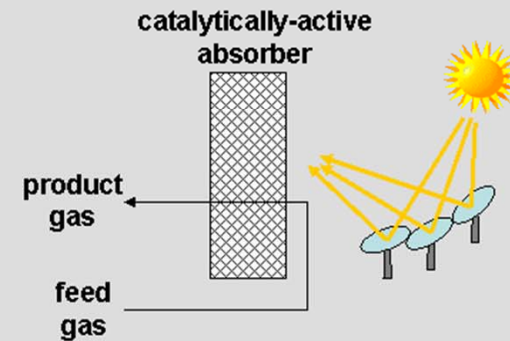
- Reformer heated externally (700 to 850° C)
- Optional heat storage (up to 24/7)
- E.g. ASTERIX project

b) -indirect (tube reactor)



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

c) Integrated, direct, volumetric



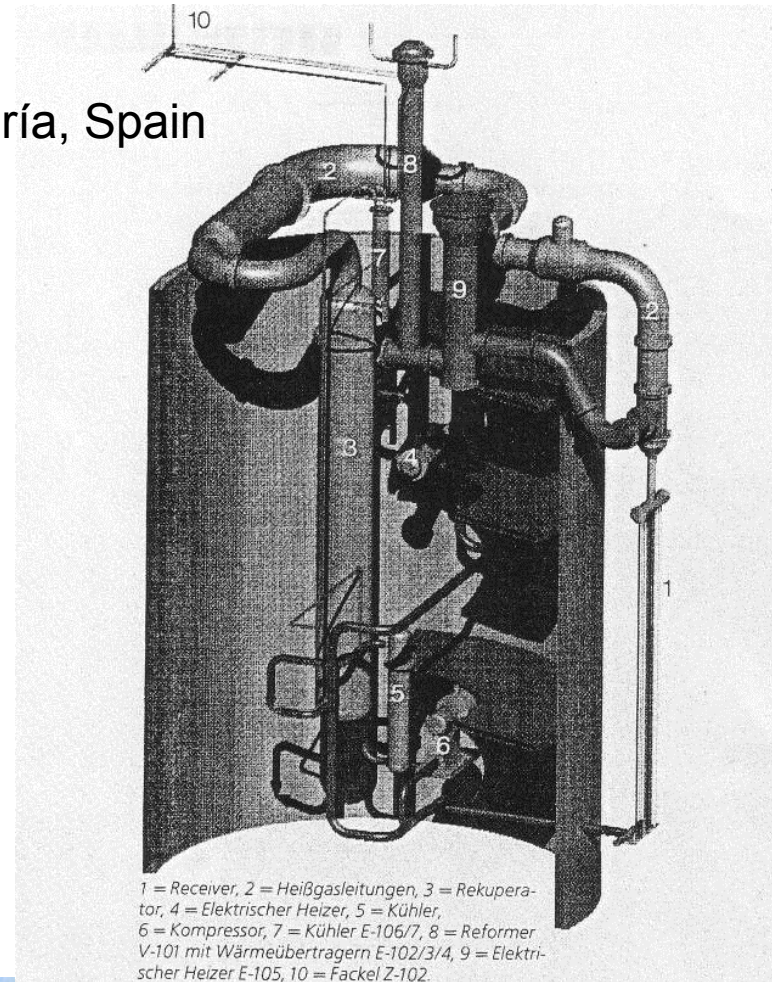
- Catalytic active direct irradiated absorber
- Approx. 90 % Reformer-h
- High solar flux, works only by direct solar radiation
- DLR coordinated projects: Solasys, Solref; Research in Israel, Japan

Source: DLR



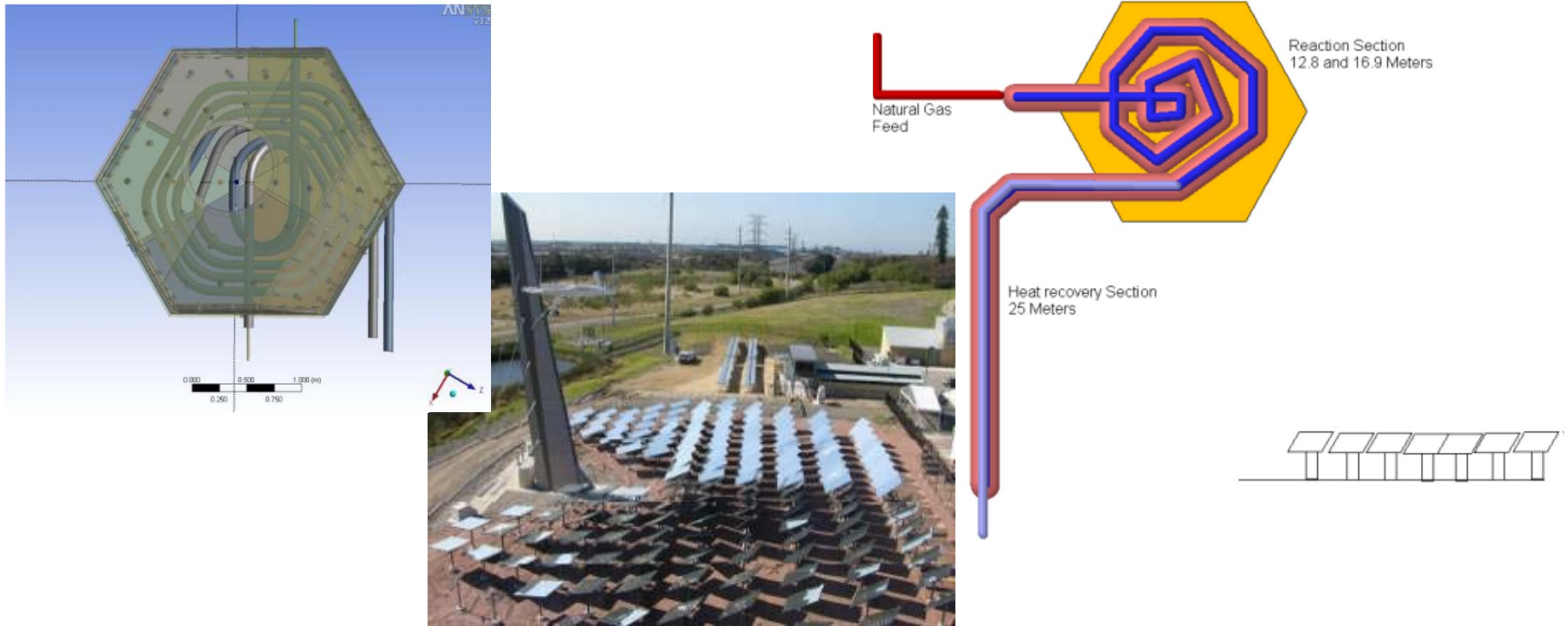
Project Asterix: Allothermal Steam Reforming of Methan

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



Pilot Scale Solar Chemical Reactors - SolarGas

Experimental set-up of the 200 kW SolarGas reactor, 600 kW plant under construction



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

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

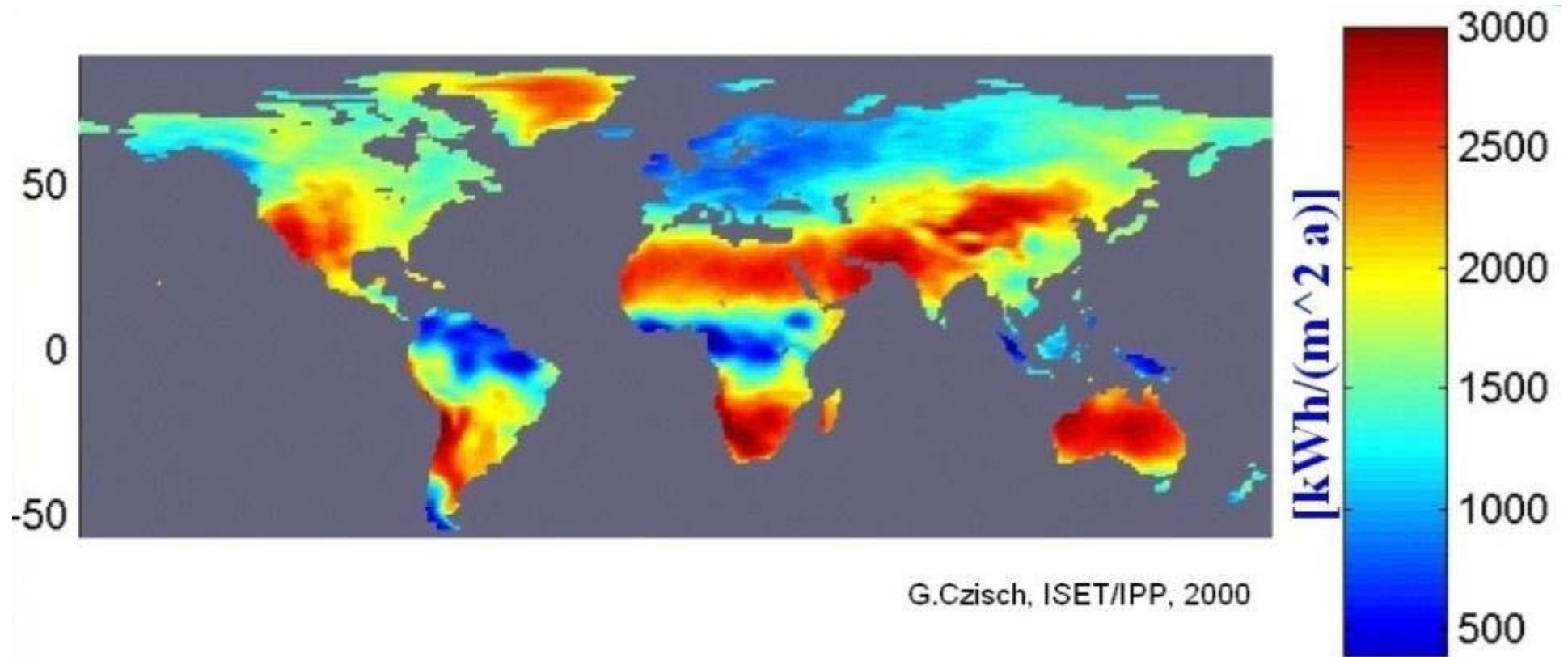


Direct heated volumetric receivers: SOLASYS, SOLREF (EU FP4, FP6)

- 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)

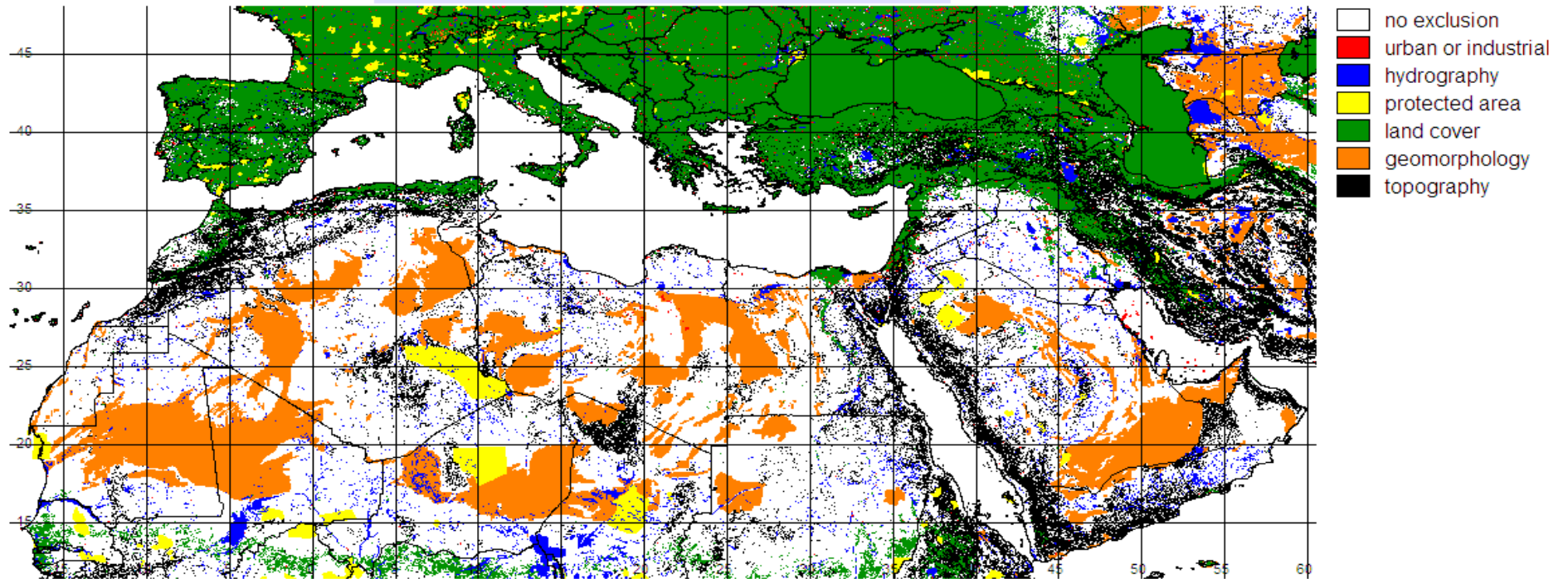


Potential Solar sites

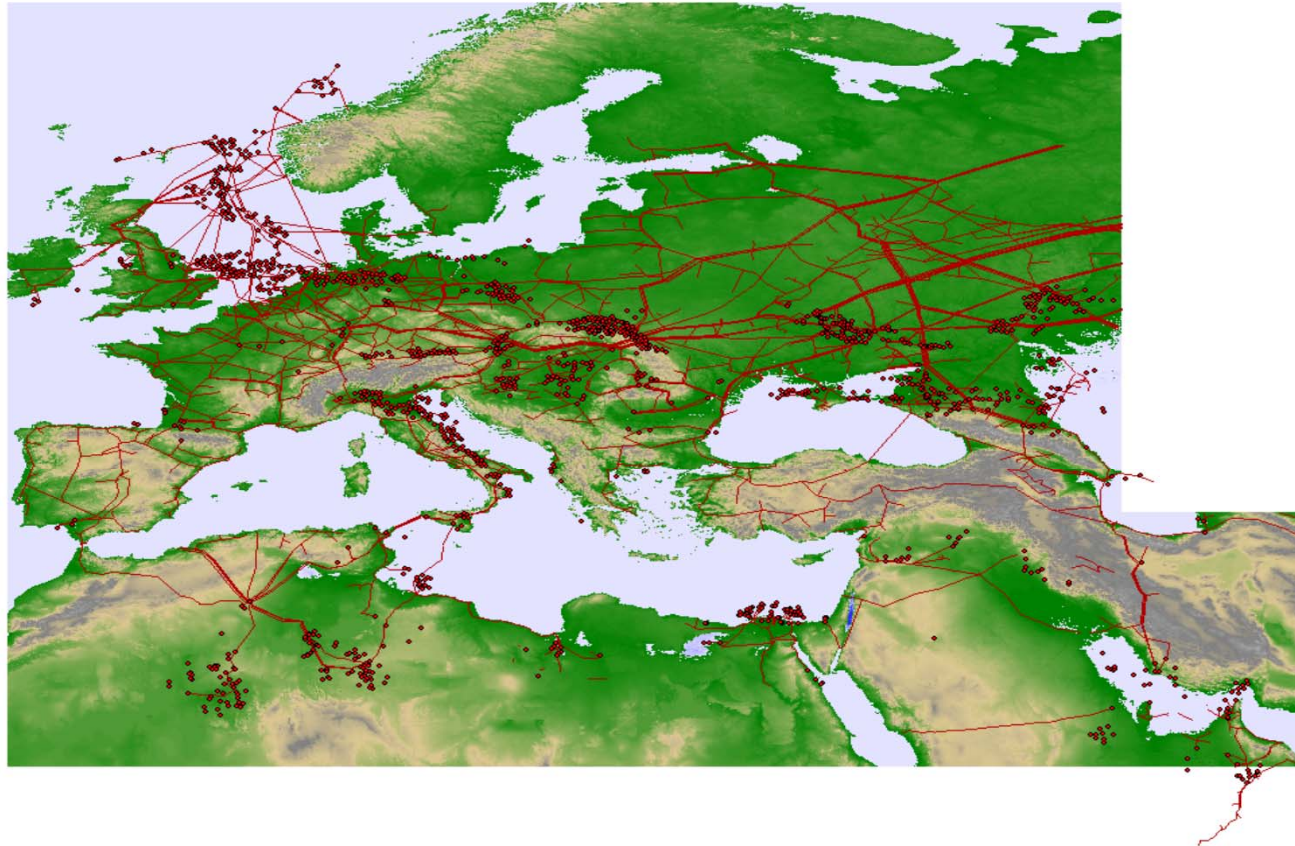


Suitable locations for CSP in Northern Africa

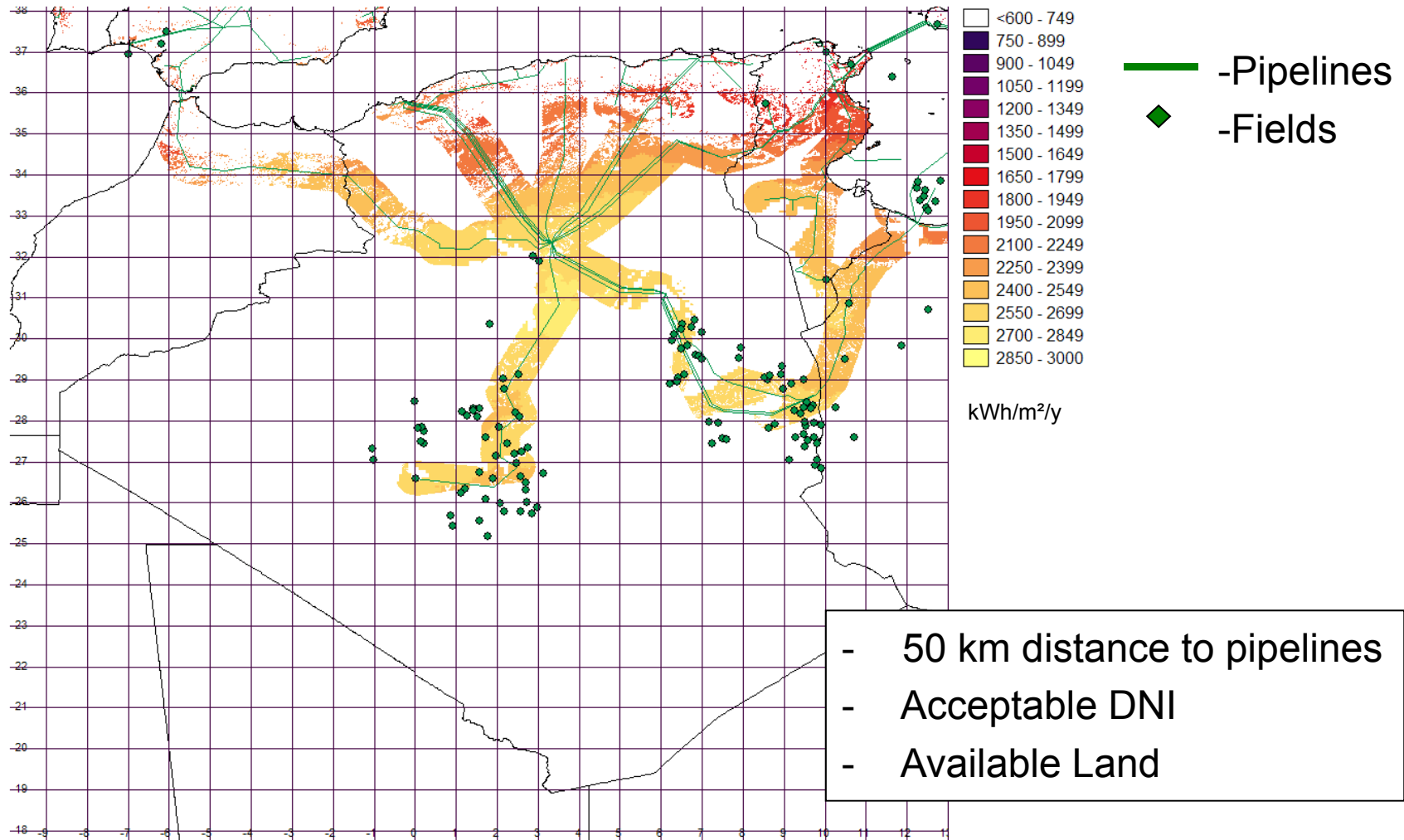
Ausschlusskriterien - Mittelmeerraum



Natural Gas Pipeline Grid and Natural Gas Fields



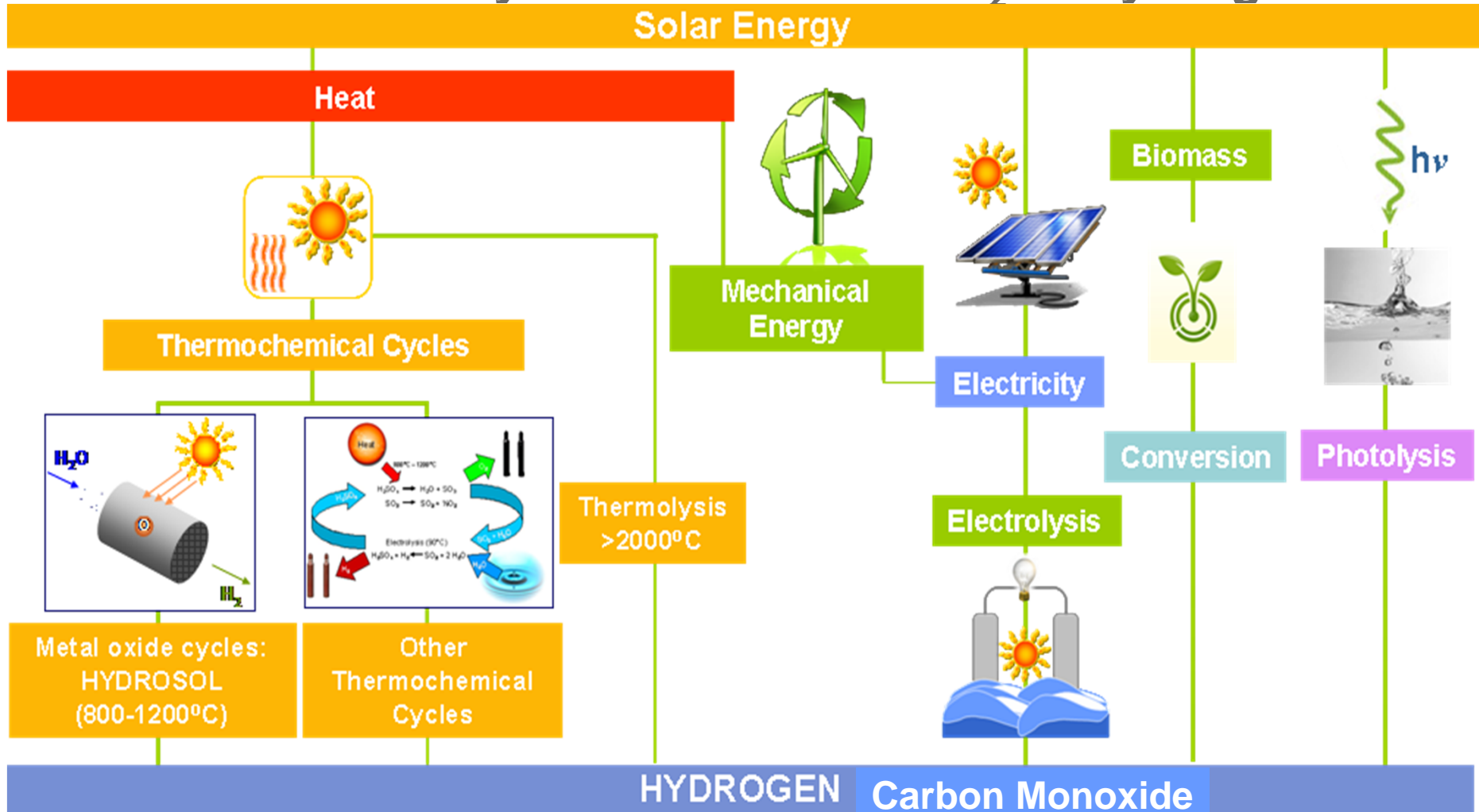
Suitable locations for solar reforming - Example Algeria and Tunisia



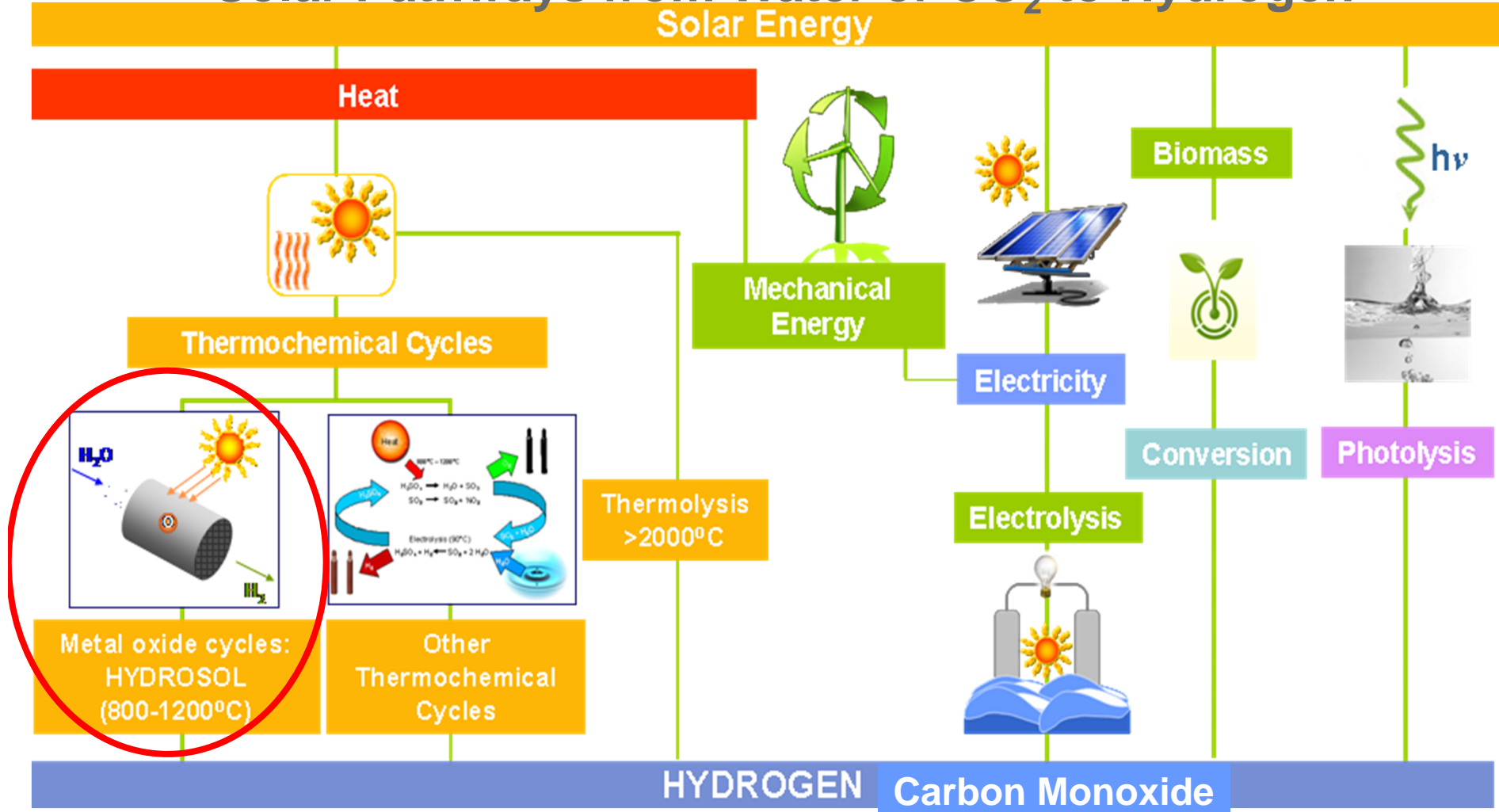
Long-term: Water splitting processes



Solar Pathways from Water or CO₂ to Hydrogen



Solar Pathways from Water or CO₂ to Hydrogen



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



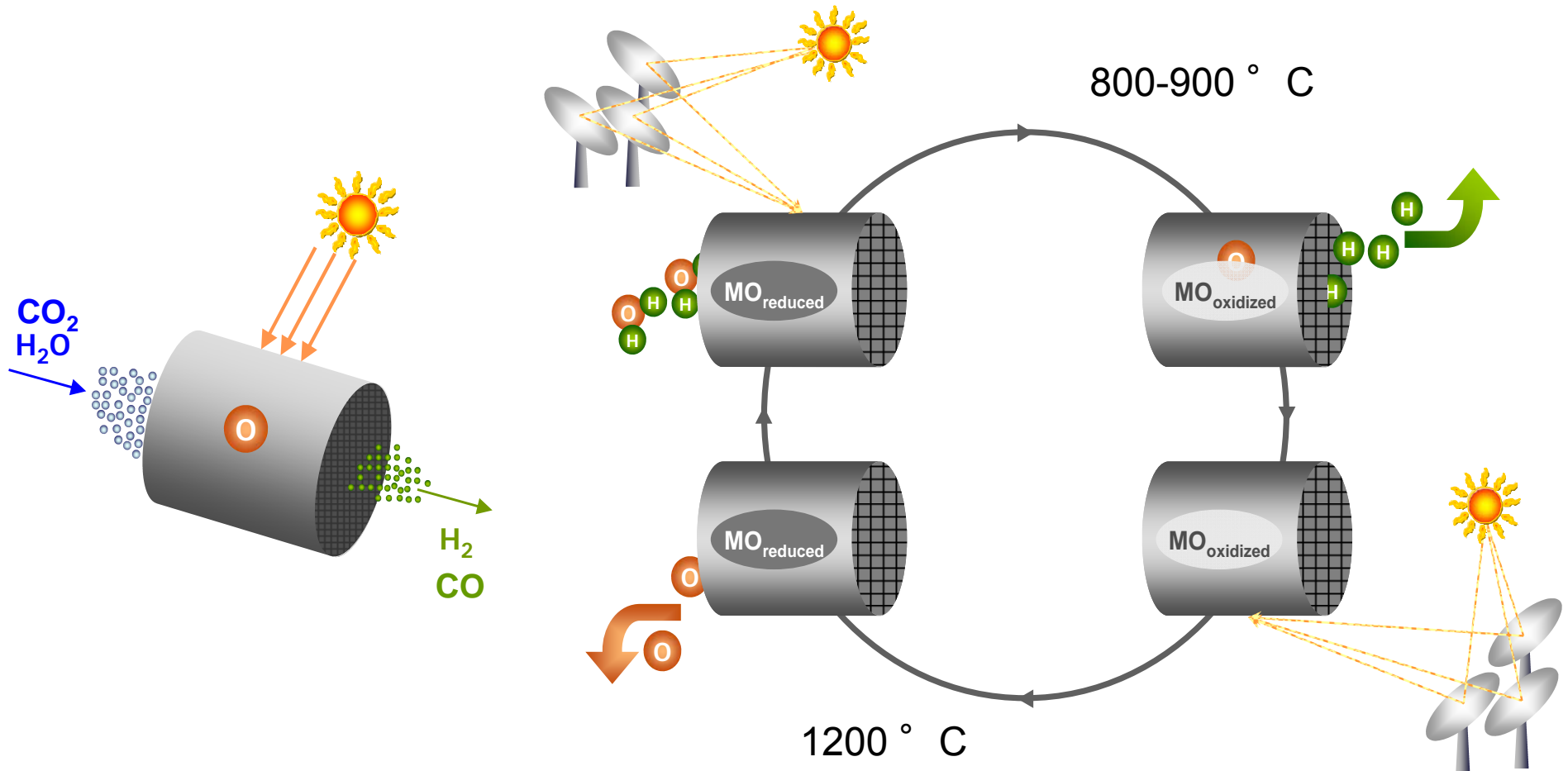
Efficiency comparison for solar hydrogen production from water (SANDIA, 2008)*

Process	T [°C]	Solar plant	Solar-receiver + power [MWth]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H ₂
Electrolysis (+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 H₂O and CO₂ by Solar Radiation



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



Hydrosol technology scale-up



2008:
Pilot reactor (100 kW)

PSA solar tower



2005:
Continuous H₂ production



2004:
First solar thermochemical
H₂ production

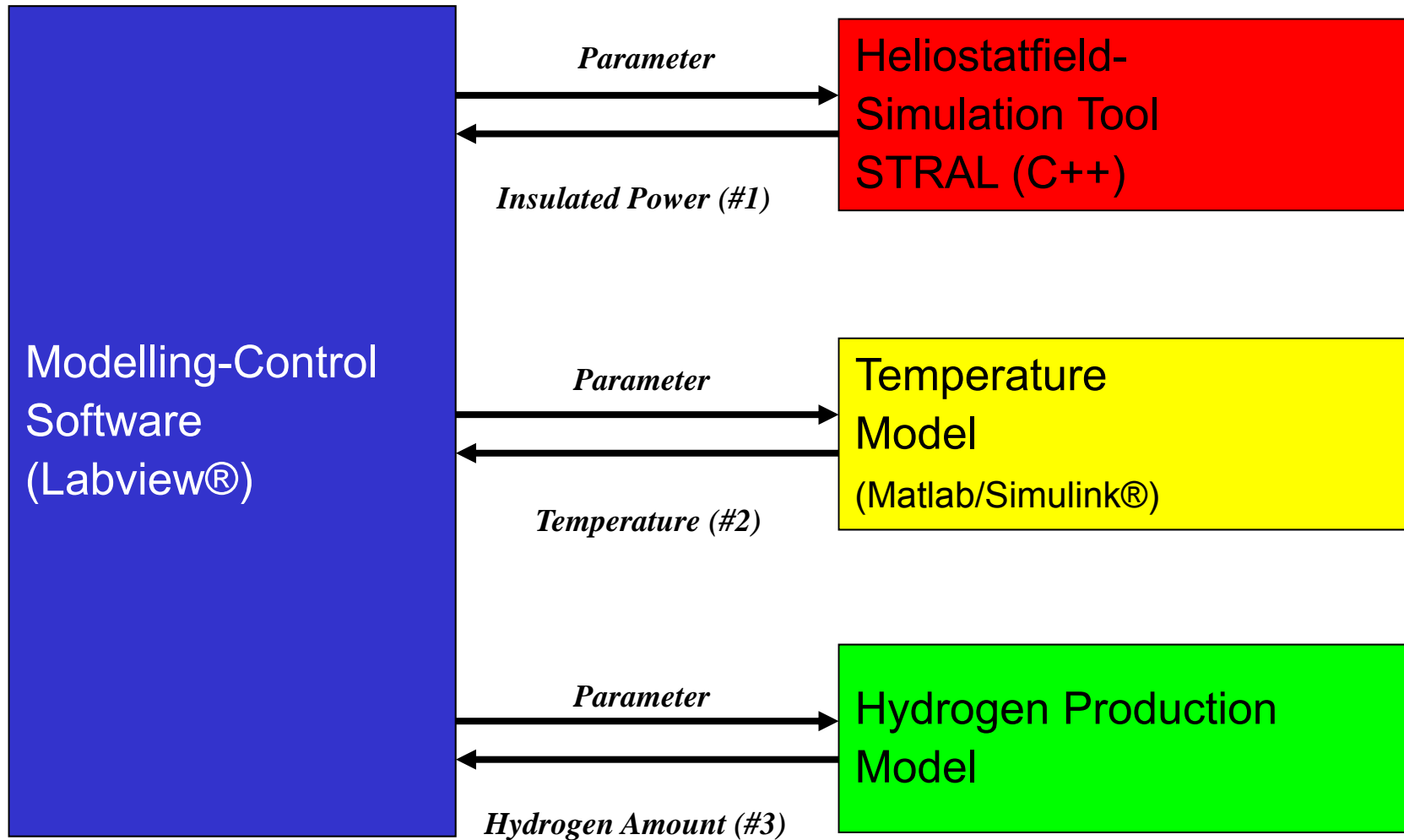
DLR solar furnace



Pilot-plant in operation since March 2008

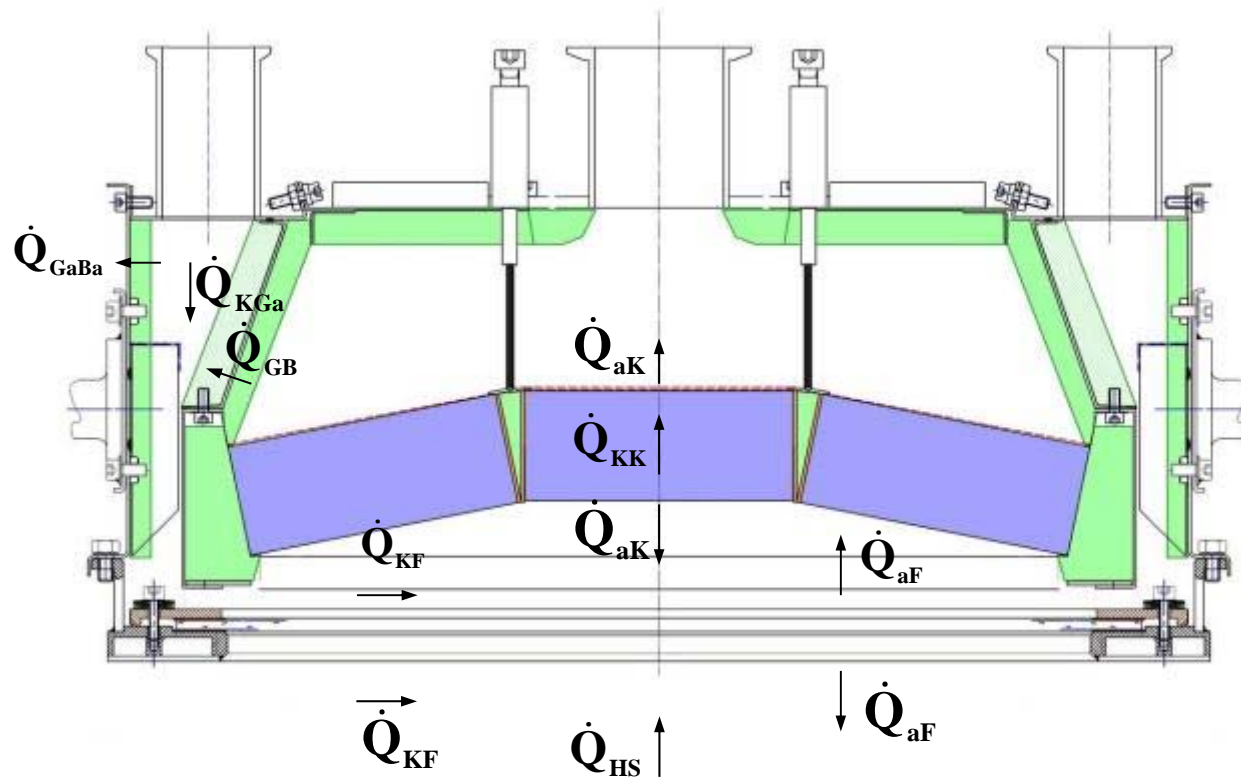


Modelling of the pilot plant - Overview Modelling:



Modelling – Temperature model:

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

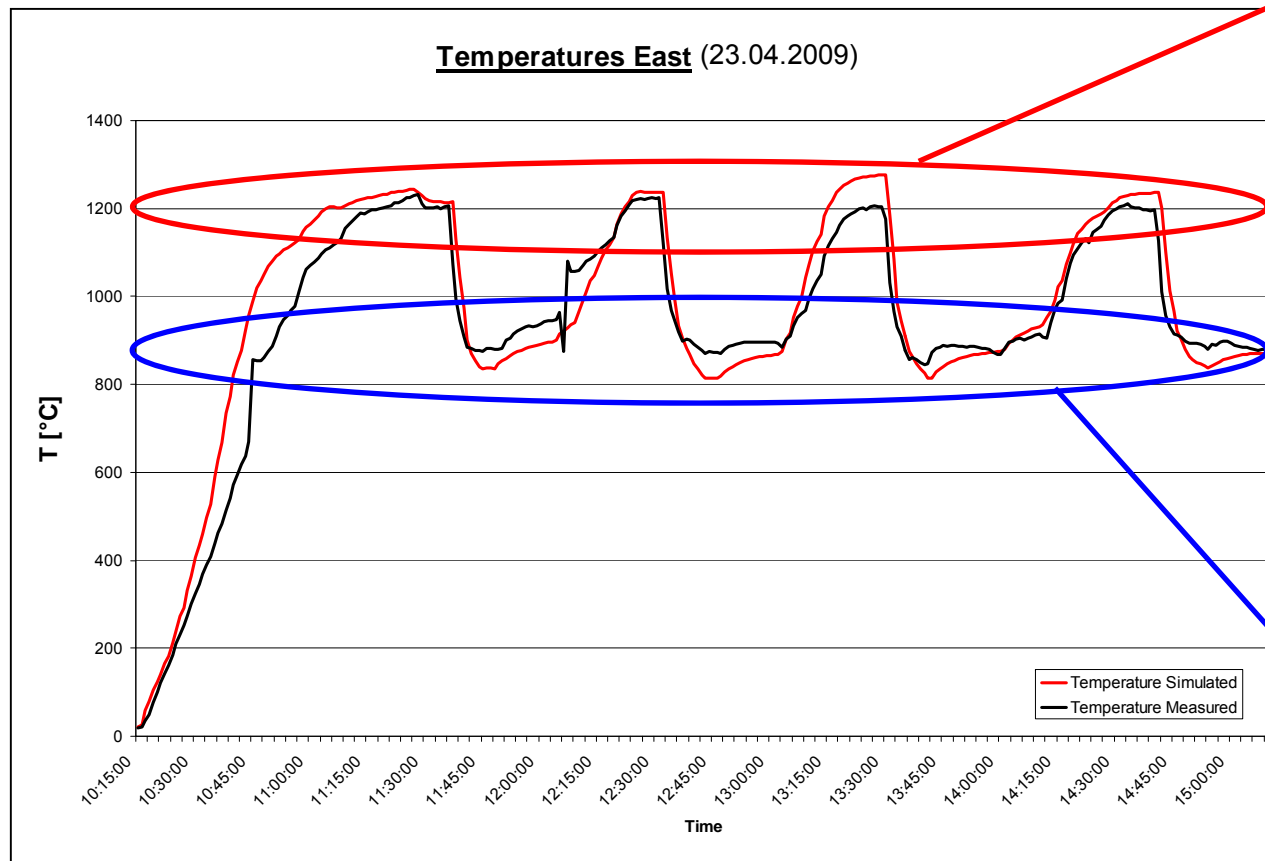


Heat flows: heat radiation, heat conduction and convection



Modelling – Temperature model:

First Verification of open loop control system



Regeneration

Input:

Simulated power East

Sampling rate (Sim.):

every second

Sampling rate (Exp.):

Every second

Average Deviation: 6.5%

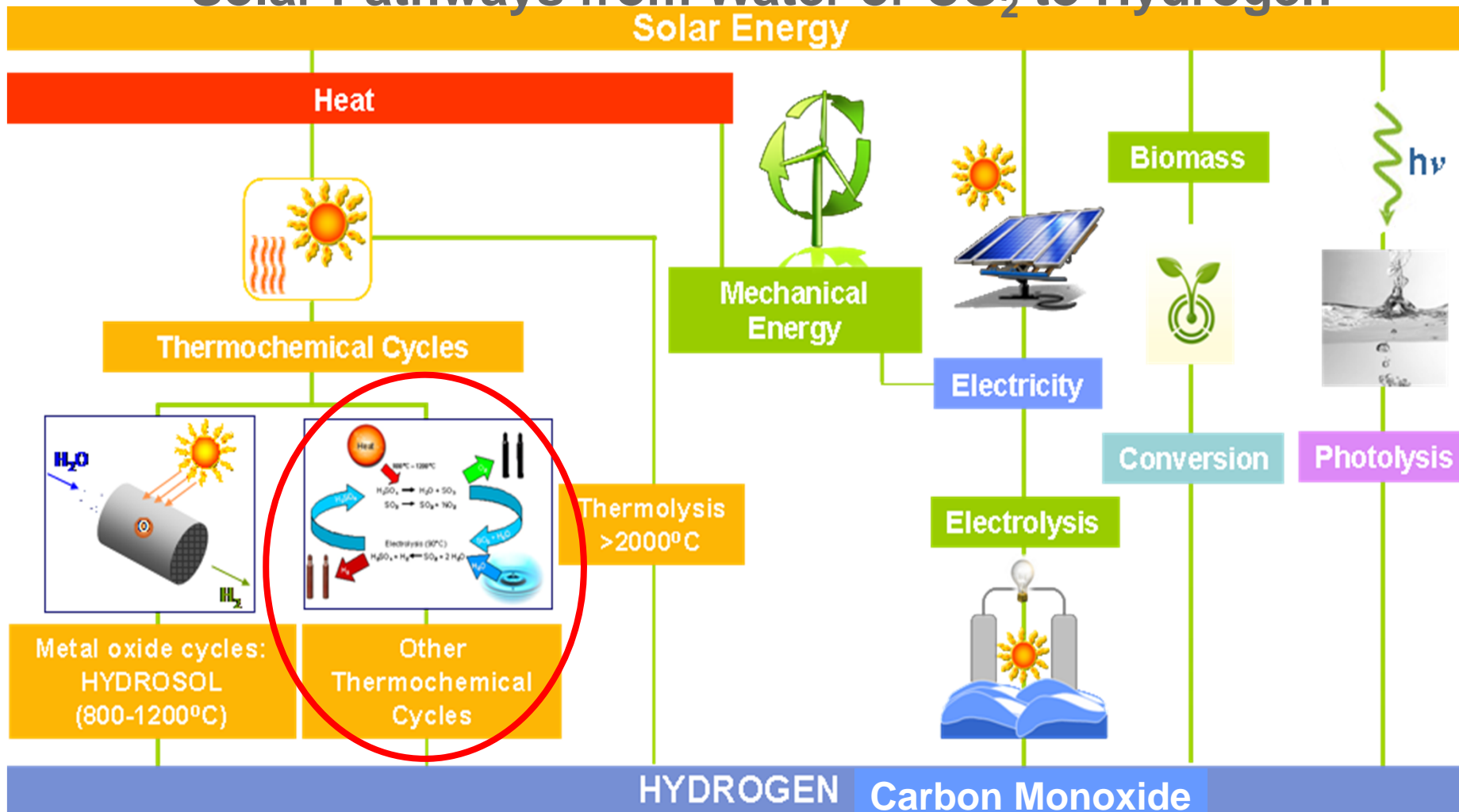
Production



Pilot Plant arranged on the research platform of the ST Jülich (artist view)

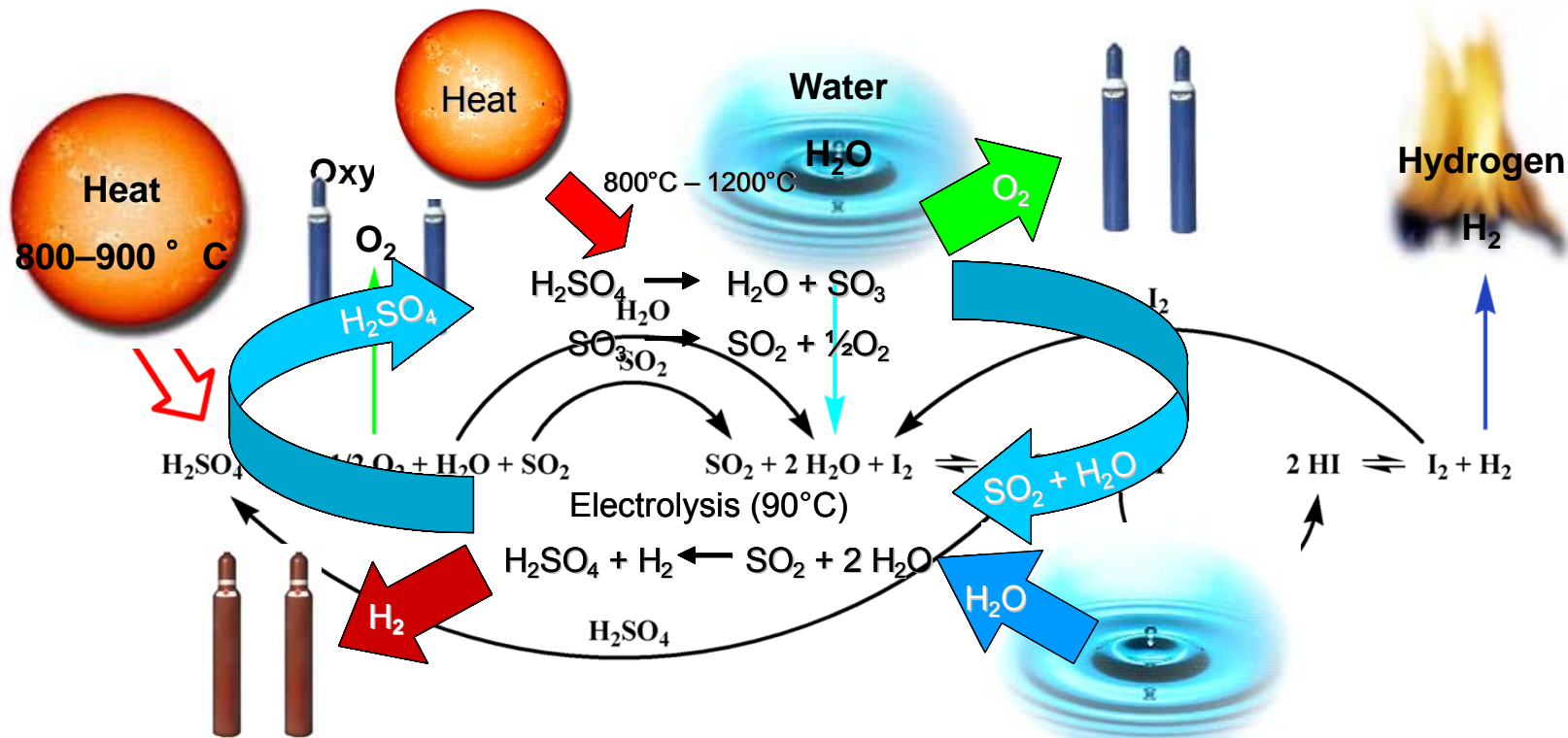


Solar Pathways from Water or CO₂ to Hydrogen

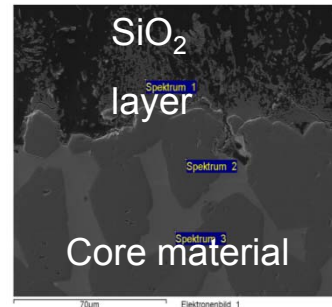
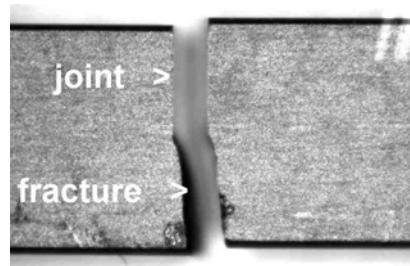
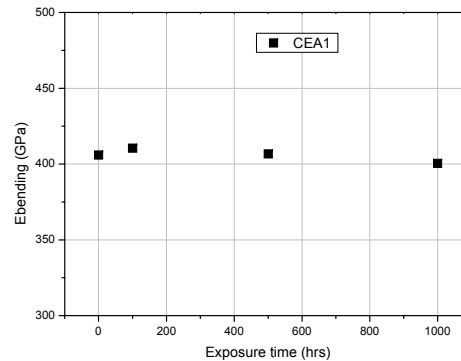
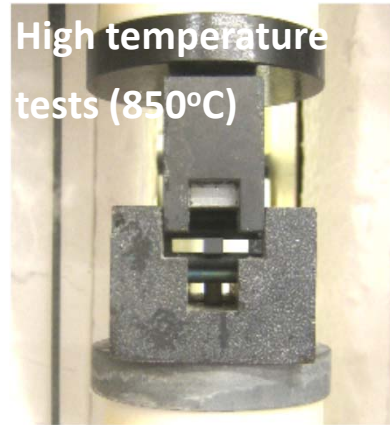


The thermochemical cycles covered in HycycleS

Sulfuric Acid Cycle



Stability of construction materials



- Performance of long-term corrosion campaigns (SO₂, SO₃ rich, boiling H₂SO₄) 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 H₂SO₄ decomposition

- ‘In-house’ synthesized materials (metal oxide based) with high catalytic activity in terms of SO₂ production from H₂SO₄:

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



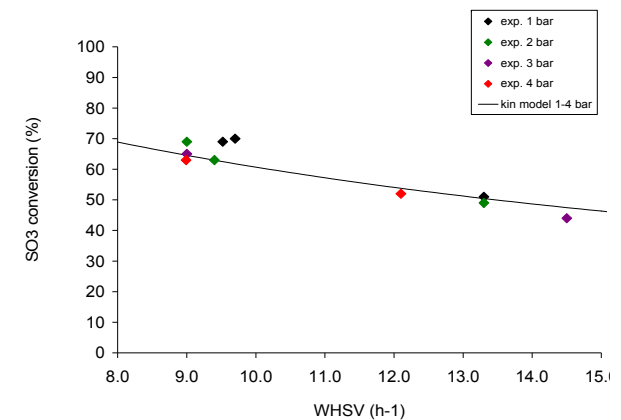
- Satisfying stability of samples coated with ‘in-house’ materials under ‘long-term’ operation

- Derivation of an empirical kinetic model

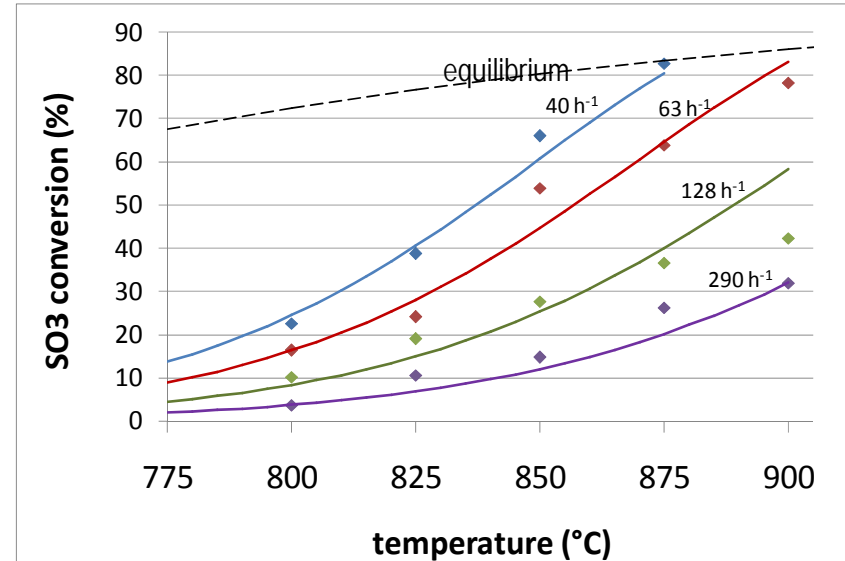
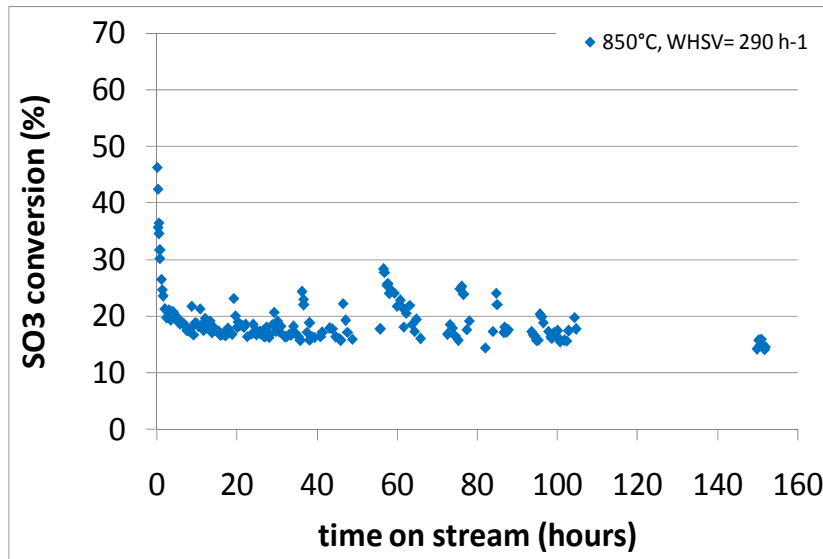
- Evaluation of the employed materials chemical stability

- Extraction of an SO₃ dissociation mechanism

- CrFe oxide identified as the most suitable catalyst



Example of Catalyst qualification: CuAl_2O_4



- Durability tests performed at “high” space velocity values
- After initial deactivation, catalyst shows < 5% loss of activity (100hrs on stream)
- Change of colour observed, due to phase separation phenomena

CuAl_2O_4 -coated SiSiC fragments (kinetic model for decomposer design)

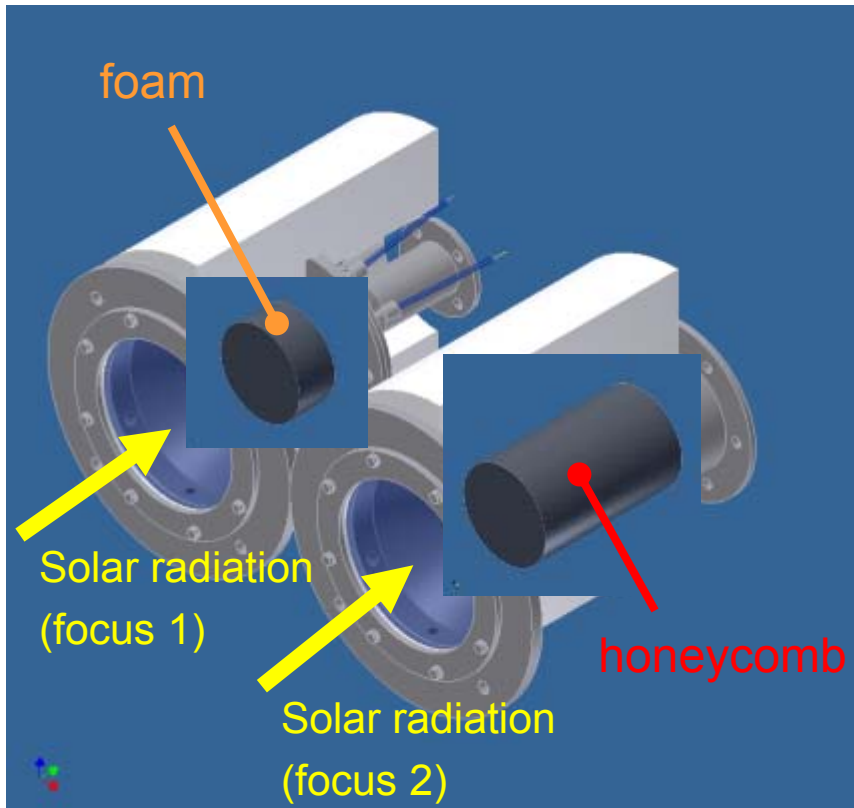
Exp. campaign	E_a (kJ/mol)	A (h ⁻¹)	dn (mm)*
No. 1	240.3	$5.6 \cdot 10^{12}$	1-4

$$-\ln(1 - X) = \frac{k}{WHSV}$$

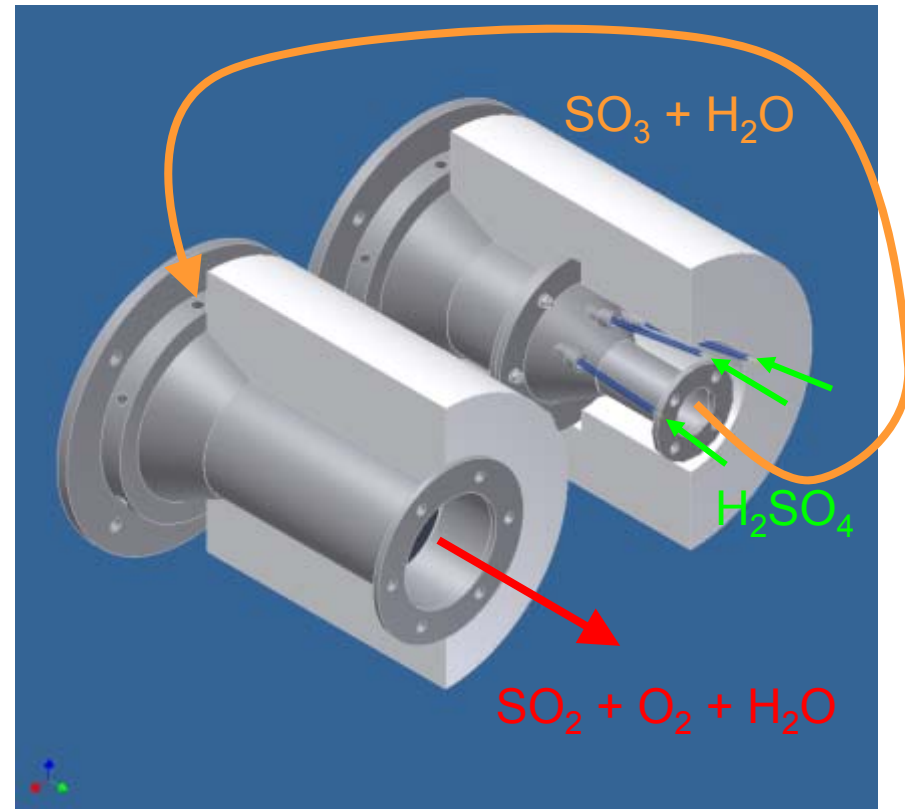
$$k = A \cdot e^{-\frac{E_a}{RT}}$$



Design of multi-chamber solar reactor



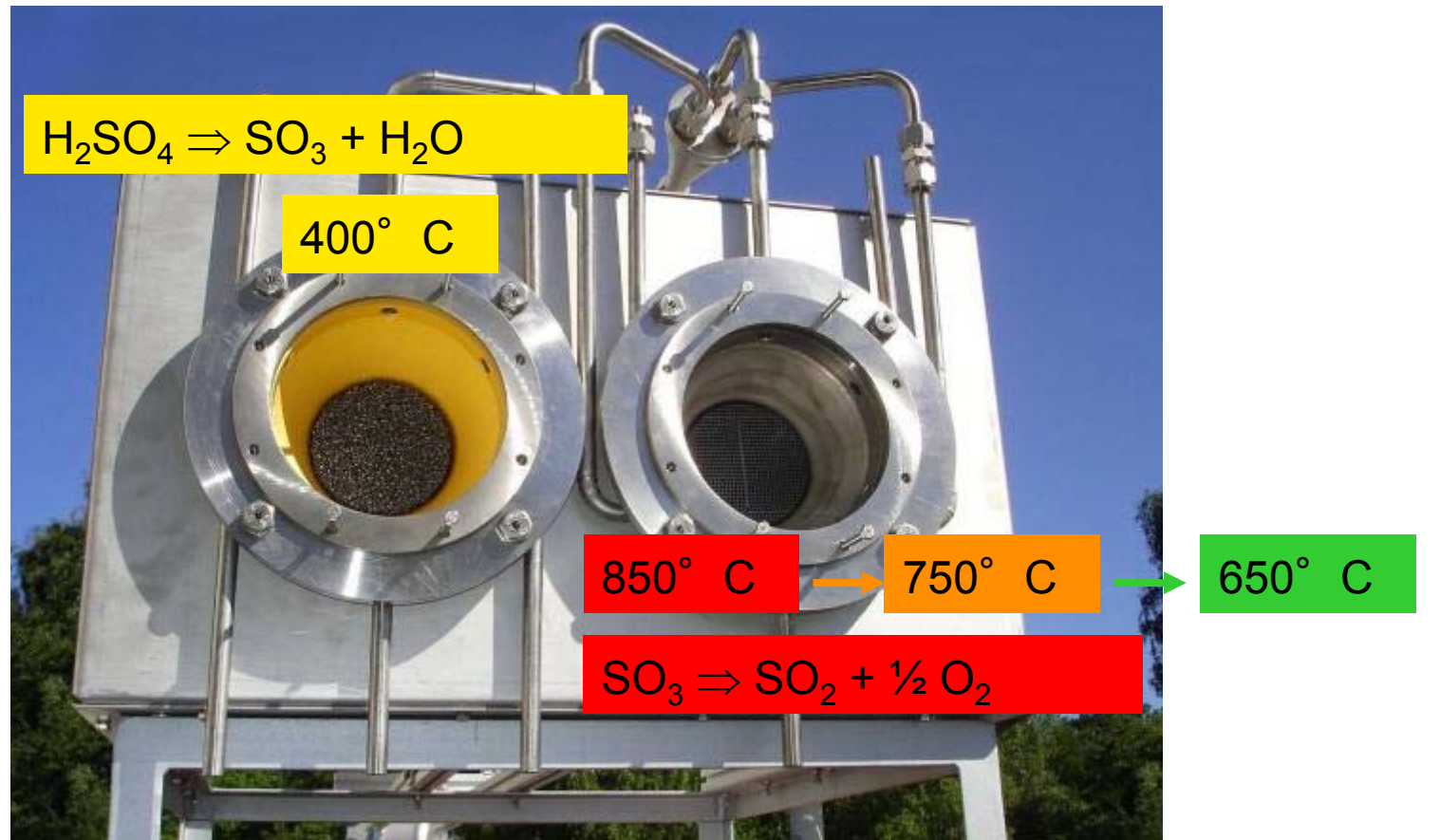
Front view of evaporator (left)
and decomposer



Rear view



Solar reactor for sulfuric acid decomposition



Operation in our solar furnace in Cologne

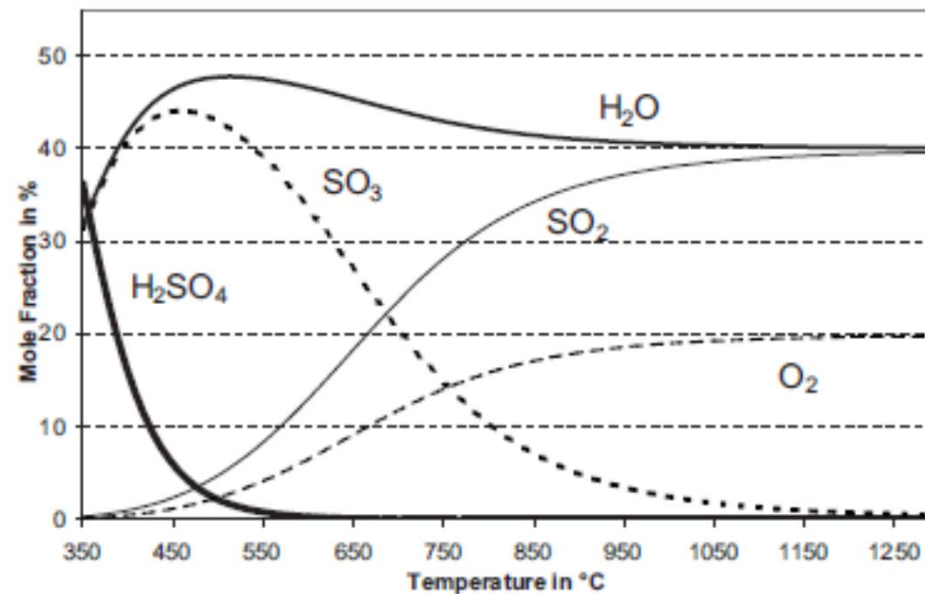


Overview of test series in solar furnace

Catalyst		Fe₂Cr₂O₄
Evaporator		solar
Number of experiments		19
Sulfuric acid concentration	w%	94
Sulfuric acid flow rate	ml/min	1...8
Mean honeycomb temperature	° C	650...850
Residence time	s	0.3...1
Weight hourly space velocity	1/h	0.6...4.7



Thermodynamic equilibrium of H_2SO_4 decomposition

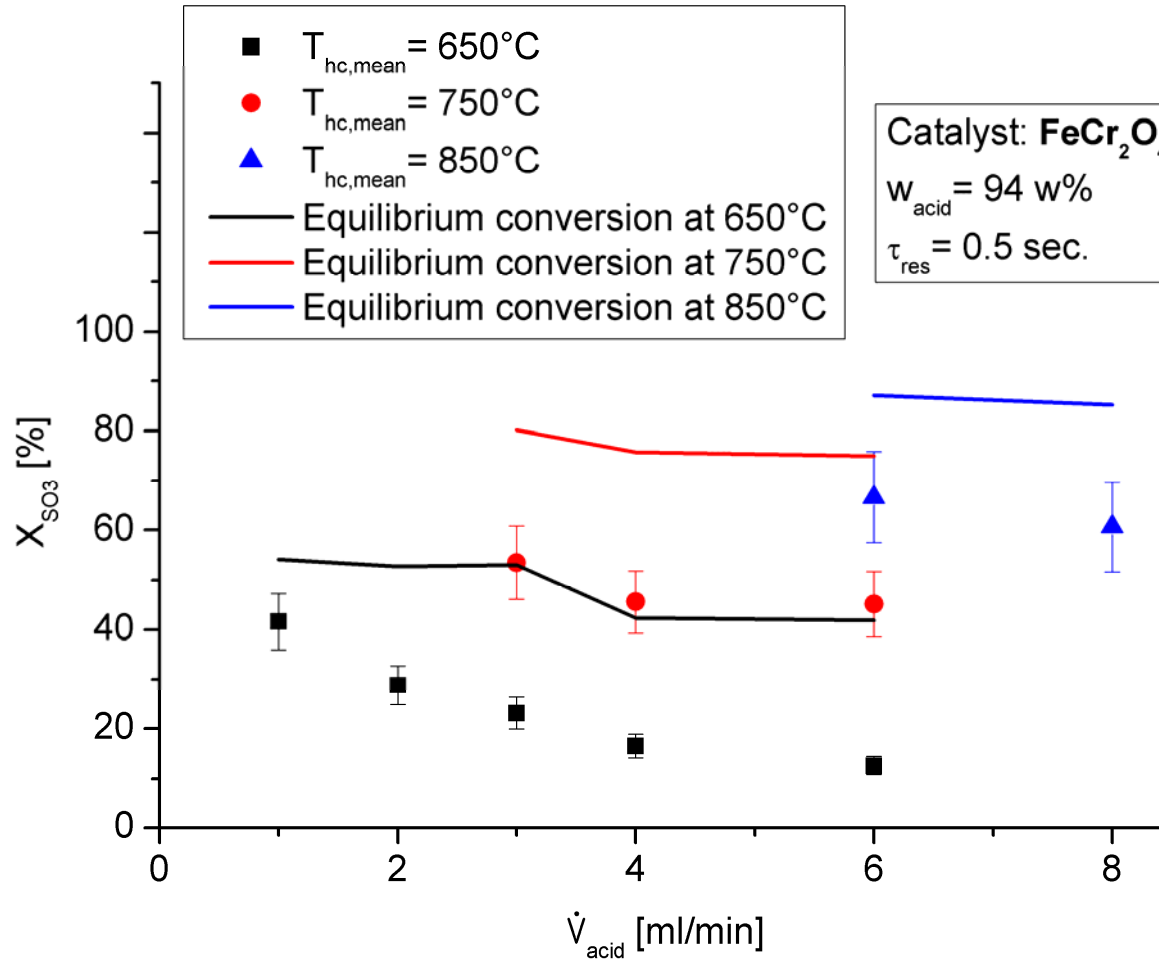


- H_2SO_4 dissociation completed at about 550°C
- 80% of SO_3 decomposed at 850°C
- 40% of SO_3 decomposed at 650°C

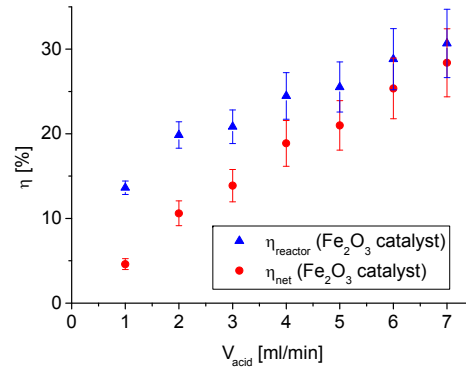
Source: Noglik et al., 2009



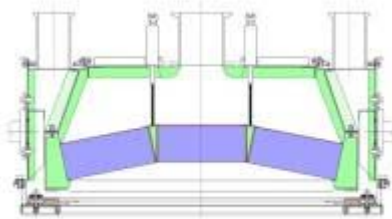
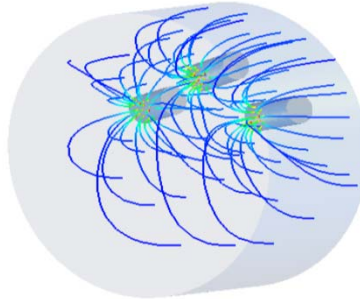
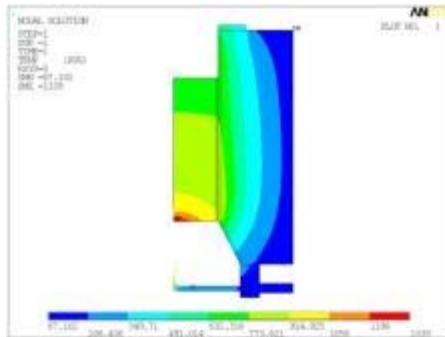
Conversion of SO₃ in honeycomb



Solar reactor as H₂SO₄ 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 SO₃ decomposition
 - Validation with experimental data
- Control procedure for scale-up solar tower system



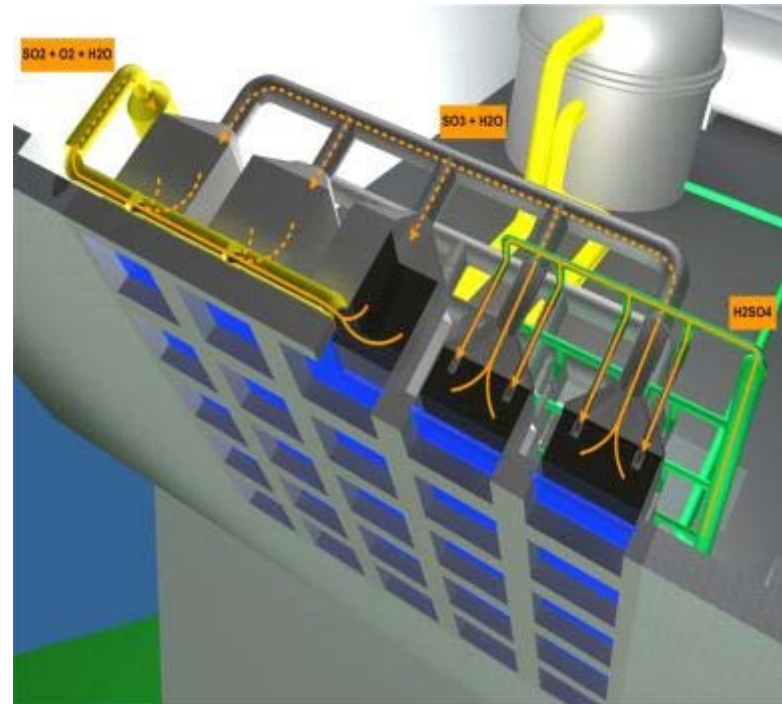
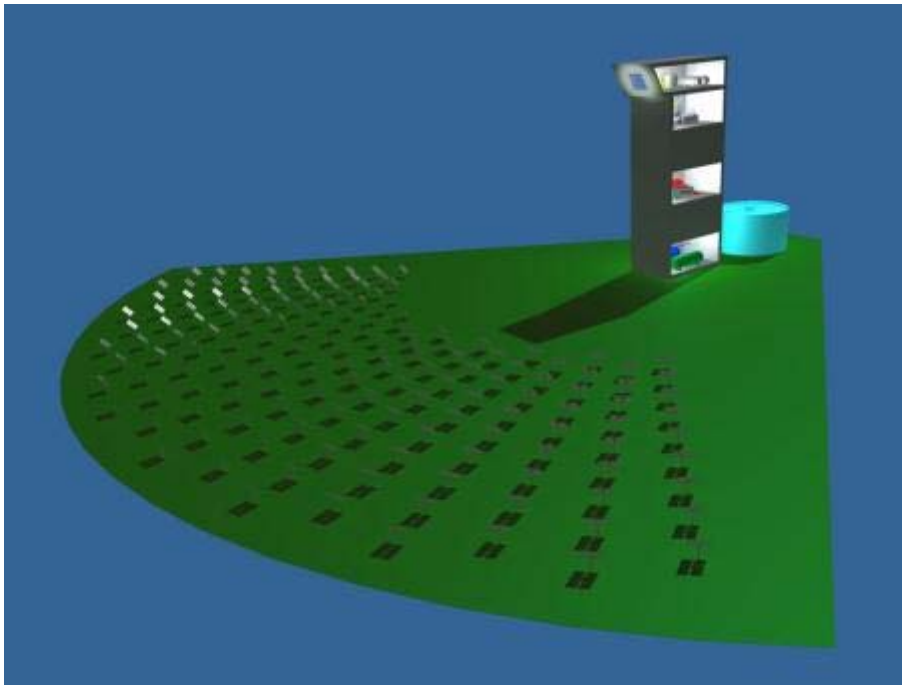
Thomey et al, IJHE 2012

Nogliki et al, IJER 2010

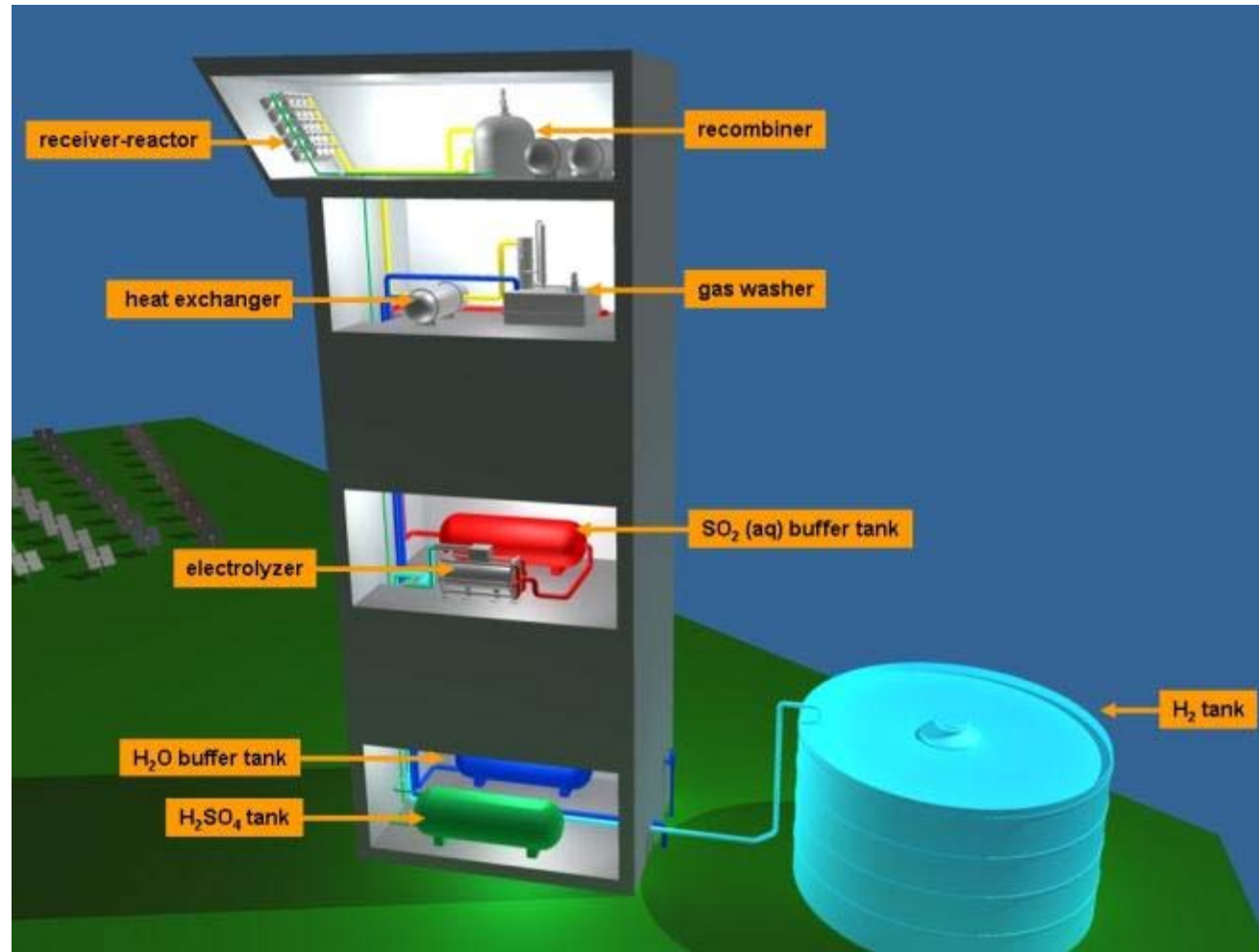
Haussener et al, ASME-JHT 2009



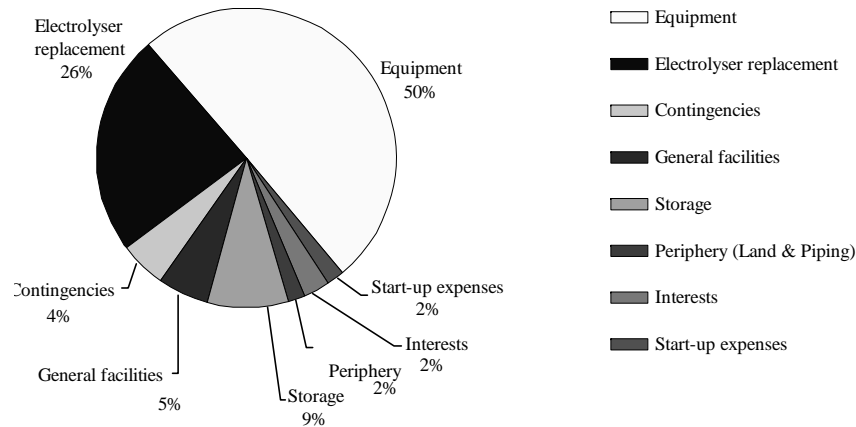
Scale-up of the solar HyS process



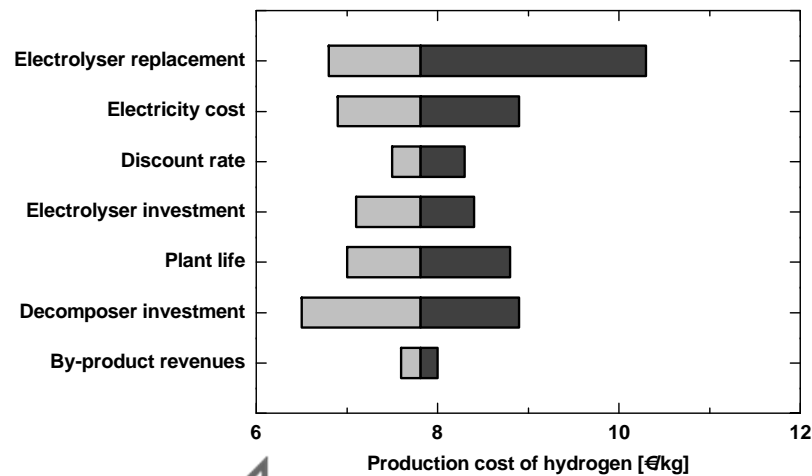
Implementation into a Solar Tower



Techno-economics



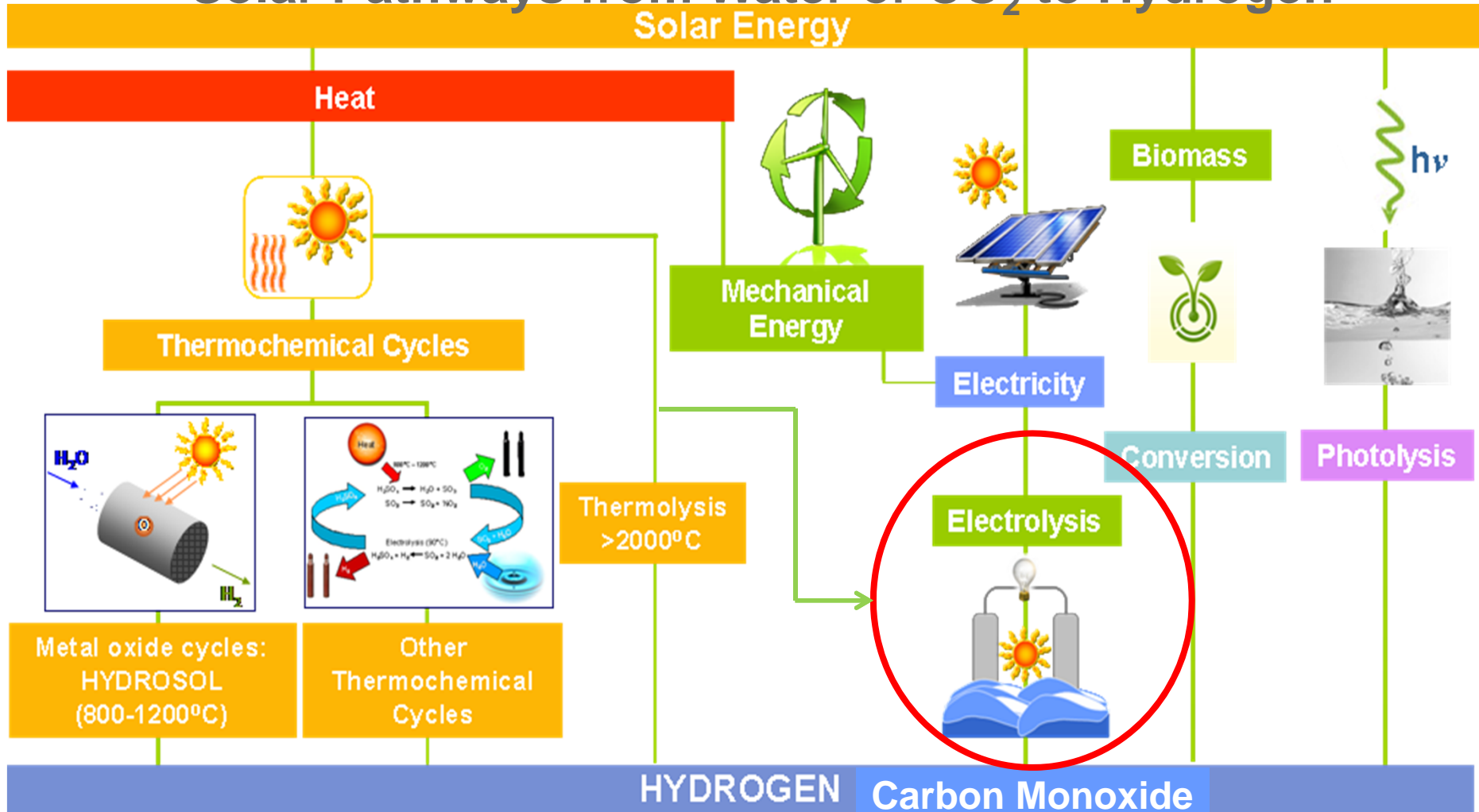
Lebros et al, IJHE 2010



- 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
 - 6-7 €/kg(H₂) for HyS
 - optimistic scenarios lead to 3.5 €/kg(H₂)
- 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

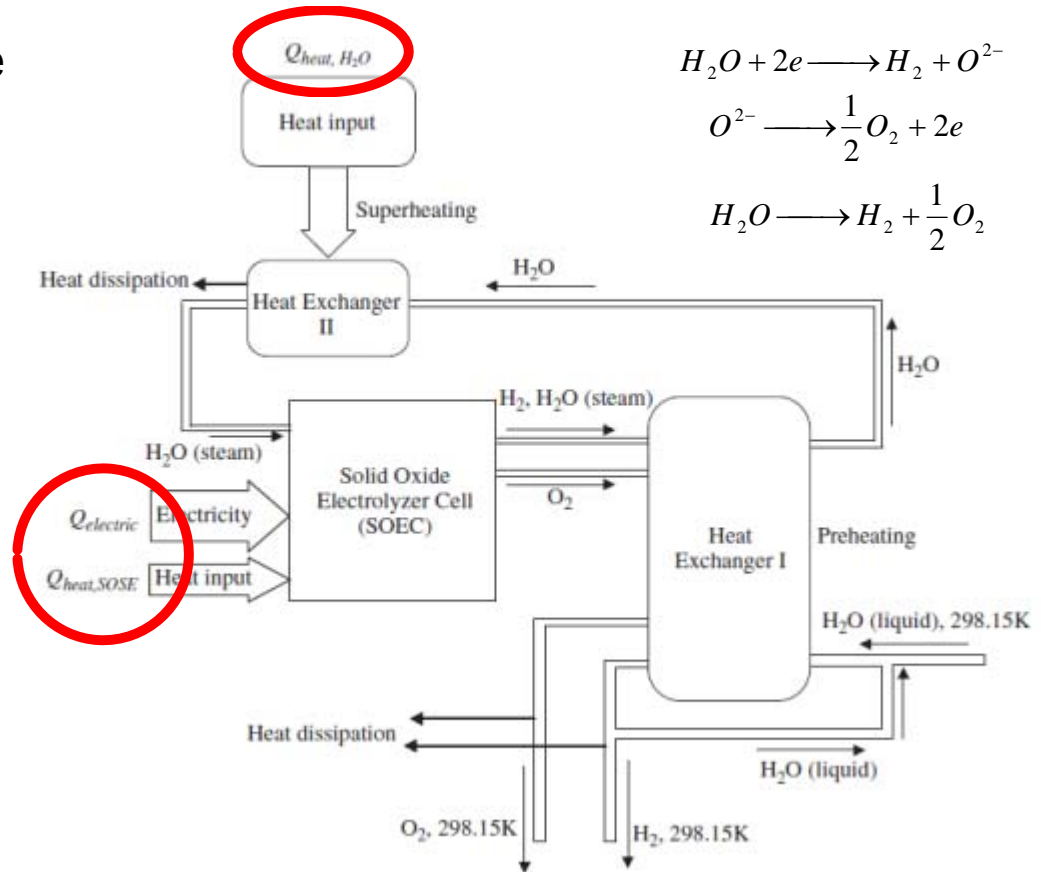


Solar Pathways from Water or CO₂ to Hydrogen



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 H₂ and O₂ gas streams existing the cell is used to evaporate water.
- The H₂O stream is further heated by the second Heat exchanger to raise the temperature of the electrolyser.

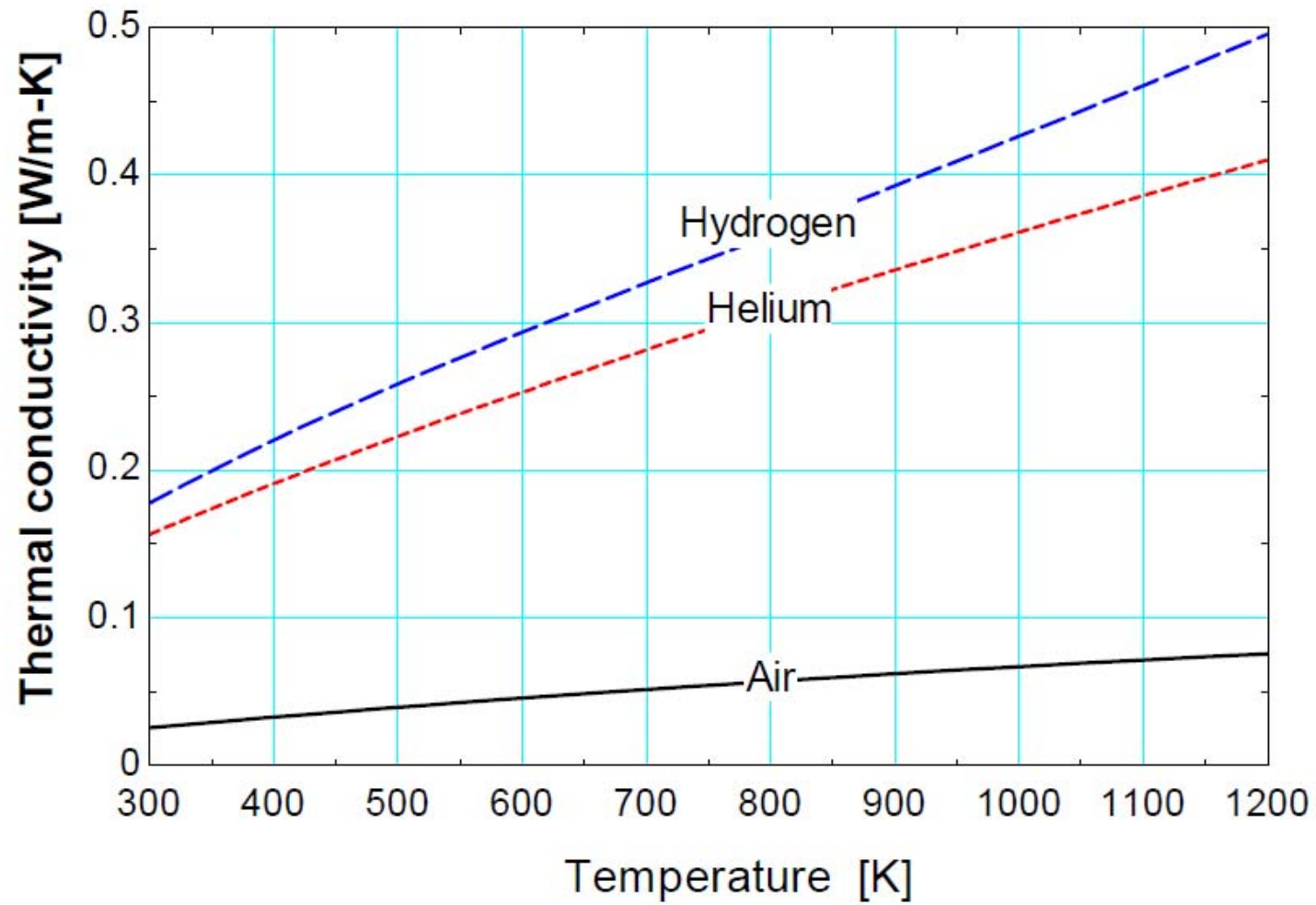


Economic analysis

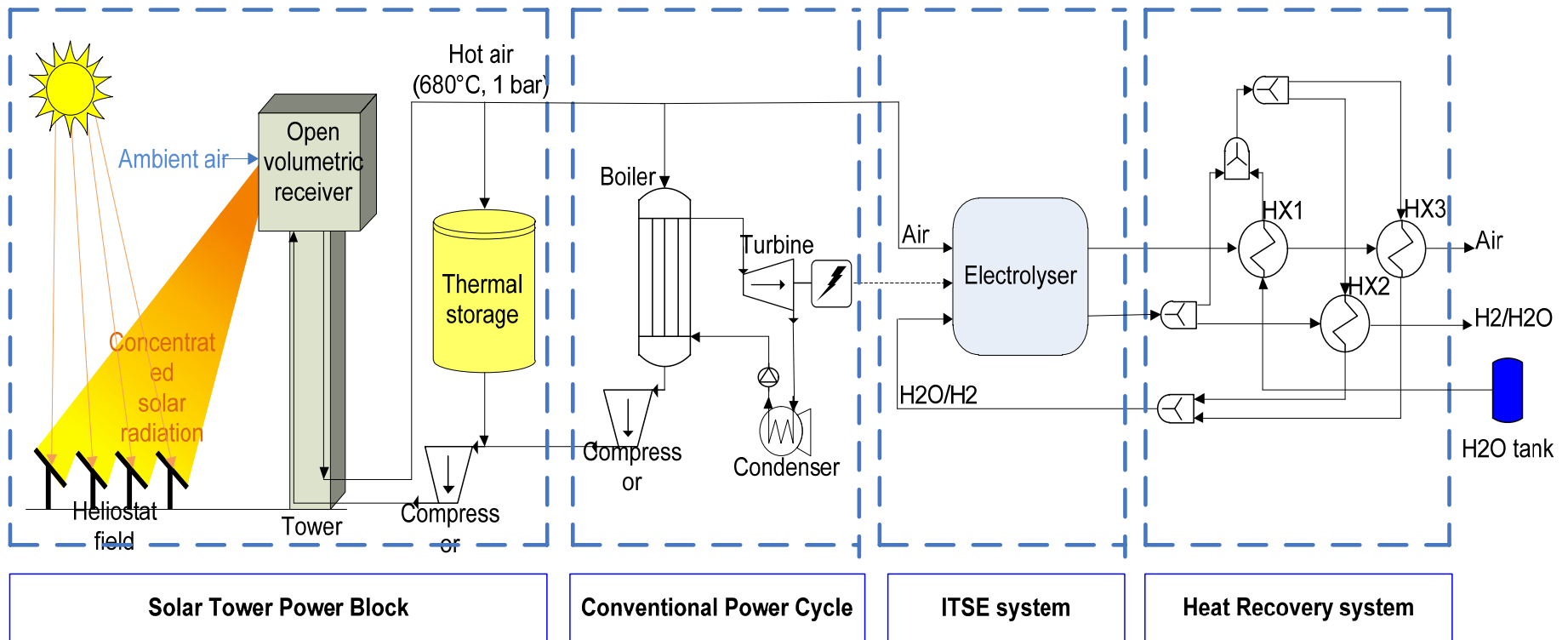
- Key parameters of the hydrogen production cost with the a concentrating solar installation coupled to a high temperature electrolyzer:
 - Efficiency of the plant
 - Efficiency of the solar installation
 - Electricity consumption of the electrolyzer
 - Site of the plant (annual solar irradiation, availability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



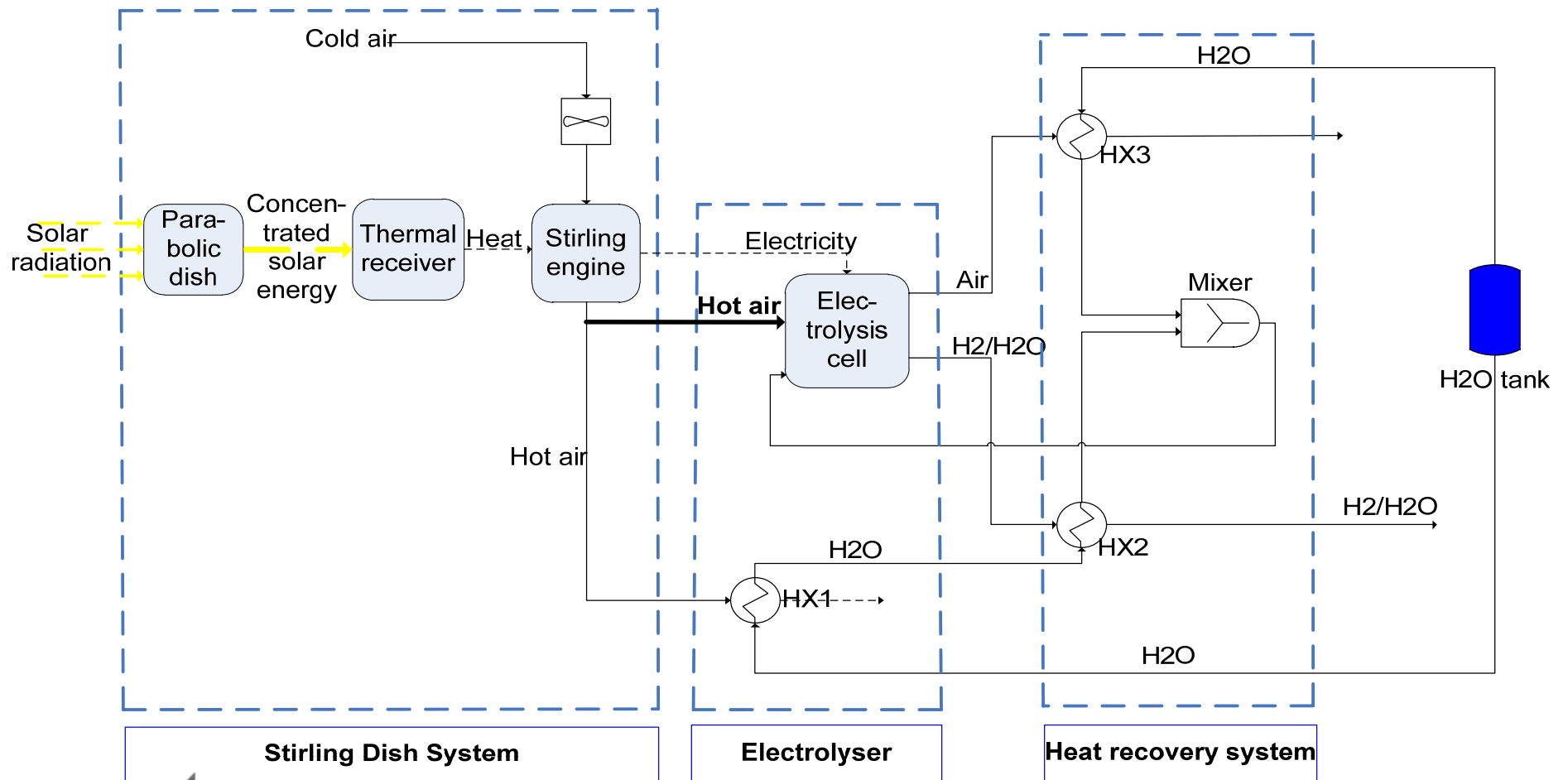
Thermal conductivity of working fluids



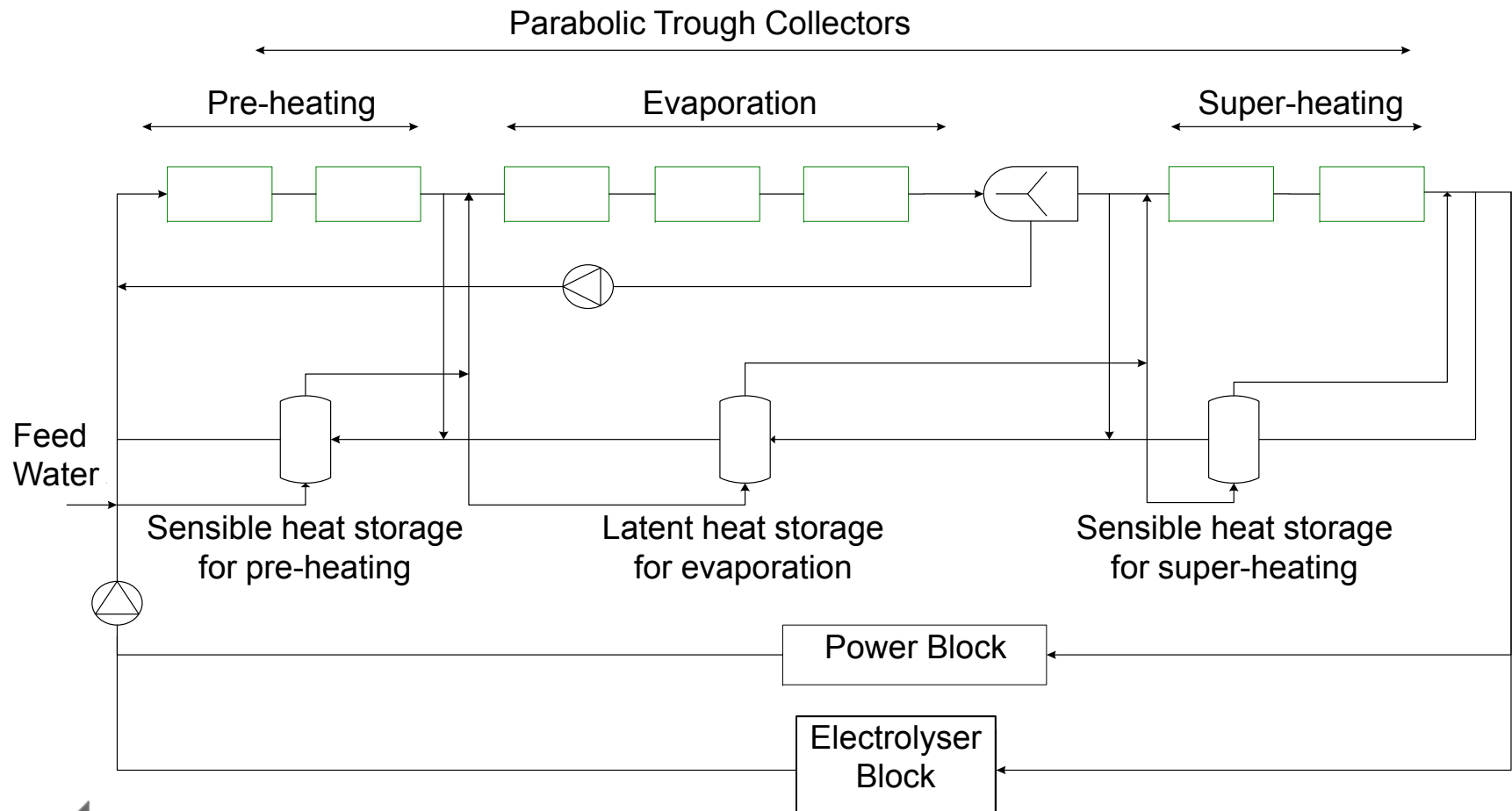
Flow diagram of the coupling of the solar power tower with the electrolyser



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



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

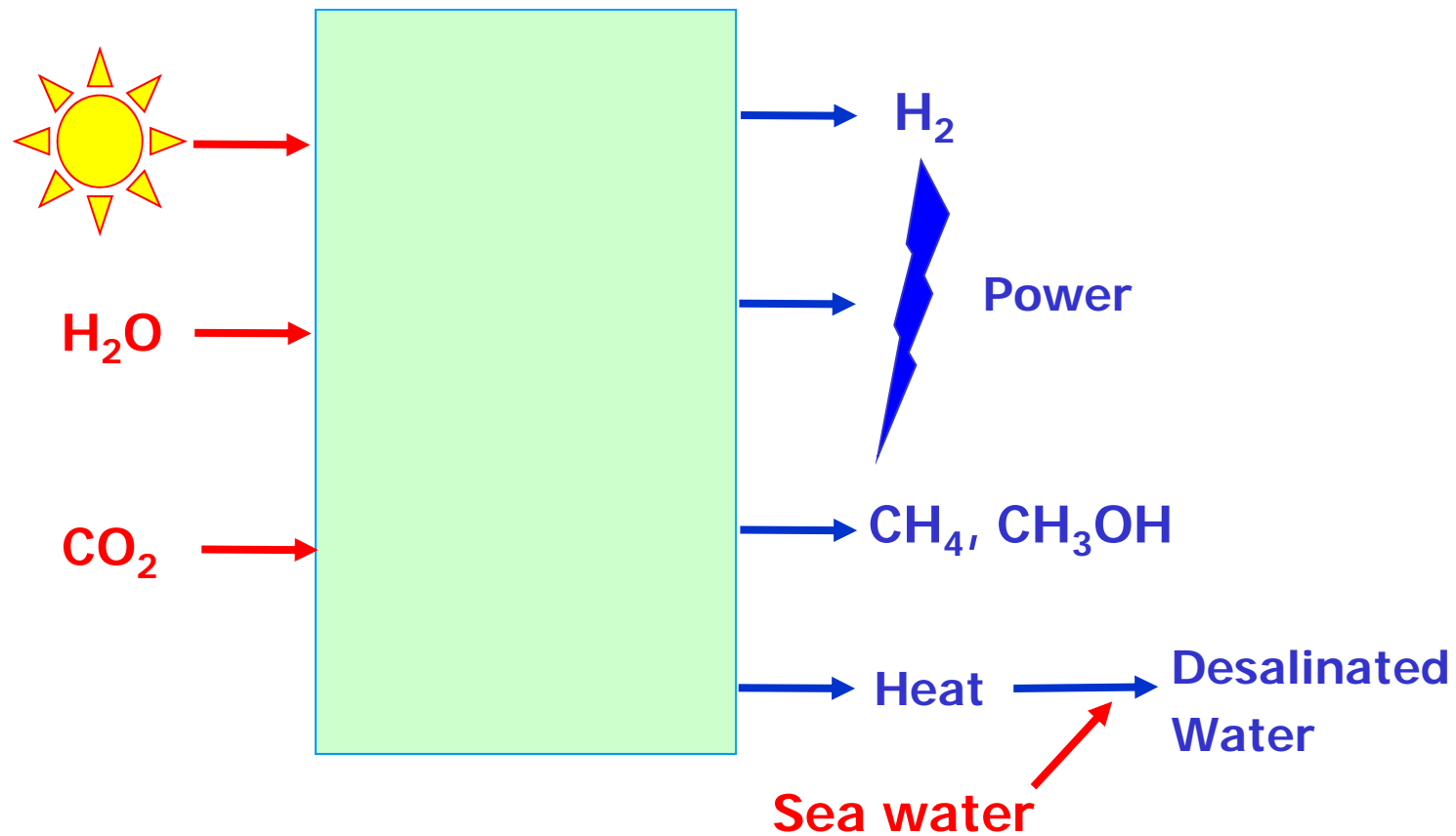


Conclusion and Outlook



Future Solar Thermal Plants – more than power!

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



Acknowledgement

- Thanks to all our funding agencies especially the European Commission and our industrial partners.
- Thanks to all colleagues and partners who provided various contributions to this work.



DLR H₂ Aircraft
ANTARES

Next appearance
Paris, October 12th





Thank you very much for your attention!

