Solar Fuels

Overview on the work carried out at the German Aerospace Center

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Contents

German Aerospace Center (DLR)

DLR

DLR
German Aerospace Center

- Research Institution
- Space Agency
- Project Management Agency

Research Areas

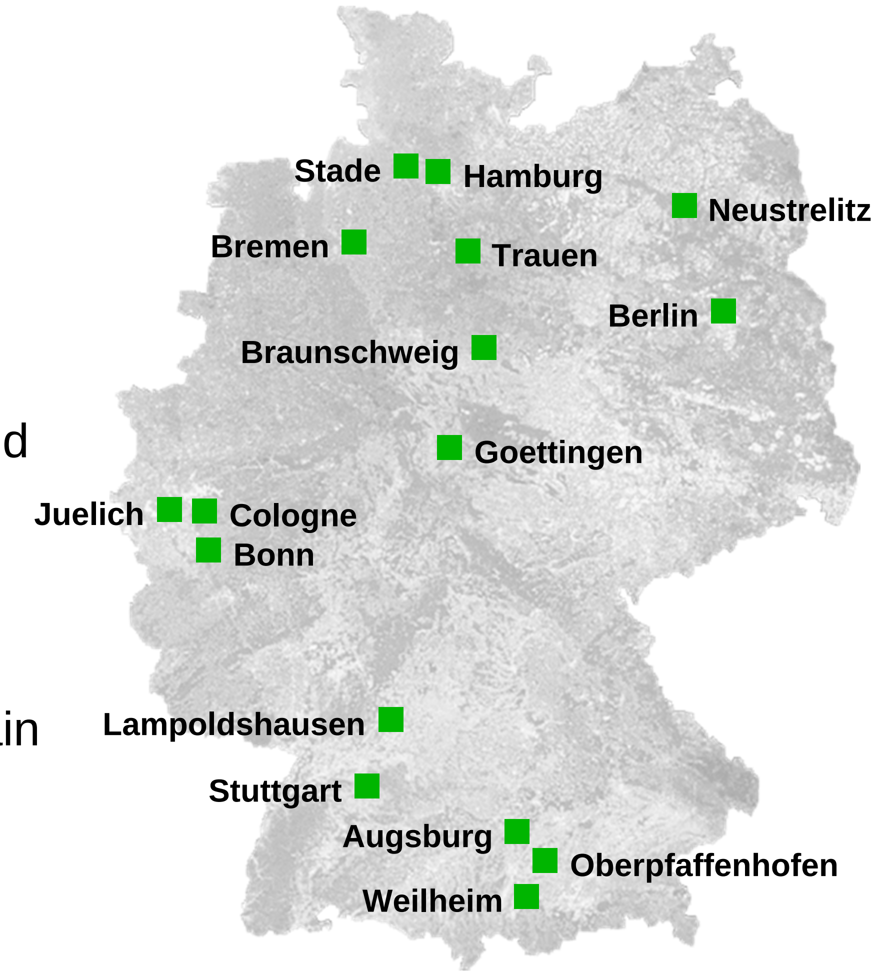
- Aeronautics
- Space Research and Technology
- Transport
- Energy
- Space Administration
- Project Management Agency

Locations and employees

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

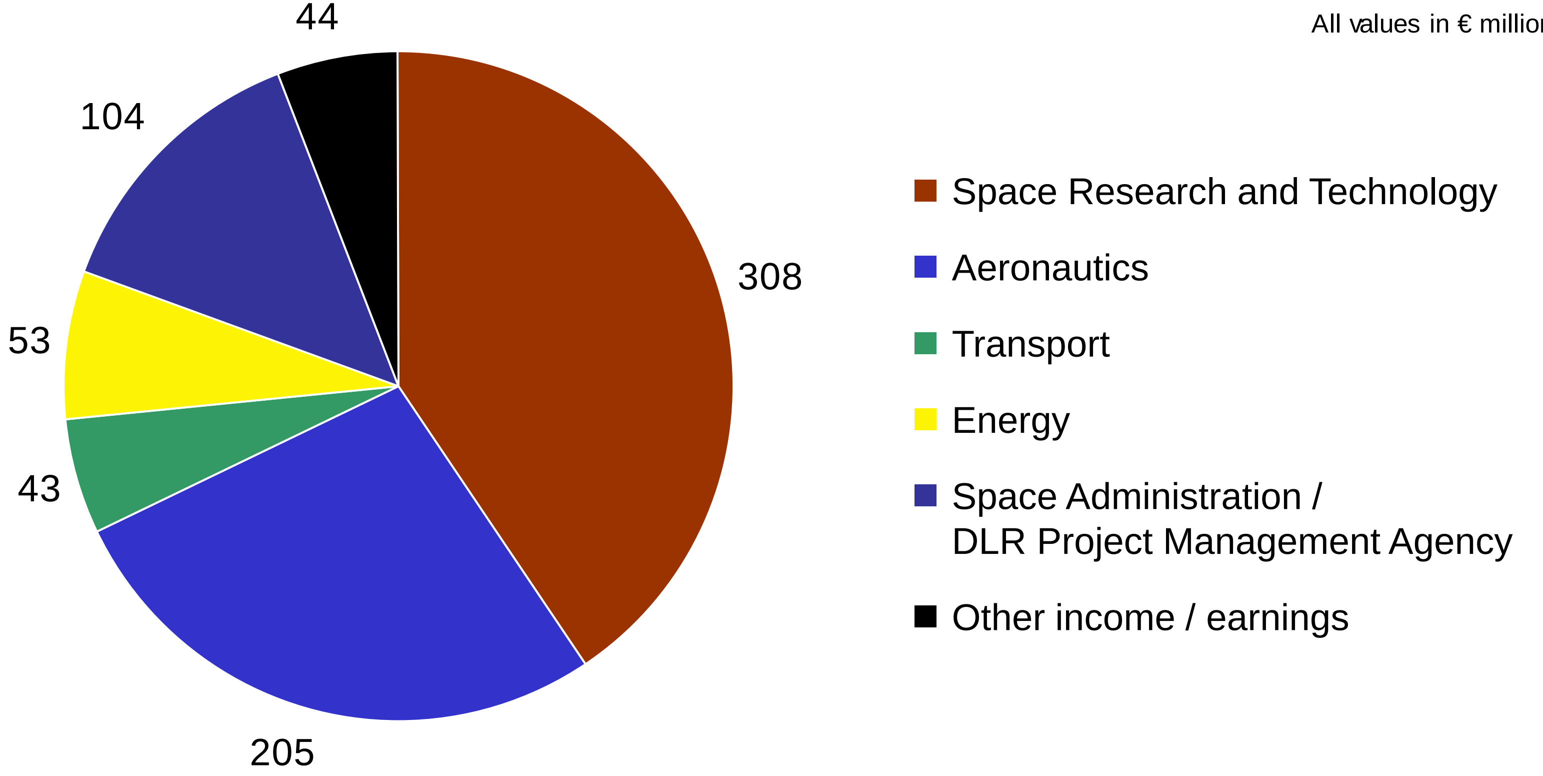
Offices in Brussels,
Paris, Washington, Singapore, and
Almería.

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



Total income 2010 – Research, operations and management tasks (excluding trustee funding from the Space Administration / DLR Project Management Agency): **€ 745 Mio. (¥74 bn)**

All values in € million



DLR

National and International Networking

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

World

Europe

EADS
cnes
NLR
EREA
esa
ONERA
ECTRI

Germany

HELMHOLTZ
GEMEINSCHAFT

Bundesministerium
für Bildung
und Forschung

Bundesministerium
für Wirtschaft
und Technologie

Bundesministerium
der Verteidigung

LIEBHERR
SIEMENS
DIEHL
OHB TECHNOLOGY
AIRBUS
ASTRIUM
AN EADS COMPANY

DLR
Deutsches Zentrum
für Luft- und Raumfahrt

Energy

DLR Energy

DLR Energy Research concentrates on:

- CO_2 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

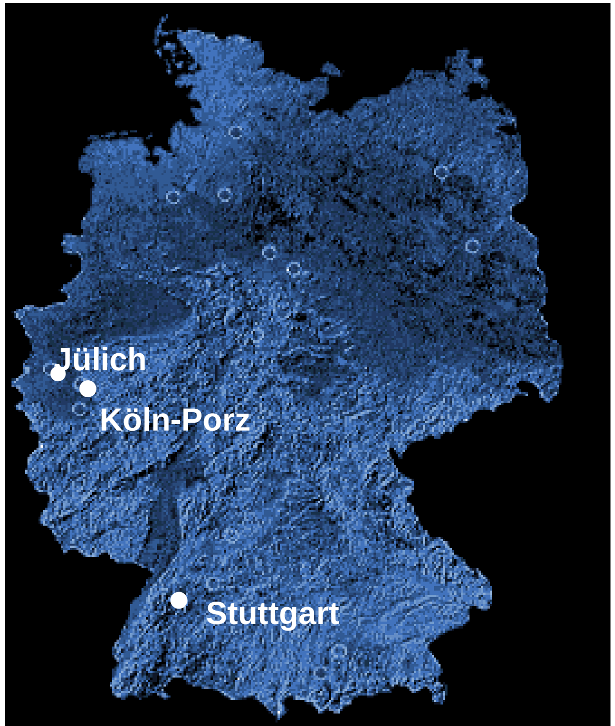
Main Topic:

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

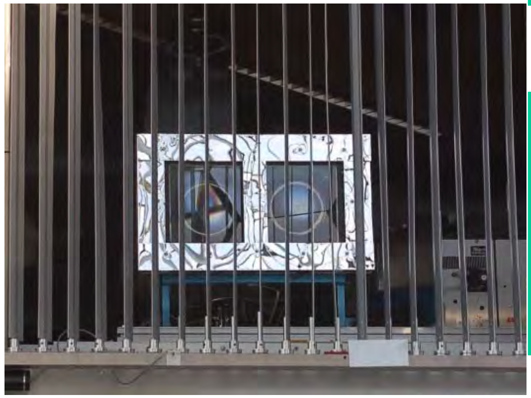
DLR

Department of Solar Chemical Engineering

Head
Organisation
Strategy
Representation in boards

Group
High temperature CE
Solar tower >500° C

Group
Low temperature CE
Reactors up to Parabolic troughs < 500° C



Solar Fuels
Solar Materials

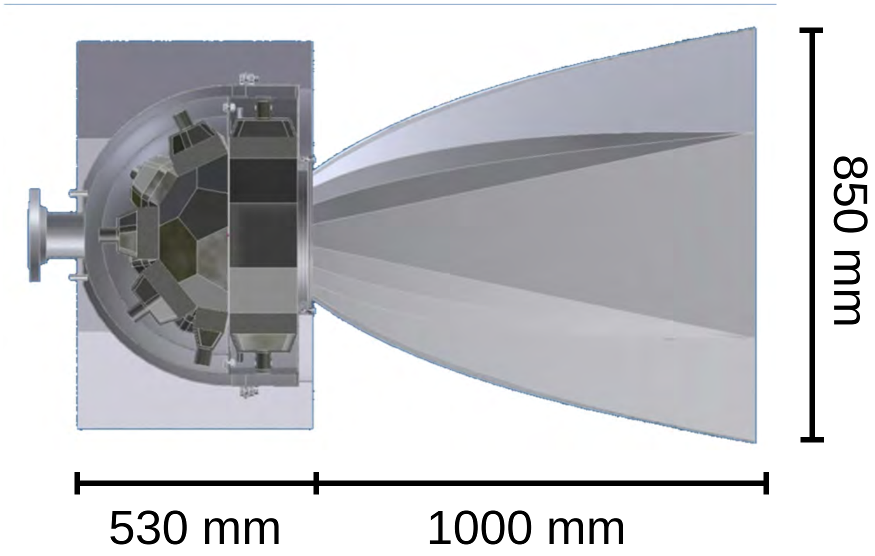
Heat transfer fluids
Solar fuels
Water treatment

SOWΛRLΛ GmbH

25 Persons + Students, 65% external funding

DLR

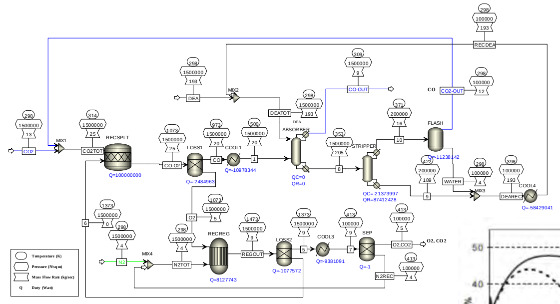
Competences

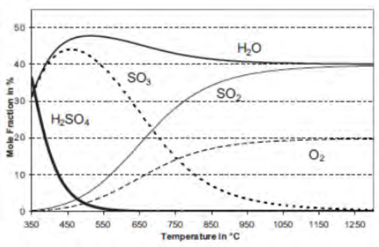


Development of components and processes

and

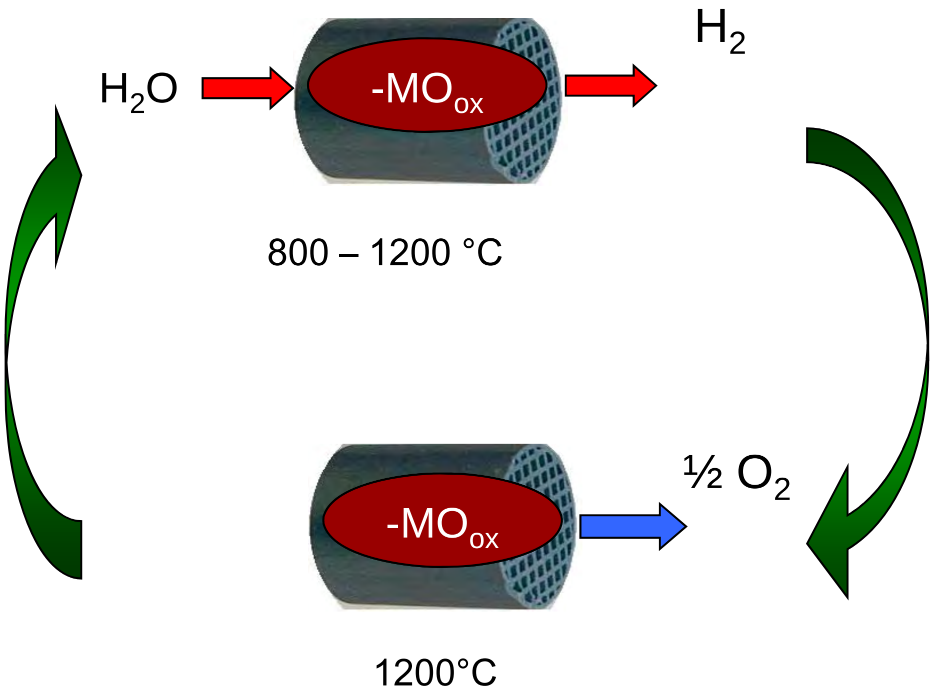
scientific, technologic and economic evaluation





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
  - H_2, syn-gas, methanol, FT-Synfuels …



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

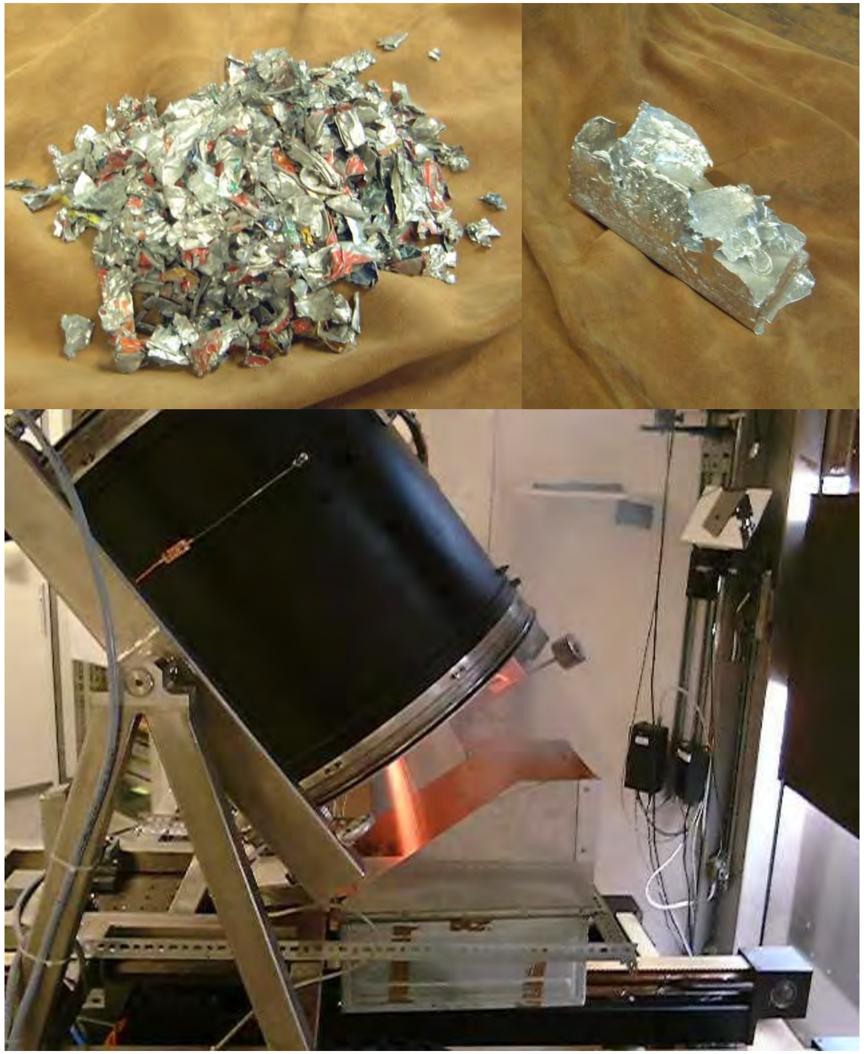
Contact DLR: Dr. Martin Roeb, (martin.roeb@dlr.de Tel.: +49(0)2203 601 2673)

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



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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 soluability
- Interaction with power plant components
  Hydrogen diffusion, influence of material contacts and impuritieson 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 CO_2
  Determination of spectral quantum yields by special lamp technologies,
  Determination of the solar efficiency in our solar test fascilities,
  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

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Photochemical Water Treatment

- Untersuchung photochemischer Verfahren (VUV bis solar)
  Actinometry of light sources, degradation tetst by photolytic and photo-catalytic processes; water analytics
- Development of photo-reactors
  Solar receiver-reactor technology and photo-reactors for nnovative 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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SOWARLA

Solar Fuels

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Solar Chemistry - Basics

- Role models
    - photosynthesis - use of photons for photochemistry
    - burning glass – use of heat for thermochemistry

- Principle in chemical reactions:
    - photochemistry ≠ thermochemistry

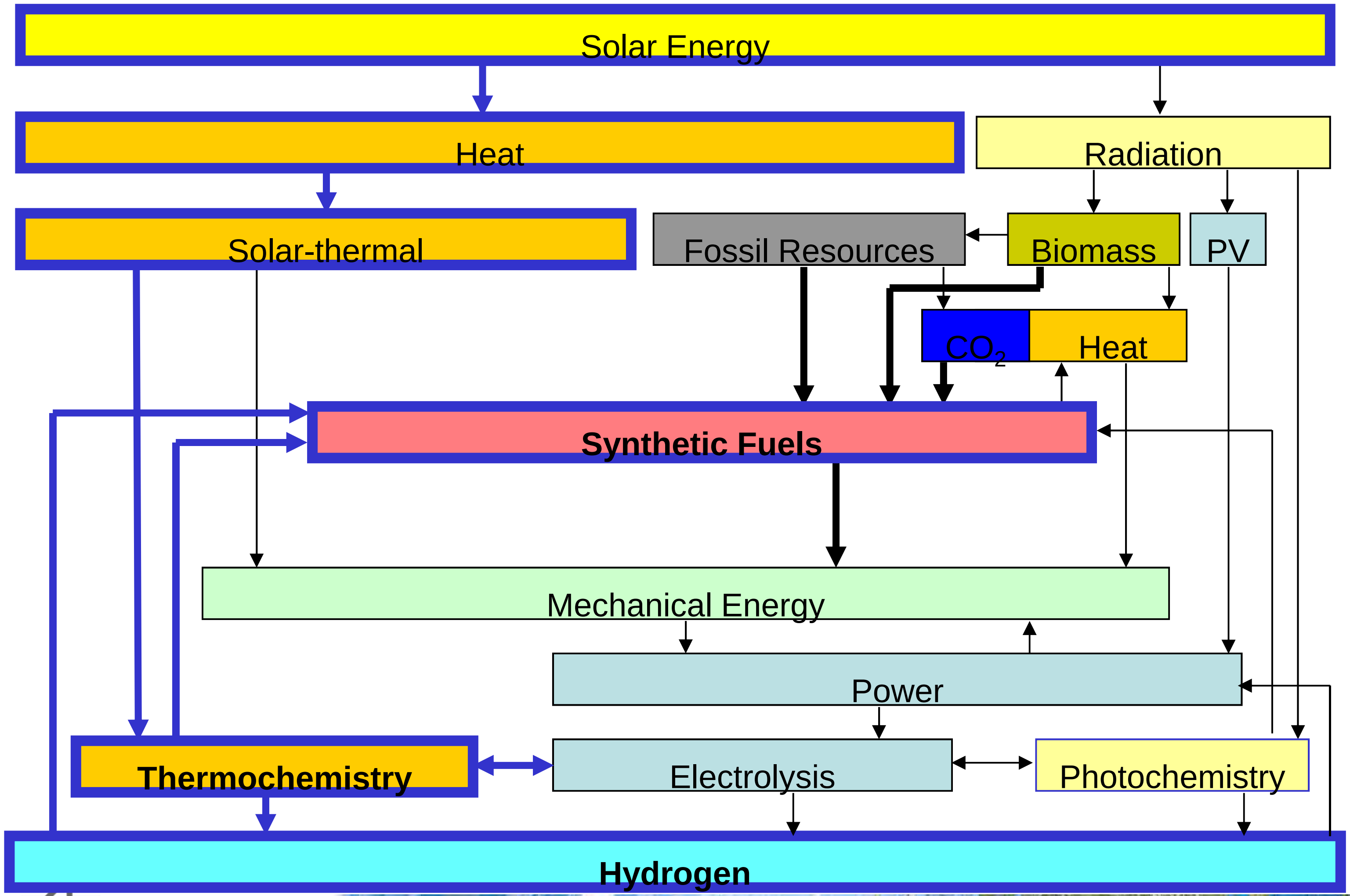
- However in some cases there are synergies in chemical processes, especially if not only one reaction takes place
    - Example: degradation of wastes

Solar Chemistry instead of Solar Power

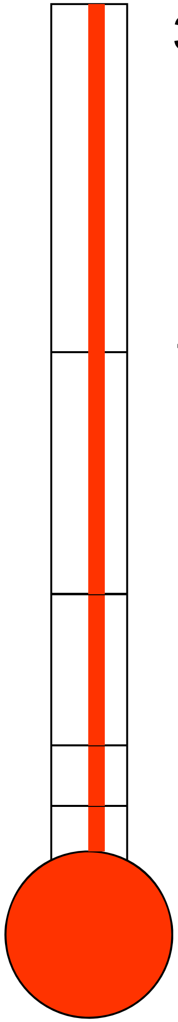
- Solar Thermochemistry is efficient because energy conversion steps are reduced!
  - Example: Hydrogen production: $H_2O \rightarrow H_2 + ½ O_2$
  - Solarchemical: 2 conversions
    - Solar radiation – heat – Chemical reaction
  - Via solar power: 4 conversions
    - Solar radiation – heat – mechanical 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)

Solar Fuels – Production pathways



Temperature Levels of CSP Technologies



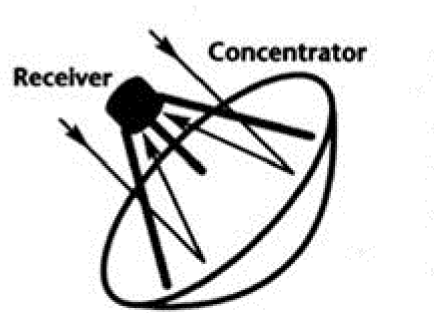
3500°C

1500°C

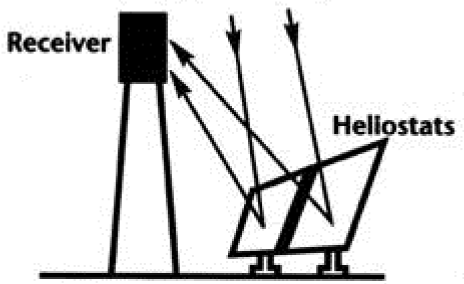
390°C

150°C

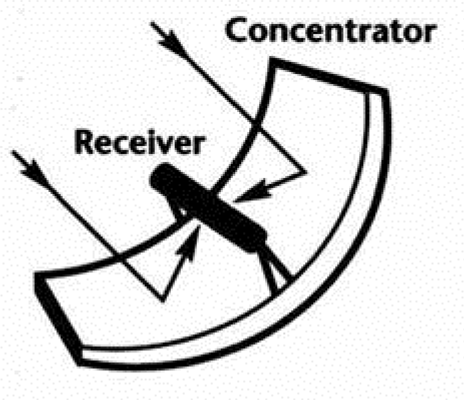
50°C



-Paraboloid:
„Dish“



-Solar Tower
(Central Receiver
System)

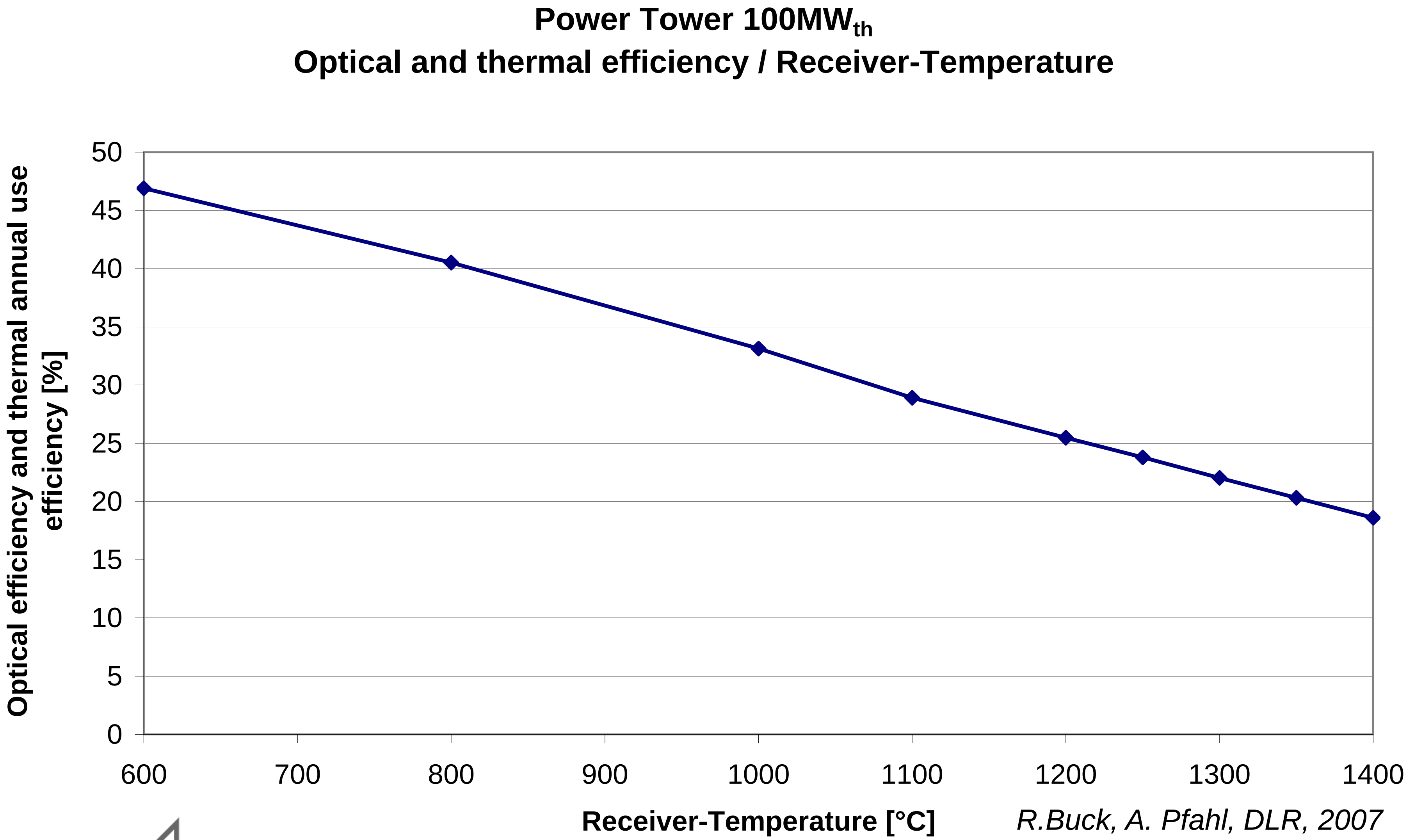


-Parabolic Trough /
Linear Fresnel

Solar Towers, “Central Receiver Systems”

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

Annual Efficiency of Solar Power Towers



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)

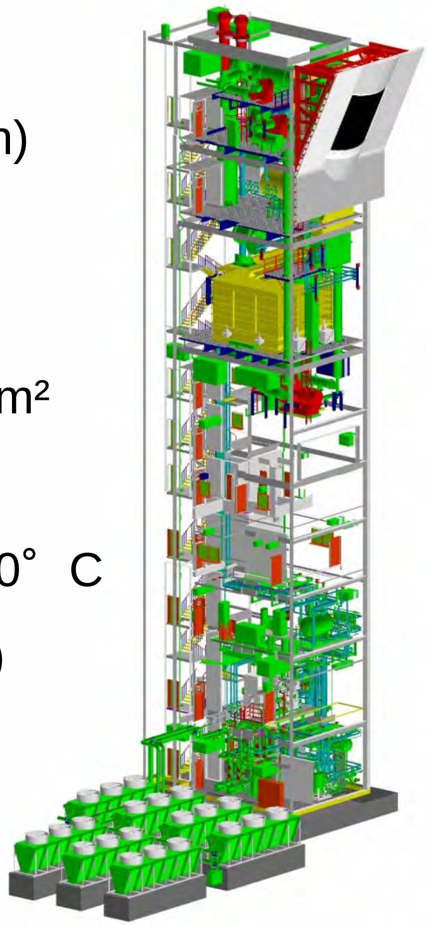
Vessel 9t/h, 30 bar/500° C

(VKK-Standardkessel)

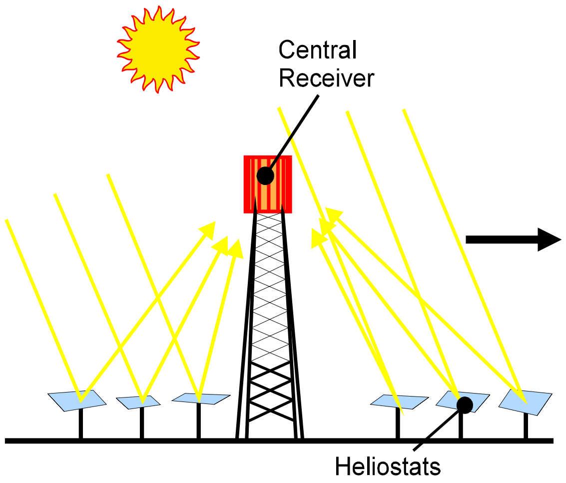
Thermal storage 1h

Turbine 1.5 MWe

(KKK-Siemens)



Principle of the solar thermal fuel production



Solar Tower

Heat

Recourses
-Natural Gas
-Water, CO_2

Chemical Reactor

Fuel
-H_2
-$CO + H_2$

-Industry
-Transportation

Energy Converter
-Fuel Cell

-Transportation
-Power Production

Short-term CO_2-Reduction: Solar Reforming

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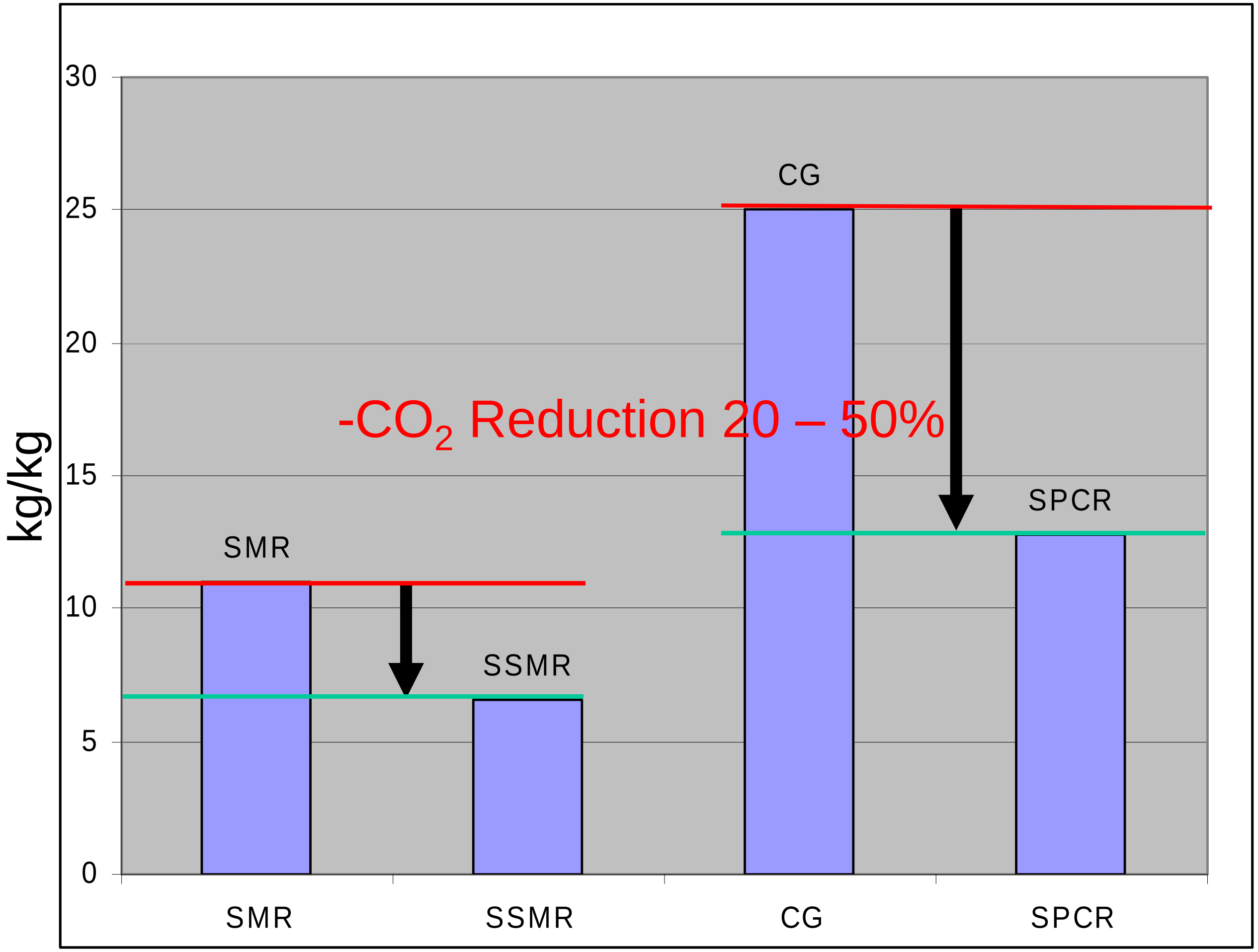
CO_2 Reduction by solar heating of state of the art processes like steam methane reforming and coal gasification



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Steam and CO_2-Reforming of Natural Gas

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

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

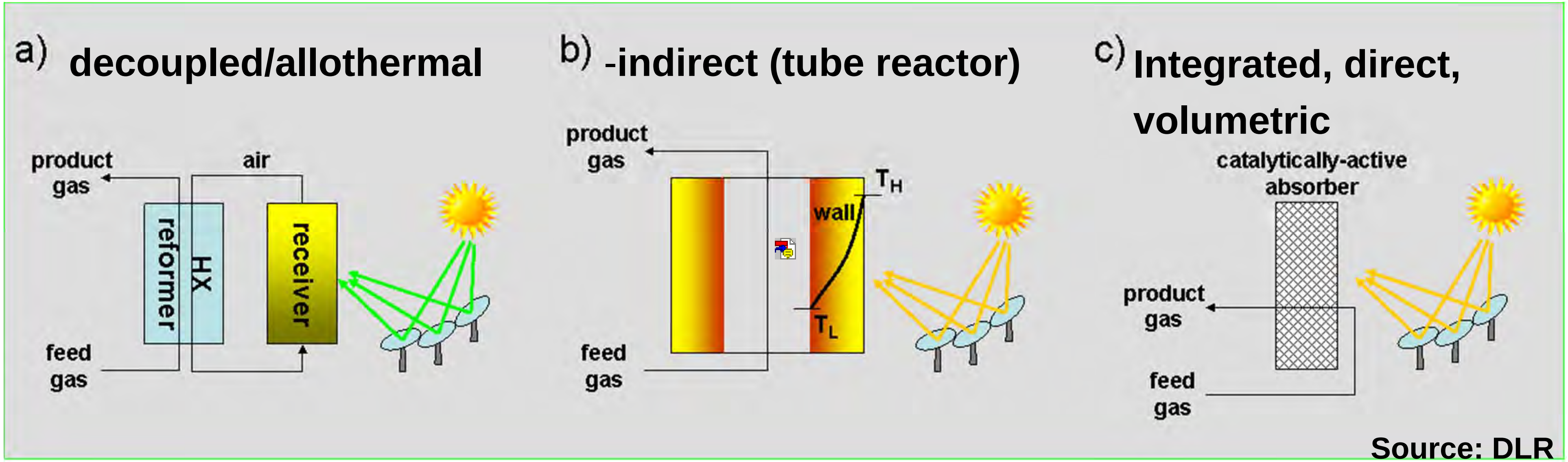
Reforming of mixtures of CO_2/H_2O is possible and common

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

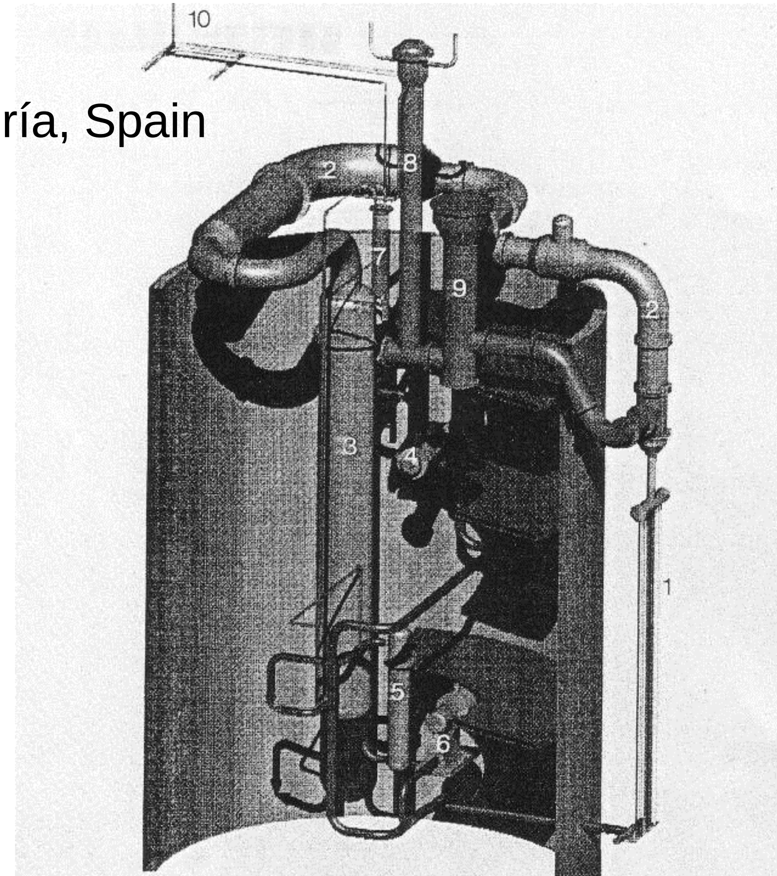
- Irradiated reformer tubes (up to 850° C), temperature gradient
- Approx. 70 % Reformer-h
- Development: CSIRO, Australia and in Japan; Research in Germany and Israel
- Australian solar gas plant in preparation

- 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
- Tubular receiver for air heating

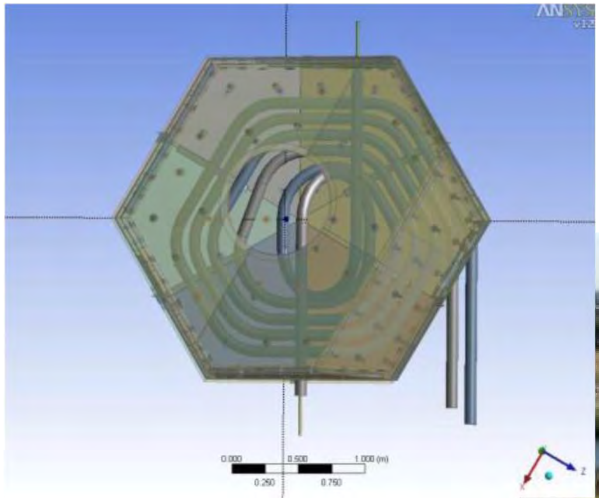
CESA-1, PSA, Spain. The solar radiation is collected by a field of heliostats and redirected to a tower, where different platforms allow the tests of various receiver technologies.

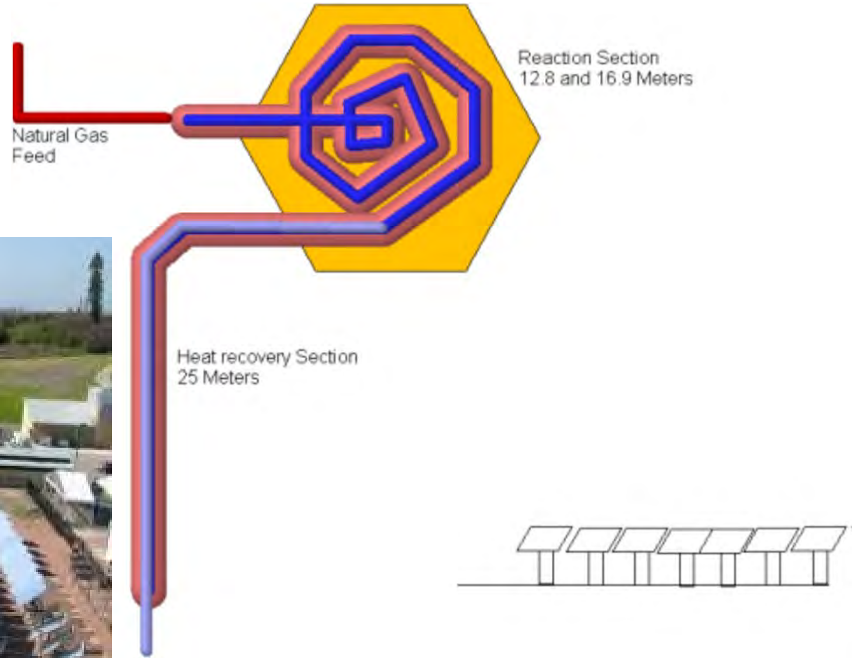


1 = Receiver, 2 = Heißgasleitungen, 3 = Rekuperator, 4 = Elektrischer Heizer, 5 = Kühler, 6 = Kompressor, 7 = Kühler E-106/7, 8 = Reformer V-101 mit Wärmeübertragern E-102/3/4, 9 = Elektrischer Heizer E-105, 10 = Fackel Z-102.

Pilot Scale Solar Chemical Reactors - SolarGas

Experimental set-up of the 200 kW SolarGas reactor





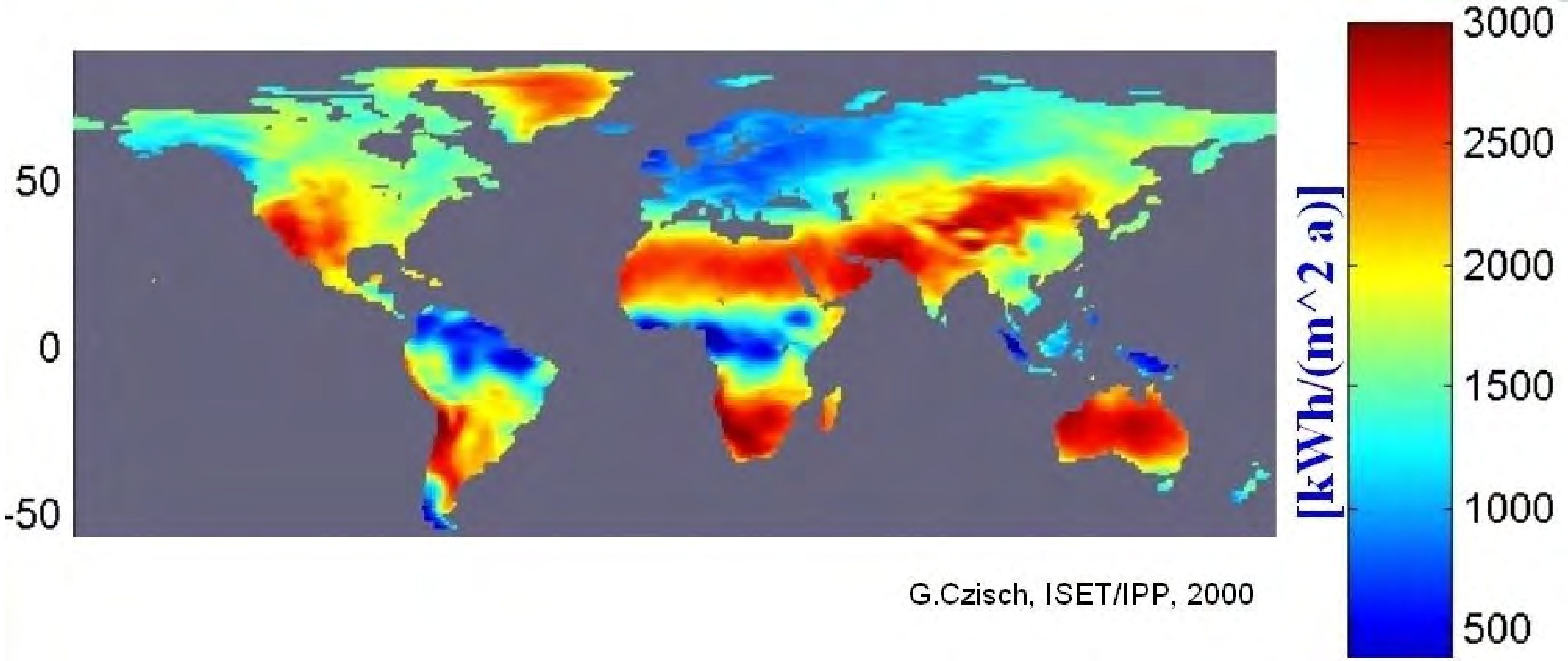
Top view of DCORE reactor (right) layout of entire integrated reformer and HRU

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

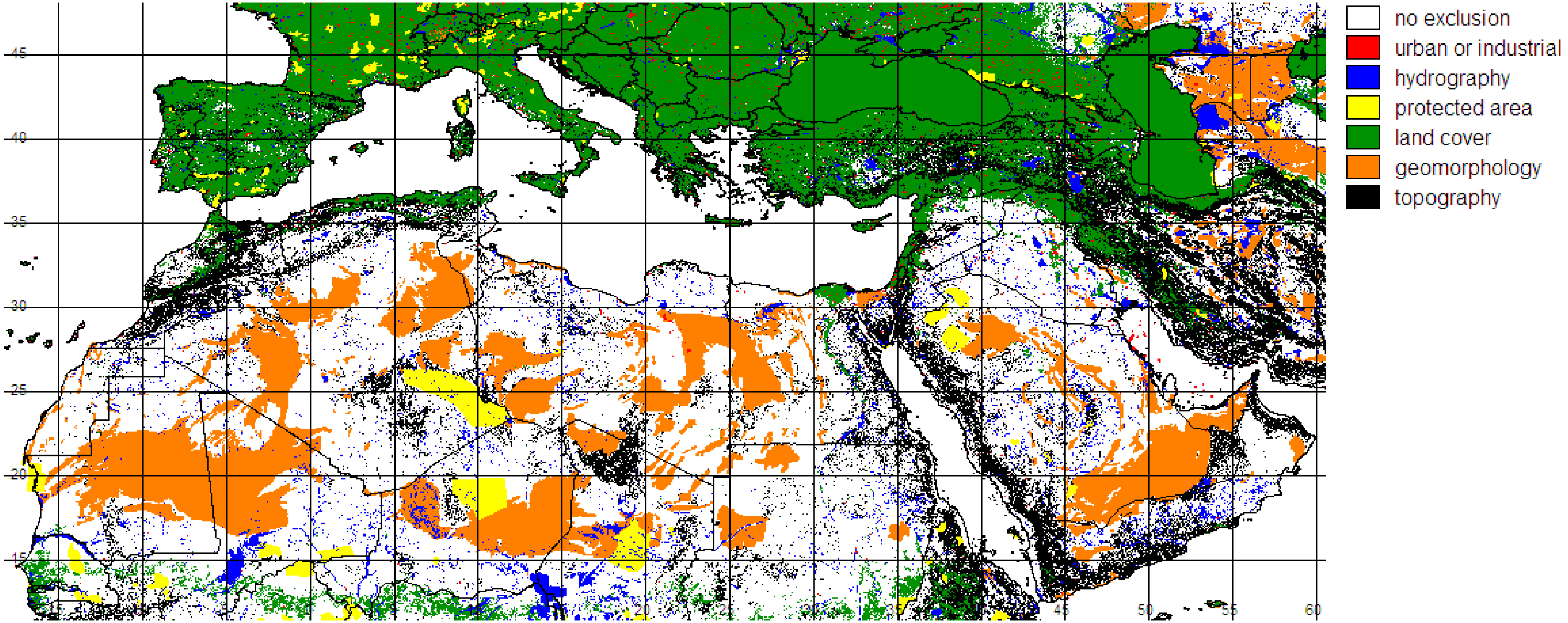
Direct heated volumetric receivers: SOLASYS, SOLREF (EU FP4, FP6)

- 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)

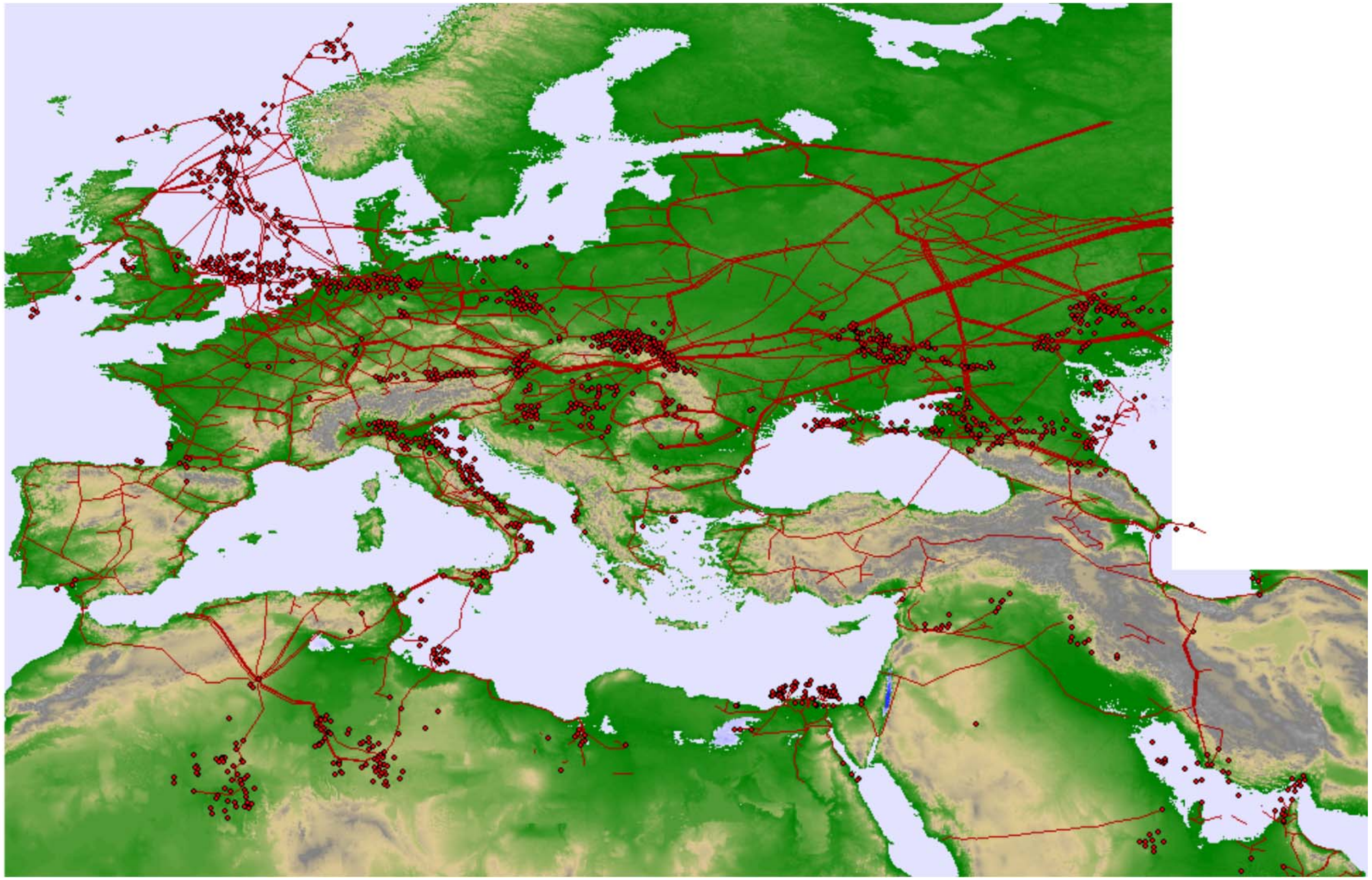
Potential Solar sites



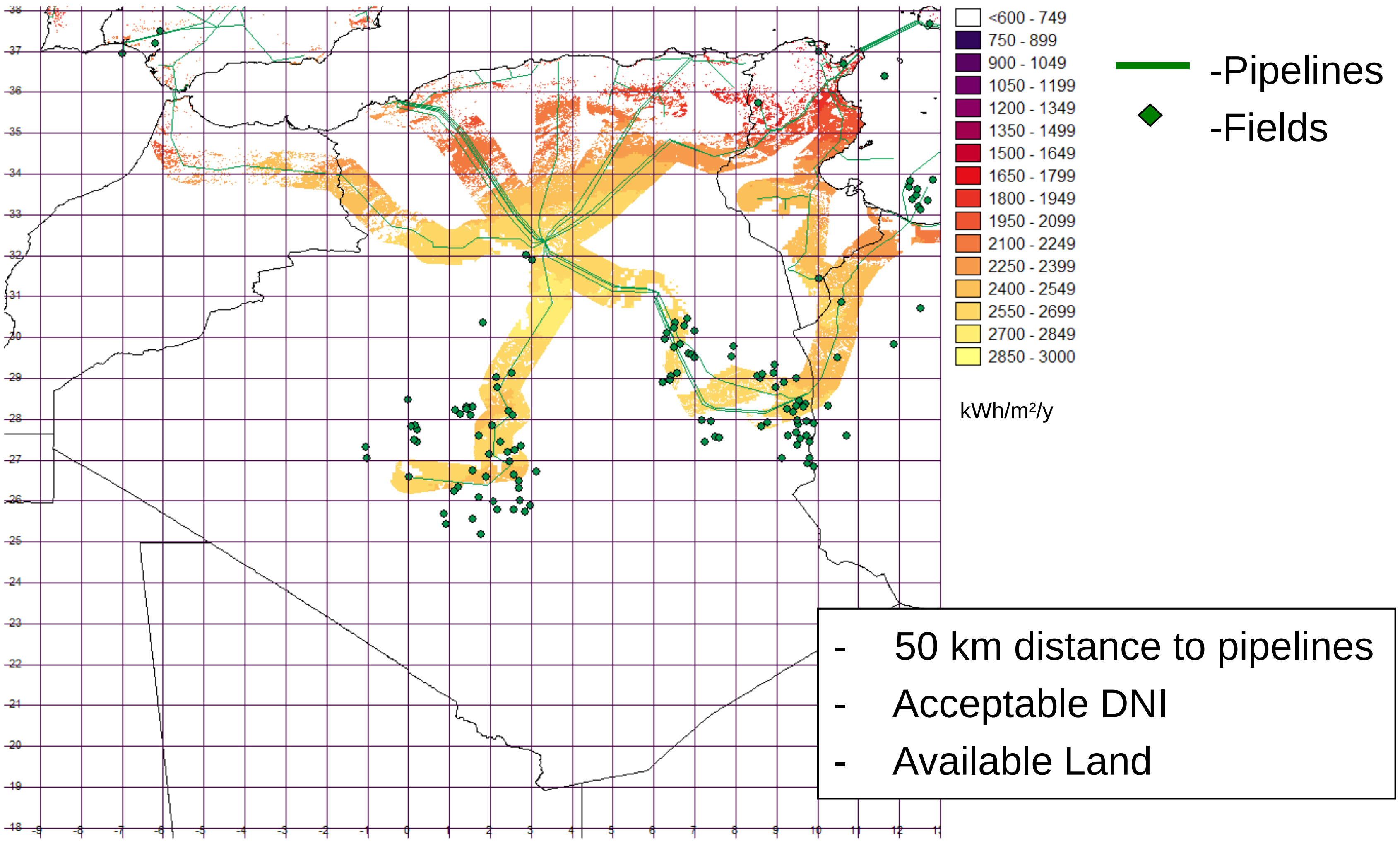
Suitable locations for CSP in Northern Africa



Natural Gas Pipeline Grid and Natural Gas Fields



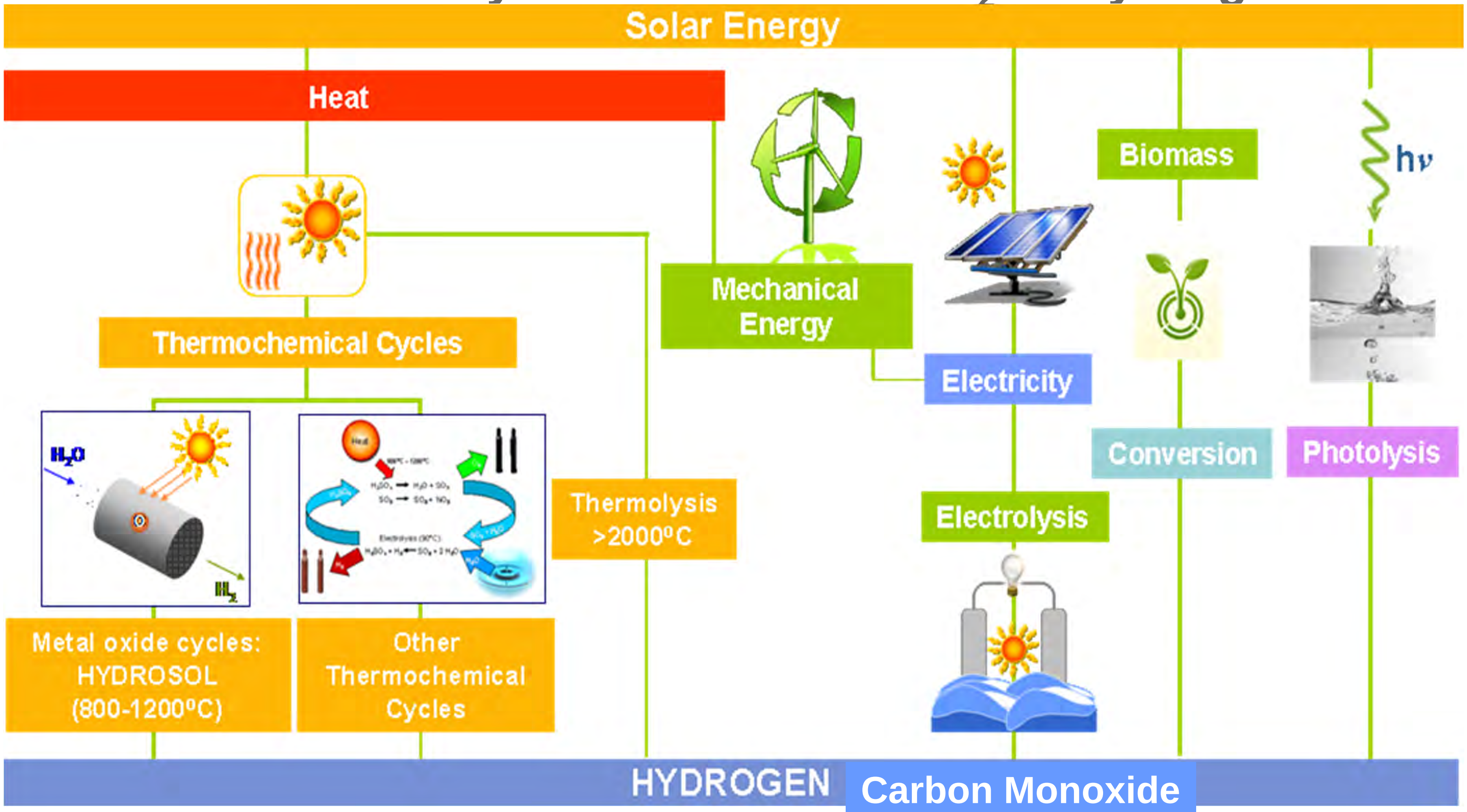
Suitable locations for solar reforming - Example Algeria and Tunisia



- 50 km distance to pipelines
- Acceptable DNI
- Available Land

Long-term: Water splitting processes

Solar Pathways from Water or CO_2 to Hydrogen



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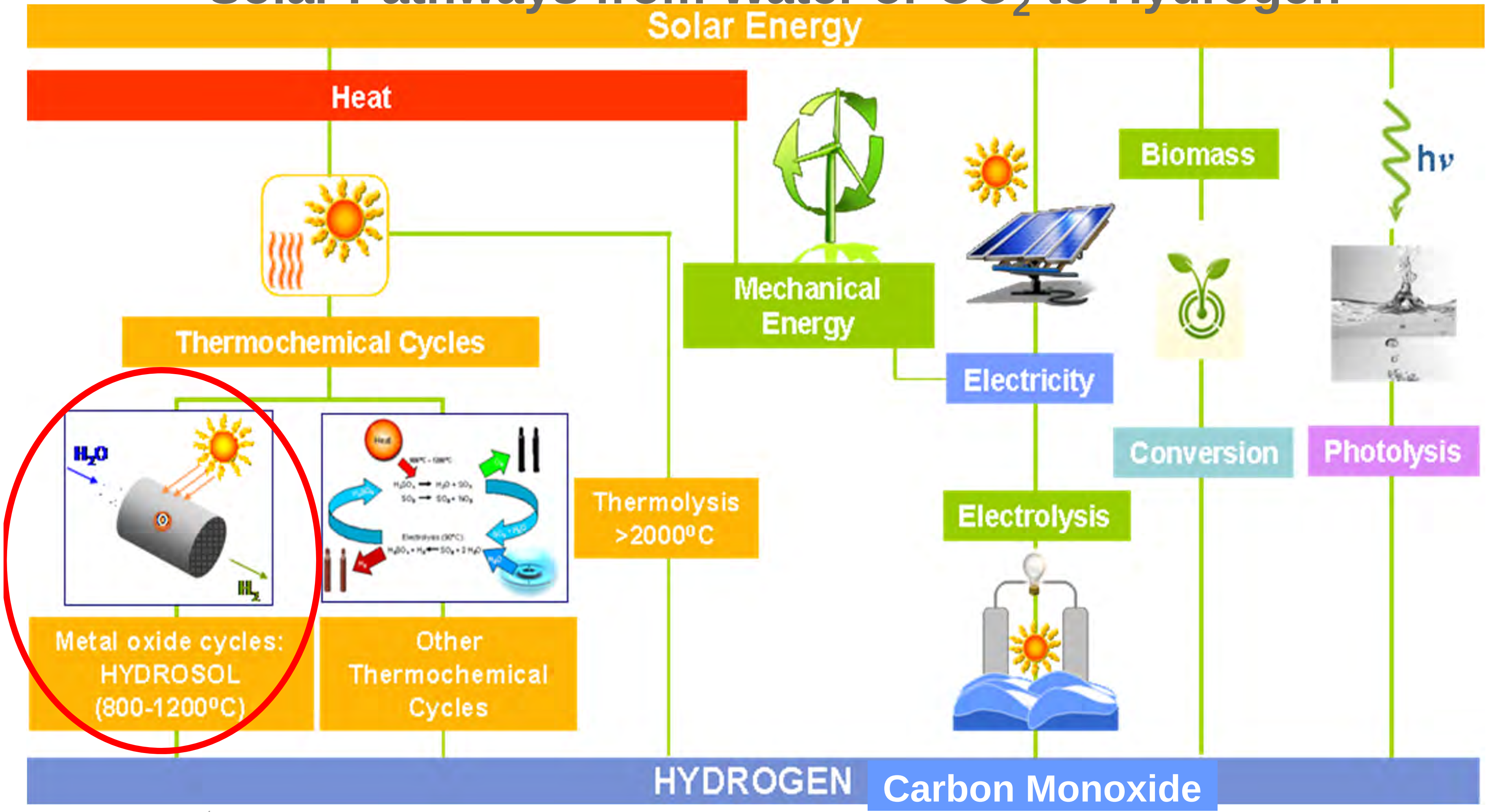


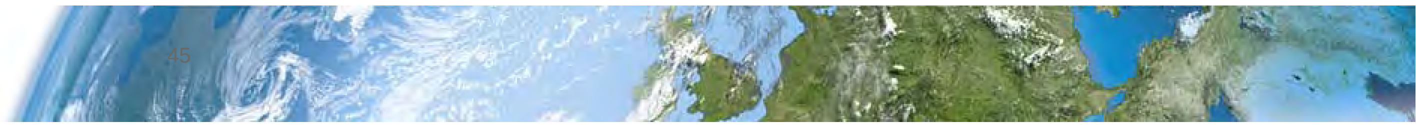
Promising and well researched Thermochemical Cycles

	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

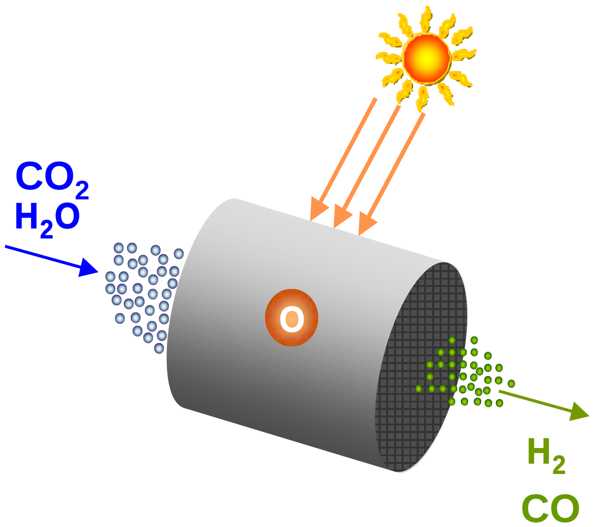
Efficiency comparison for solar hydrogen production from water (SANDIA, 2008)*

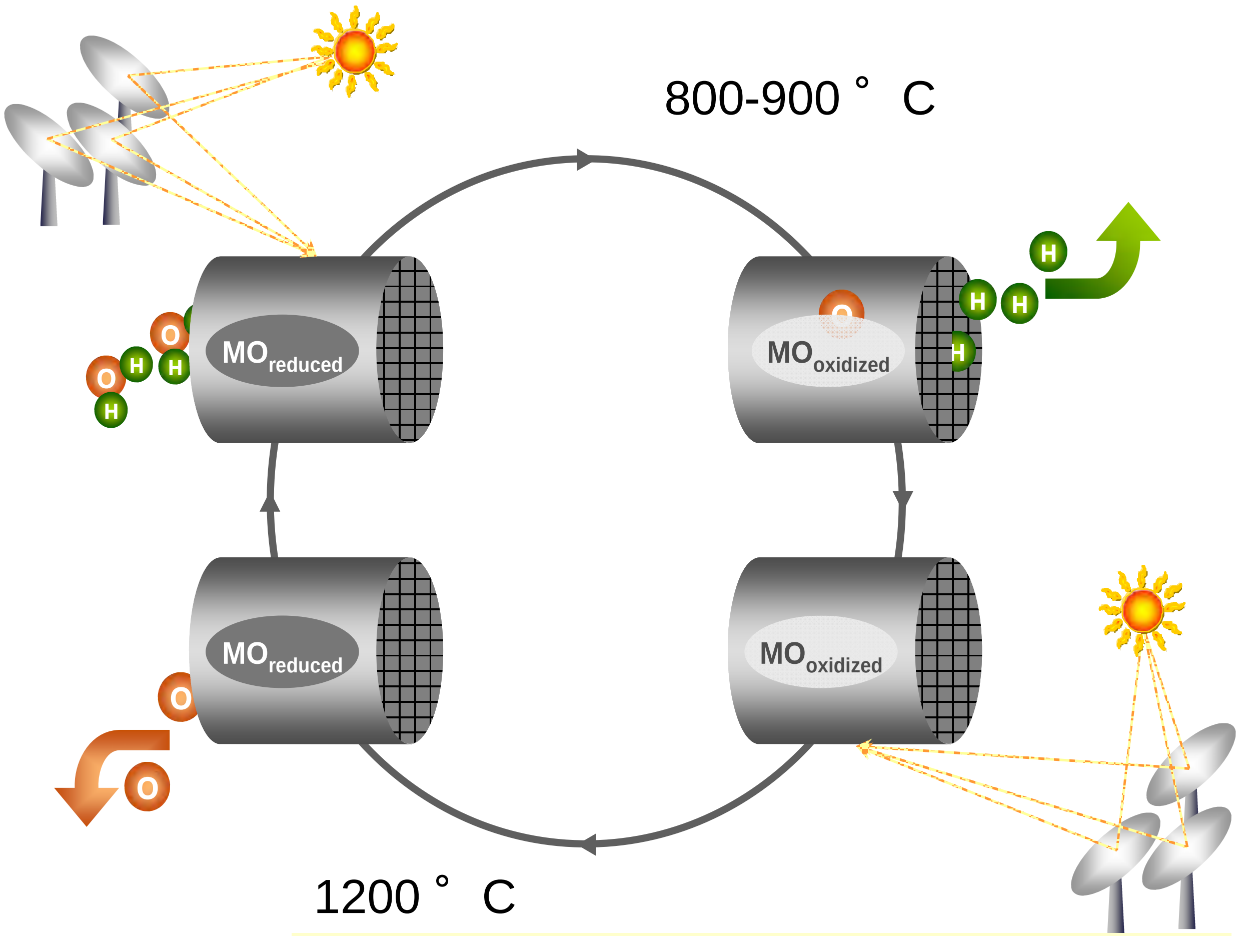
Process	T [°C]	Solar plant	Solar-receiver + power [MWth]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H_2
Elctrolysis (+solar-thermal power)	NA	Actual Solar tower	Molten Salt 700	30%	57%	83%	14%
High temperature steam electrolysis	850	Future Solar tower	Particle 700	45%	57%	76,2%	20%
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



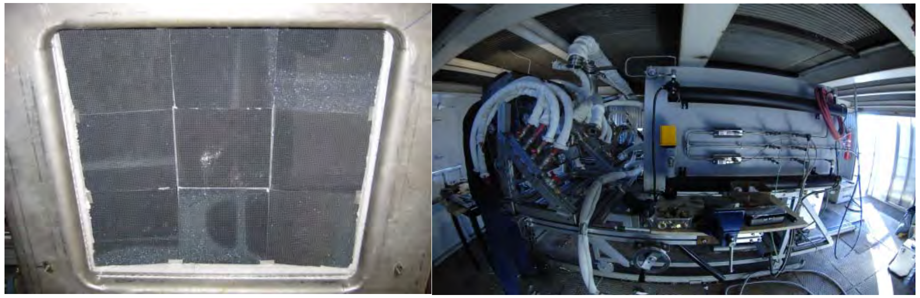
Fuel Production from H_2O and CO_2 by Solar Radiation





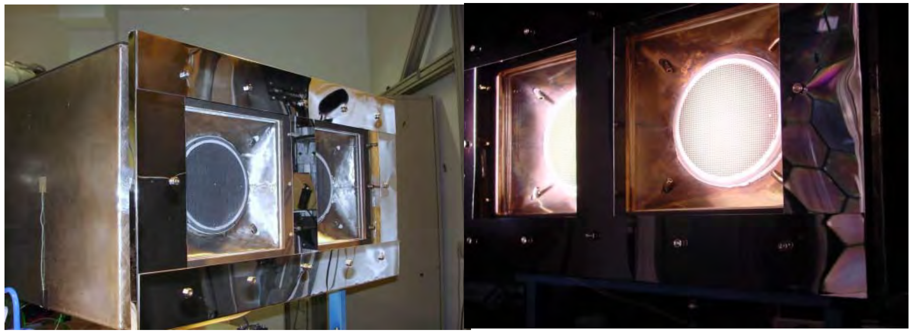
DLR: Roeb, Müller-Steinhagen, *Science*, Aug. 2010

Hydrosol technology scale-up



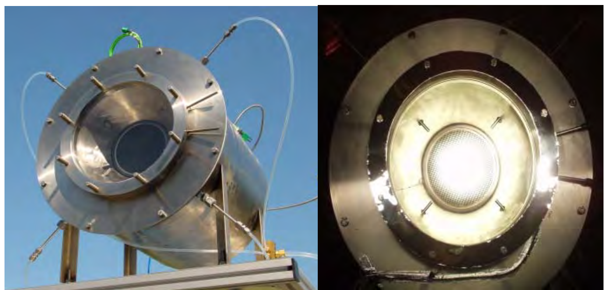
2008:

Pilot reactor (100 kW)



2005:

Continuous H_2 production



2004:

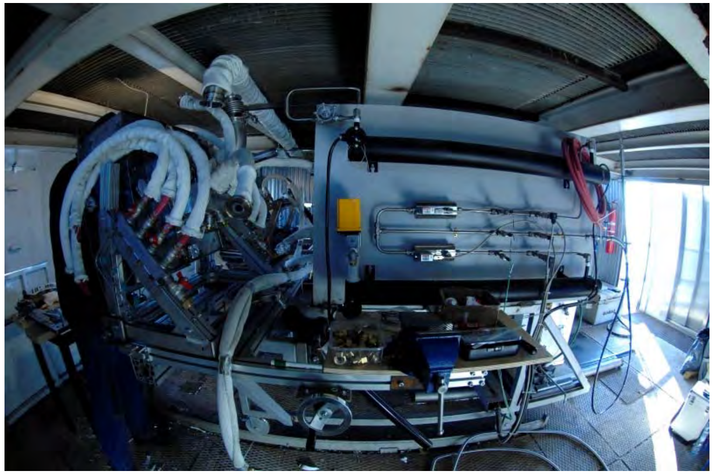
First solar thermochemical

H_2 production

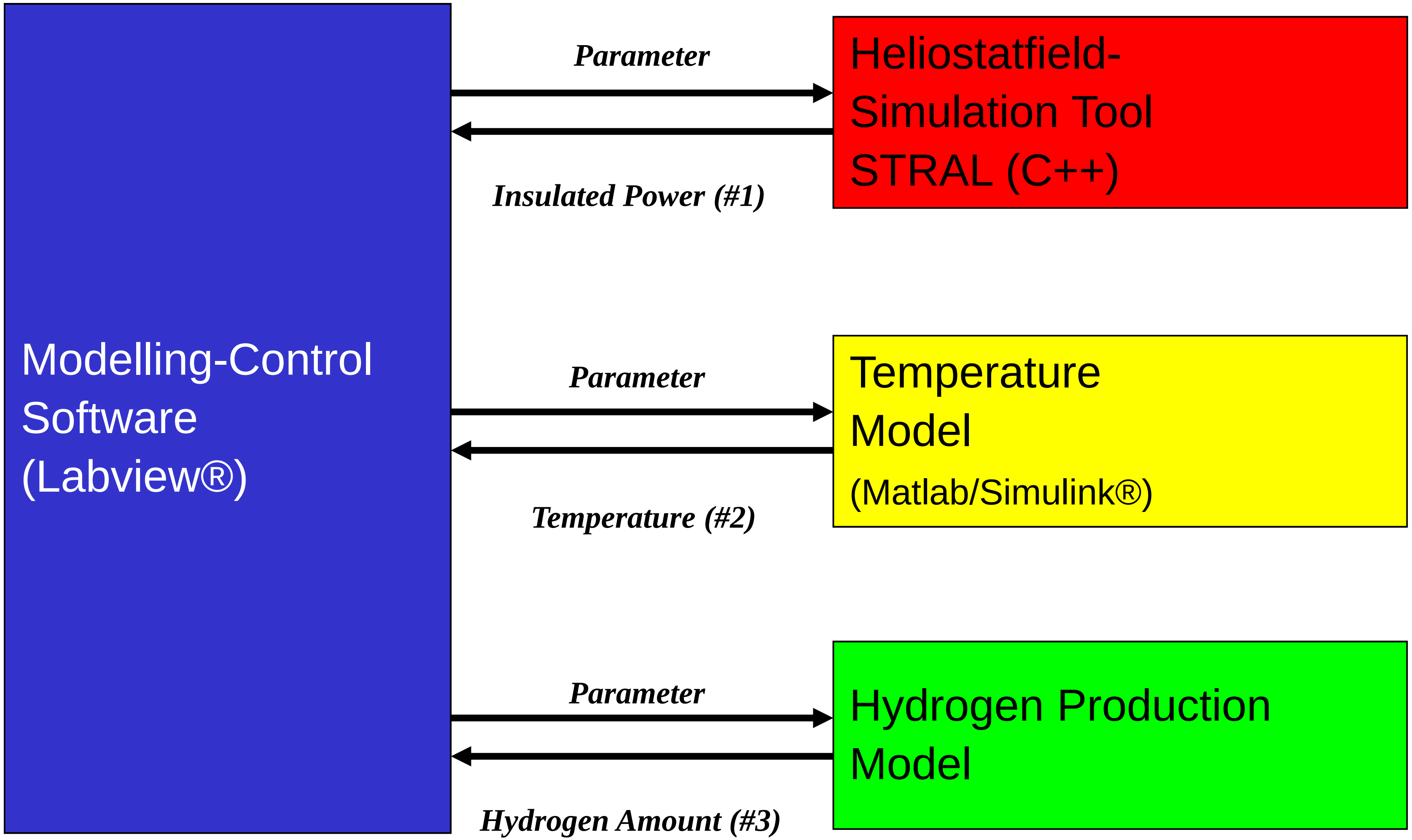
PSA solar tower

DLR solar furnace

Pilot-plant in operation since March 2008

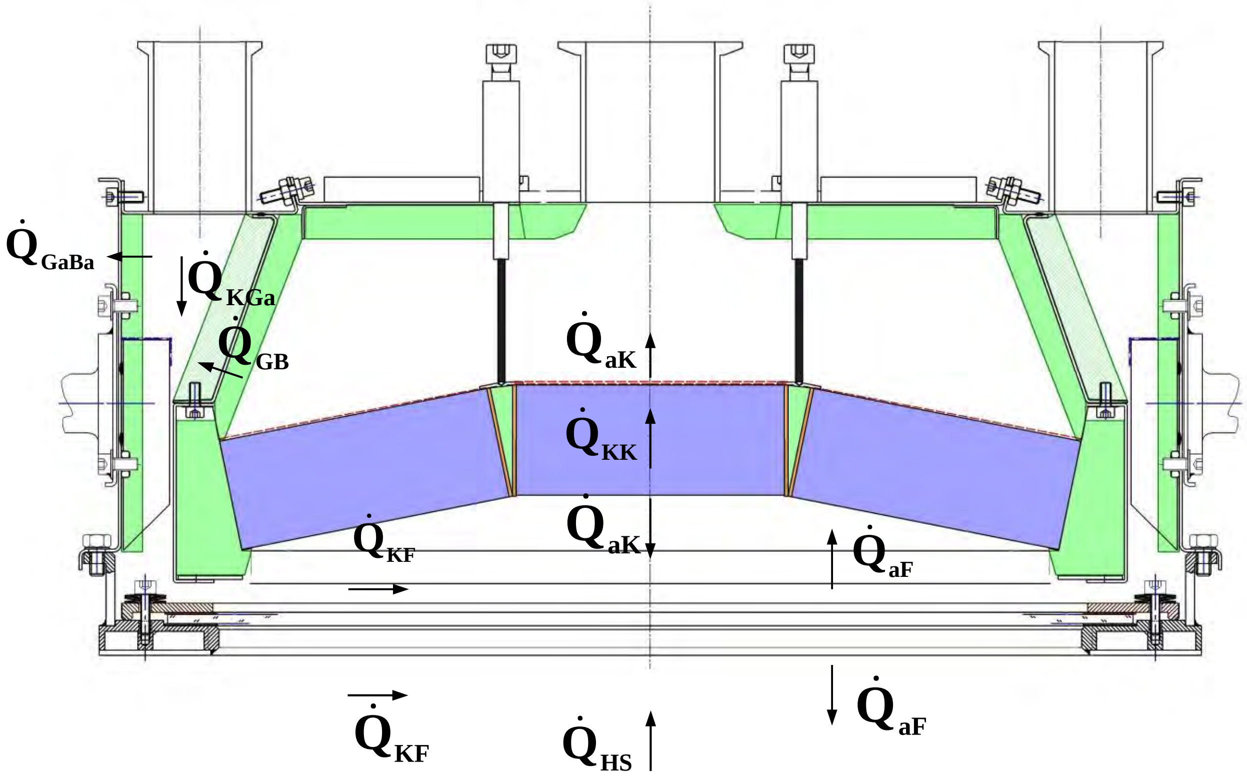


Modelling of the pilot plant - Overview Modelling:



Modelling – Temperature model:

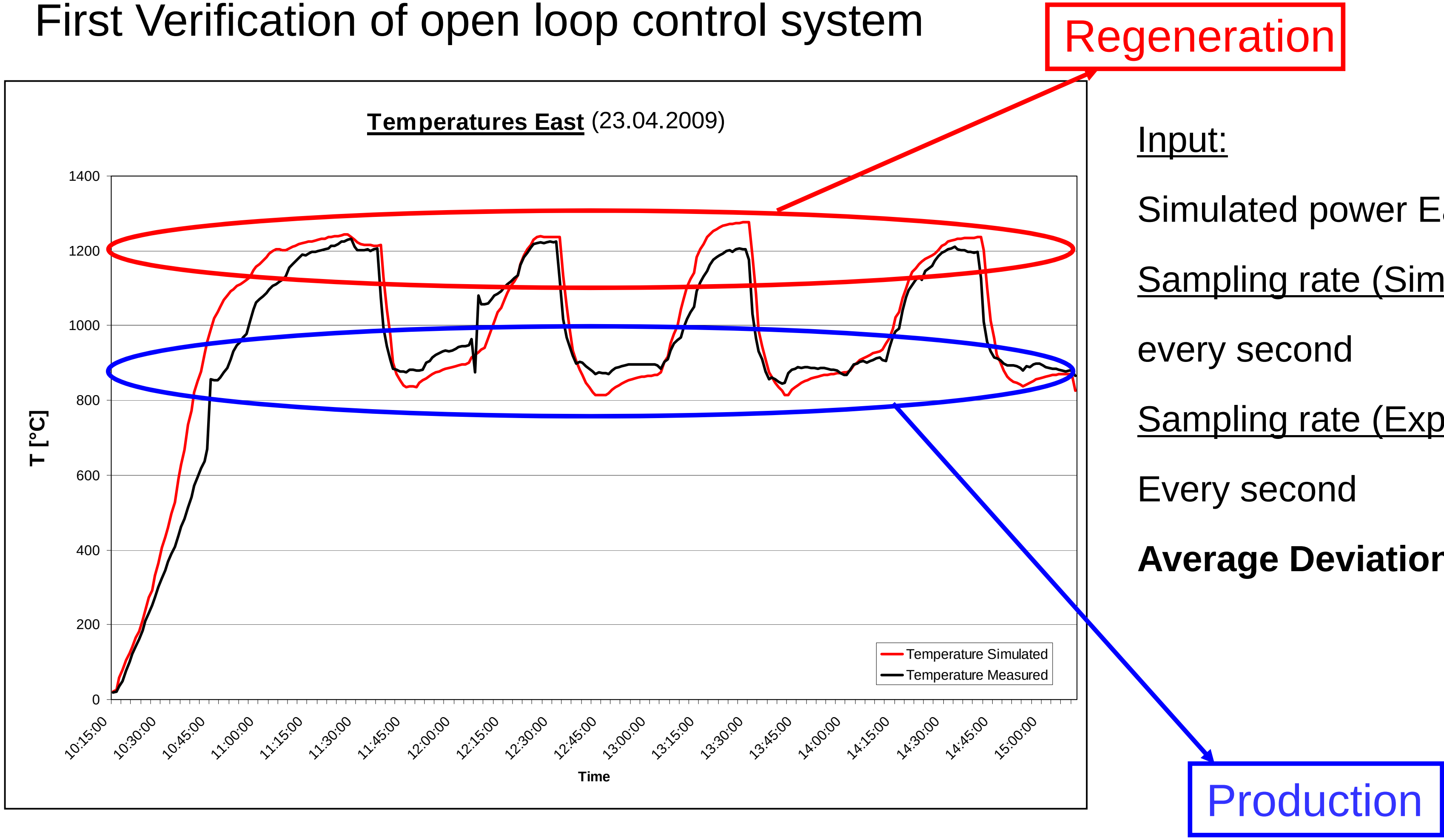
Collecting formulas of the **heat flows** (simplified balance!)



Heat flows: heat radiation, heat conduction and convection

Modelling – Temperature model:

First Verification of open loop control system



Input:

Simulated power East

Sampling rate (Sim.):

every second

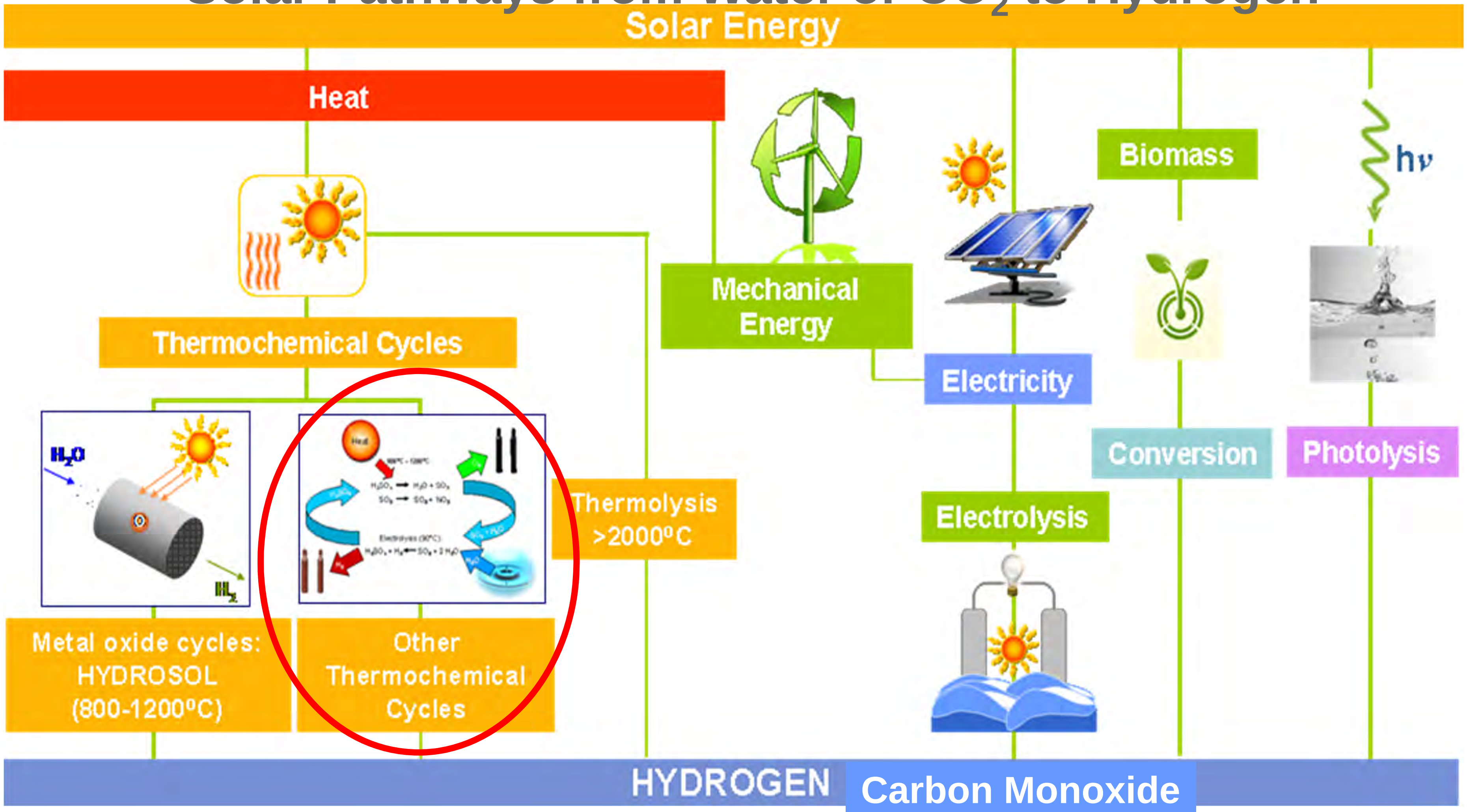
Sampling rate (Exp.):

Every second

Average Deviation: 6.5%

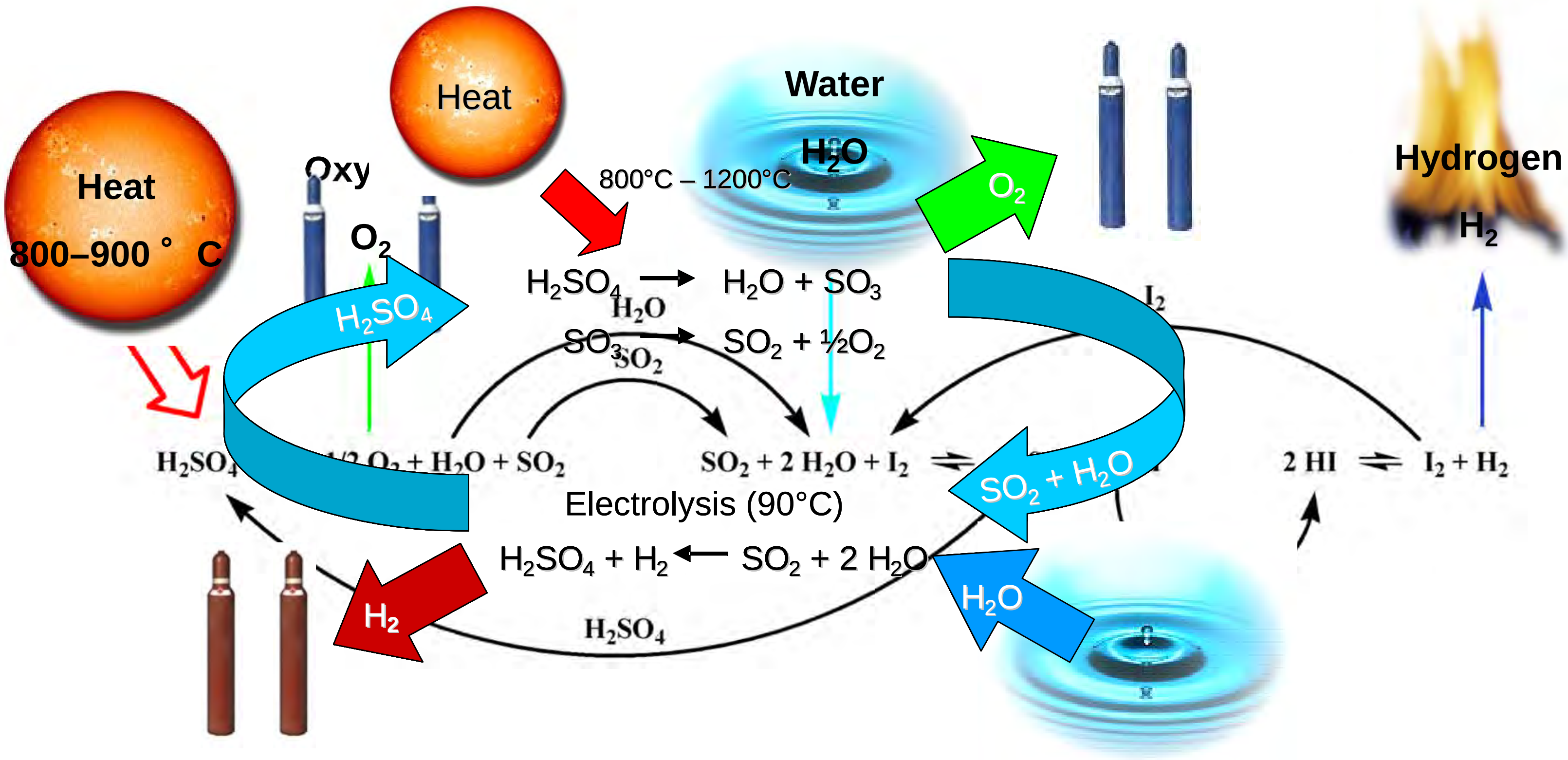
Pilot Plant arranged on the research platform of the ST Jülich (artist view)

Solar Pathways from Water or CO_2 to Hydrogen



The thermochemical cycles covered in HycycleS

Sulphur-Iodine Process
Hybrid Sulphur Cycle



DLR

H_2SO_4 decomposition in 2 steps

1. Evaporation of liquid sulfuric acid (400° C)

$$H_2SO_4 \rightleftharpoons SO_3 + H_2O$$

-2. Dissociation of sulfur trioxide (850° C)

$$SO_3 + H_2O \rightleftharpoons SO_2 + \tfrac{1}{2}\, O_2 + H_2O$$

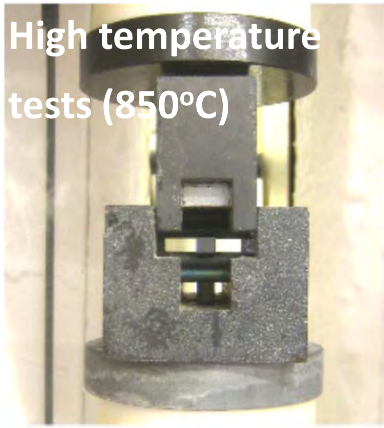
-**Absorbers**

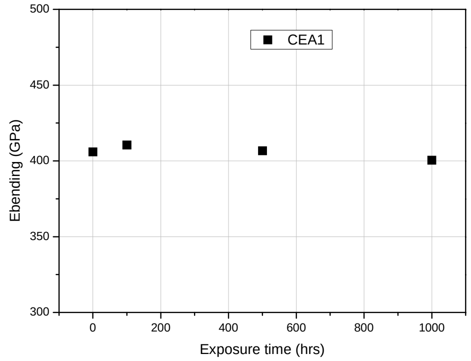
:

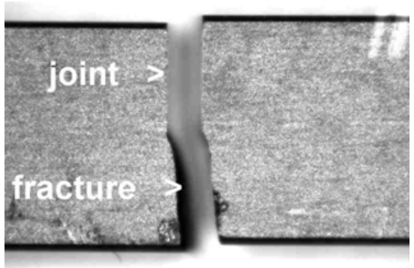
-SiSiC foam

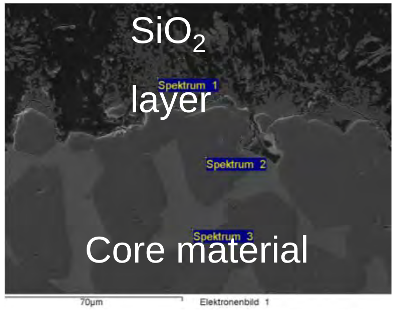
-SiSiC honeycomb

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.

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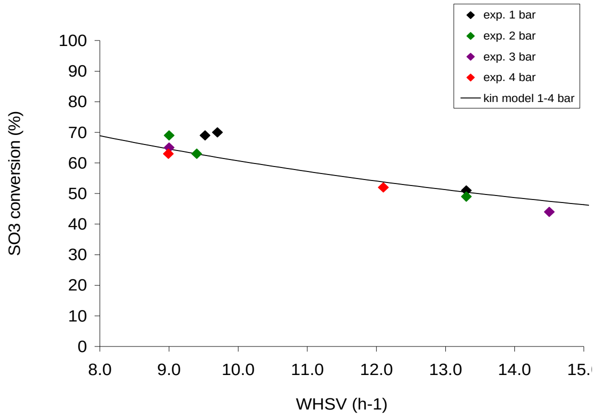
Advanced catalysts and coatings for H_2SO_4 decomposition

– ‘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



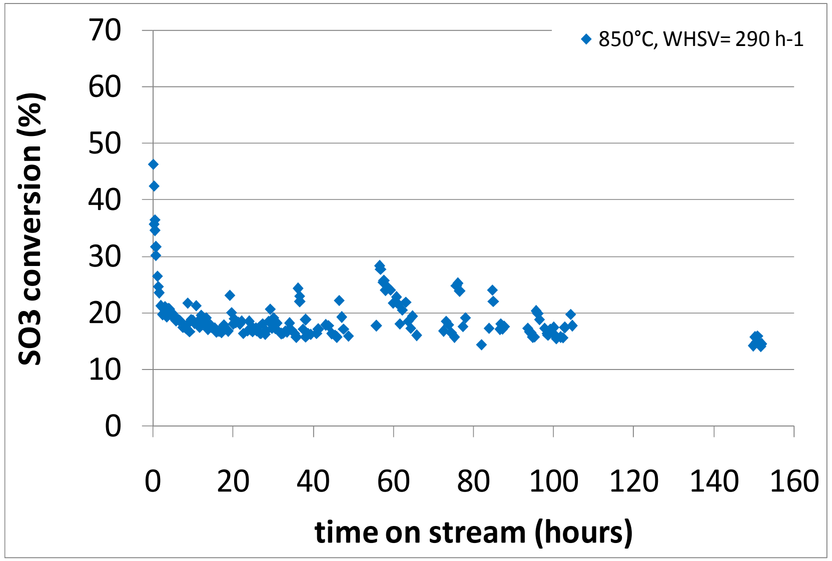
– Evaluation of the employed materials chemical stability

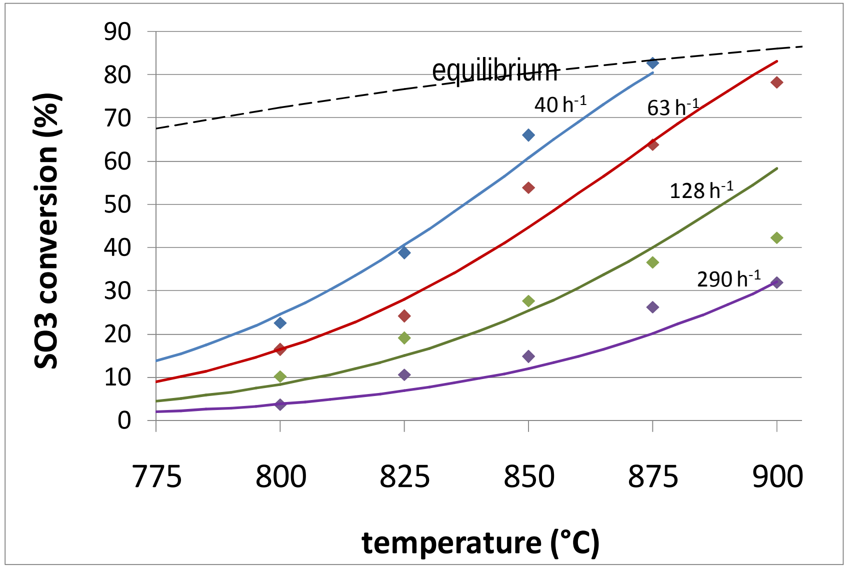
– Extraction of an SO_3 dissociation mechanism

– CrFe oxide identified as the most suitable catalyst

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

Example of Catalyst qualification: $CuAl_2O_4$





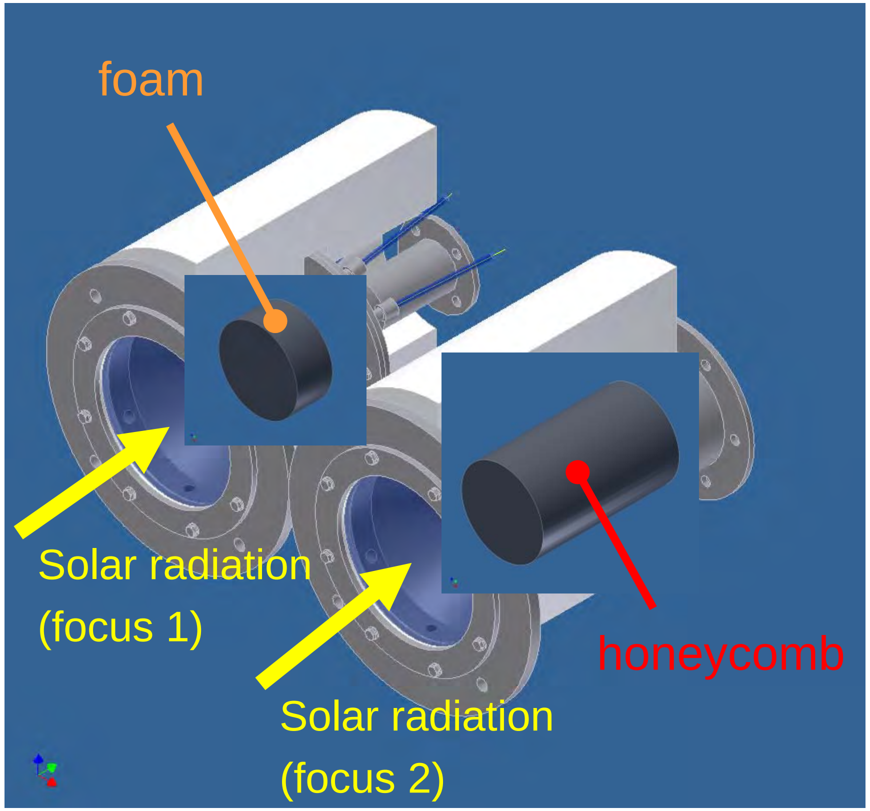
- Durability tests performed at “high” space velocity values
- After initial deactivation, catalyst shows < 5% loss of activity (100hrs on stream)
- Change of colour observed, due to phase separation phenomena

$CuAl_2O_4$-coated SiSiC fragments (kinetic model for decomposer design)			
Exp. campaign	*Ea* (kJ/mol)	*A* (h^{-1})	*dn (mm)**
No. 1	240.3	$5.6*10^{12}$	1-4

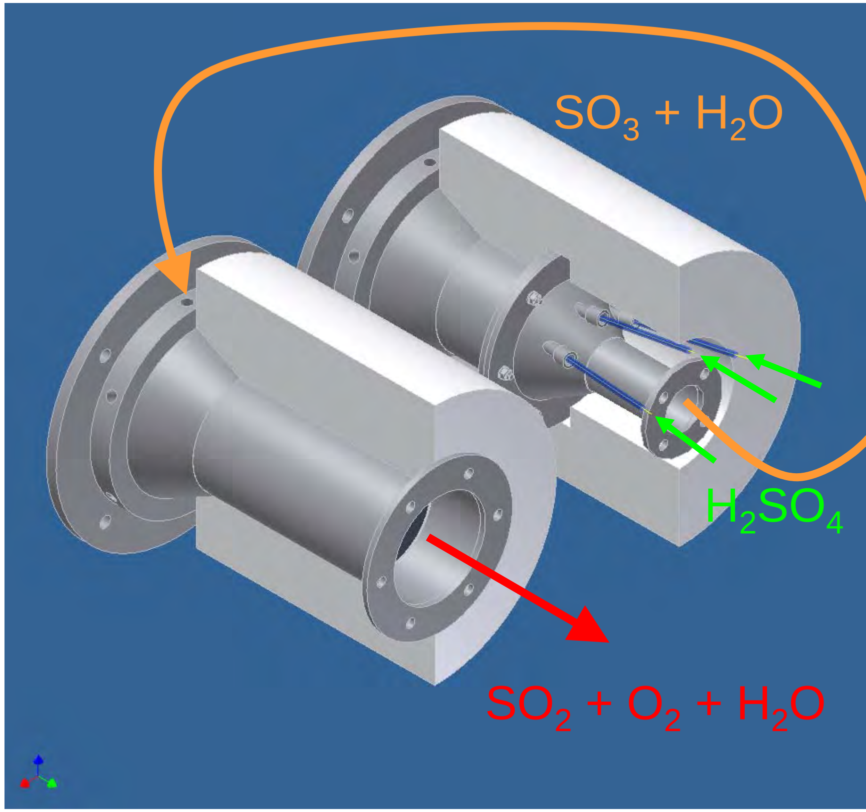
$$-\ln(1-X) = \frac{k}{WHSV}$$

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

Design of multi-chamber solar reactor

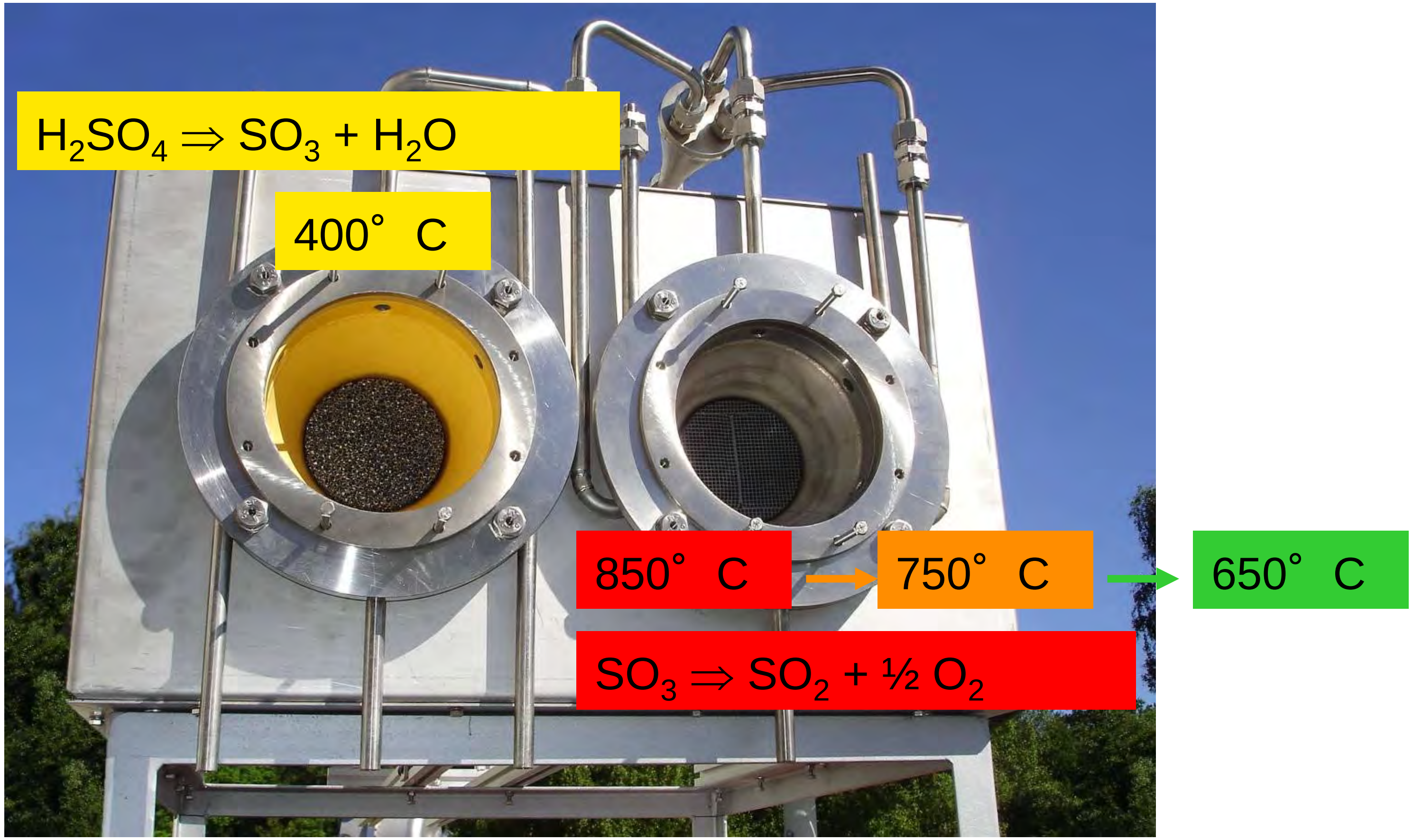


Front view of evaporator (left)
and decomposer

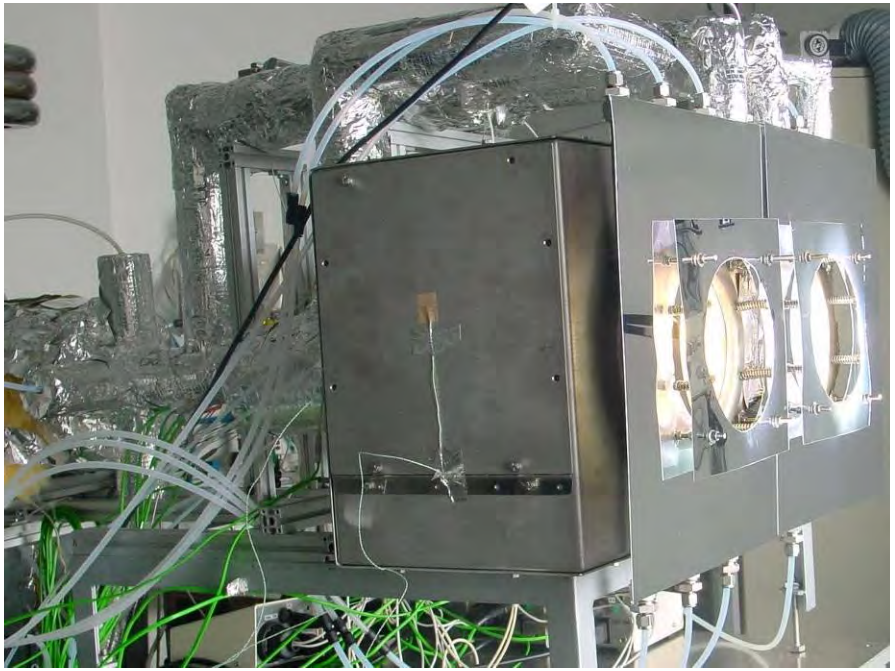


Rear view

Solar reactor for sulfuric acid decomposition



Operation in our solar furnace in Cologne



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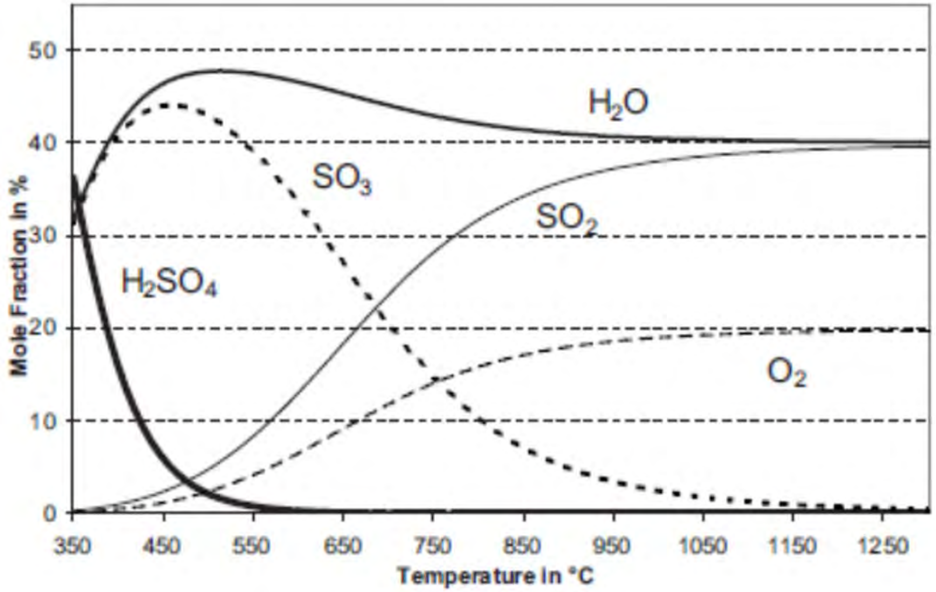
Overview of test series in solar furnace

Catalyst		**$Fe_2Cr_2O_4$**
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

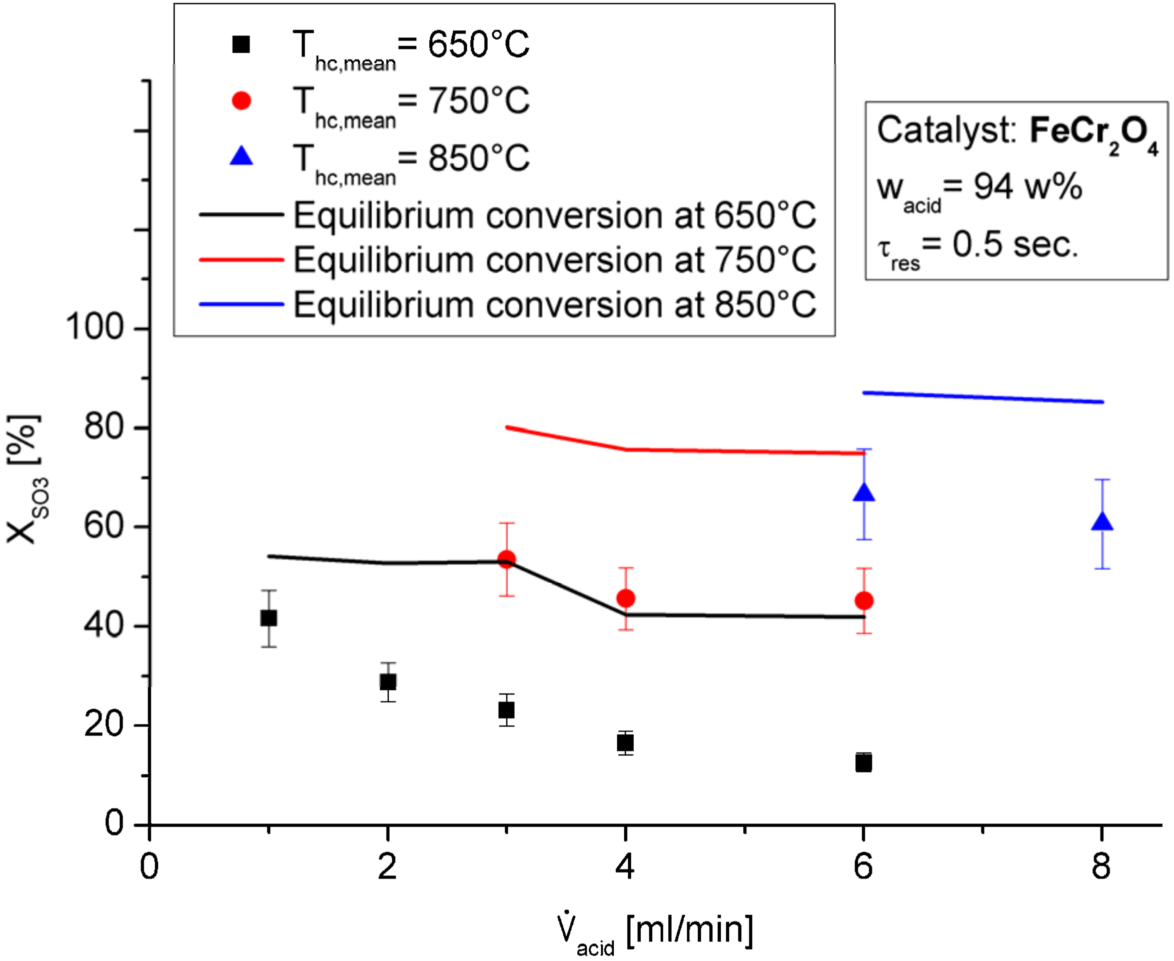
Thermodynamic equilibrium of H_2SO_4 decomposition



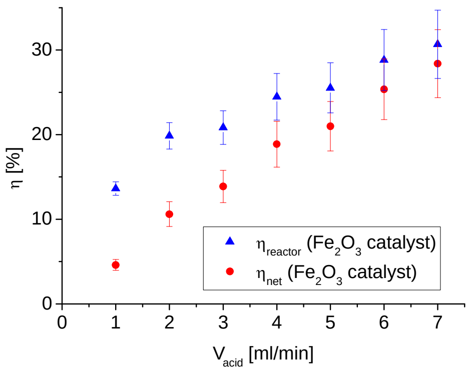
- H_2SO_4 dissociation completed at about 550° C
- 80% of SO_3 decomposed at 850° C
- 40% of SO_3 decomposed at 650° C

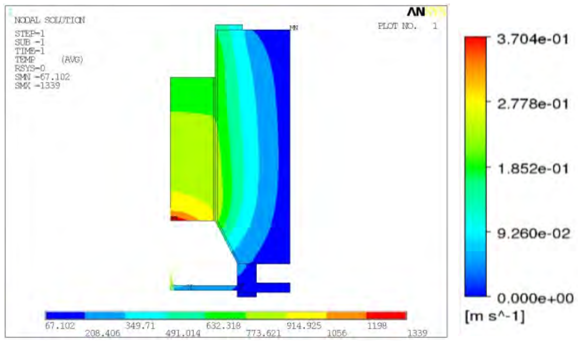
Source: Noglik et al., 2009

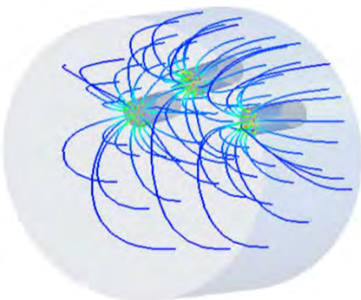
Conversion of SO_3 in honeycomb

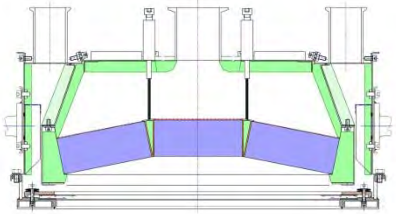


Solar reactor as H_2SO_4 decomposer









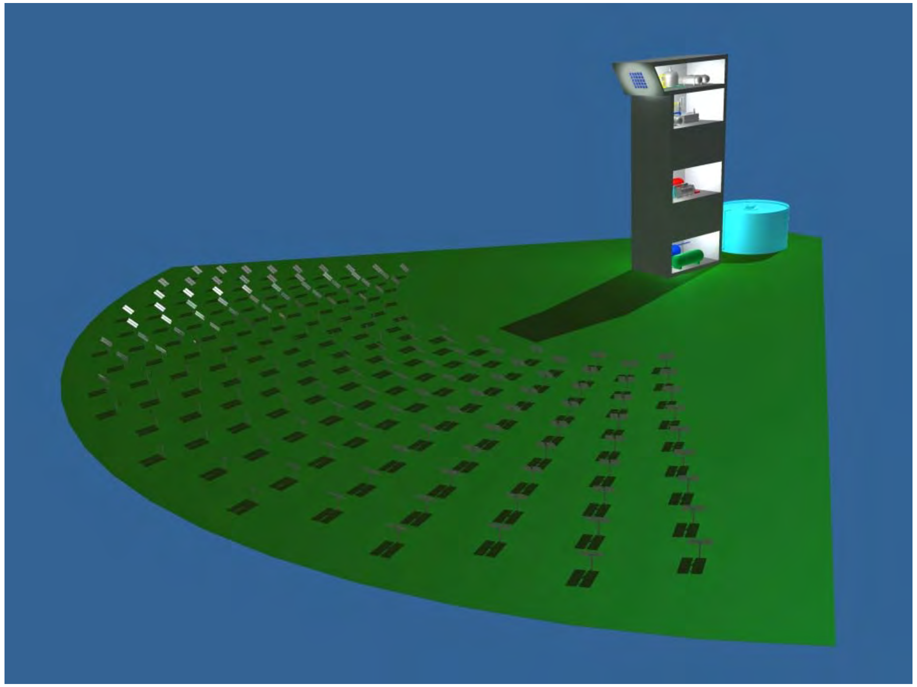
- Development and operation of a scalable prototype
  - FEM analysis
  - trouble-free operational > 200 h
  - conversions > 80 %
  - reactor efficiency > 25 %
- Continuum model of foam vaporiser
  - Computer tomography
- Modelling of SO_3 decomposition
  - Validation with experimental data
- Control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

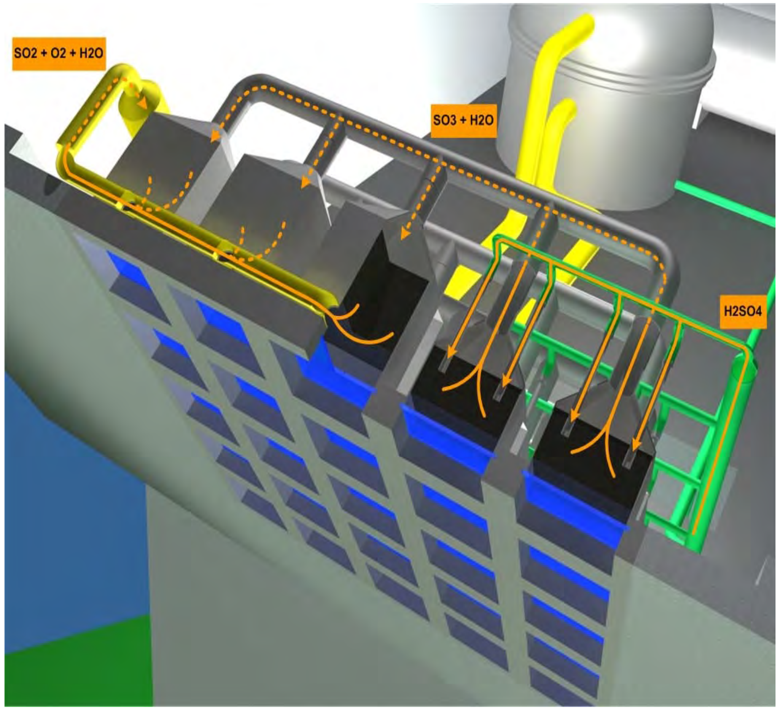
Thomey et al, IJHE 2012

Noglik et al, IJER 2010

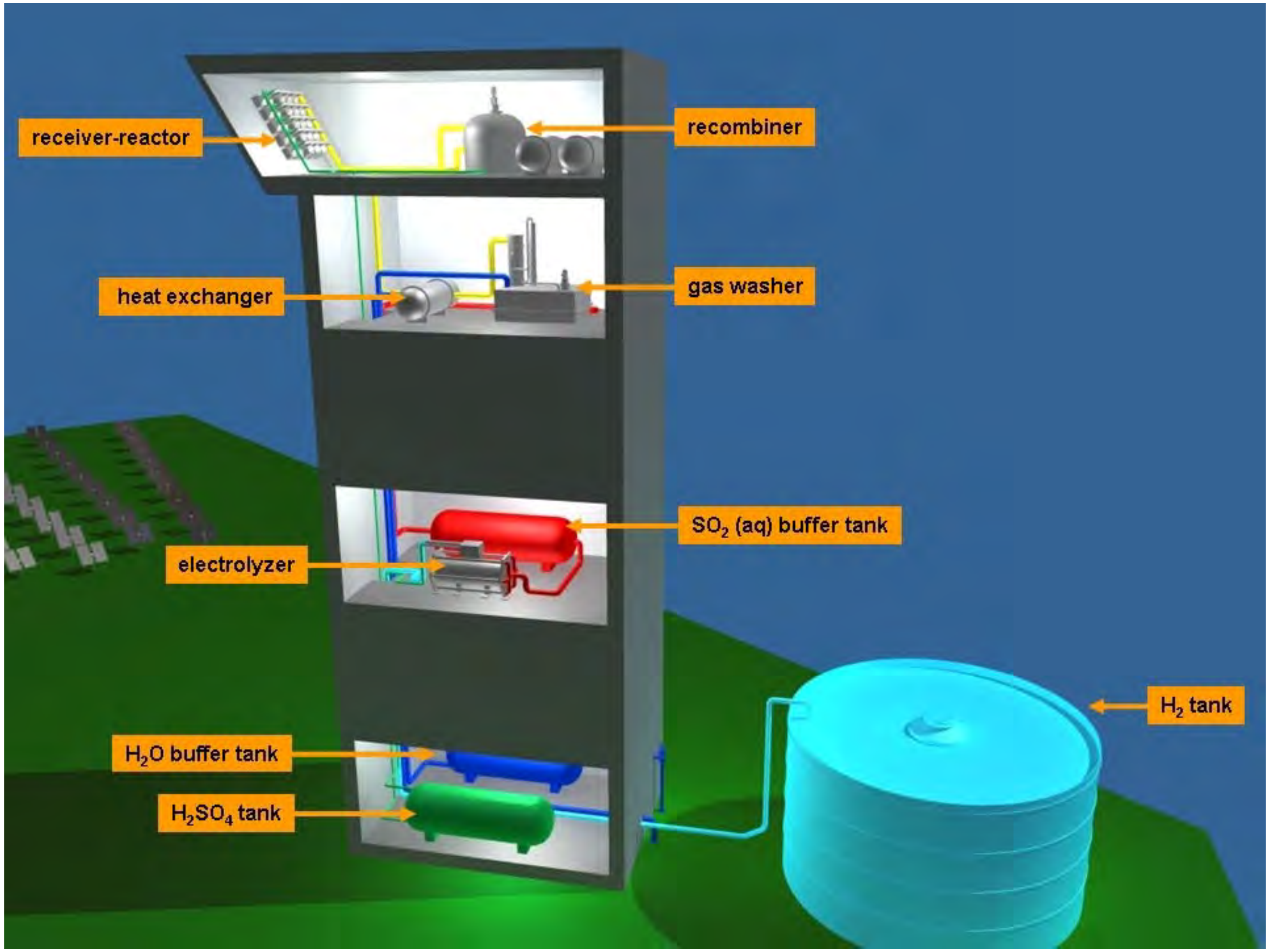
Haussener et al, ASME-JHT 2009

Scale-up of the solar HyS process

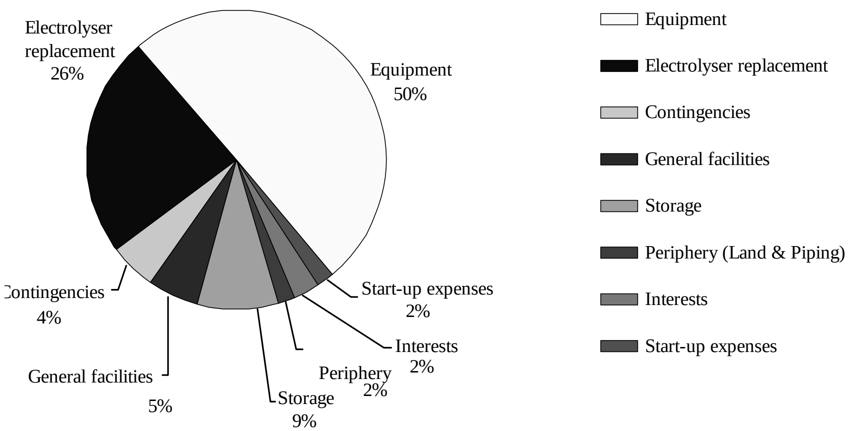




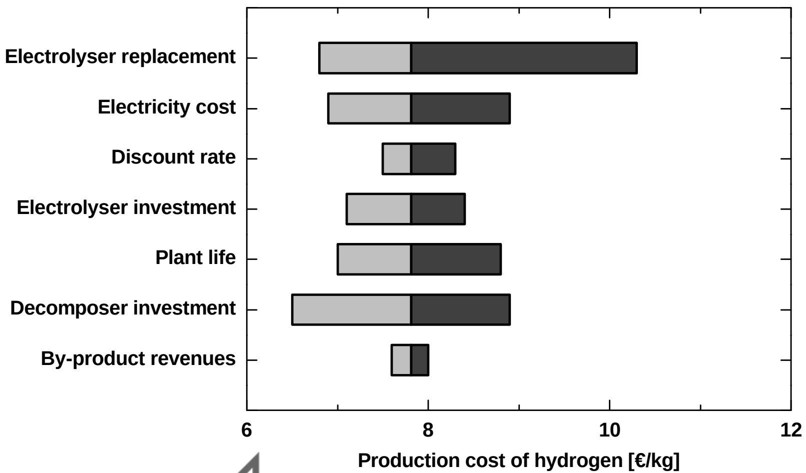
Implementation into a Solar Tower



Techno-economics

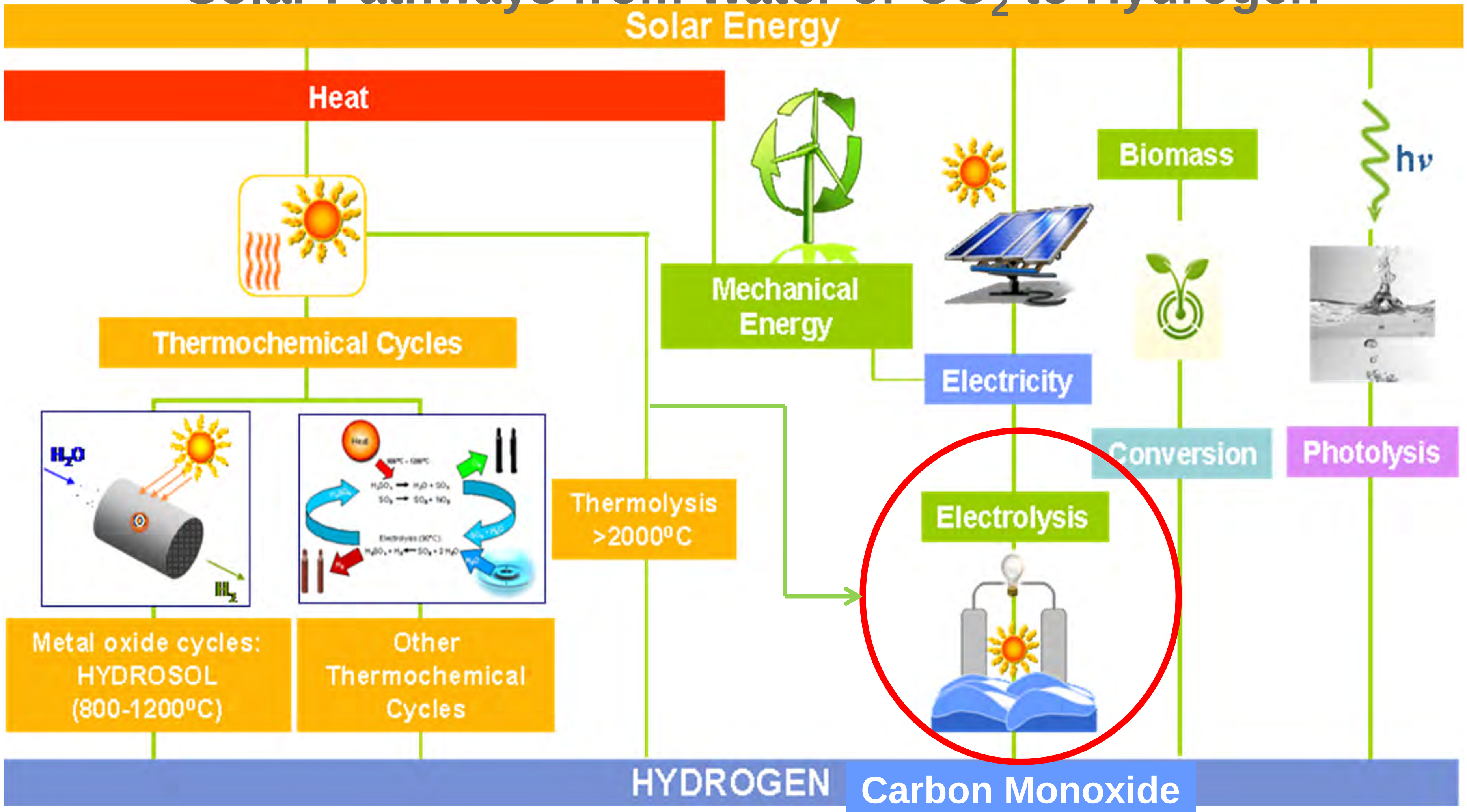


Lebros et et al, IJHE 2010



- 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
  $\rightarrow$ optimistic 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 Hydrogen



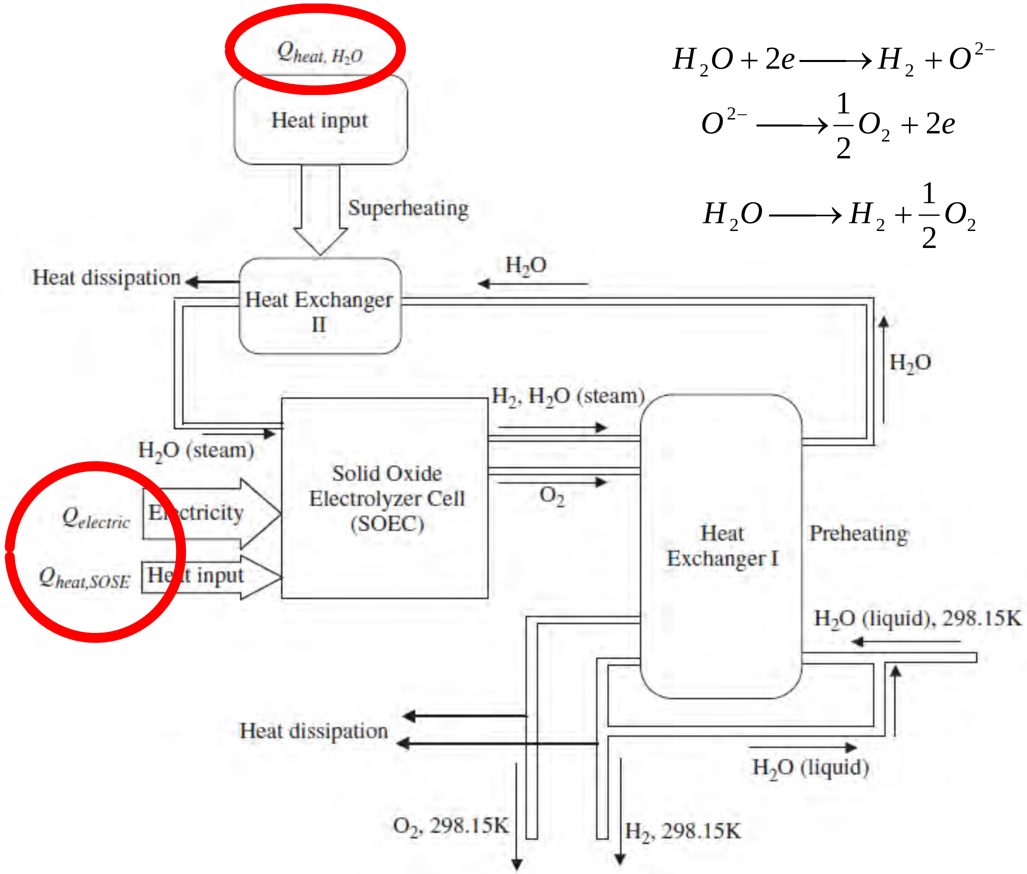
High temperature electrolysis process

- 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 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.

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

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

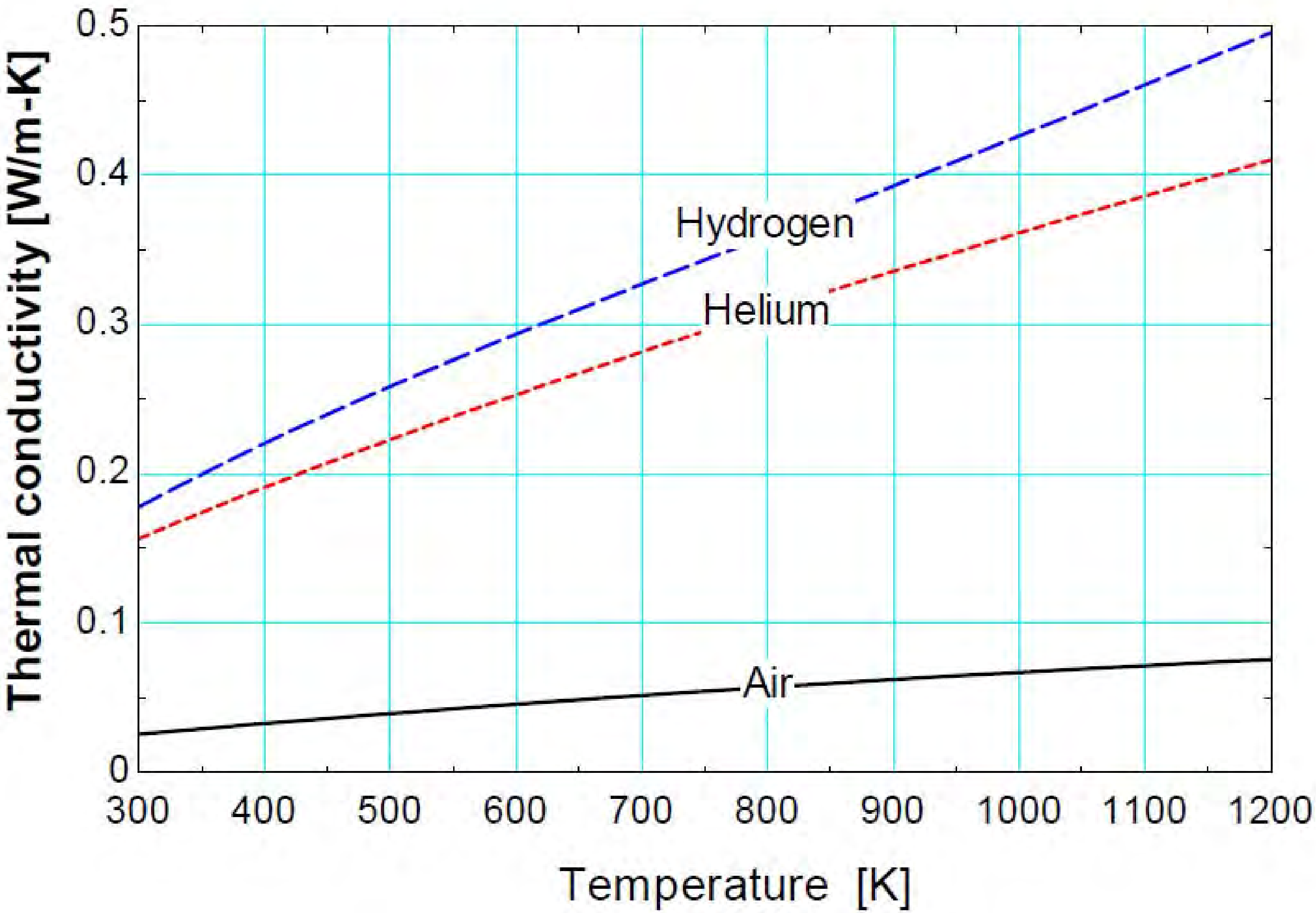
$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$



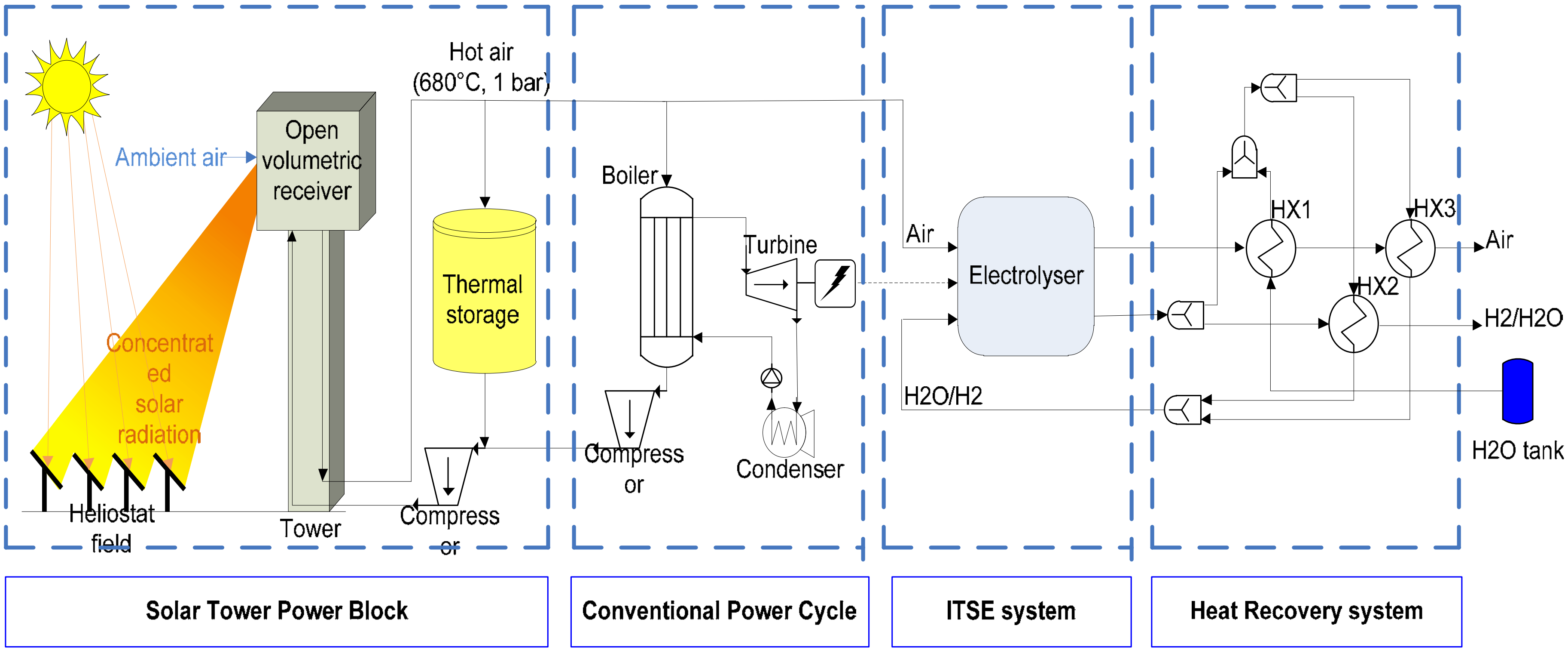
Economic analysis

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

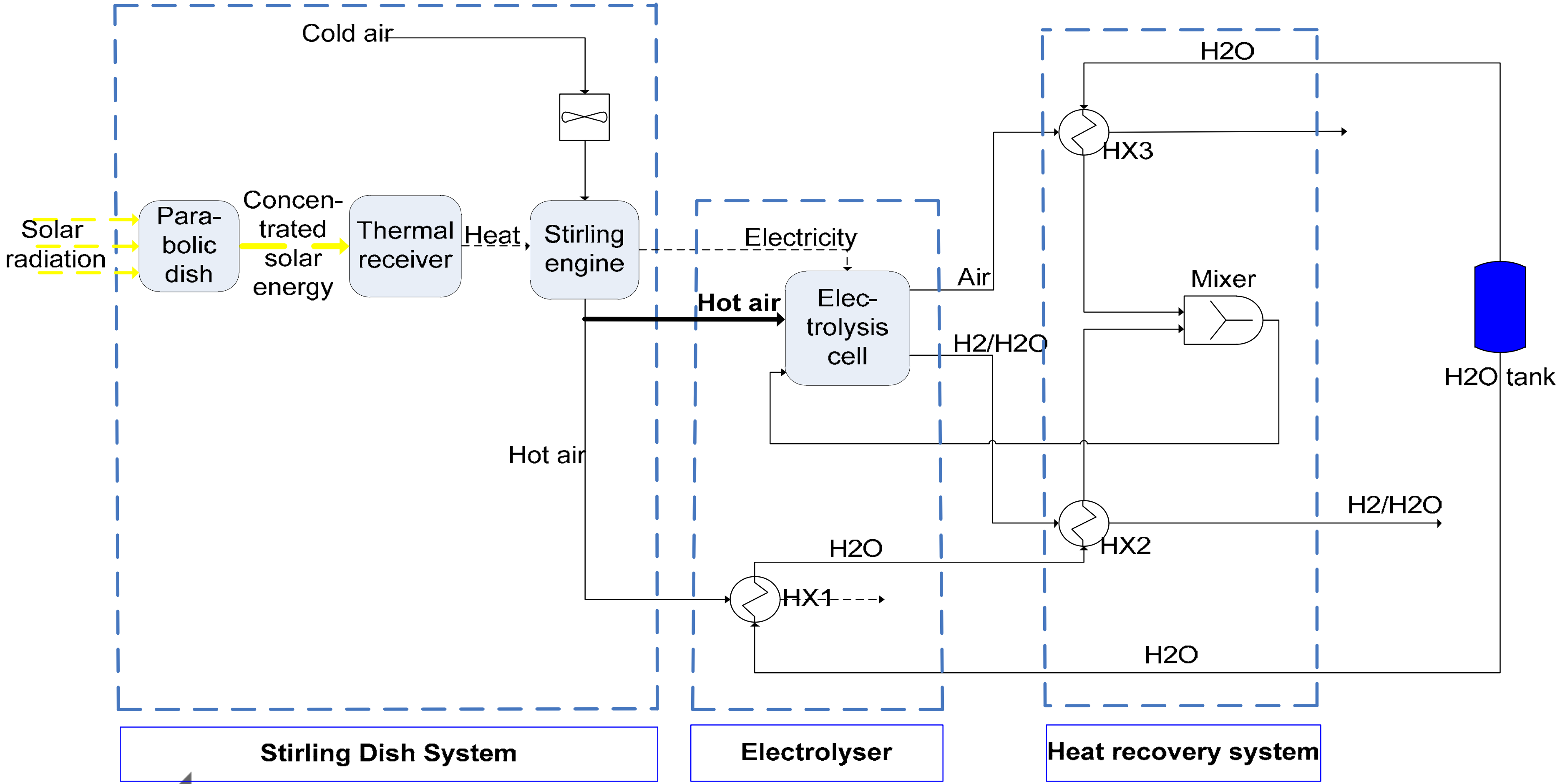
Thermal conductivity of working fluids



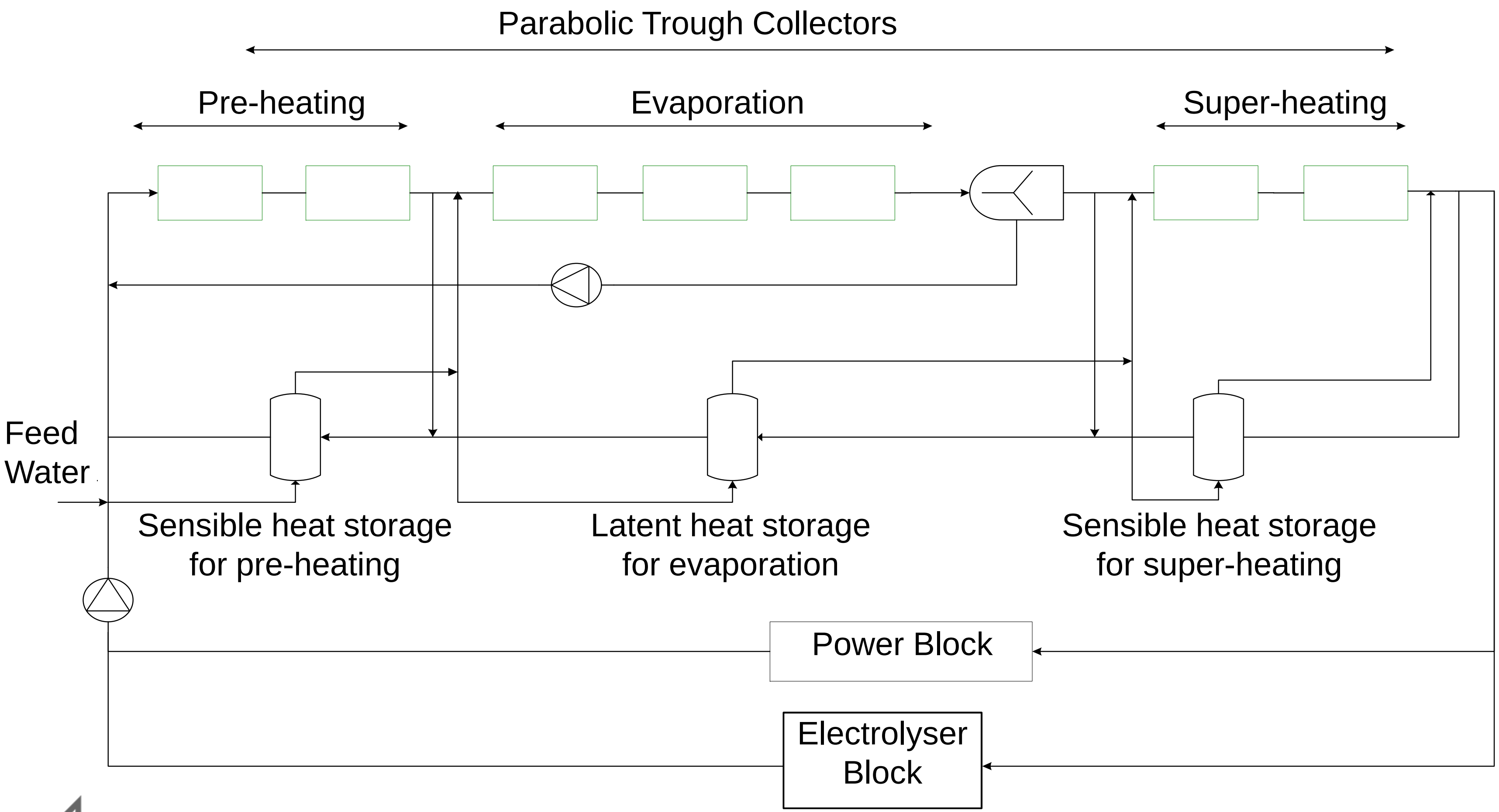
Flow diagram of the coupling of the solar power tower with the electrolyser



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



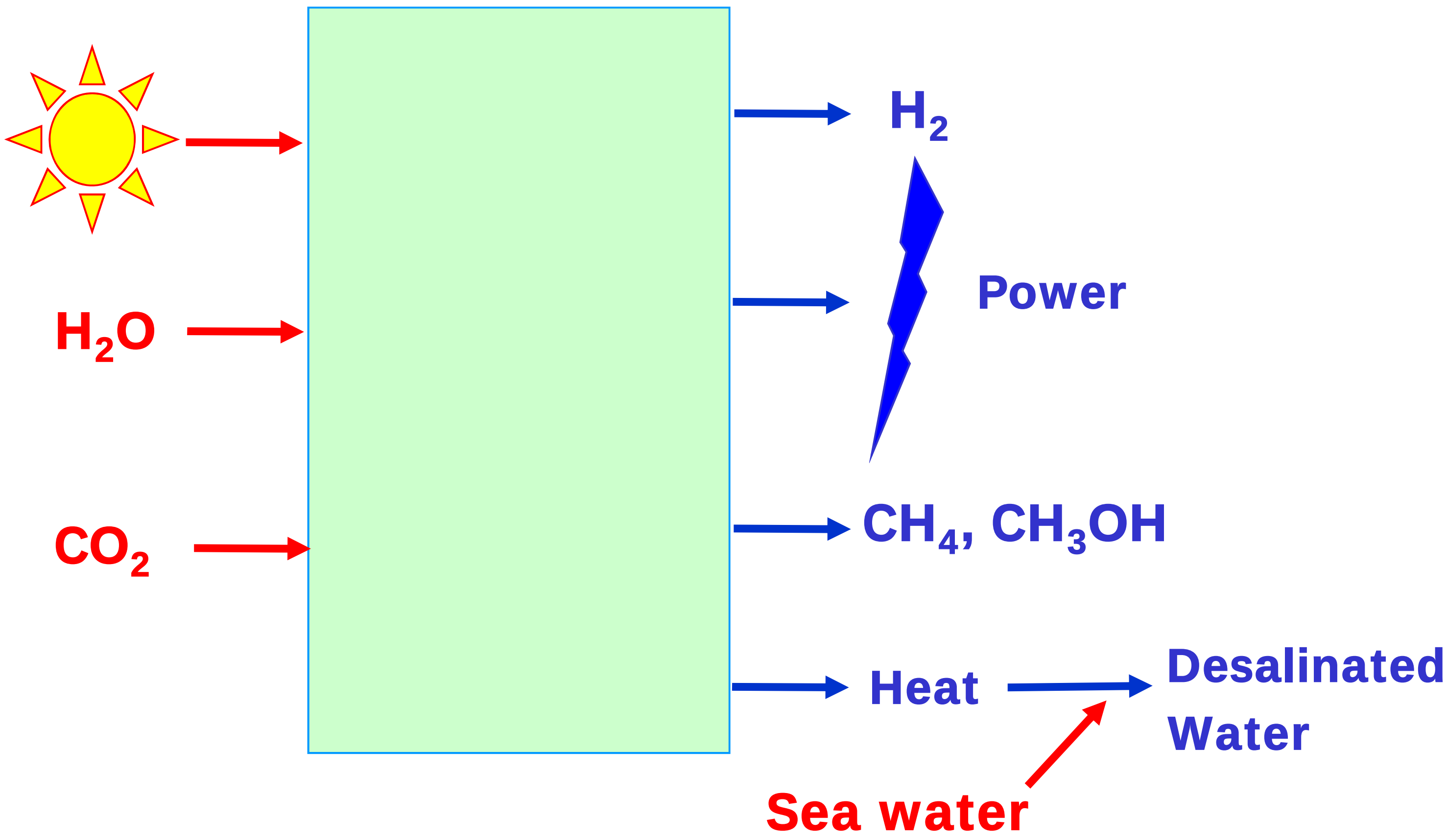
Flow Diagram of the coupling of the parabolic trough to the electrolyser



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.

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DLR H_2 Aircraft
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Thank you very much for your attention!

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