

Solar Hydrogen

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**Deutsches Zentrum
für Luft- und Raumfahrt e.V.**
in der Helmholtz-Gemeinschaft



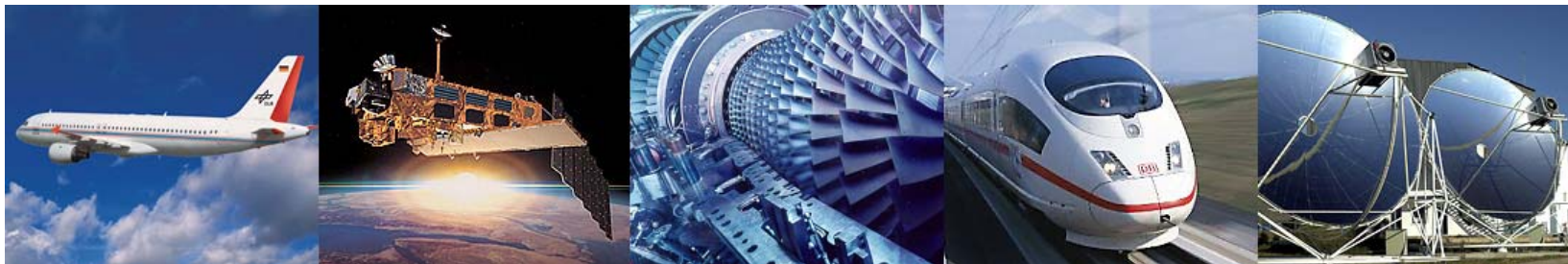
Overview

- Introduction of DLR
 - Energy
- Solar Hydrogen
 - From Fossil Recourses
 - Thermochemical Cycles
- HYDROSOL, HYDROSOL 2, HYDRSOOL 3-D
- Summary and Outlook





DLR German Aerospace Center



- Research Institution
- Space Agency
- Project Management Agency



Research Areas

- Aeronautics
- Space
- Transport
- Energy
- Space Agency
- Project Management Agency



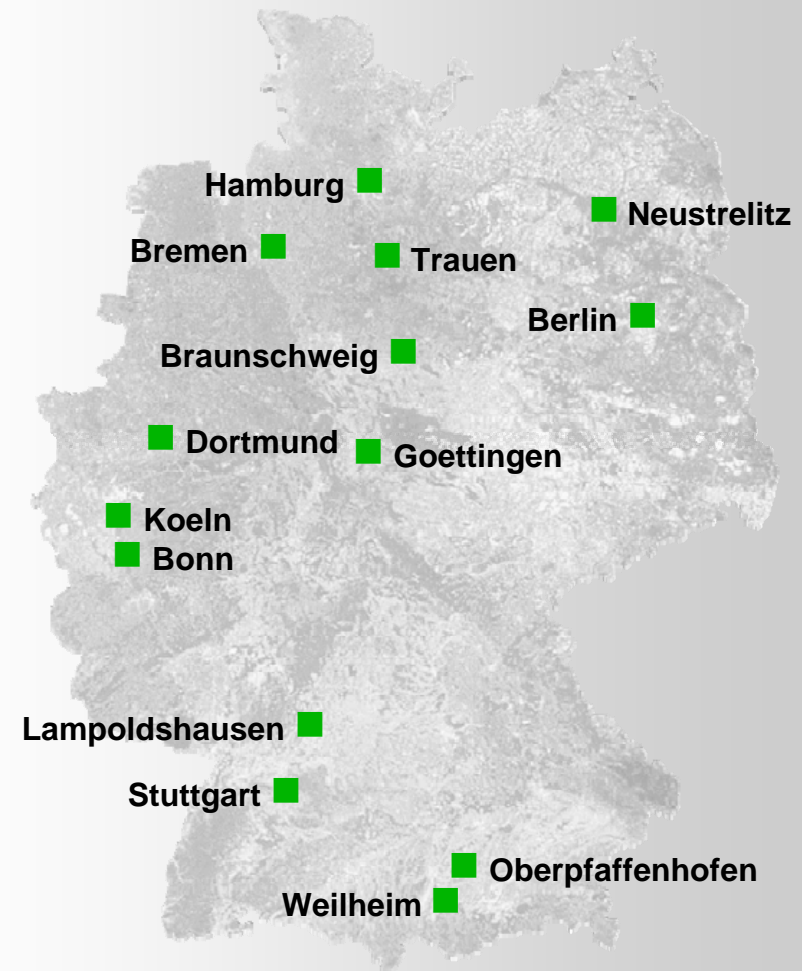


Locations and employees

6500 employees across
29 research institutes and
facilities at

■ 13 sites.

Offices in Brussels,
Paris, Washington, and Almería
(plus permanent Delegation on the
Plataforma Solar de Almería)





Energy



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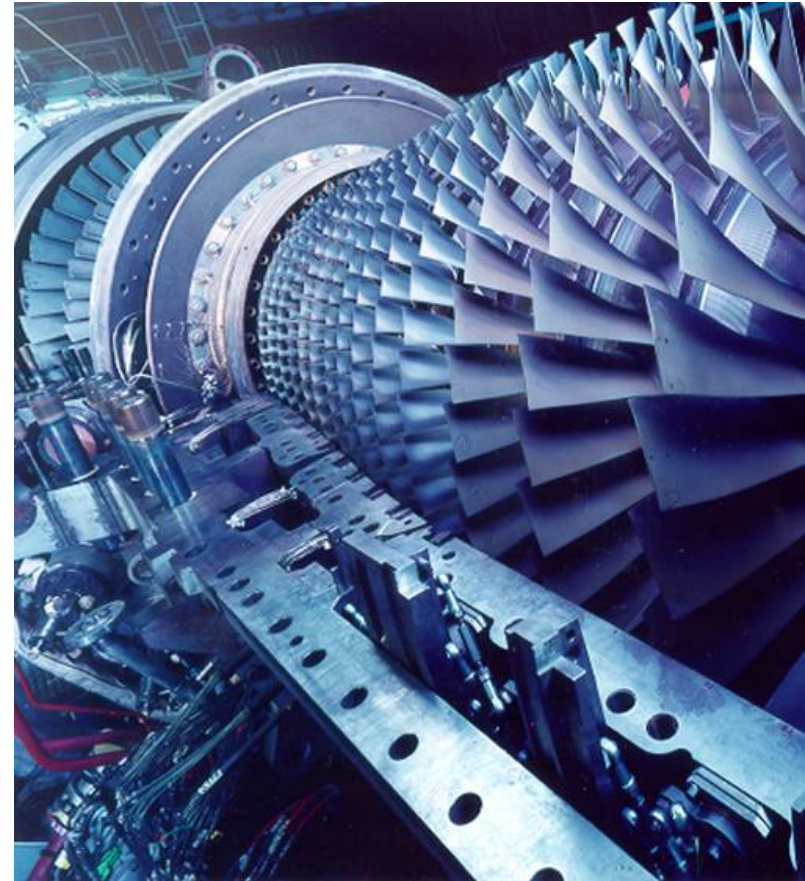
Slide 6

Stellenbosch University > 2 Sept. 2010

DLR Energy Research Area

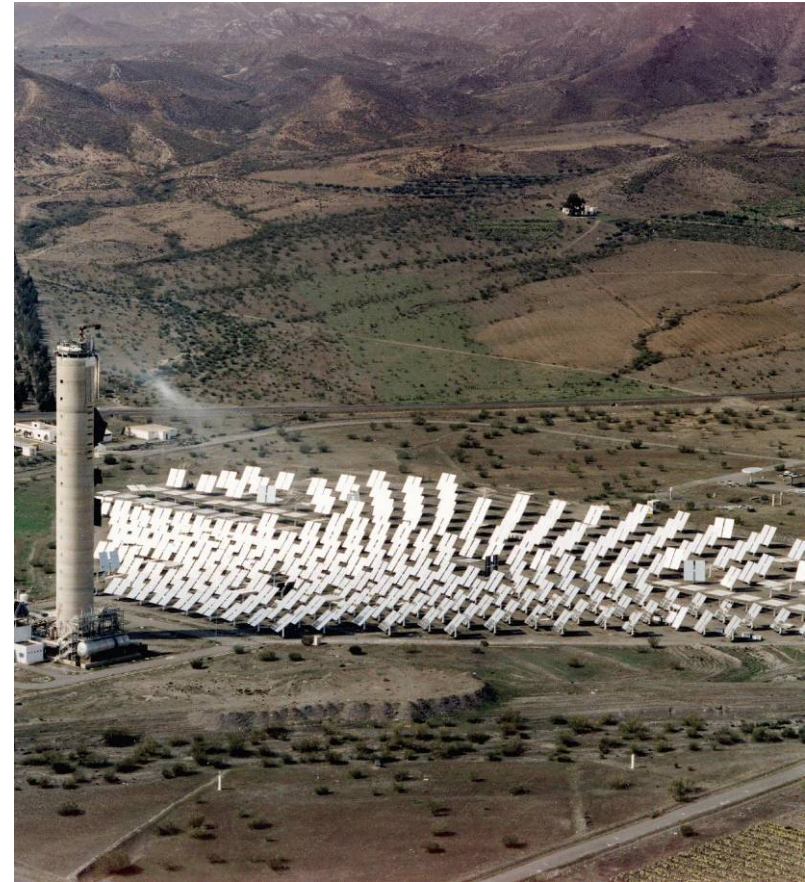
DLR Energy Research concentrates on:

- CO₂ avoidance through efficiency and renewable energies
- synergies within the DLR
- major research specific themes that are relevant to the energy economy
- Second largest research centre in Germany for non-nuclear energy
- Approx. 400 employees

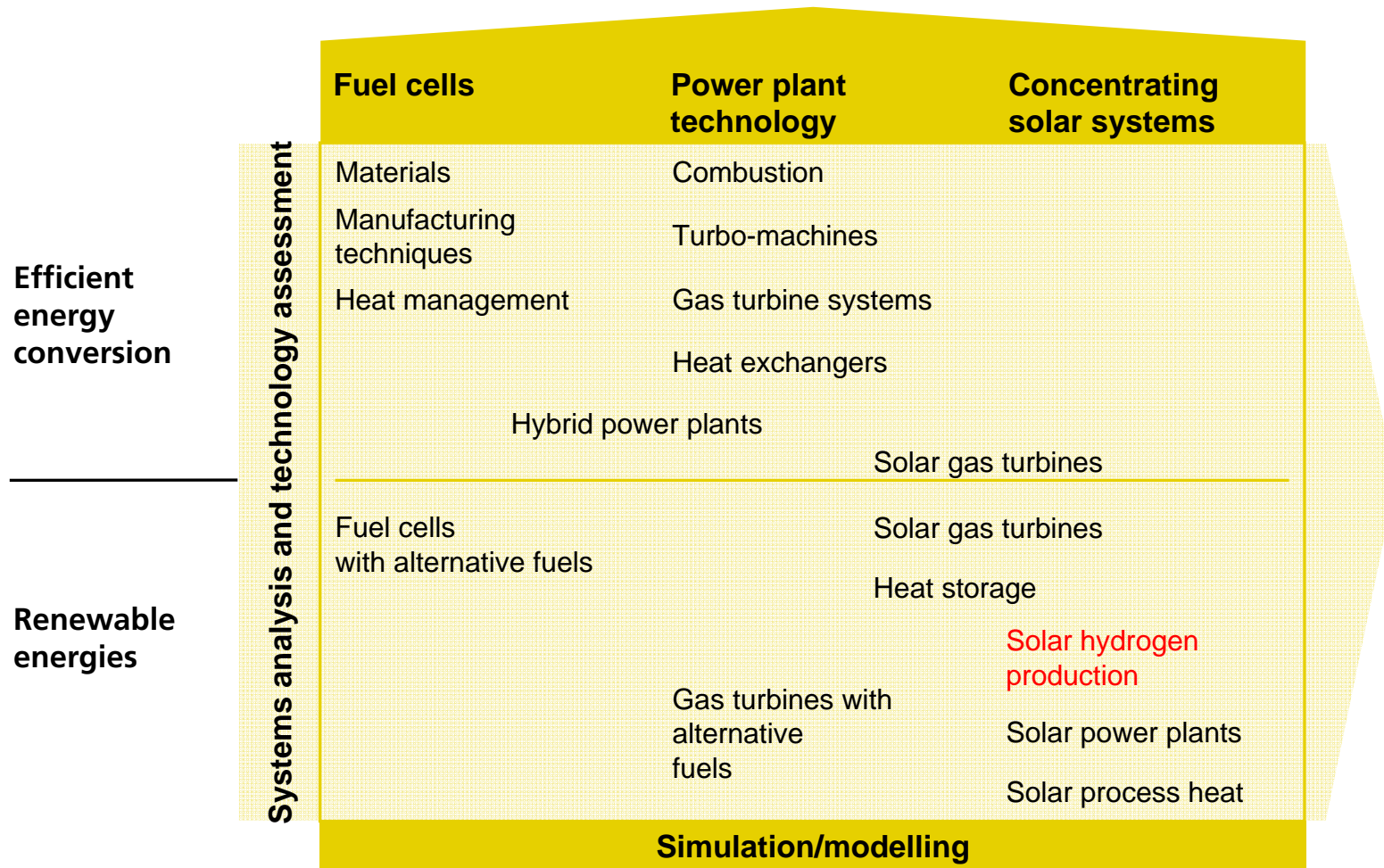


Energy Research Program Themes

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



Portfolio of Competences – Energy





Solar Hydrogen



Vision

- Producing hydrogen for mass markets means implementing as efficient processes as possible to convert available energy sources like renewables or nuclear into the chemical energy vector.
(De Beni G. 1970; Marchetti 1973; Winter 2000)

- Hydrogen should be produced from water
 - to reduce dependencies on fossil fuels
 - To reduces environmental impact



Technical and Economic Efficiency

Technical: In which process is the most energy stored in the hydrogen

Is the process technical feasible?

Are there any knock-out criteria?

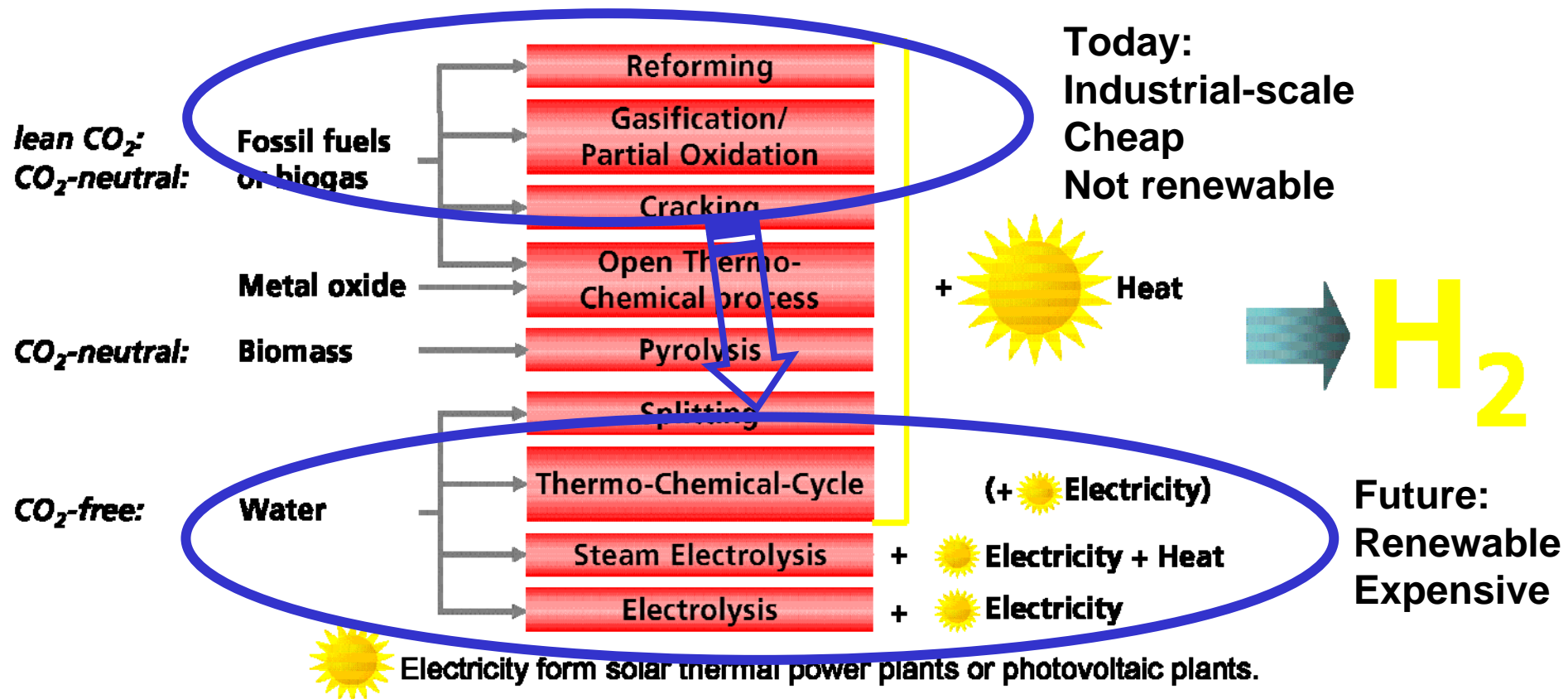
Economic: Is the product (hydrogen) cost competitive?

Are there any other economic reasons that make the process not competitive?

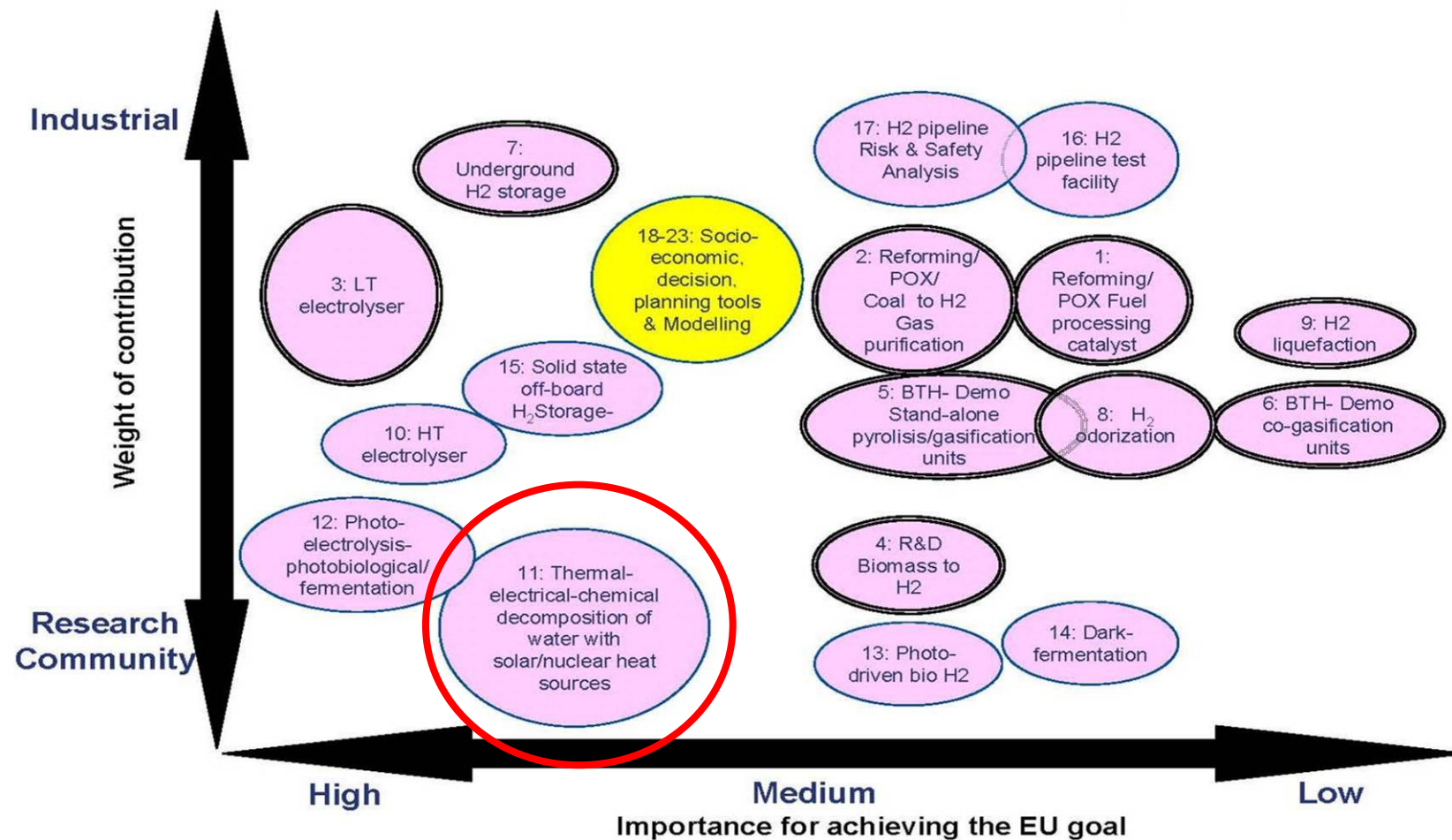
Hydrogen Production Today

- Steam Methane Reforming
 - Thermal efficiency 78%
 - 1 kg H₂ by means of SMR yields to 9.42 kg of CO₂
 - The production cost of hydrogen is estimated at 0.04 €/kWh (**1.33 €/kg**)
- Coal Gasification
 - The Lurgi Process (Fixed-Bed) 500 – 1000 °C
 - The Winkler Process (Fluidized-Bed) 800 - 1100 °C
 - The Koppers-Totzek/Texaco Process (Entrained-Bed) 1040 – 1540 °C
 - Thermal efficiency 58 - 63%
 - 23 kg CO₂ / kg H₂
 - Hydrogen costs from coal gasification are **1.21 to 1.79 €/kg** H₂(coal price not reported)
- Partial Oxidation
 - 1300 - 1500 °C
 - **1.45 – 1.67 €/kg**

Solar Thermal Processes for Hydrogen Production



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





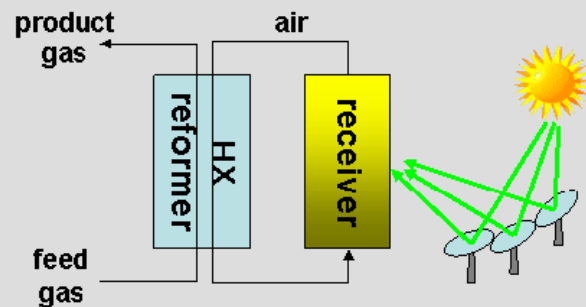
Solar Hydrogen from Hybrid Fossil Processes

Carbon Based Transition Processes

- Starting from applied technologies
- Reduced risk compared to water splitting technologies
- Solar Reforming of Natural Gas
 - Development by a number of groups since at least 25 years
 - Cost are estimated to 1.4 €/kg H₂
- Solar Gasification and Reforming of Petcoke
 - Development by ETH Zurich, CIEMAT, and PDVSA
 - Cost are estimated to about 2.1 €/kg H₂
- SOLZINC – Carbothermal reduction of ZnO
 - Pilot reactor successfully tested
 - Zinc is produced not hydrogen!
- Solar Cracking of Methane
 - No CO₂ emission but C, C might be a product too
 - challenging reactor design: solids and high temperatures

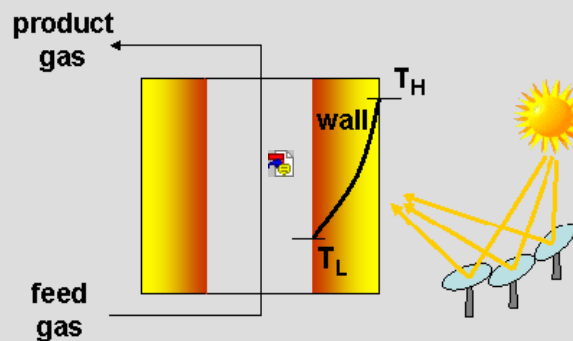
Solar Steam Methane Reforming – Technologies

a) decoupled/allothermal



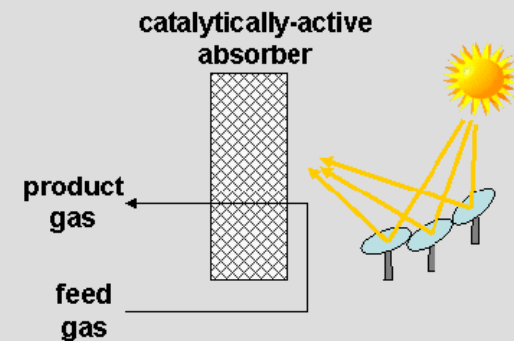
- Reformer heated externally (700 to 850°C)
- Optional heat storage (up to 24/7)
- E.g. DLR Project ASTERIX

b) indirect (tube reactor)



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

c) Integrated, direct, volumetric



Quelle: DLR

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

Direct heated volumetric receiver: 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)
- DLR (D), WIS (IL), ETH (CH), Johnson Matthey (UK), APTL (GR), HYGear (NL), SHAP (I)



Assessment of relevant H₂ pathways until 2020

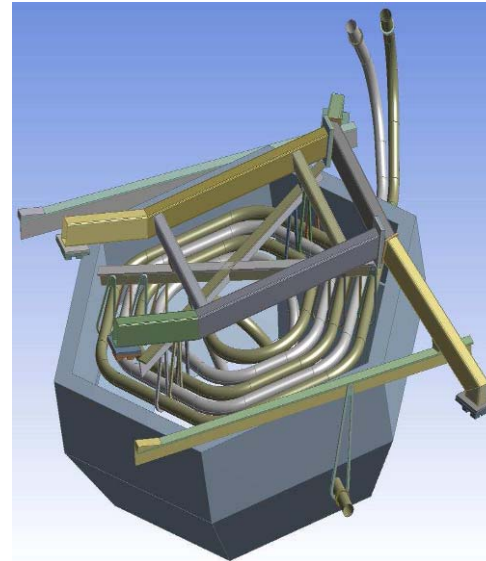
including NG Solar-SMR for comparison issues

	NG SMR	NG Solar- SMR	Grid Electricity electrolysis	Wind electrolysis	Biomass
H ₂ production cost	8* €/GJ	12* €/GJ	31 €/GJ	50-67 €/GJ	25-33 €/GJ
Positive impact on security of energy supply	modest	modest - high	high	high	high
Positive impact on GHG emission reduction	neutral - modest	modest - high	negative -neutral	high	high

***assuming a NG price of 4€/GJ; NG Solar-SMR: expected costs for large scale, solar-only**

Project Perspectives

- The consortium forces the realisation of the a prototype reforming plant
- Link with Australian CSIRO by an ongoing IPHE project
- Funding was assured in October 2009
- Development phase of the joint project
- SOLREF receiver will run on a second tower at the CSIRO Solar Centre in Newcastle, NSW





Thermochemical Cycles

Thermochemical Water Splitting



PROBLEMS!

- Hydrogen + Oxygen = explosive gas!
 - Dangerous
 - Separation?
- 2500 °C Materials
 - Special ceramics – difficult to handle, expensive
- 2500 °C Temperature
 - How could such high temperatures be achieved?
 - Efficiency?



Sollution



H_2O

Are the problems solved now?

- Still high temperatures
- Materials
- Chemical reactions
- Efficiency

550 °C

O_2

1250 °C





Thermochemical Cycle

- Firstly developed in the oil crises of the 1970s
- Use of nuclear energy to produce an energy carrier
- Mainly in the USA (General Atomics, Westinghouse), but also in Europe (FZJ, JRC Ispra) and Japan (JAEA)
- Up to 900 different cycles are known
- Main groups:
 - Sulphur cycles
 - Volatile metal oxide cycles
 - Non-volatile metal oxide cycles
 - Low temperature cycles
- In the 1980s and 1990s the interest went down because of lower oil prices
- Come back in the 2000s
 - Solar thermal more in the focus
 - Studies to identify the most promising cycles (e.g. USA, France)



Thermochemical vs. Electrochemical?

- Thermochemical

- No conversion steps necessary = possibly very high efficiency

- Electrochemical

- Conversion steps necessary for power production = lower efficiency

- No contradiction: use energy forms as efficient as possible

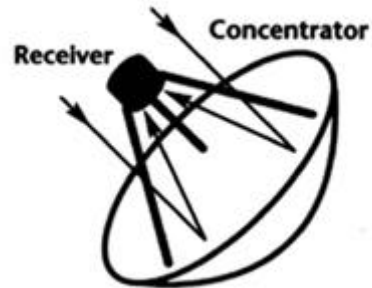
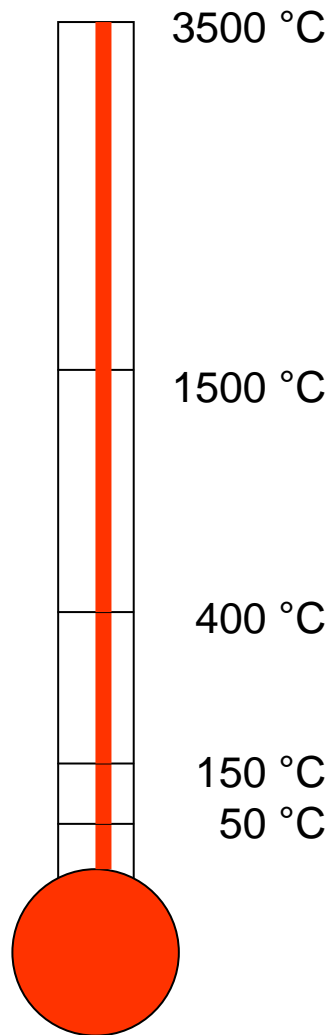
Promising and well researched Cycles

	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

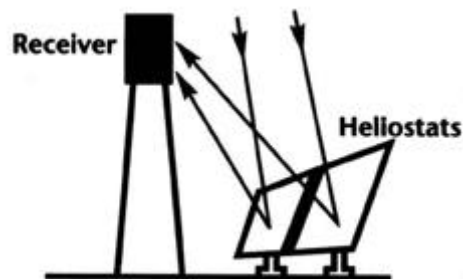
Temperature nuclear

Reactor Type	Temperature (°C)	Carnot-Efficiency
Boiling Water Reactor	285	47%
RBMK (Graphite moderated)	285	47%
CANDU Reactor (Heavy Water Reactor)	300	48%
Pressurised Water Reactor	320	50%
Breeder Reactor, Sodium cooled	550	64%
Advanced Gas Cooled Reactor	650	68%
(Very) High Temperature Reactor	750+	71+%

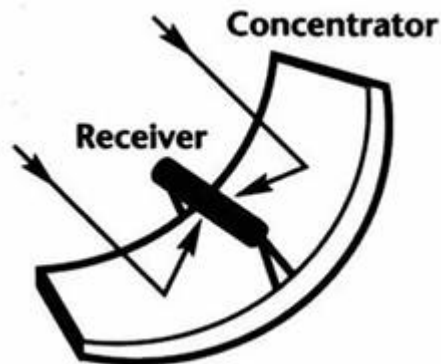
Temperature – Concentrating Solar Power



Paraboloid: Dish



Solar tower
(Central Receiver System)

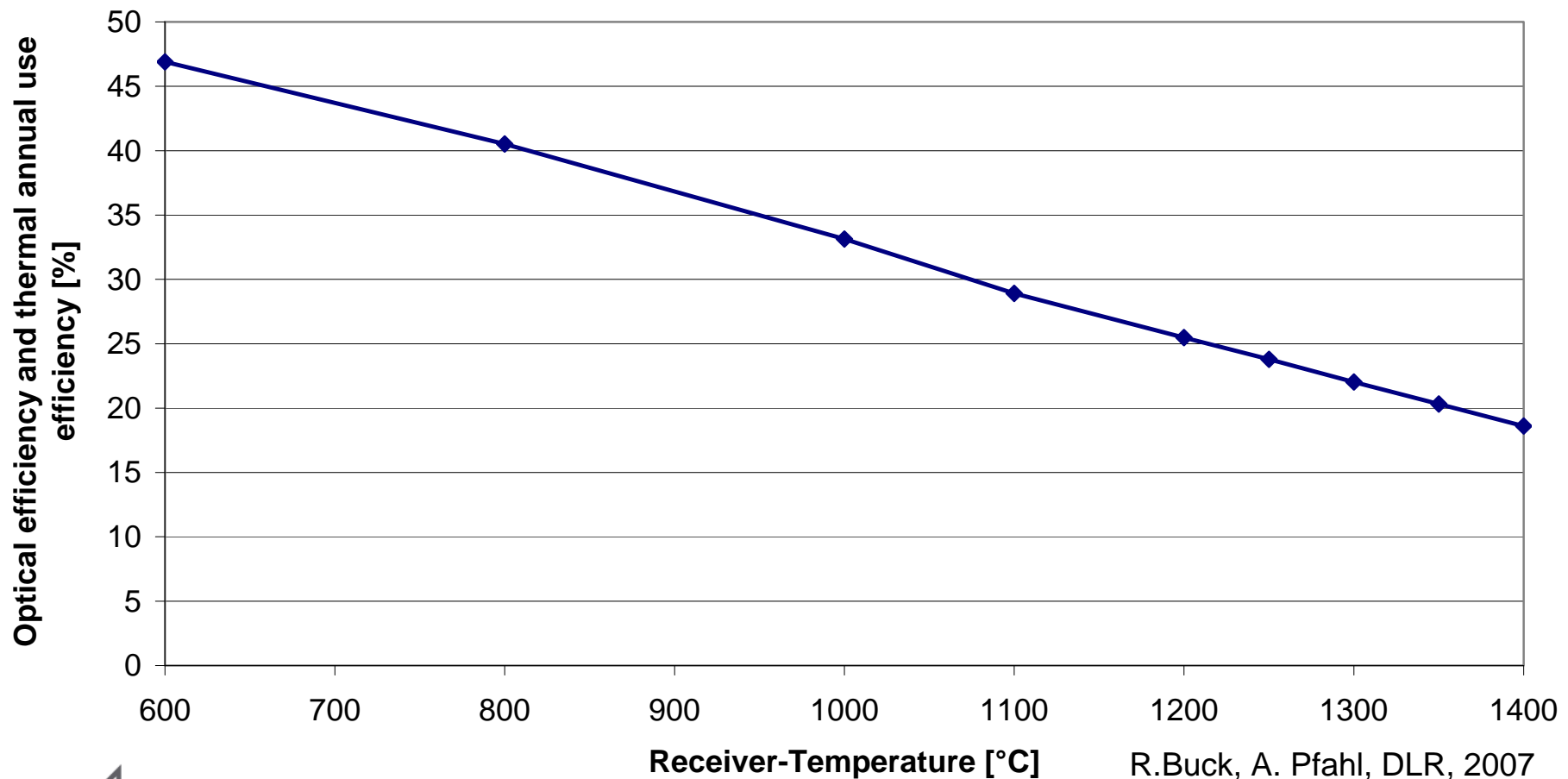


Parabolic trough



Annual Efficiency of Solar Power Towers

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



R.Buck, A. Pfahl, DLR, 2007



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Solar Towers, “Central Receiver Systems”



- Solar-Two
- PSA
- PS10+20

Efficiency comparison solar H₂ 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 Sulphur- 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

Water based processes

- Long term necessary for the de-carbonised H₂ society
- Benchmark: Renewable electricity + electrolysis
- Challenging technologies
- Metal/Metal oxide thermo-chemical Cycles
 - Zn/ZnO (3,58 – 4,12 €/kg)
 - Mixed Iron Oxides (Ferrites)
 - Already shown in the HYDROSOL project
 - Cost based on the small scale experiments are 7 €/kg
 - Calculated improvements will lead to 3,5 €/kg
- Sulphur Cycle Family
 - Developed for use with nuclear heat
 - Hybrid Sulfur (ISPRA Mark 11)
 - Cost calculation 0,8 €/kg H₂ nuclear
 - Sulphur-Iodine Process (ISPRA Mark 16)
 - Cost calculation 1,17 – 1,66 €/kg nuclear, 4,53 €/kg solar

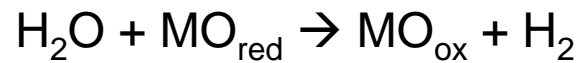


HYDROSOL, HYDROSOL 2, HYDROSOL 3D

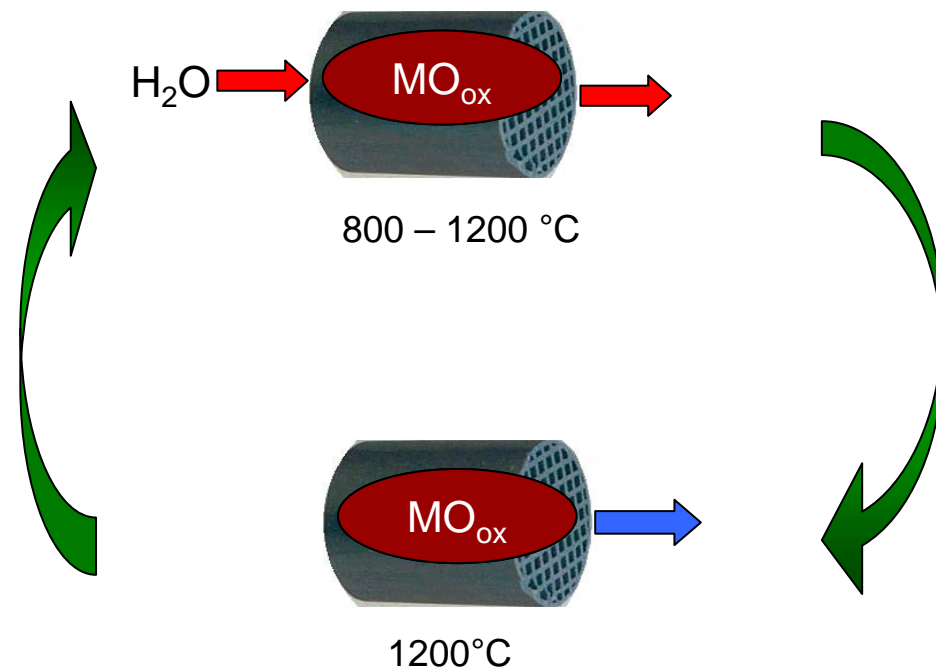
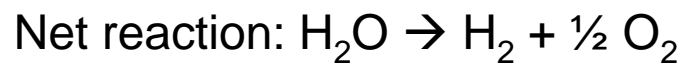
Thermochemical Cycle using Mixed Iron Oxides

Process Operation

1. Step: Water Splitting



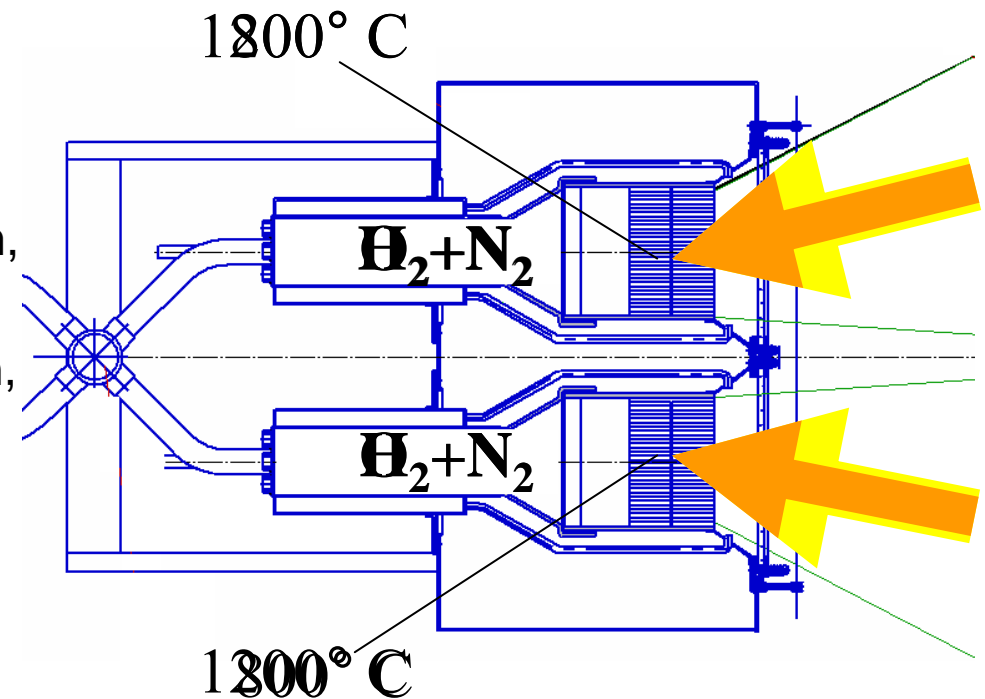
2. Step: Regeneration



**Redox materials used in the
HYDROSOL-2 project:**
 ZnFeO , NiZnFeO

Reactor for continuous hydrogen production:

- Reactor with two modules
- 15 kW two-chamber system
- Two different alternating processes:
 - Production: 800°C, water steam, nitrogen, exothermic
 - Regeneration: 1200°C, nitrogen, endothermic
- Transient steps like
 - Switching between half cycle
 - Start-up / Shutdown
- Closed system: quartz window
- Four-way-valve

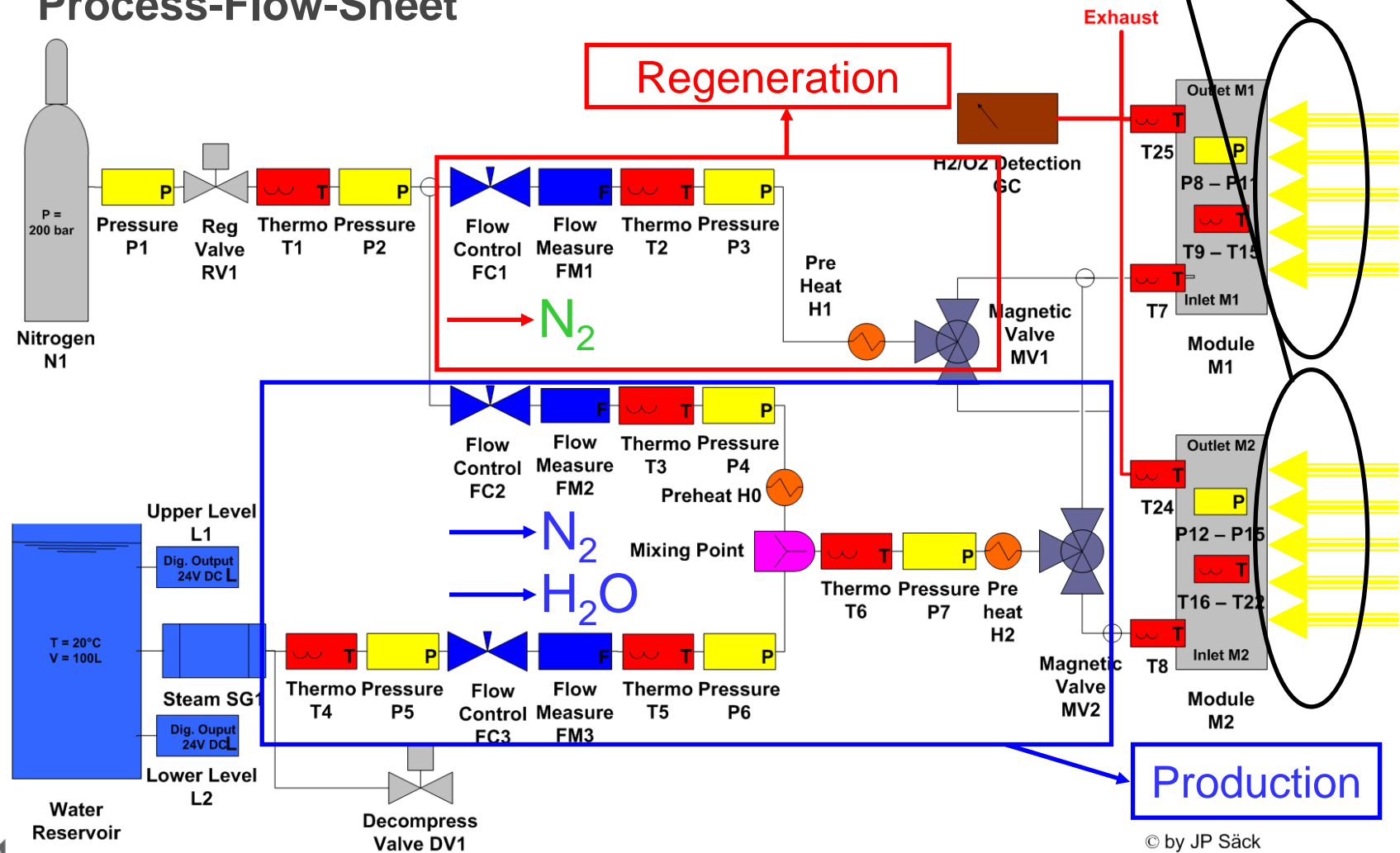


HYDROSOL II Pilot Reactor in Operation



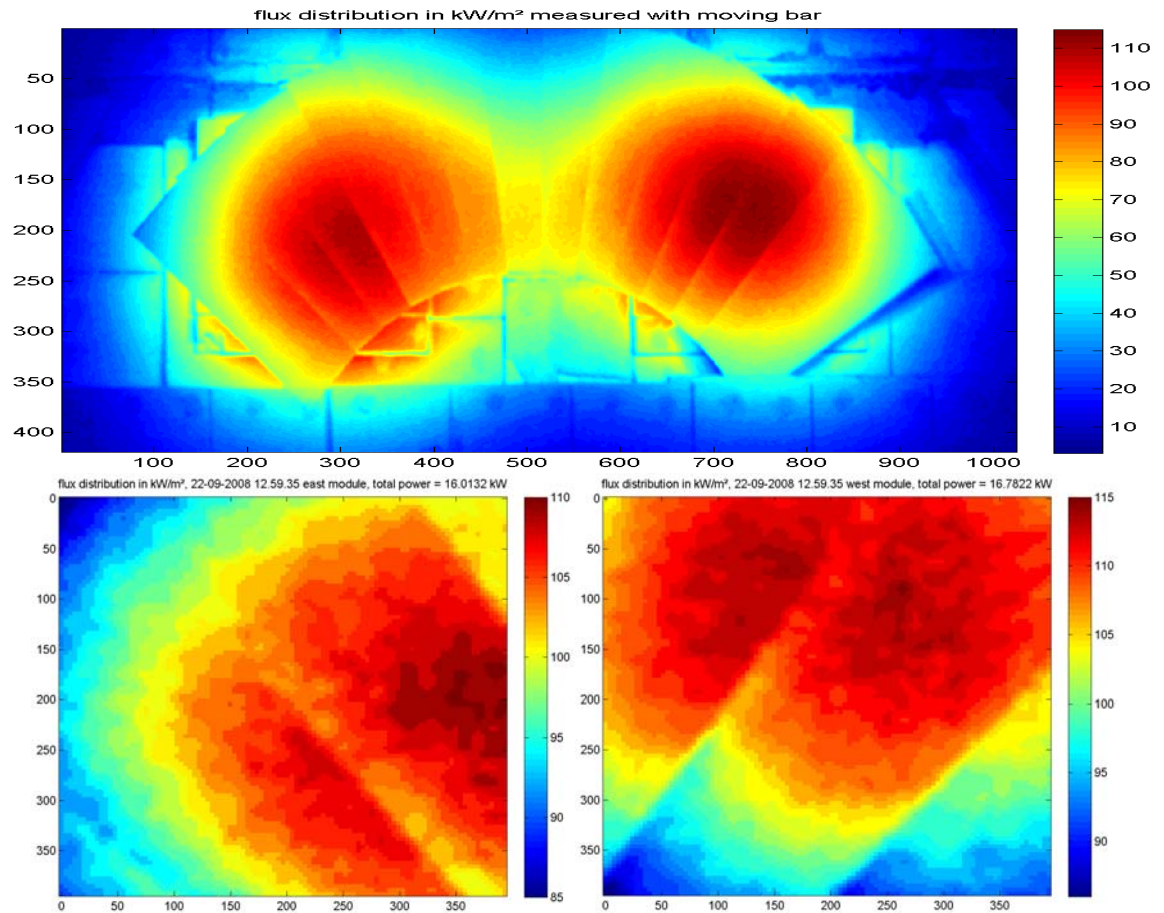
Experiments – Process Control Software:

Process-Flow-Sheet

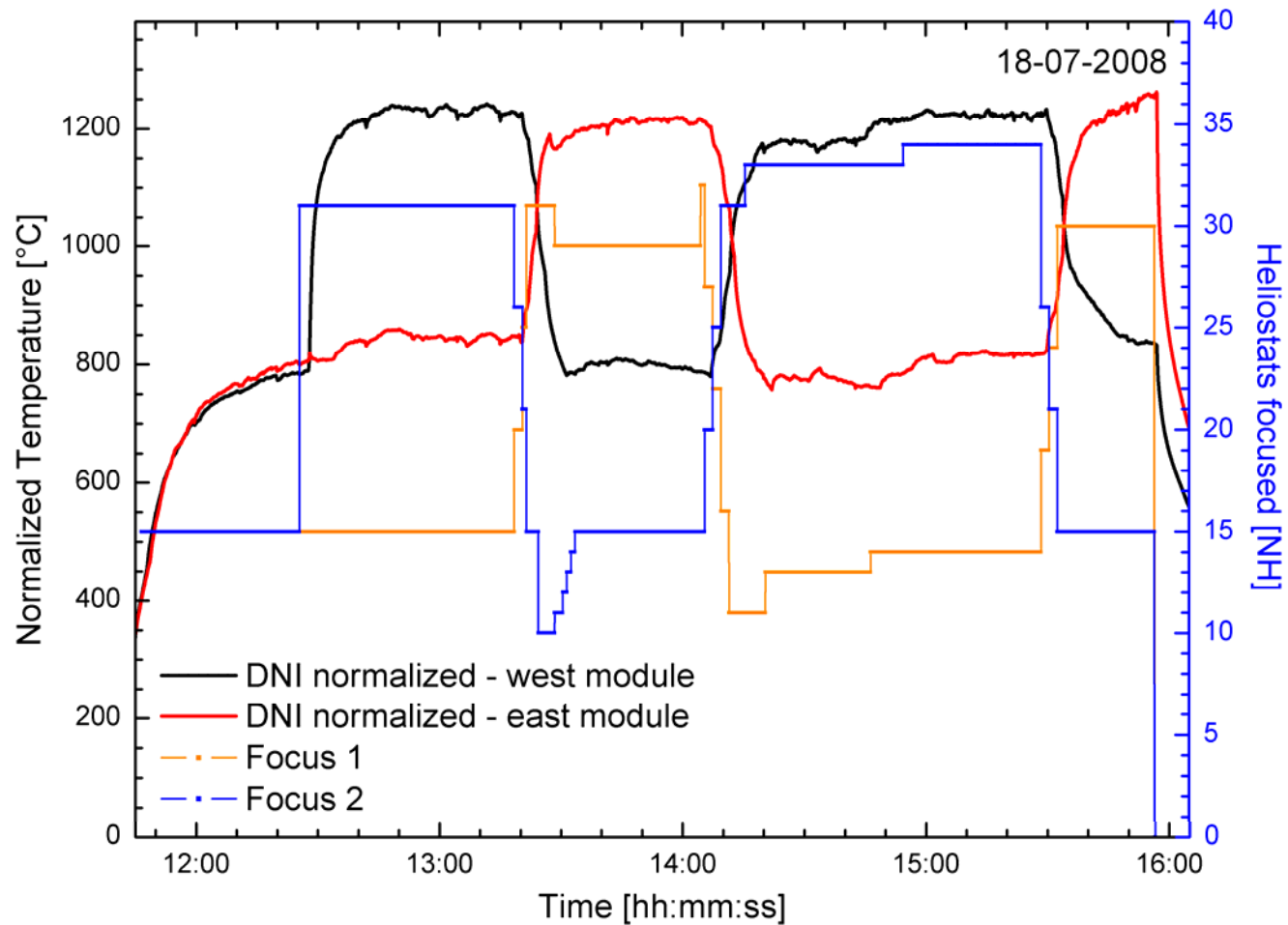


Experiments – Process Control Software:

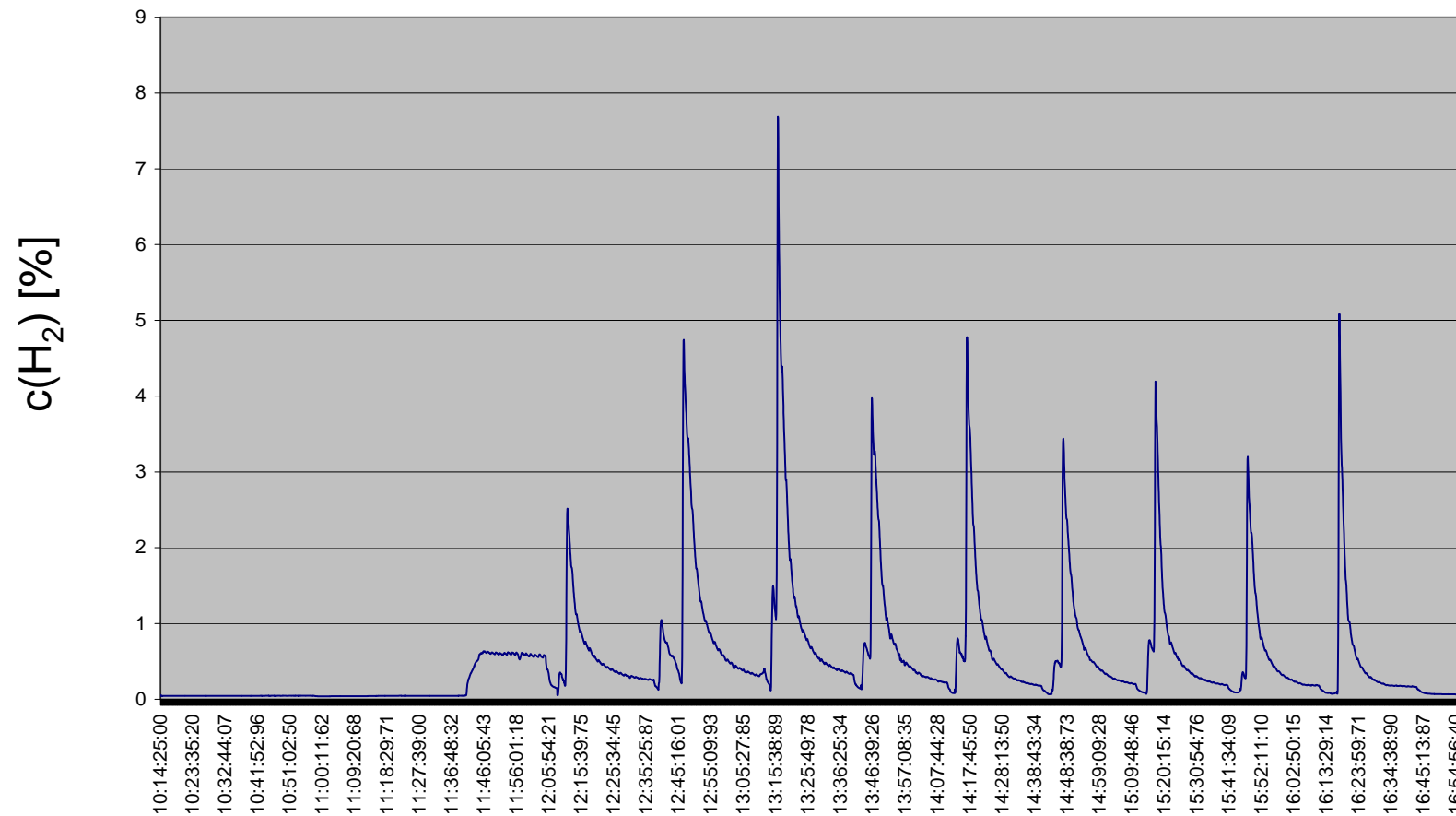
Flux Measurement at test operation $\text{Flux}_{\text{Maxboth Modules}} = 115 \text{ kW/m}^2$



Results: Thermal cycling



Hydrogen production of 4th day of experimental series





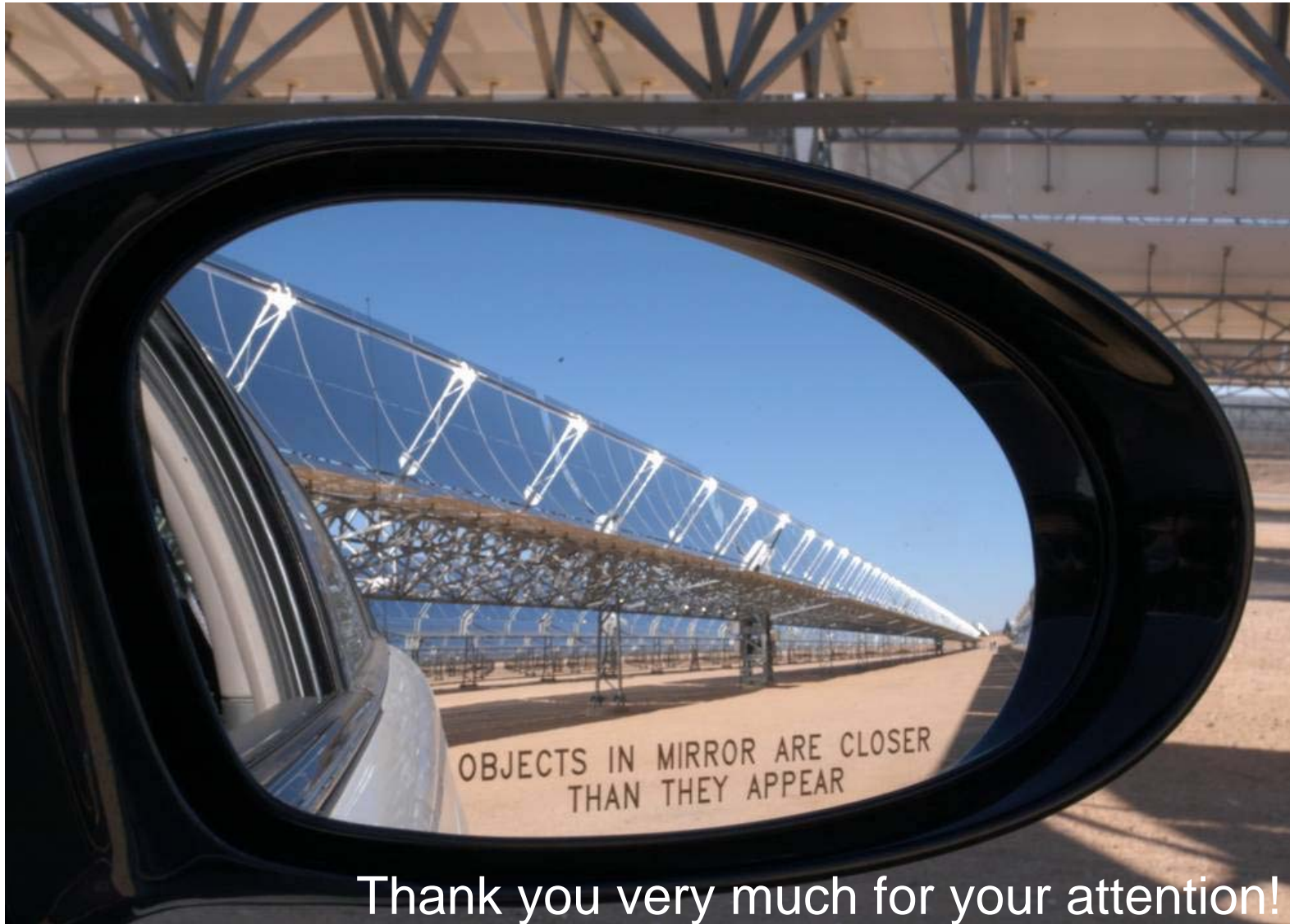
Summary and Outlook

- Technologies like solar steam reforming should be short term technologies to introduce solar technology into the chemical industry
- Thermochemical cycles will provide renewable hydrogen with very high efficiency compared to other renewable technologies
- The HYDROSOL reactor concept was scaled up in HYDROSOL 2 from the solar furnace to a 100 kW pilot plant on the tower of the PSA
- Topic of the ongoing HYDROSOL 3-D project is the design of a MW test plant
- Also sulfur cycles should be scaled-up since the development is already on a very advanced level and the temperature level is lower than of other TCCs

Acknowledgement

- The Projects
HYDROSOL, HYDROSOL II; HYTHEC,
HYCYCLES, Hi2H2, INNOHYP-CA,
SOLHYCARB und SOLREF are co-funded by
the European Commission
- HYDROSOL 3-D is co-funded by the European
Joint Technology Initiative on Hydrogen and
Fuel Cells
- HYDROSOL was awarded
 - Eco Tech Award Expo 2005, Tokyo
 - IPHE Technical Achievement Award
2006
 - Descartes Research Price 2006





Thank you very much for your attention!