Solar Fuels – work carried out by the German Aerospace Center

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DLR

Introduction

- Introduction of DLR
- Solar Fuels – wide variety with great perspectives
- Drivers for solar (thermal) fuels
- Synergies with industrial processes
    - Connections to fossil ressources
- Innovative processes
- Summary and Outlook

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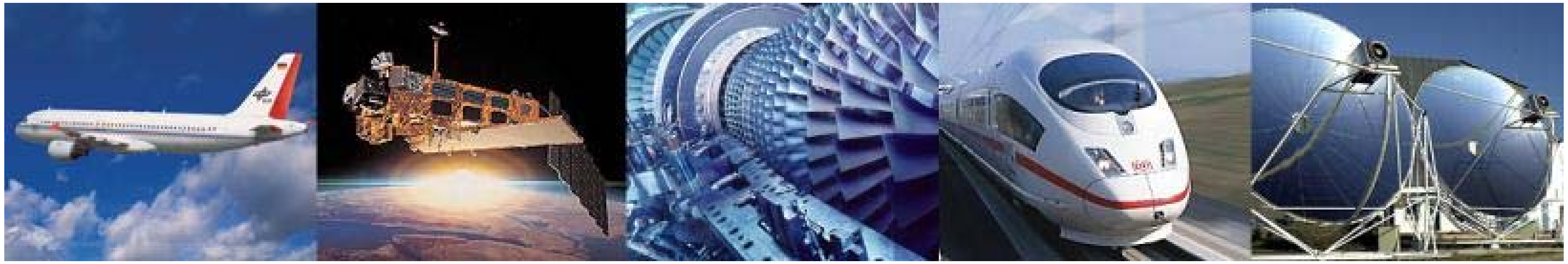

- Research Institution
- Space Agency
- Project Management Agency

Research Areas

- Aeronautics
- Space Research and Technology
- Transport
- Energy

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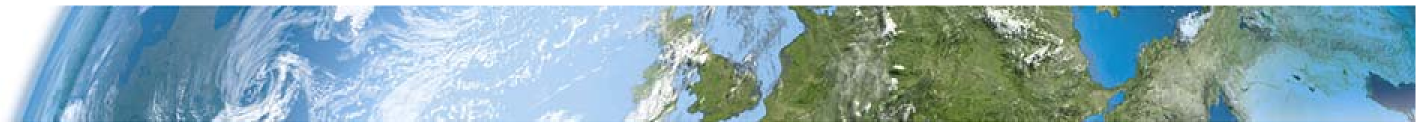


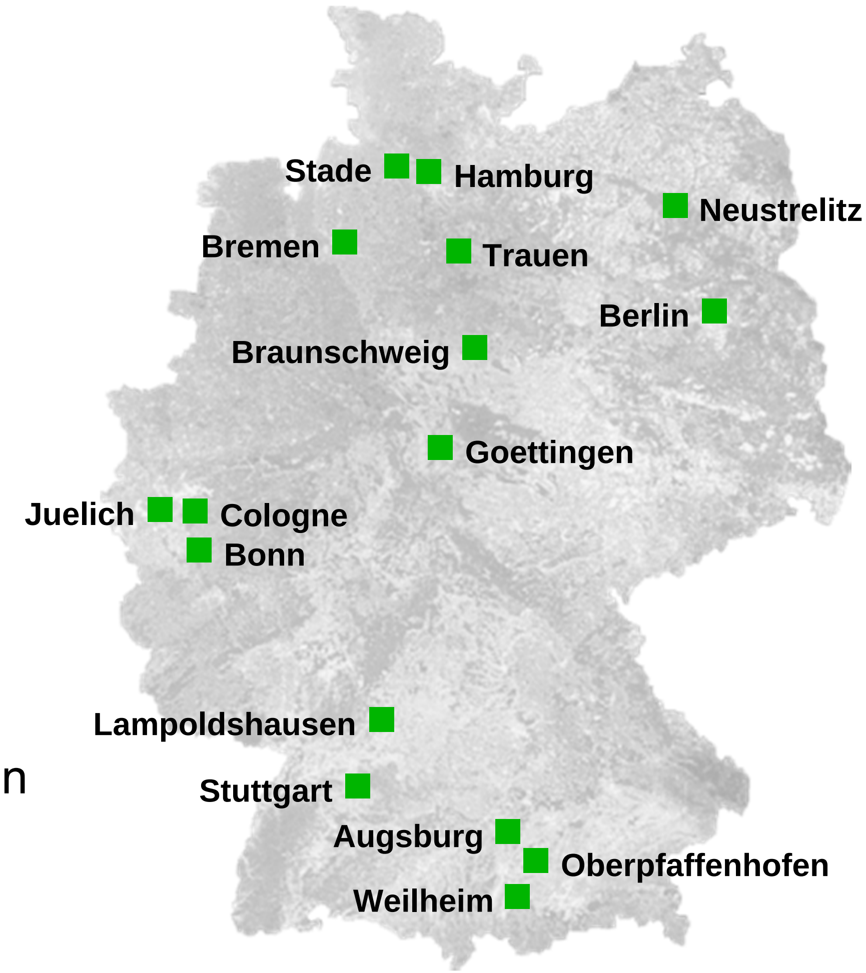
Locations and employees

7700 employees across
32 institutes and facilities at

- 16 sites.

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

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



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

HGF POF III - TOPIC: *Solar Fuels*

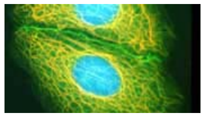
Speaker: R. van de Krol (HZB)
Deputy: C. Sattler (DLR)

Goal: To demonstrate stand-alone, viable systems for the production of chemical fuels with sunlight

Sub-Topics:

Thermochemical Routes — DLR

Photoelectrochemical Routes — HZB



Bioartificial Photosynthesis — UFZ

Systems Design — DLR, HZB, UFZ

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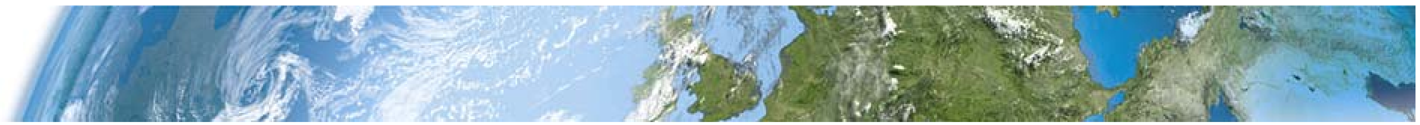

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Main Topic:

Solar Thermal Power Plants

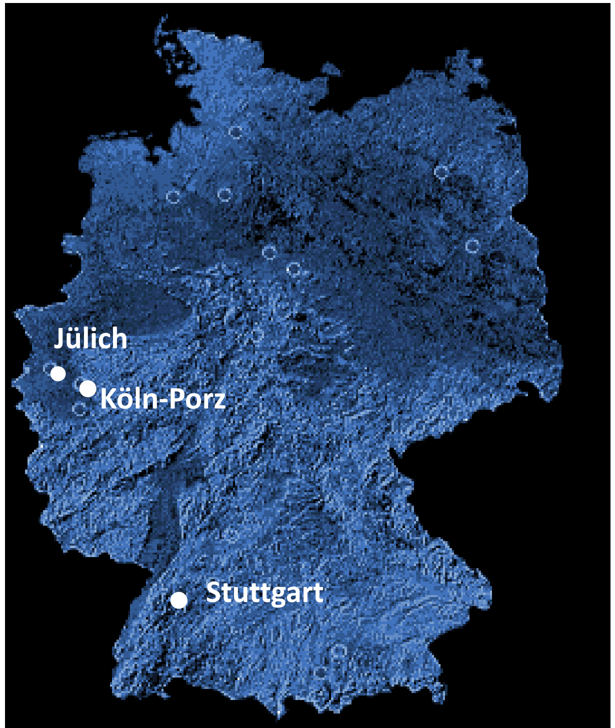
140 Persons

5 Departments, 4 Sites

Köln-Porz, Jülich

Stuttgart

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

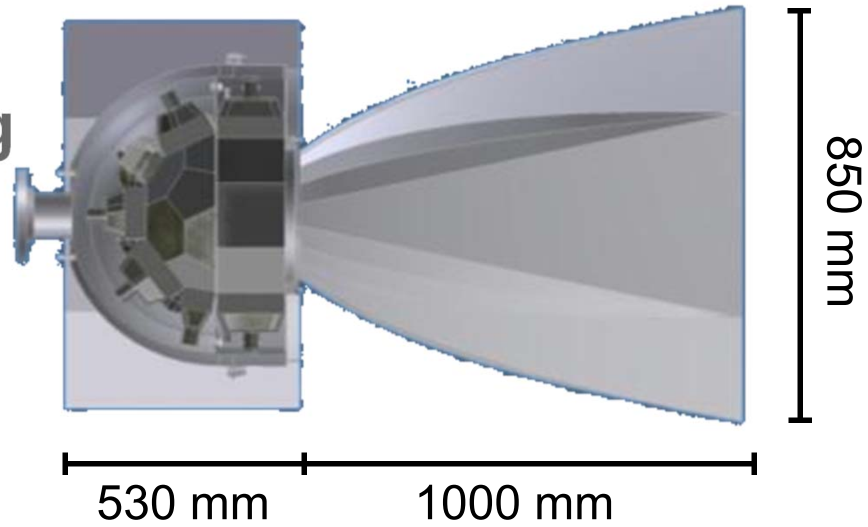


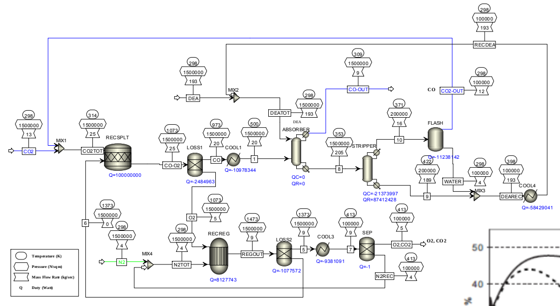
Competences of the Department of Solar Chemical-Engineering

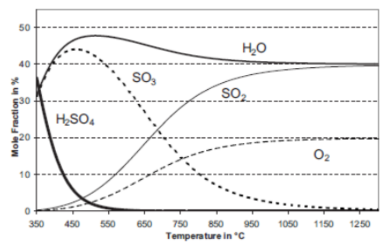
Development of components and processes

and

scientific, technologic and economic evaluation

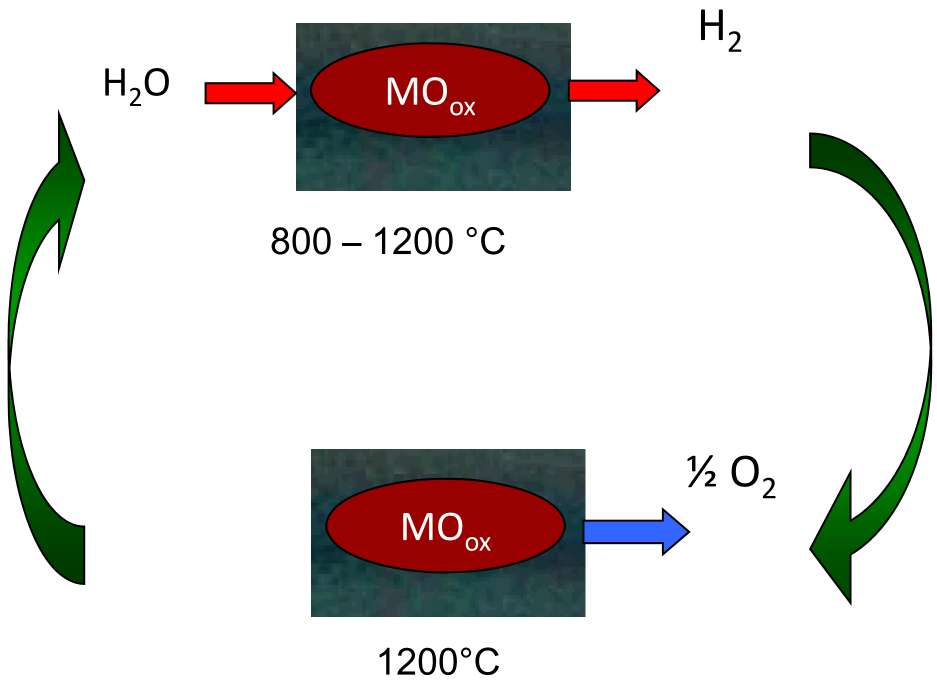






Solar Fuels

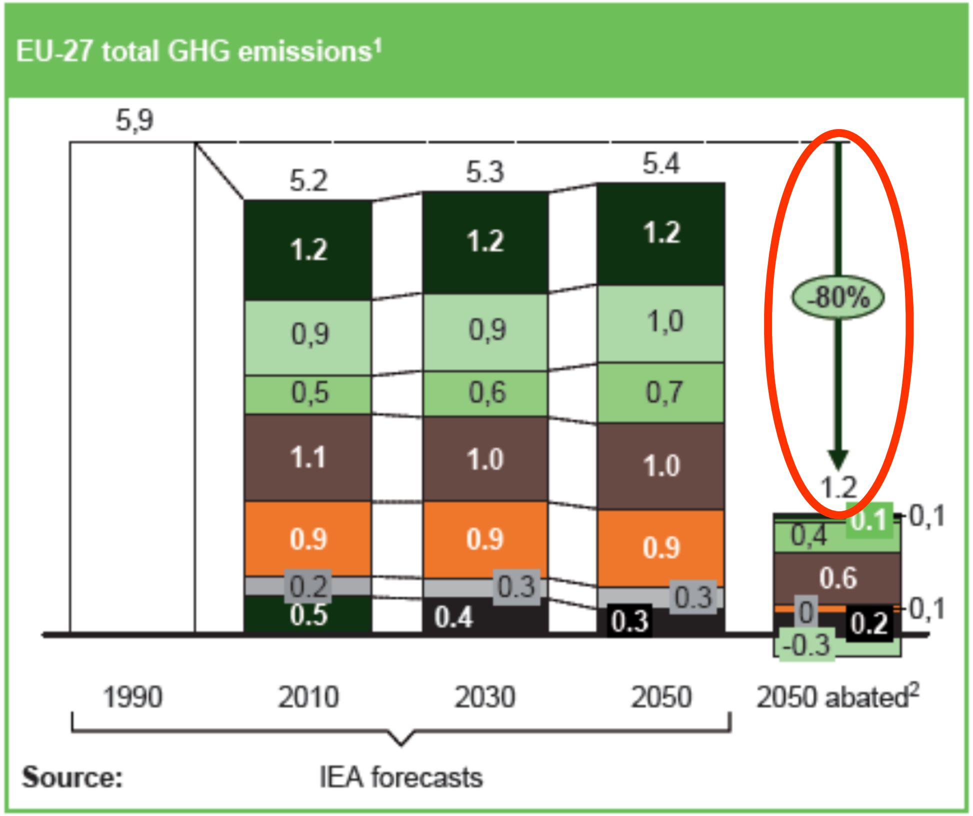
- > 20 years experience and international cooperation
- Processes
  - Reforming of NG
  - Thermo-chemical cycles
    - Sulfur
    - metal oxides
  - Solar HT electrolysis
  - Cracking of methane
  - Photo-catalysis
- Products
  - H_2, syn-gas, methanol, FT-Synfuels …



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

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

Development of EU GHG emissions [Gt CO_2e]



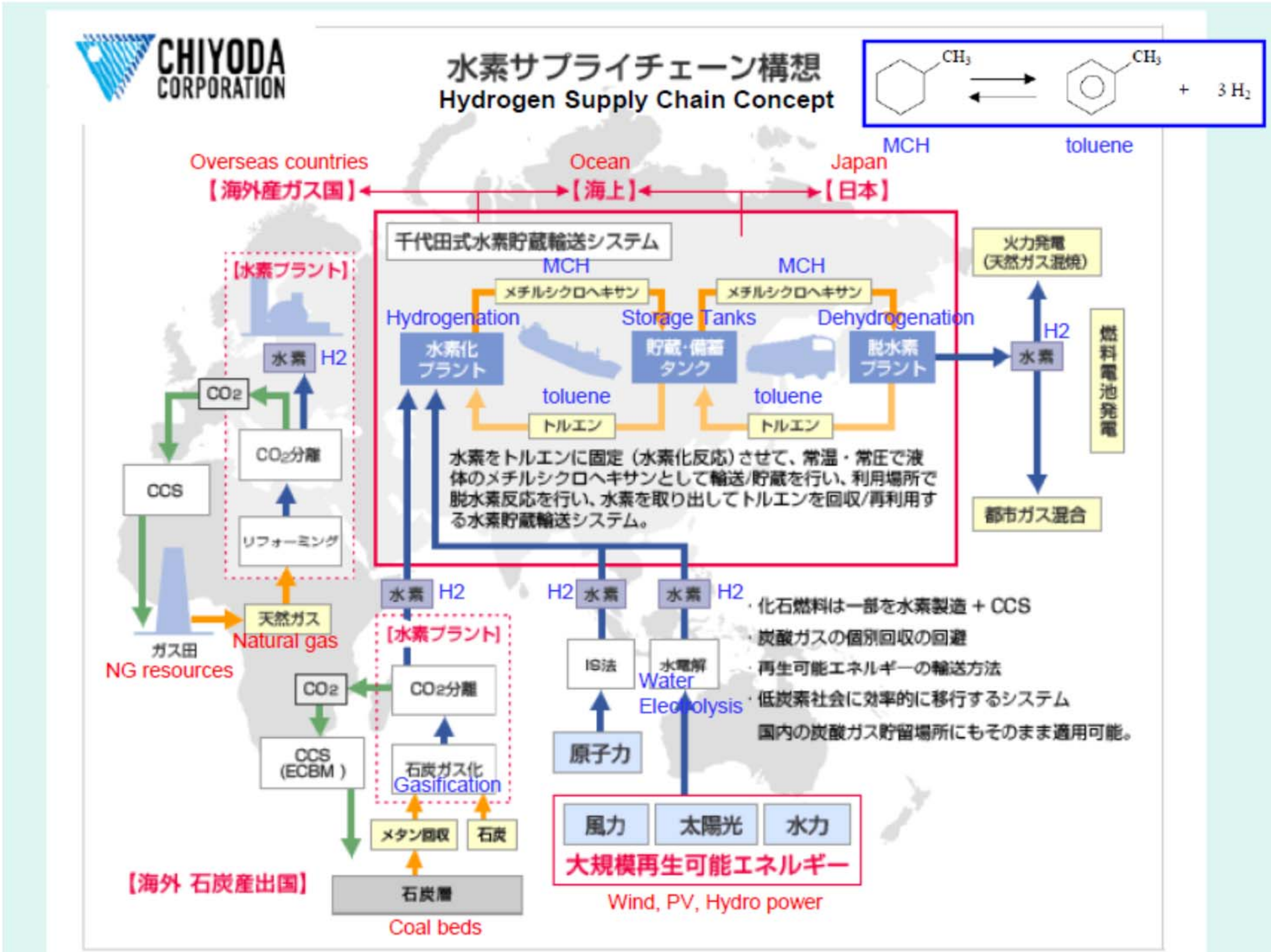
Sector	Total abatement
Power	95-100%
Road transport	95%
Air & sea transport	50%
Industry[3]	40%
Buildings	95%
Waste	100%
Agriculture	20%
Forestry	-0.25 Gt CO_2e

1 Large efficiency improvements are already included in the baseline based on the International Energy Agency, World Energy Outlook 2009, especially for industry
2 Abatement estimates within sector based on Global GHG Cost Curve
3 CCS applied to 50% of large industry (cement, chemistry, iron and steel, petroleum and gas, not applied to other industries)

SOURCE: www.roadmap2050.eu

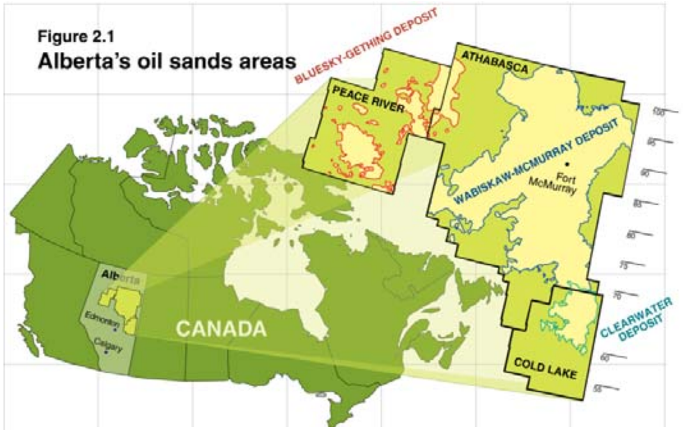
Hydrogen Vision by the CHIYODA Corporation

- Import of renewable hydrogen from Australia
- Cycling of the liquids Toluen and MCC (Methyle Cyclohexane)
- High storage capacity of 3 mols of H_2 in 1 mol of MCC

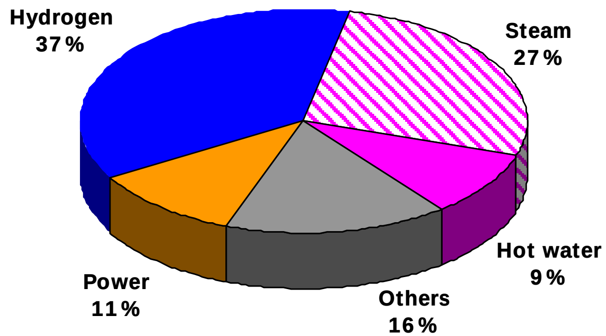


Canadian Oil Sands – Vision by Alberta Innovates

- In 2011, 3MM bpd of oil from Alberta, 59% from oil sands
    - Oil sands account for 38.2% of GHG in Alberta (2010)
- H_2 production is #1 source of CO_2 emissions/bbl
    - Up to 2000 scf H_2/bbl needed to turn bitumen into synthetic crude
    - SMR is the main technology
- Solar fuels as GHG mitigation alternative to CCS



GHG sources - synthetic crude



Source: S. Trottier et al., Alberta Innovates, Canada

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Hydrogen for Mobile Applications - Hyundai

- In early 2012, a Hyundai ix35 Fuel Cell set a range record for hydrogen cars by driving from Oslo to Monaco using only existing fuelling stations
- Production of the Hyundai ix35 Fuel Cell began in January 2013, making Hyundai the first automaker to begin commercial production of a hydrogen-powered vehicle.
- Hyundai plans to manufacture 1.000 units of the hydrogen-powered ix35 Fuel Cell vehicles by 2015, targeted predominantly at public sector and private fleets, with limited mass production of 10.000 units beyond 2015.

Toyota

- Successful startup: -30° Celsius
- Extended cruising range: 830km (JC08 mode) without refueling

- A sedan-type next-generation fuel-cell concept is planned for launch in about 2015.

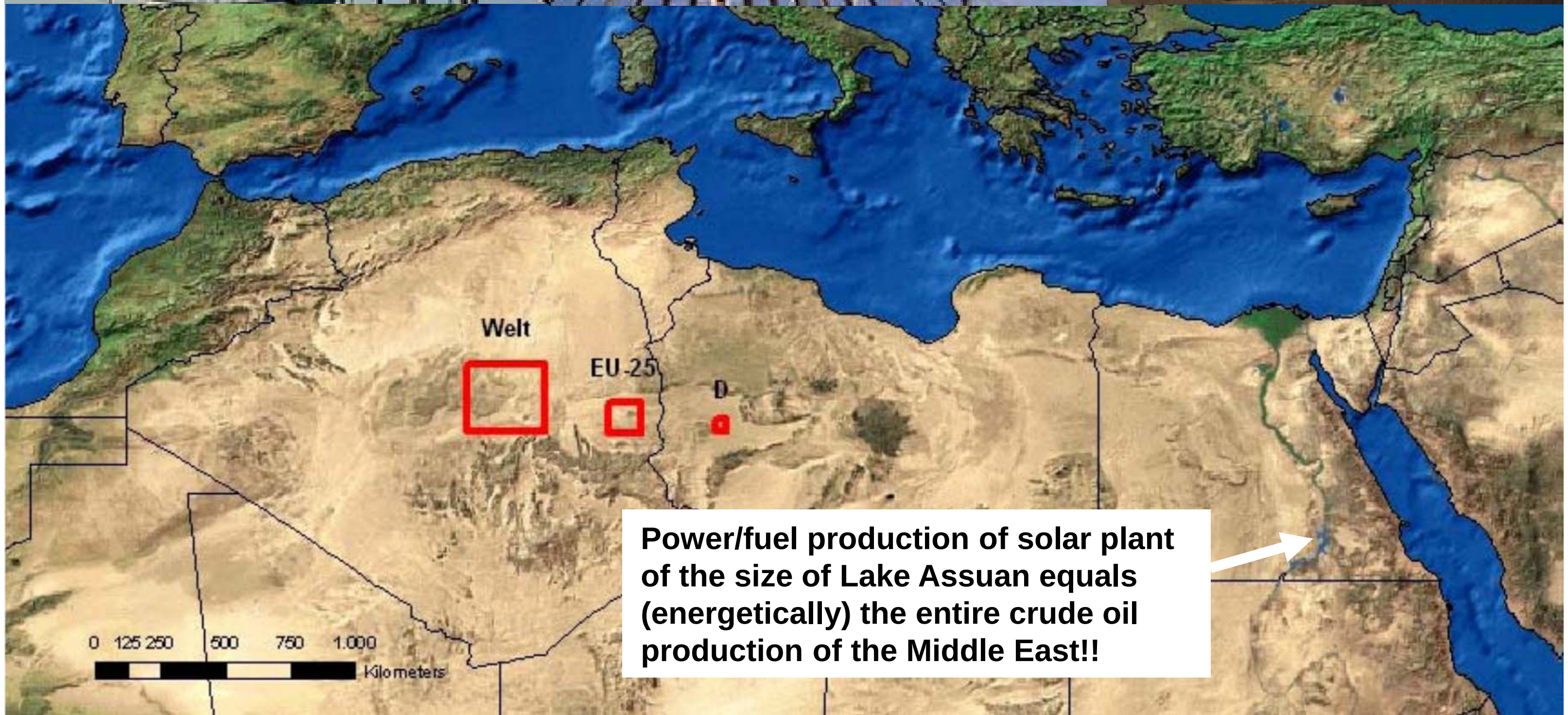
- Toyota says it will be among the first manufacturers to bring hydrogen-powered vehicles to the European market in 2015. The company has also said it will start selling fuel cell vehicles in the US in 2015, first in California.

Hydrogen Planes?

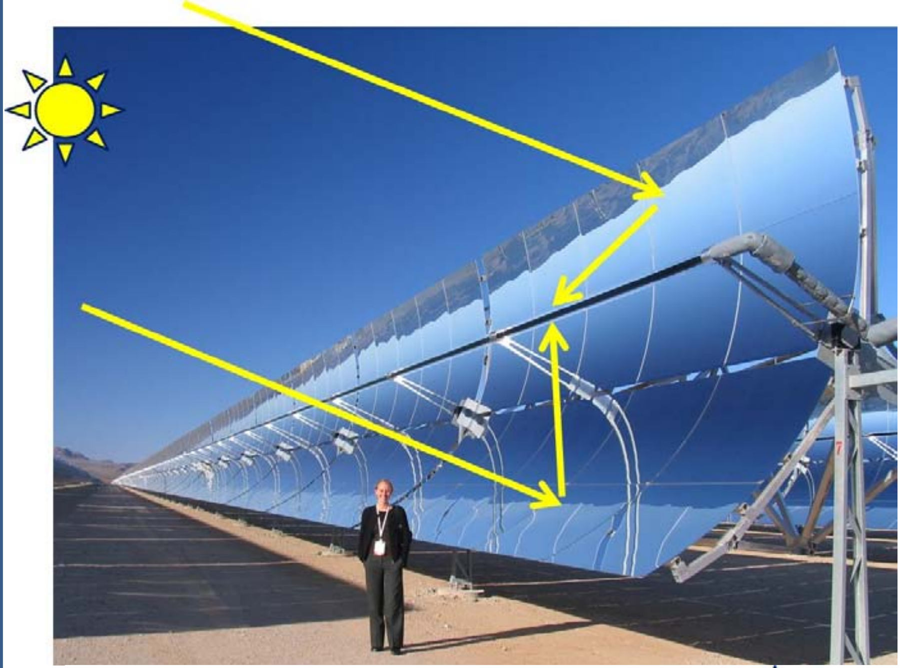
- Standard for rockets – e.g. ARIANE V
- Proven for jet planes in the 1980s e.g. by Tupolev and for small fuel cell aircrafts e.g. DLR Antares
- Safety advantage – most casualties because of burning cerosene, hydrogen would be gone instantly (burning batteries are even worse)
- But unlikely for mass application in the next decades because of the existing proven and expensive infrastructure, long lifetime of aircrafts

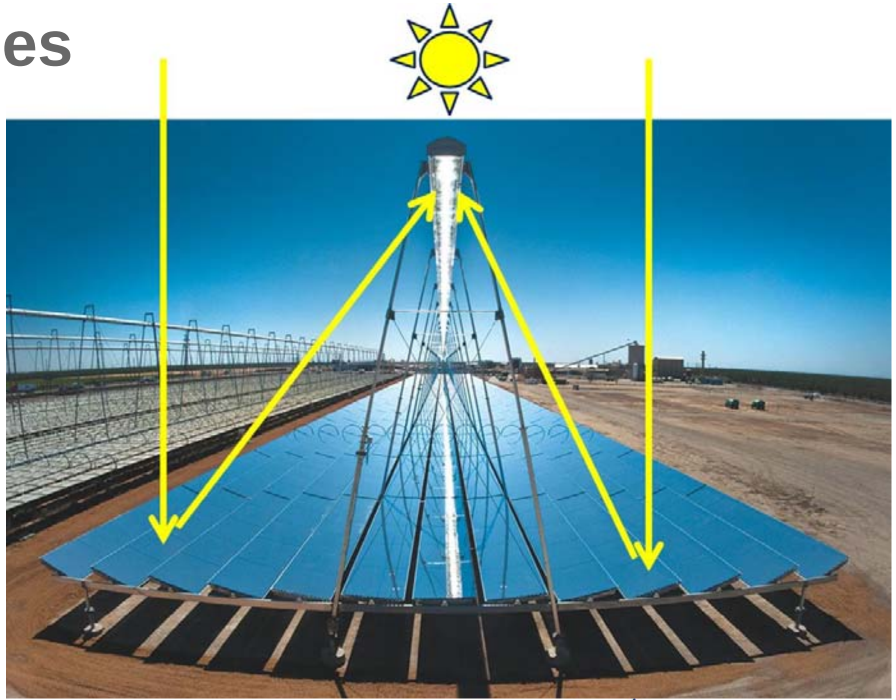
Need for liquid fuels with very high quality and reduced carbon foot print - Solar Jet Fuels!

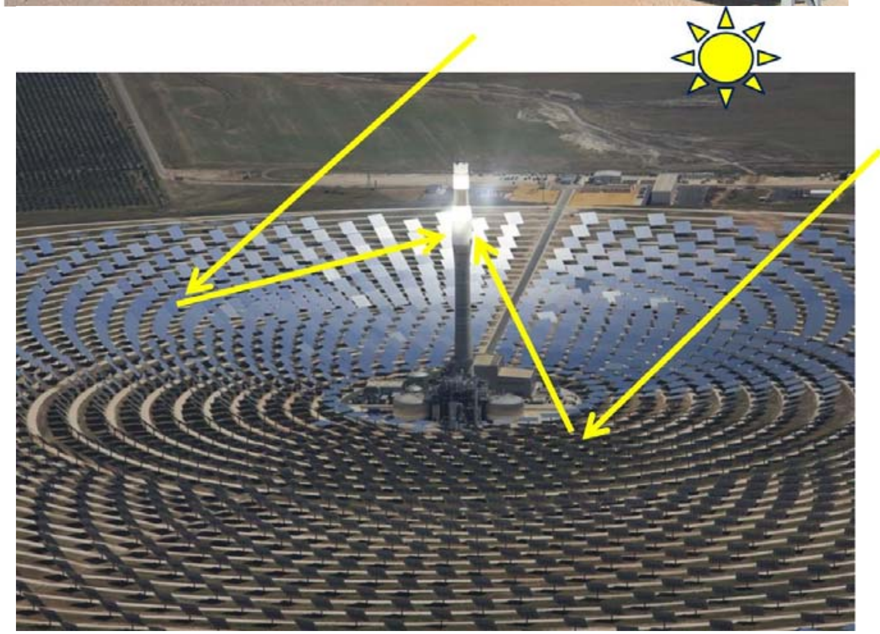
Potential of Solar Energy

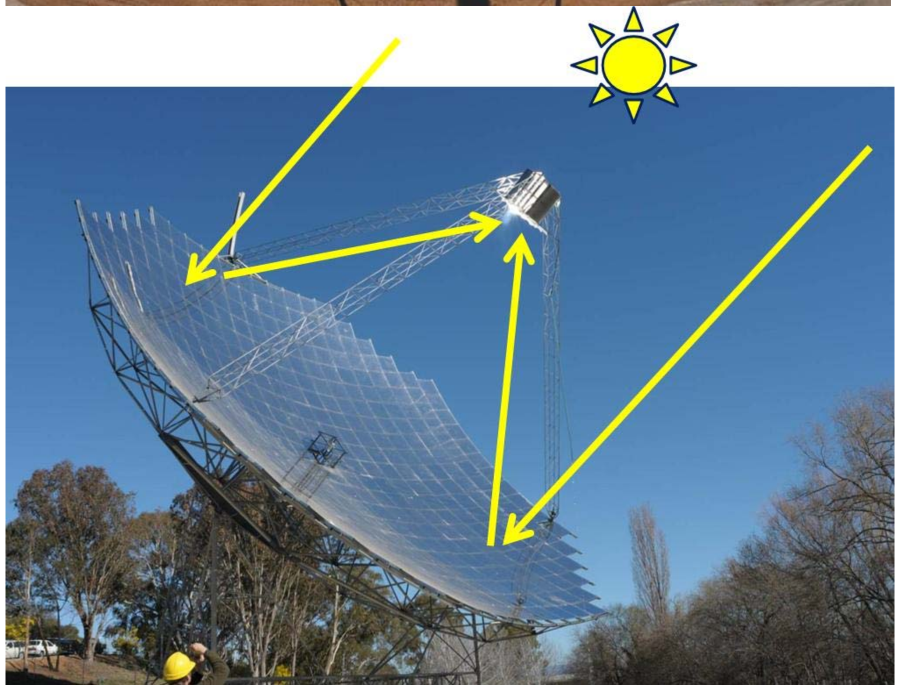


Concentrating Solar Approaches





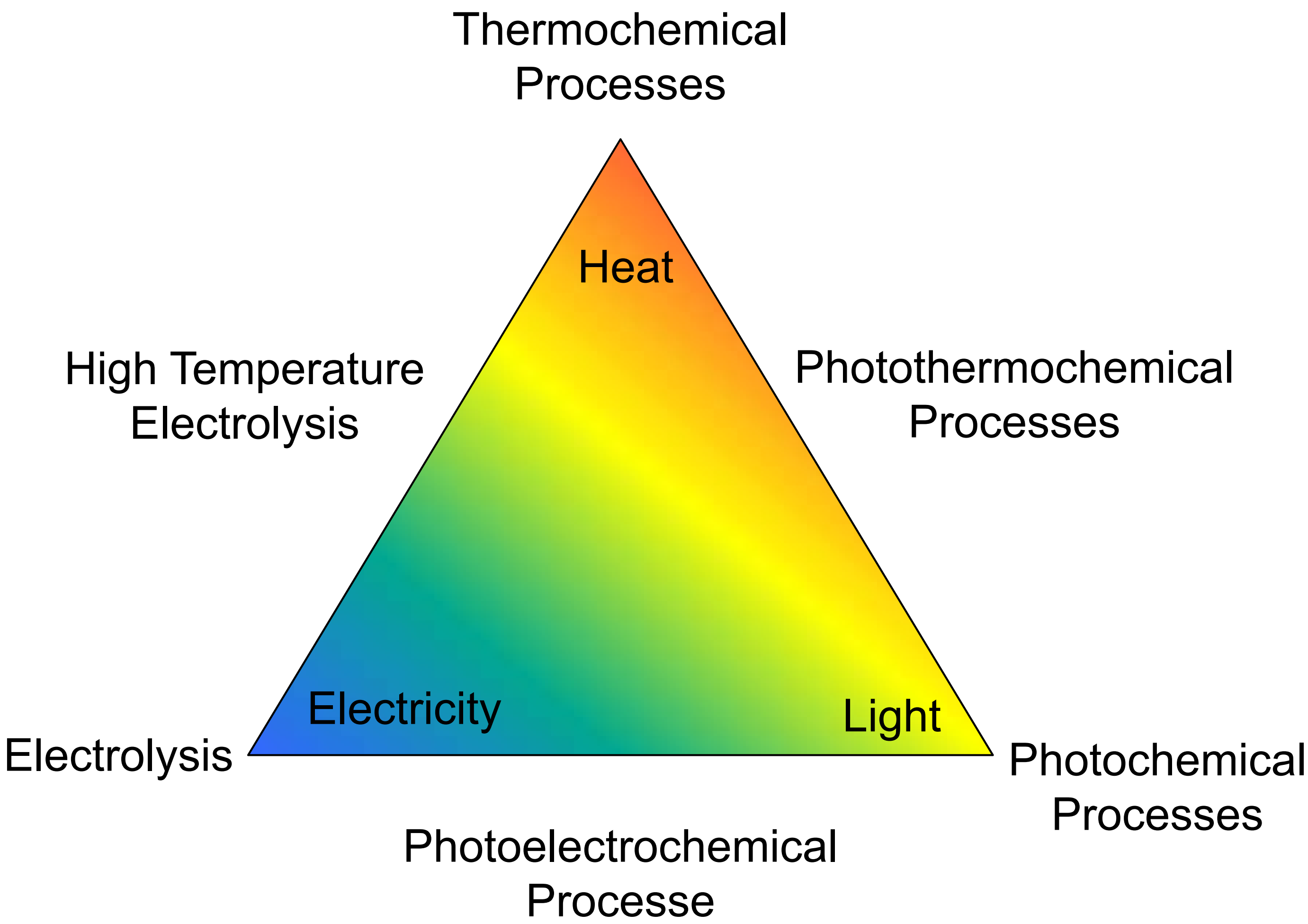


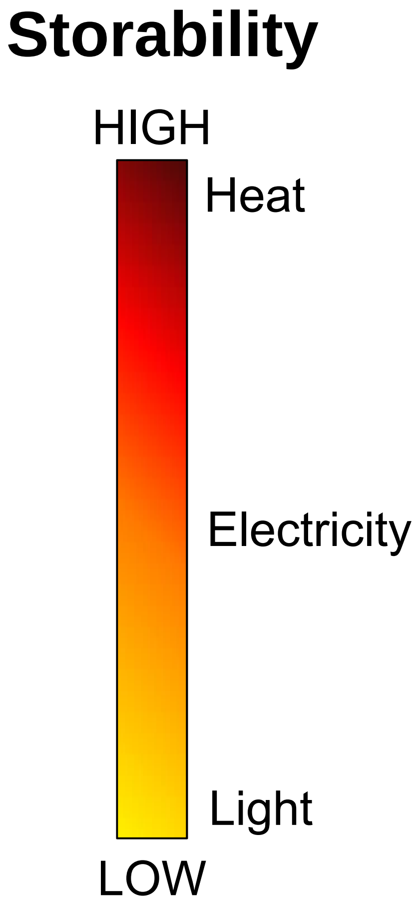


Chemical energy storage = very high energy densities

Technology	Energy Density (kJ/kg)
Hydrogen	142000
Gasoline	45000
Sulfur	12500
Cobalt Oxide Redox-cycle	850
Lithium Ion Battery	580
Molten Salt (Phase Change)	230
Molten Salt (Sensible)	155
Elevated water Dam (100m)	1

Energy Provision and Storability





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Solar Chemistry instead of Solar Power

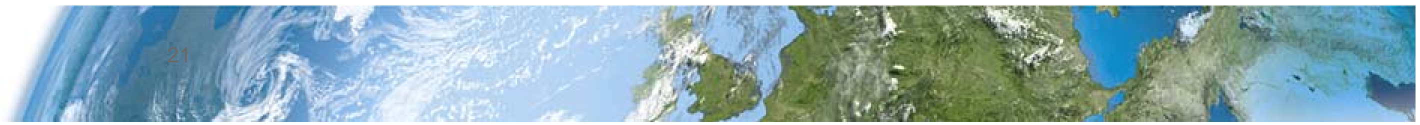
- Solar Thermochemistry is efficient bcompared to solar powered Electrochemistry because energy conversion steps are reduced!
  - Example: Hydrogen production: $H_2O \rightarrow H_2 + \frac{1}{2} O_2$
  - Solarchemical: 2 conversions
    - Solar radiation – heat – Chemical reaction
  - Via solar power: 4 conversions
    - Solar radiation – heat – mechanical energy – electrical energy – chemical reaction
- Solar photo-chemistry uses the light directly without any conversion. Photo-chemistry can be economical if the reaction needs a large amount of photons
  - Example: Production of Caprolactam an intermediate for Nylon

    Annual production > 200,000 t (artificial light reduces the efficiency)

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



Established High Temperature Industrial Processes

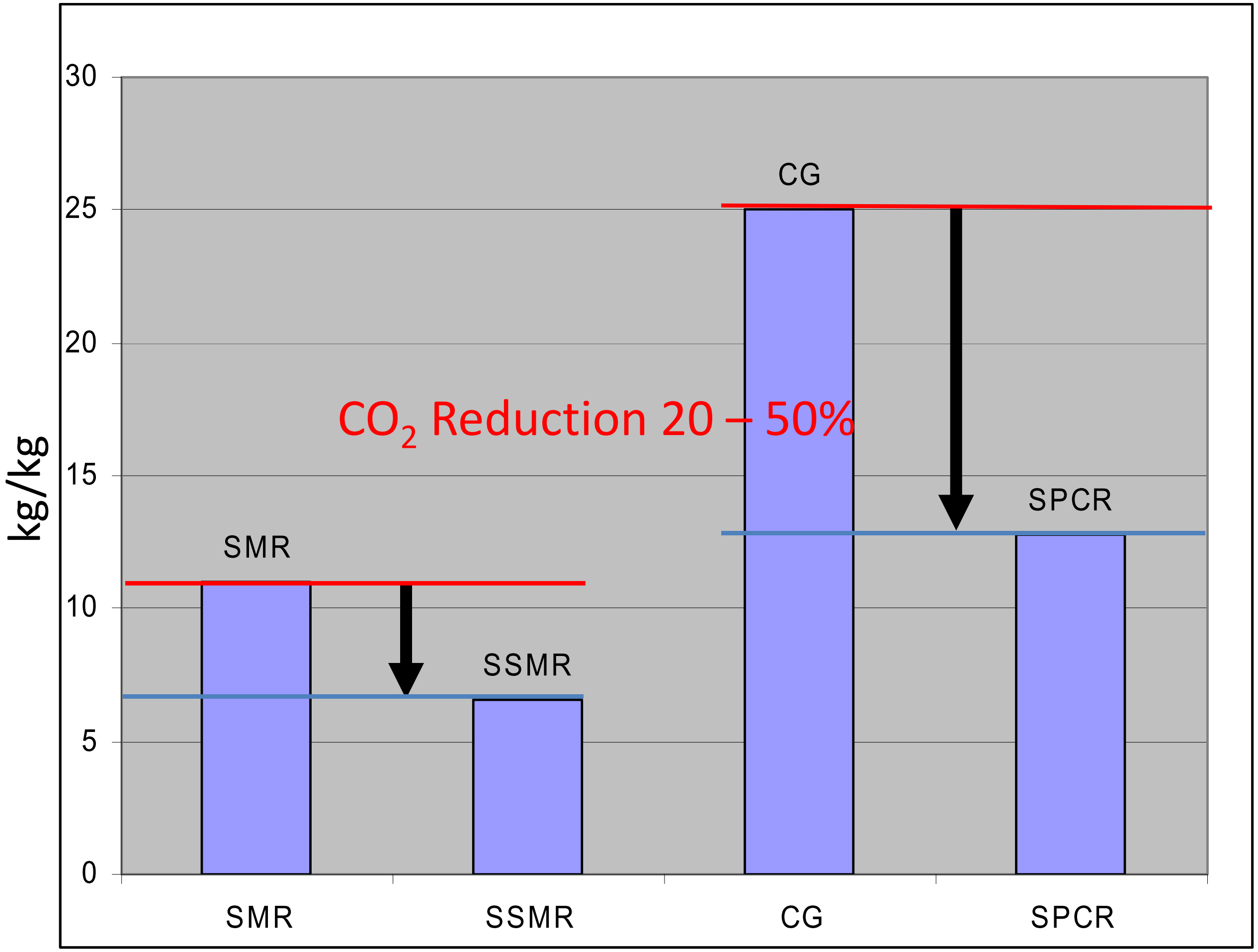
- Gasification and reforming of carbonaceous feedstock for the production of synthesis gas
    - Natural gas
    - Coal
    - Petcoke
    - Waste
    - Biomass

Goal: Fuels with reduced CO_2 emissions for power production but also for air, land, and, sea transportation

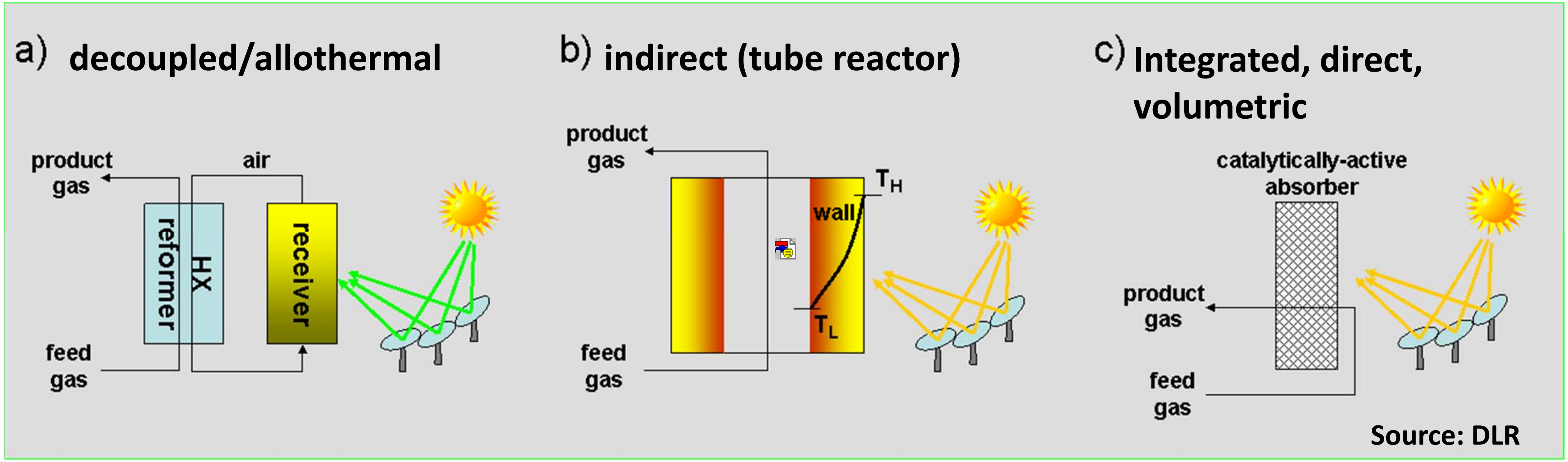
- Sulfuric acid splitting
    - Sulfuric acid production

Goals: Reduction of emissions, raise of efficiency, production of heat and hydrogen

CO_2 Reduction by solar heating of steam methane reforming and coal gasification



Solar Methane Reforming – Technologies



a) decoupled/allothermal

Reformer heated externally (700 to 850°C)

Optional heat storage (up to 24/7)

Development: Australia, Germany, Israel, Spain, USA

E.g. ASTERIX project

b) indirect (tube reactor)

Irradiated reformer "tubes" filled with catalysts or molten salt (up to 850°C), temperature gradient

Approx. 70 % Reformer-h

Development: Australia, Germany, Israel, Italy, Japan, and the USA

E.g. Australian solar gas reformers,

c) Integrated, direct, volumetric

Catalytic active direct irradiated absorber

Approx. 90 % Reformer-h

High solar flux, works only by direct solar radiation

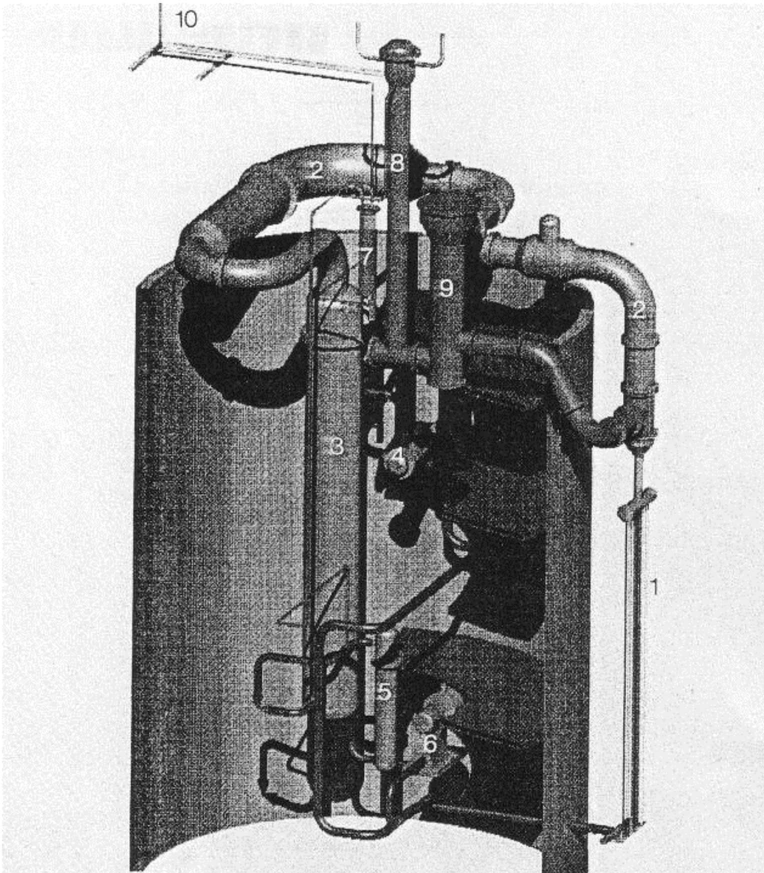
Development: Germany, Israel, Japan

e.g. SOLREF project

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
- 2011 CSIRO, Australia, tested a 600 kW plant

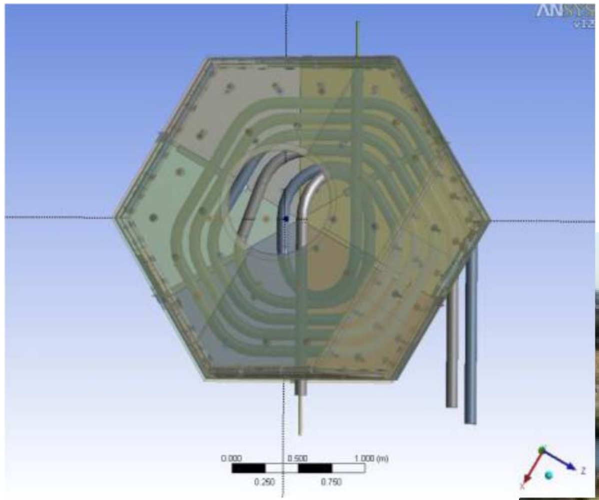
CESA-1, PSA, Spain. The solar radiation is collected by a field of heliostats and redirected to a tower, where different platforms allow the tests of various receiver technologies.

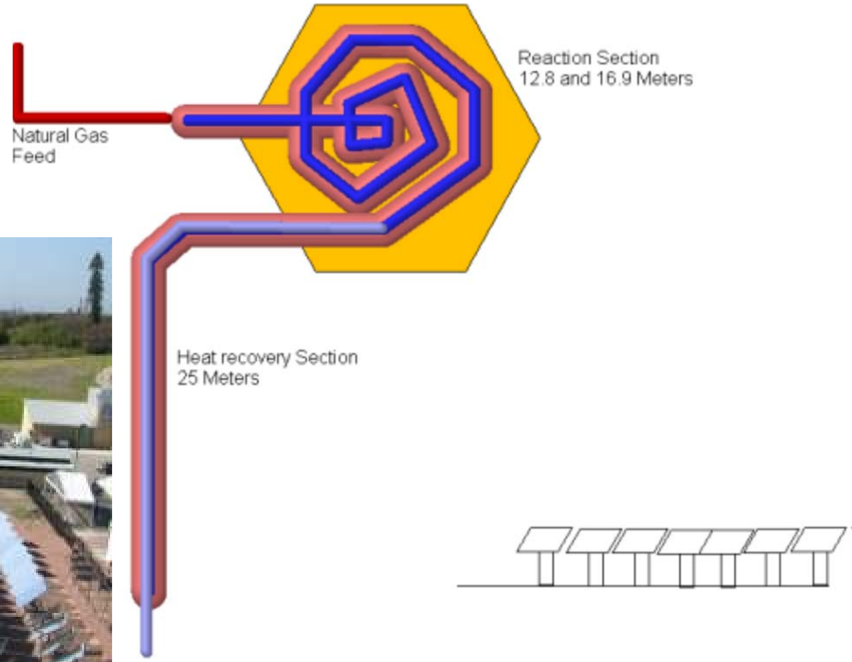


1 = Receiver, 2 = Heißgasleitungen, 3 = Rekuperator, 4 = Elektrischer Heizer, 5 = Kühler, 6 = Kompressor, 7 = Kühler E-106/7, 8 = Reformer V-101 mit Wärmeübertragern E-102/3/4, 9 = Elektrischer Heizer E-105, 10 = Fackel Z-102.

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)

New High Temperature Industrial Processes

- Water splitting
  - Hydrogen is necessary for the production of all gaseous or liquid solar fuels

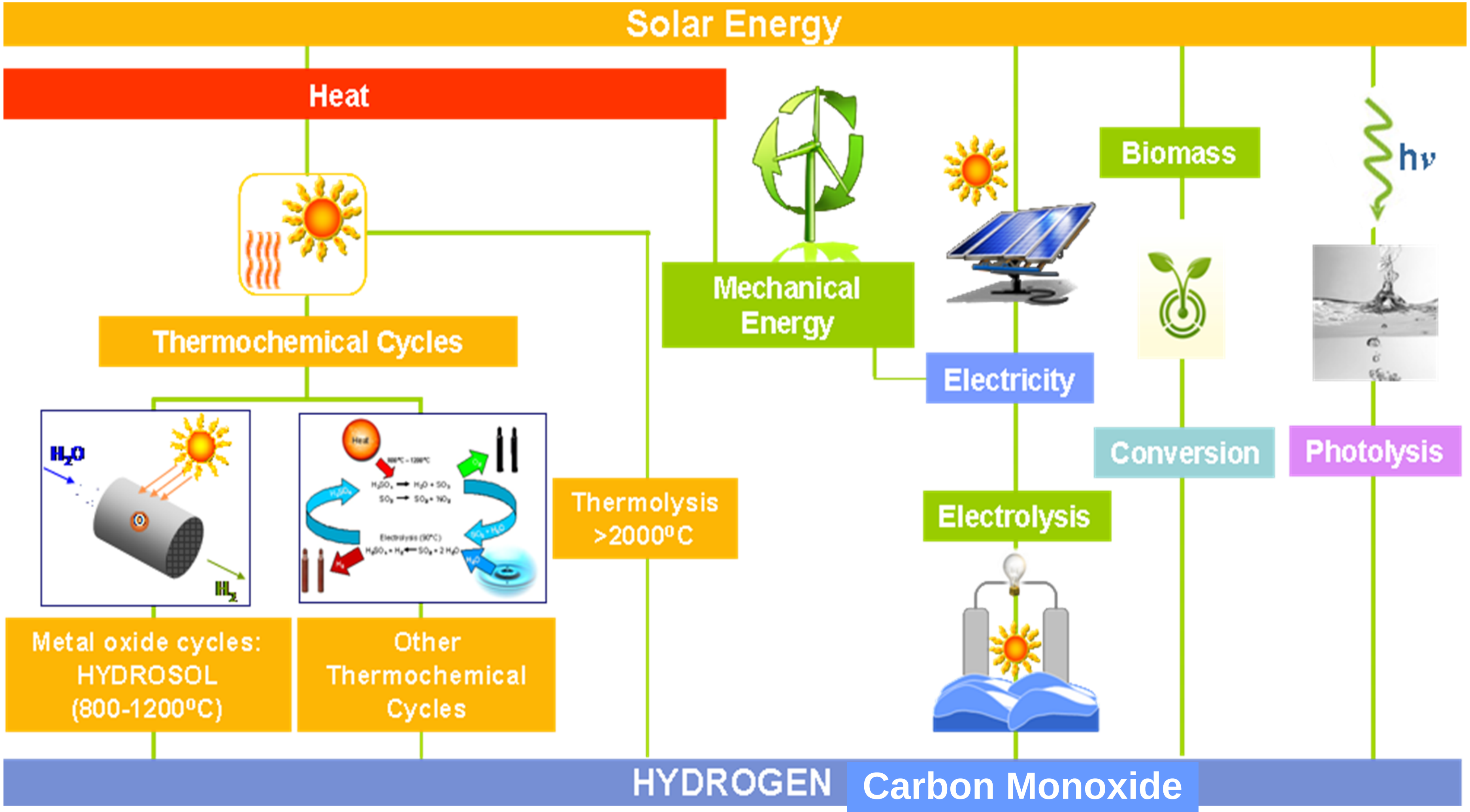
Goals:

  - Production of hydrogen for power generation and transportation (land, sea, and air?)
  - Upgrade of fossil recourses (oil sands, coal, natural gas)
  - Fertilizer production

- CO_2 splitting
  - If a suitable source is available it is possible to recycle CO_2 into new fuels
  - It needs lower temperatures but the efficiency depends crucially on the generation of a useful gas flow

Goals: Synthetic gaseous and liquid fuels

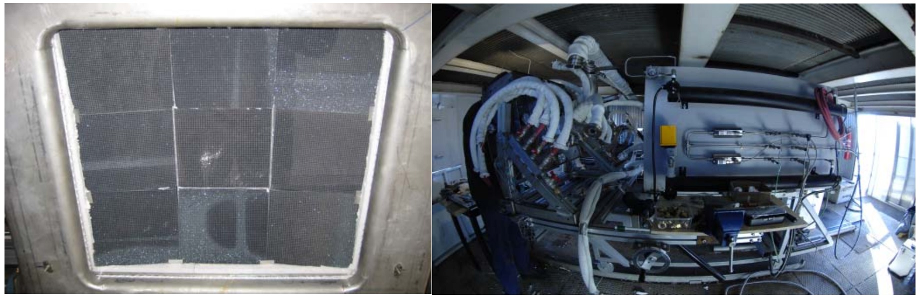
Solar Pathways from Water or CO_2 to Hydrogen or SynGas



Well researched Thermochemical Cycles

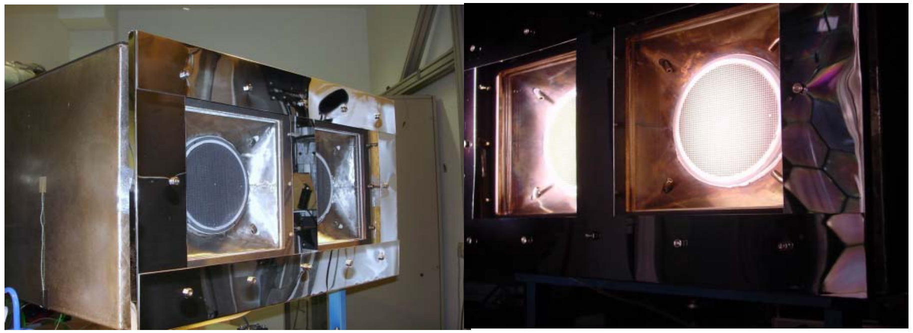
	Steps	Maximum Temperature (°C)	LHV Efficiency (%)
Sulphur Cycles			
Hybrid Sulphur (Westinghouse, ISPRA Mark 11)	2	900 (1150 without catalyst)	43
Sulphur Iodine (General Atomics, ISPRA Mark 16)	3	900 (1150 without catalyst)	38
Volatile Metal Oxide Cycles			
Zinc/Zinc Oxide	2	1800	45
Non-volatile Metal 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

HYDROSOL as a technology scale-up example

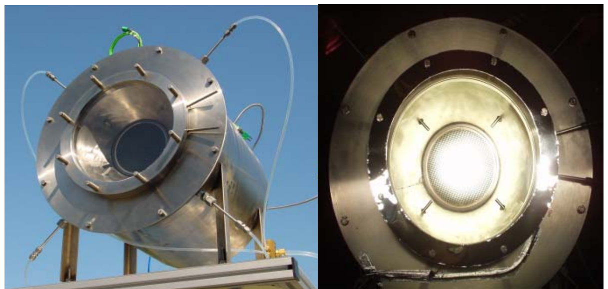


2008:
Pilot reactor (100 kW)

PSA solar tower



2005:
Continuous H_2 production

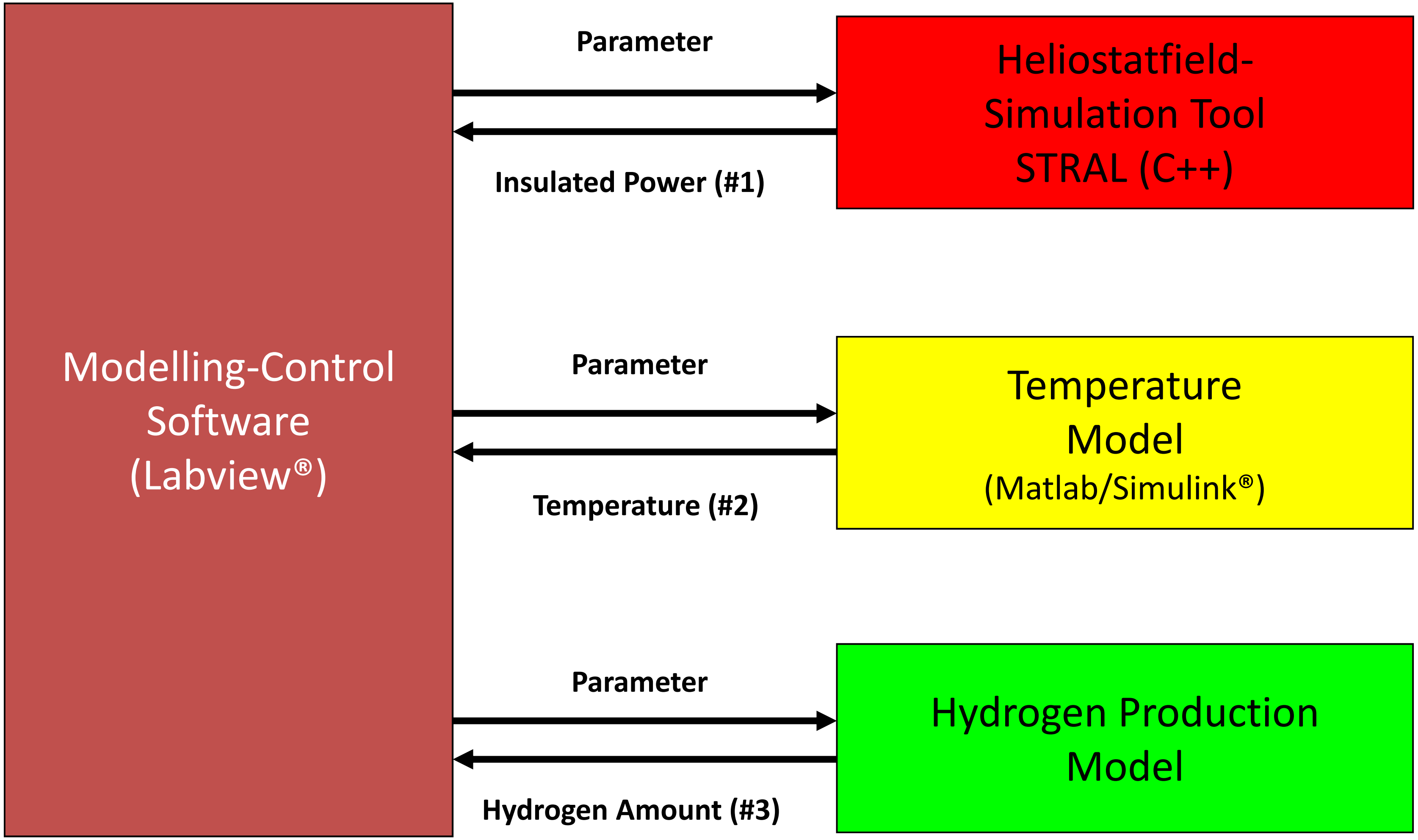


2004:
First solar thermochemical
H_2 production

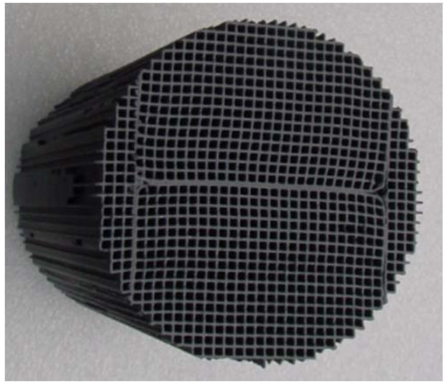
DLR solar furnace

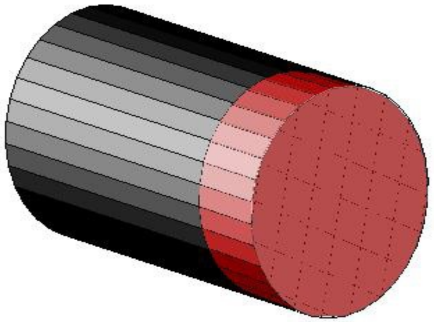
HYDROSOL II Pilot Reactor in Operation

Modelling of the pilot plant - Overview Modelling:

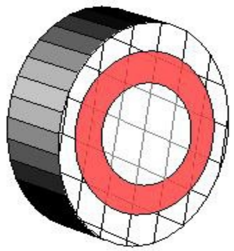


Discretization of honeycomb absorber

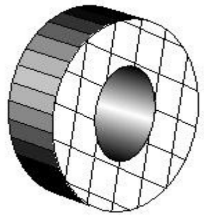




honeycomb structure



slice of honeycomb
(axial discretization)



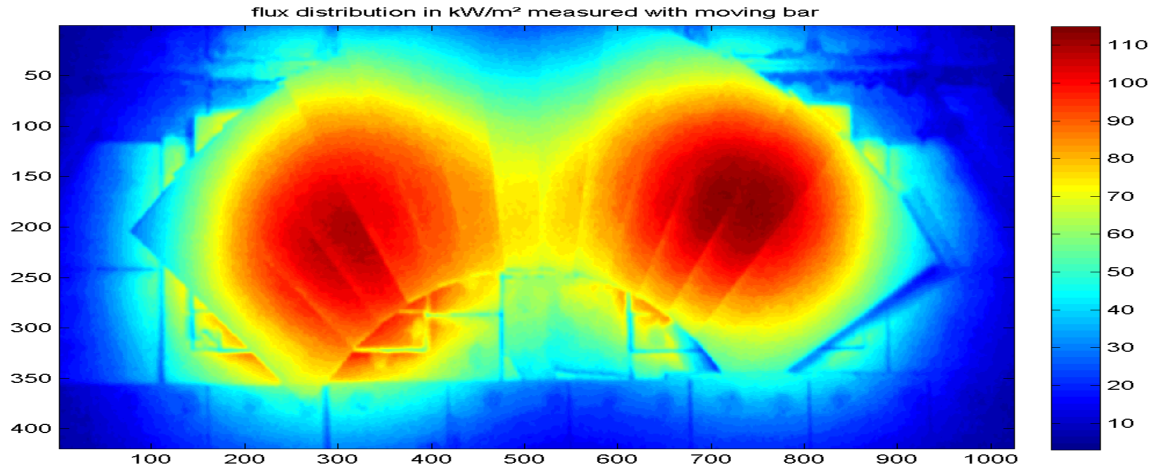
ring element of slice
(radial discretization)

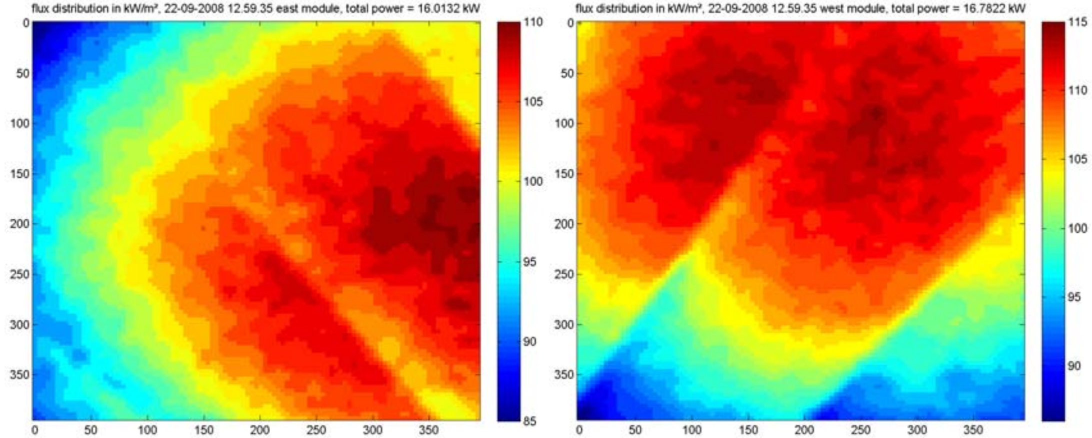
- Not every single channel is modeled separately
- Honeycomb discretized into
  - Rotation-symmetric rings in radial direction
  - Slices in axial direction
- For each ring element one channel is modeled representing all channels of ring

Experiments – Process Control Software:

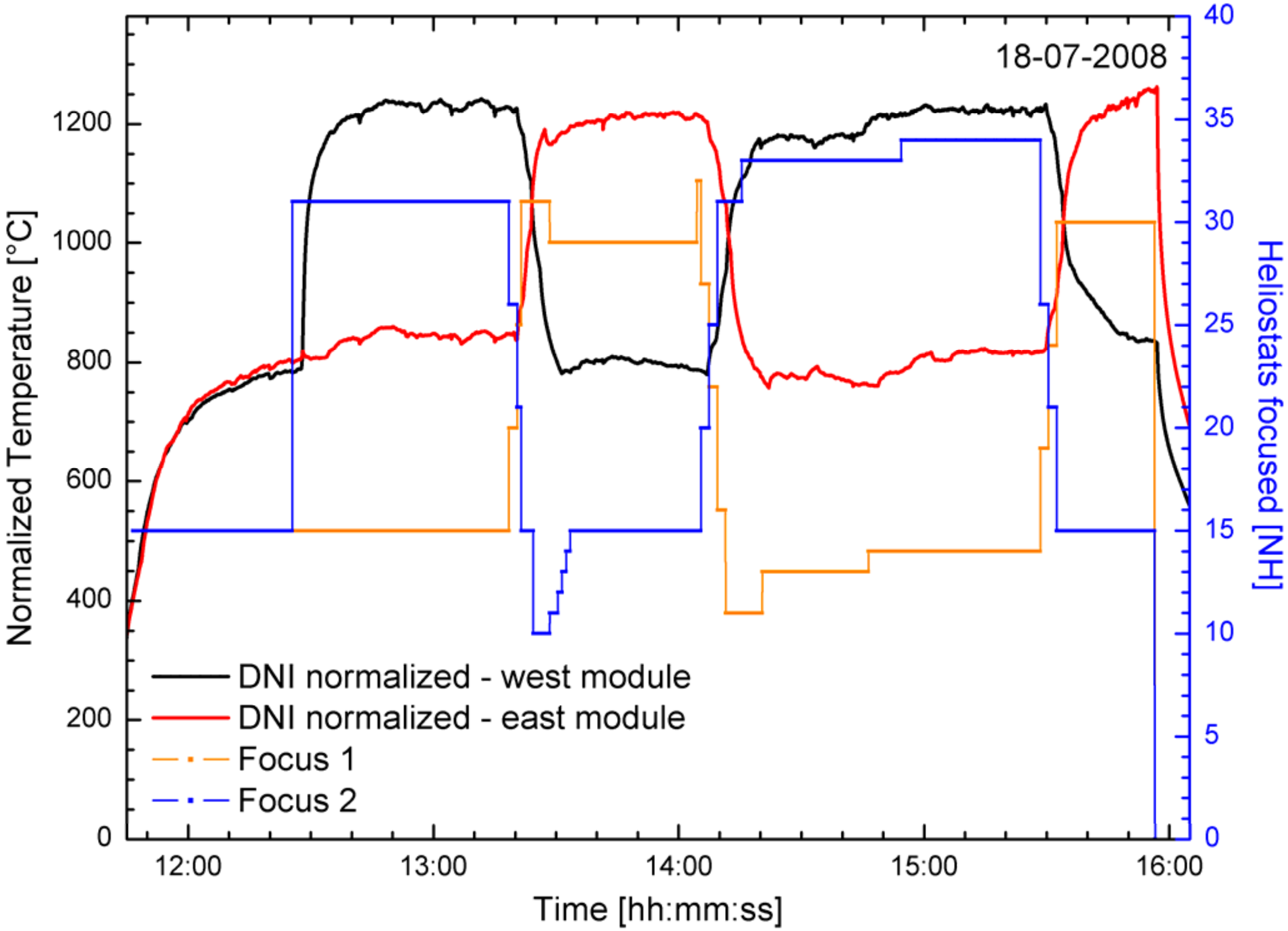
Flux Measurement at test operation

$Flux_{Max\,both\,Modules} = 115 kW/m^2$

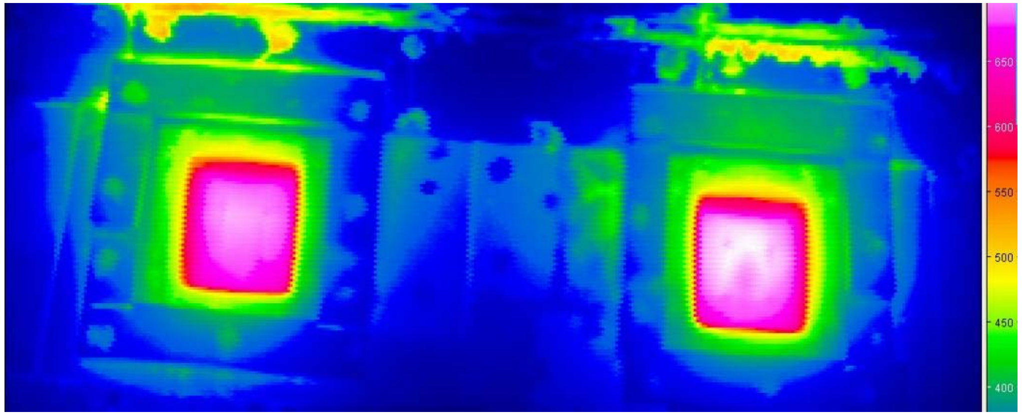


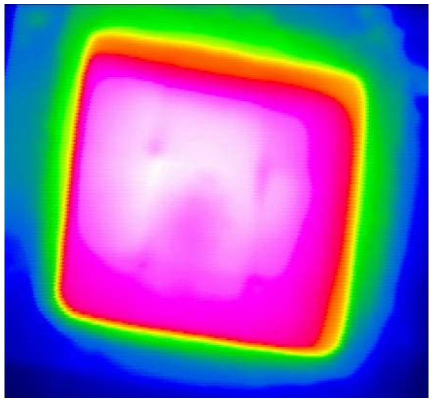


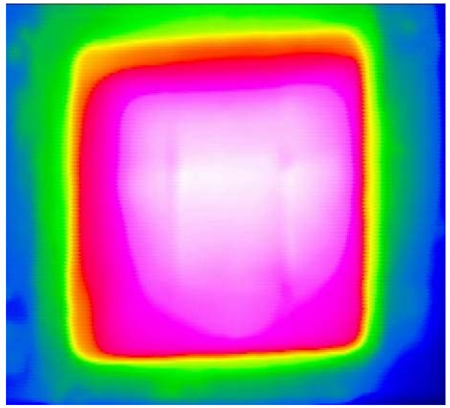
Results: Thermal cycling



Thermal test at CRS Tower at PSA, Spain







Controll of a Heliostat Field

- Ivanpah, Ca., Brightsource
  - Three Towers
  - 390 Mw_{el}
  - 170,000 Heliostats
  - Length 5 Miles
  - Easy profile
- Thermochemical Plant
  - Very constant temperature
  - On whole receiver

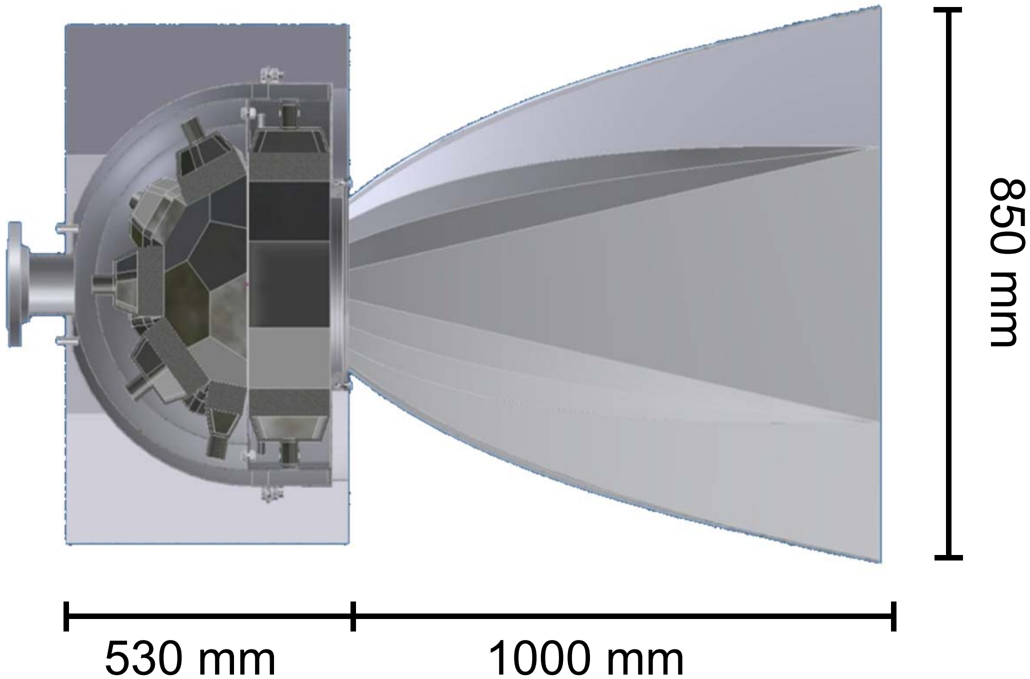
- See:

http://ivanpahsolar.com/

http://www.solarreserve.com/what-we-do/csp-projects/crescent-dunes/

2012: HYDROSOL 3D: 1 MW Pilot Plant Designs
2014: HYDROSOL PLANT Project will start

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

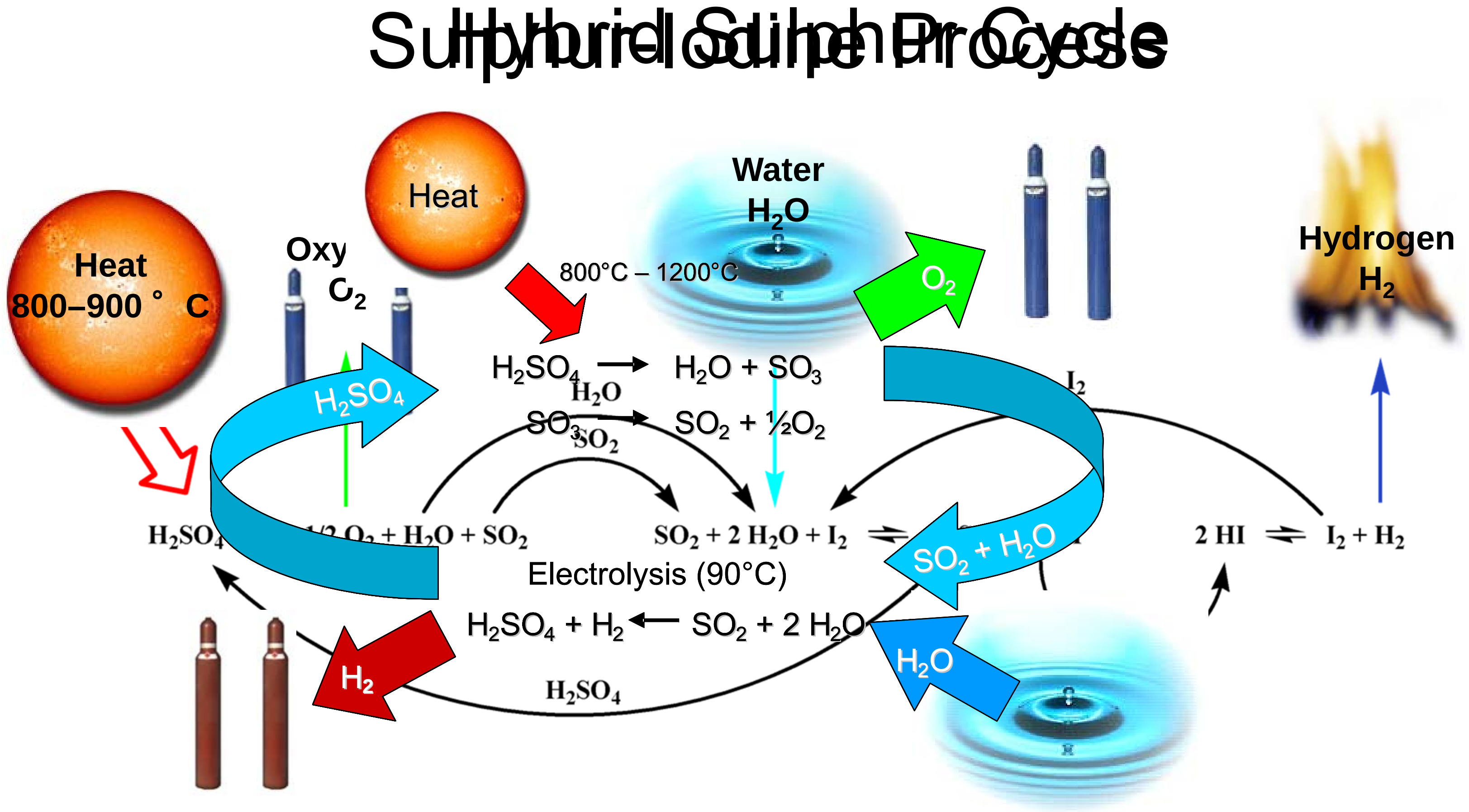


Compact 1 MW Receiver Design

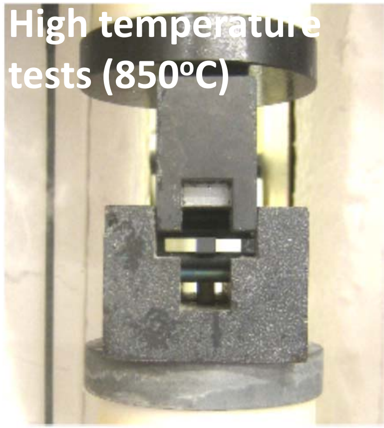
Important Recent Improvements

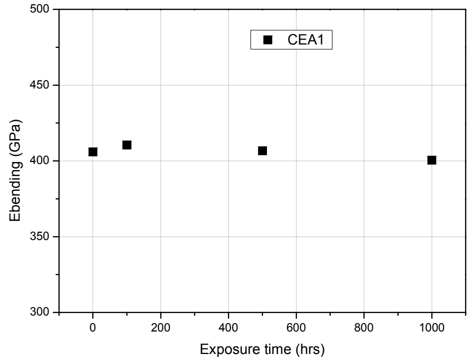
- Identification of the key losses within the processes
- Work is done on redox cycles by the leading research groups in Germany, Greece, Japan, Korea, Spain, Switzerland, the USA, …
  - Stability of the redox materials – from ferrites to ceria, to doped ceria to spinells and perovskites – reduced temperatures, increased stability
  - Sweep gas – losses by heating large volumes of non reactive gases to remove oxygen – reduction of sweep gas and pressure
  - Temperature swing – losses by cyclic heating – pressure swing
  - Reactor design – imporved particle receivers, redox material as construction material

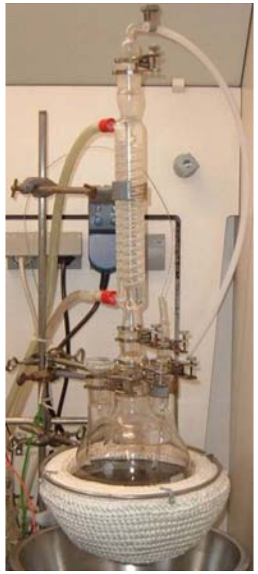
Sulfur based thermochemical cycles

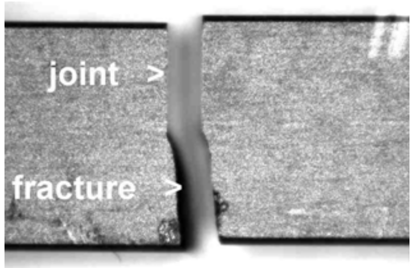


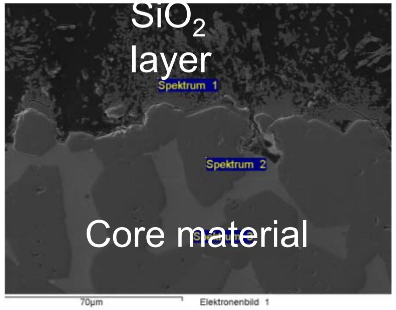
Stability of construction materials











- 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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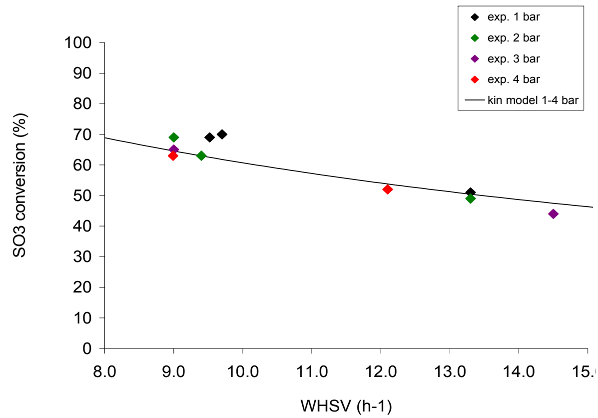
Advanced catalysts and coatings for H_2SO_4 decomposition

- ‘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

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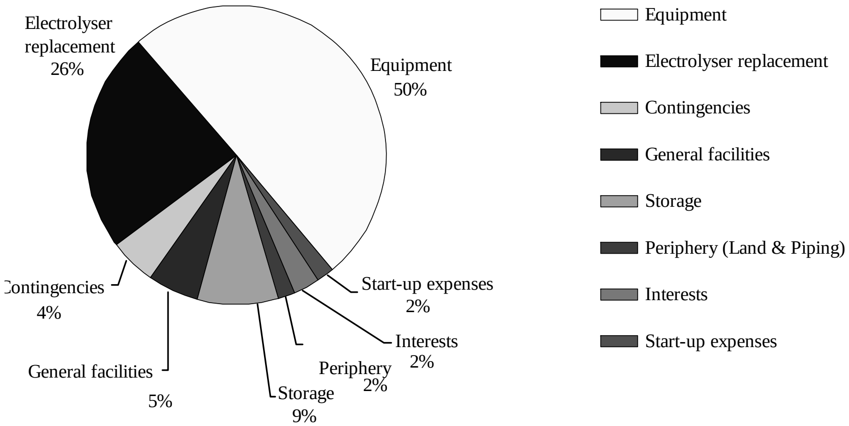
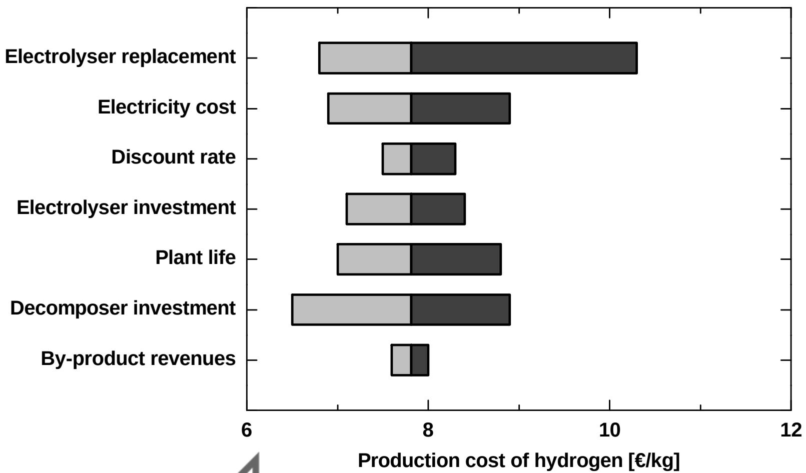
Three concecutive European Projects: HyThec, HyCycleS, Sol2Hy2: Techno-economic analysis



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
  → 6-7 €/kg(H_2) for HyS
  → 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
- Demo in the 500 kW range is under construction

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 productivity
- Chemical Engineering

  Development of solar receiver-reactors, design of concentrator technologies, scale-up, and economic evaluation

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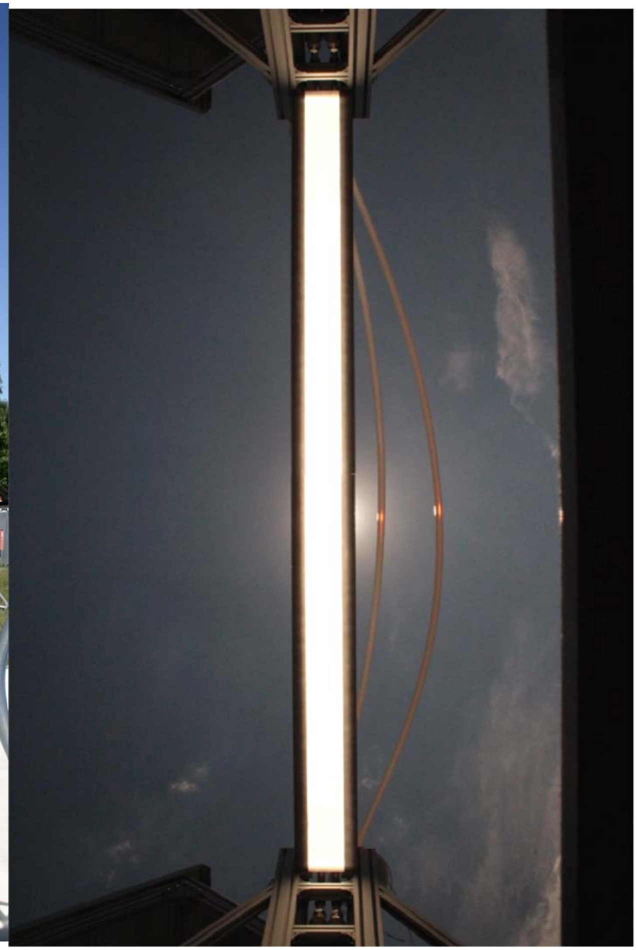
Teatfacility „SoCRatus“
Photoelectrochemistry at up to 20 suns



Concentrated Solar Fuels – CSF
The Challenges

- High temperatures, sometimes corrosive materials
- High investment cost – similar to CSP
  - Solar towers seem to be favorable
  - Some applications are forseen to be operated in dishes
  - Line focussing concentrators are not providing sufficient temperatures for most processes, but there are some opportunities e.g. steam generation
- Acceptance of competing technologies like PV+electrolysis or photoelectrochemistry might be higher
  - Information and education is needed
- Development status of the technologies – this gets slowly better
  - Lack of support compared to competing technologies
    - Not visionary enough? Not fancy enough? Marketing?
    - Thermodynamics are already well understood, therefore no „breakthroughs“ are expected?

Conclusion and Outlook

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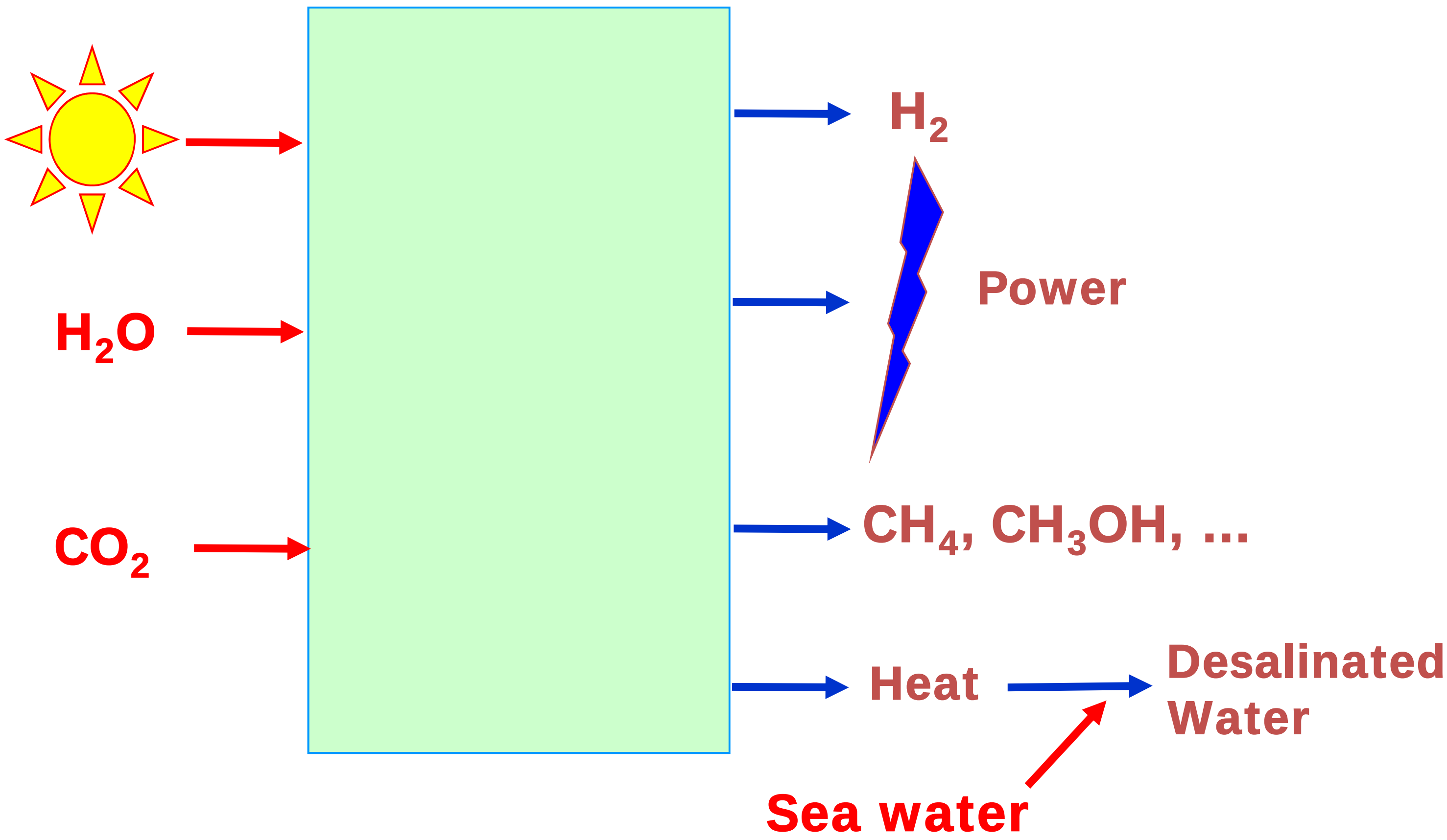
Future Solar Plants – more than power!

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



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Acknowledgement

- Thanks to all agencies funding the development of solar fuel technologies
- Thanks to all industrial partners already committed to solar fuels
- Thanks to all colleagues and partners who provided various contributions to this presentation – especially the ones that are not mentioned, all contributions are important!

Thank you very much for your attention!