Solar Fuels

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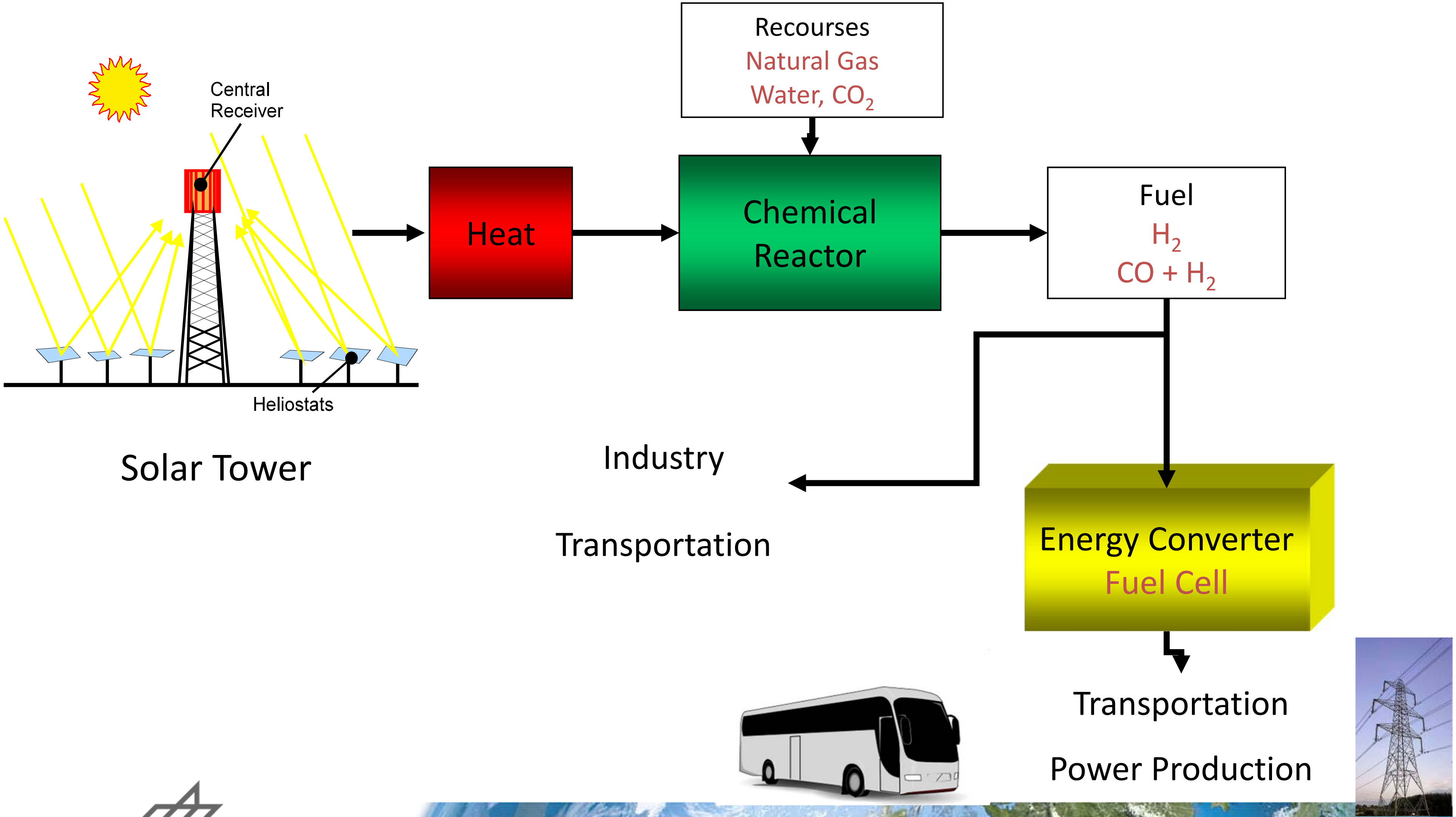
Introduction

- Solar Fuels – wide variety with great perspectives
- Drivers for solar (thermal) fuels
  - Economical
  - Political
- Synergies with industrial processes
  - Connections to fossil ressources
- Innovative processes
  - Connections to hydrogen and Fuel Cells
- Summary and Outlook

Solar Fuels

- Fuels – Materials to produce heat and power (Dictionary)
    - Hydrogen, Synthesis Gas, Methane, Fischer-Tropsch Fuels, Methanol, Metal oxides, Sulfur …
- Solar Fuels = Chemically stored solar energy!
    - Thermal, photo(electro)chemical, biochemical
- At SolarPACES 2013:
- 2 Solar Fuels sessions - 11 papers, 1 keynote, 9 posters
- 5 Storage sessions – 3 thermochemical papers, 4 posters

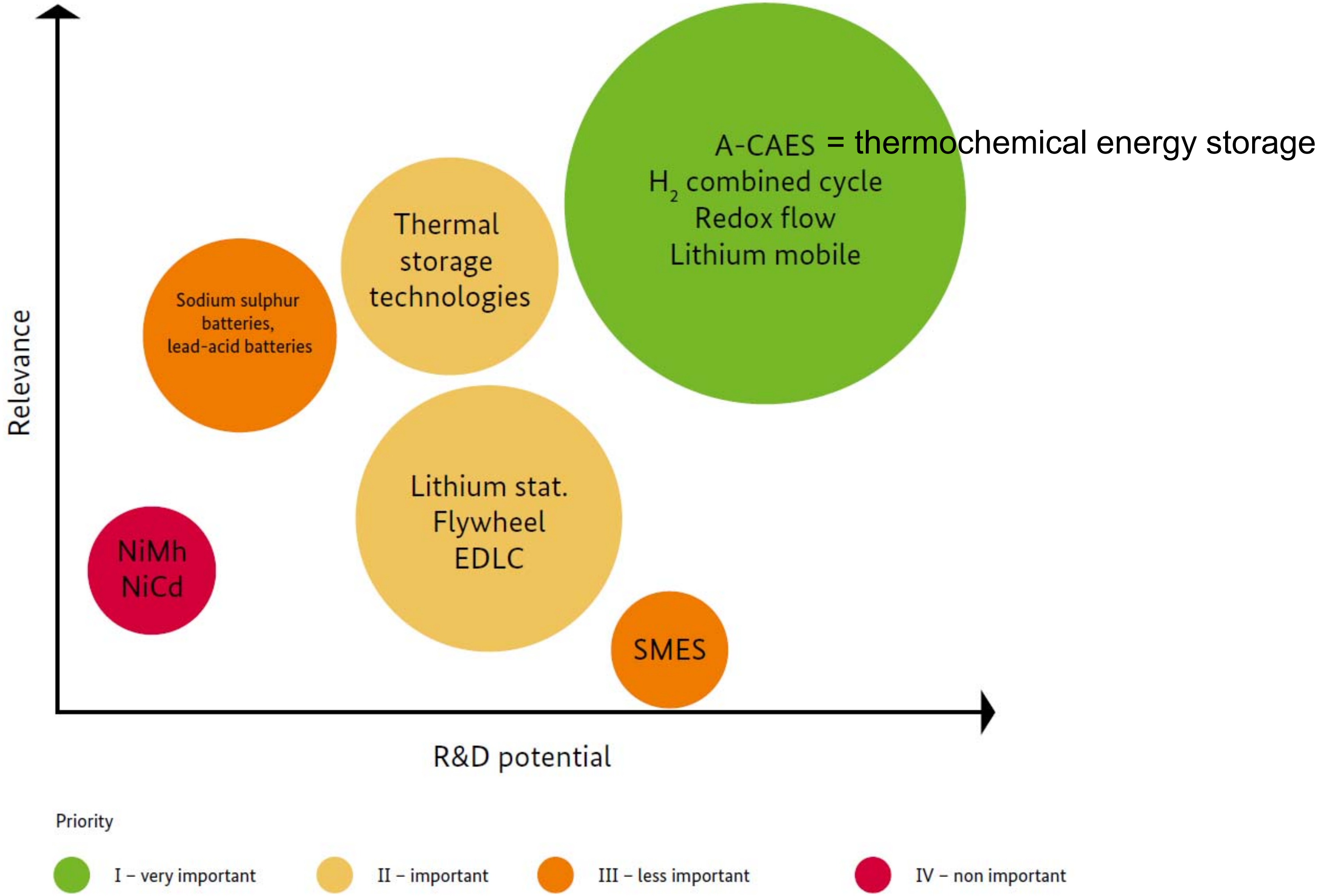
Principle of the solar thermal fuel production



Chemical heat 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

6th German Energy Reserach Programme



Concentrated Solar Fuels – CSF
The Advantages

- Very high storage densities
- Dispatchability and for some application for mobility!
- Possibly very efficient production

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 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)*

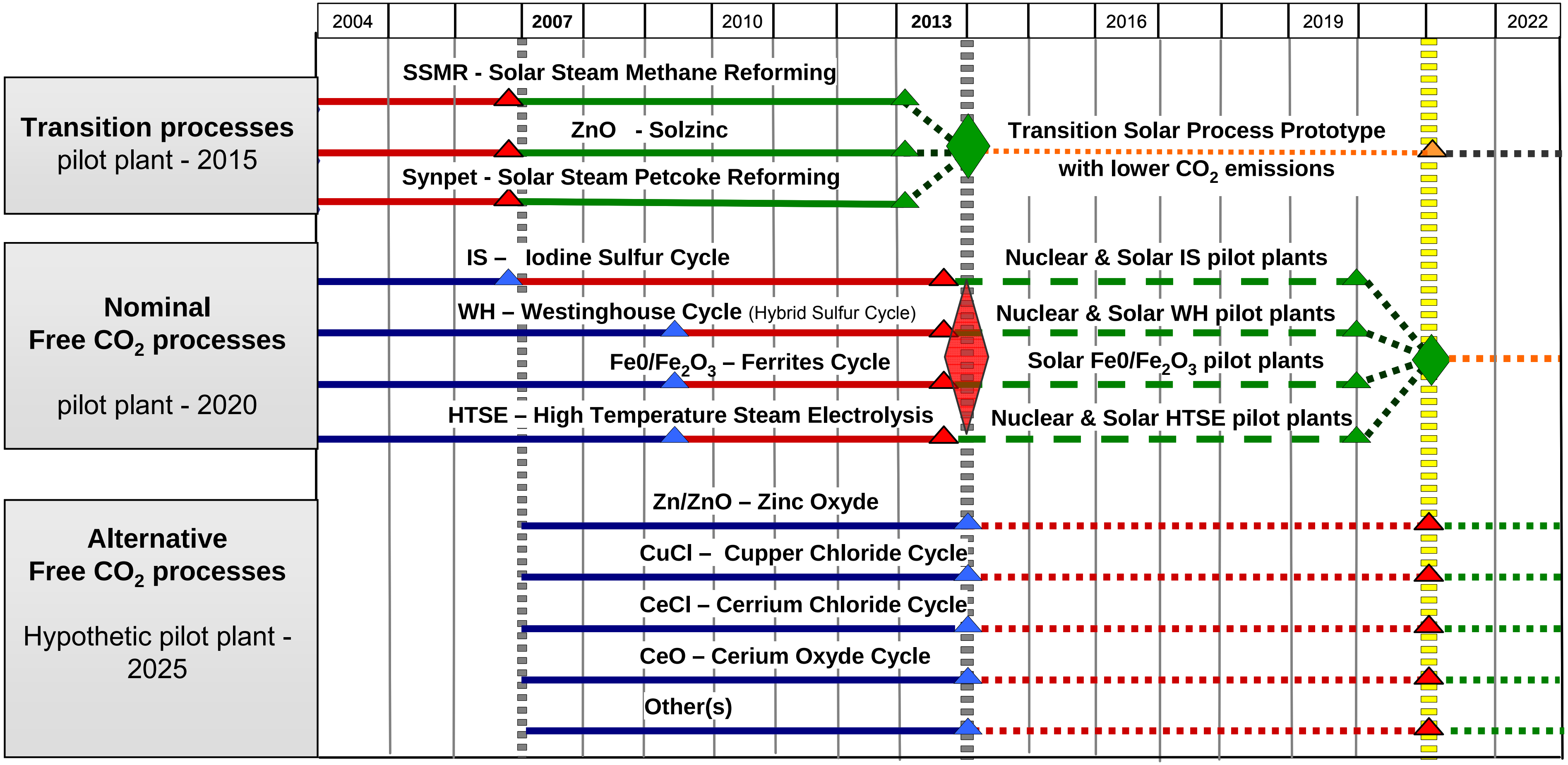
Process	T [°C]	Solar plant	Solar-receiver + power [MWth]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H_2
Elctrolysis (+solar-thermal power)	NA	Actual Solar tower	Molten Salt 700	30%	57%	83%	14%
High temperature steam electrolysis	850	Future Solar tower	Particle 700	45%	57%	76,2%	20%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

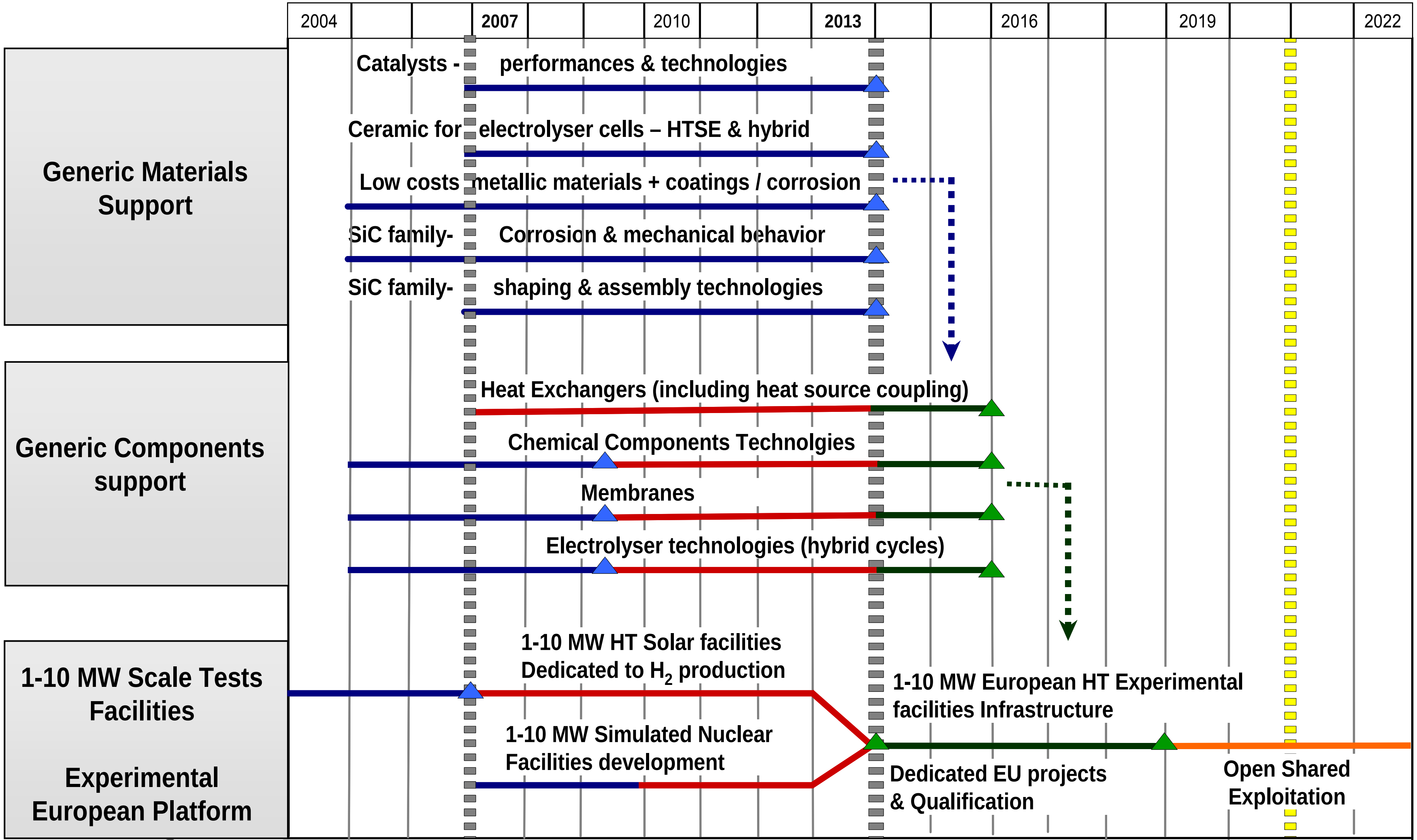
Concentrated Solar Fuels – CSF
The Challenges

- 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, besides steam generation
- Acceptance of competing technologies like PV+electrolysis or photoelectrochemistry might be higher
- Development status of the technologies
  - Lack of support compared to competitors like nuclear fusion or fission
  - Reasons?
    - Not visionary enough?
    - Thermodynamics are already well understood, therefore no „breakthroughs“ are expected?
    - Not fancy enough? Marketing?

INNOHYP-CA Roadmap 2007 can be interpreted positively
Right processes and planned actions



The cross-cutting actions Roadmap shows some delays: Materials and Test Infrastructure



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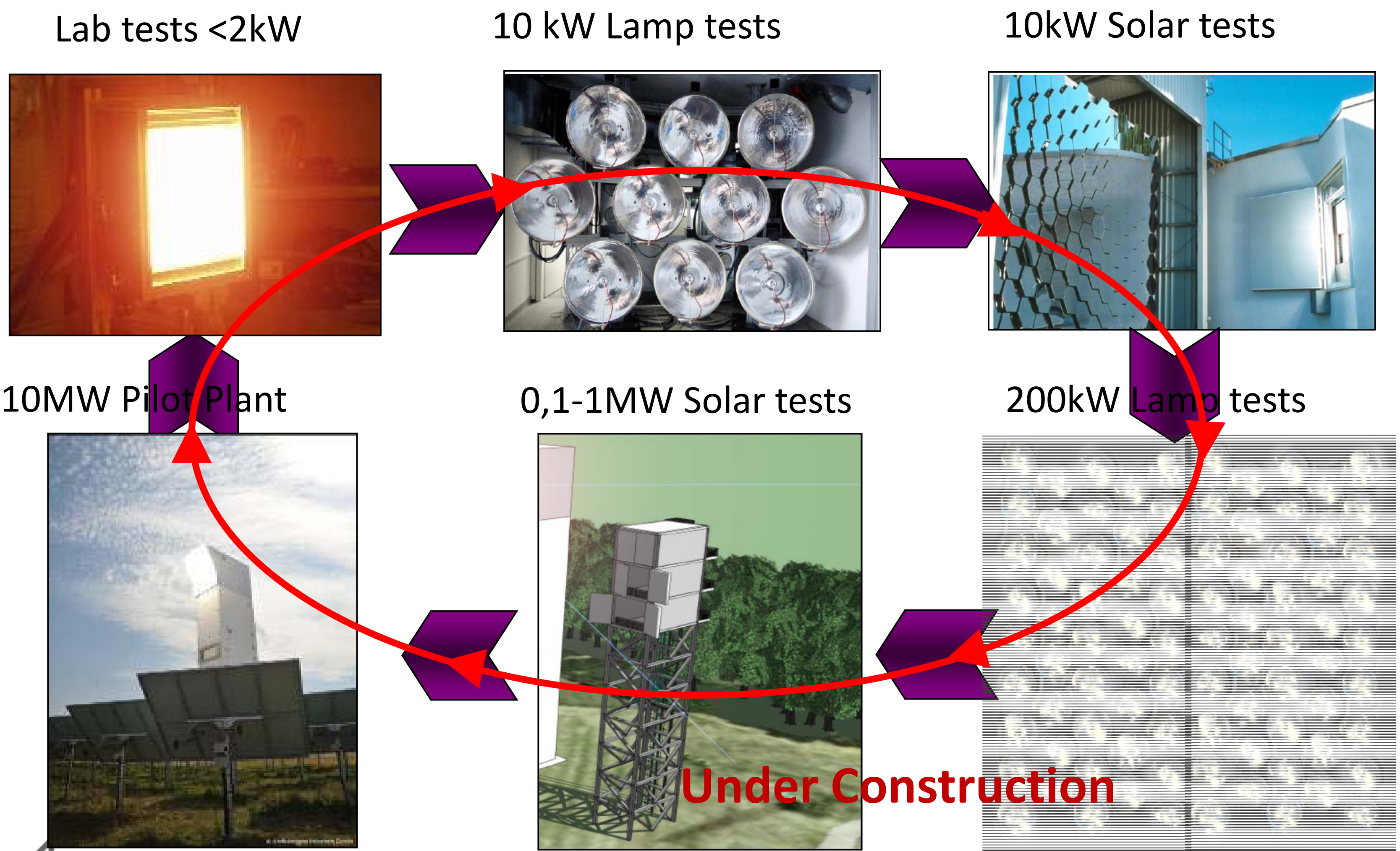
DLR Innovation Cycle - Solar Tower



Drivers for CSF

- **Economy**
  - If somebody can **make money** with the technology there will be progress
  - First business cases are most probably not obvious
- **Policy**
  - ++ Security of supply – value to control fuel production
  - ++ Changing regulations caused by pollution – Megacities (e.g. German and European emission laws, California's Zero Emission Policies …)
  - \+ Changing regulations caused by climate change, Scenarios are seriously taken into account by CO_2 intensive industry, but still discussed controversial by the society
  - \- No need to protect of jobs
- Need to support this by R&D as well as by information and education

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

- **Goals of the EU until 2020 (20/20/20)**
  - 20% higher energy efficiency
  - 20% less GHG emission
  - 20% renewable energy
- **Goal of the EU until 2050:**
  - 80% less CO_2 emissions than in 1990
- Actions in the field of energy efficiency, codes and standards, funding mechanisms, and the charging of carbon emissions necessary
- Significant research effort for the development of a new generation of CO_2 emission free energy technologies, like
  - Offshore-Wind
  - **Solar**
  - 2nd generation Biomass

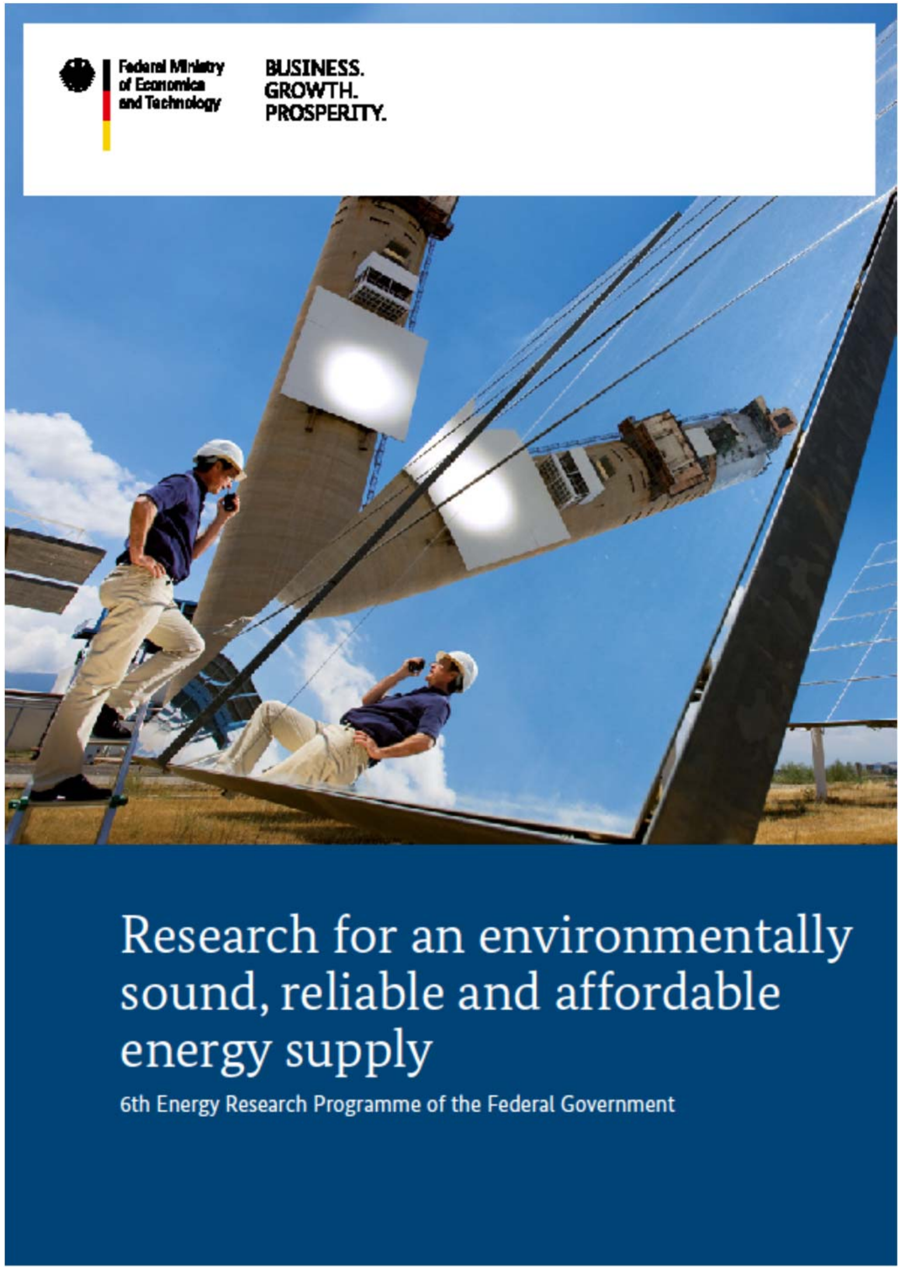
HORIZON 2020

- Most probably about 70 bn€ (2014-2020)
- Main Topics
  - Strengthen the EU's position in science. European Research Council (ERC) Person related basic research (31,73%)
  - Strengthen industrial leadership in innovation (22,09%)
  - address major concerns shared by all Europeans such as climate change, developing sustainable transport and mobility, making renewable energy more affordable, ensuring food safety and security, or coping with the challenge of an ageing population (38,53%)
- Plenary by P. de Bonis on Thursday

Programs in Germany

- 6th Energy Research Programme (3.5 billion € for the period 2011-2014).

- The Programme focuses on key topics relating to the restructuring of Germany's energy supply, i.e.
    - renewable energies,
    - energy efficiency,
    - storage and grids.



IEA SolarPACES and HIA

- SolarPACES Task II: Works on these technologies since the start of the IA
  - 27th Task 2 Meeting yesterday!
  - Study for solar fuel roadmaps in South Africa and Australia as high potential countries
    - Two workshops with 60 and 45 participants
      - Information, education, advertisement, collection of ideas and strategies
    - Connection with activities by HySA and ARENA
    - Joint efforts by experts from Australia, Canada, Germany, Israel Japan, South Africa, Switzerland, USA
    - Work goes on, roadmaps are under preparation
- New HIA Task on solar hydrogen production under preparation
  - Proposed by the US DoE, broad participation by the HIA members
  - Close connection (co-location?) with SolarPACES Task II planned

Solar Fuels

Synergies with established industrial processes

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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

Steam and CO_2-Reforming of Natural Gas

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

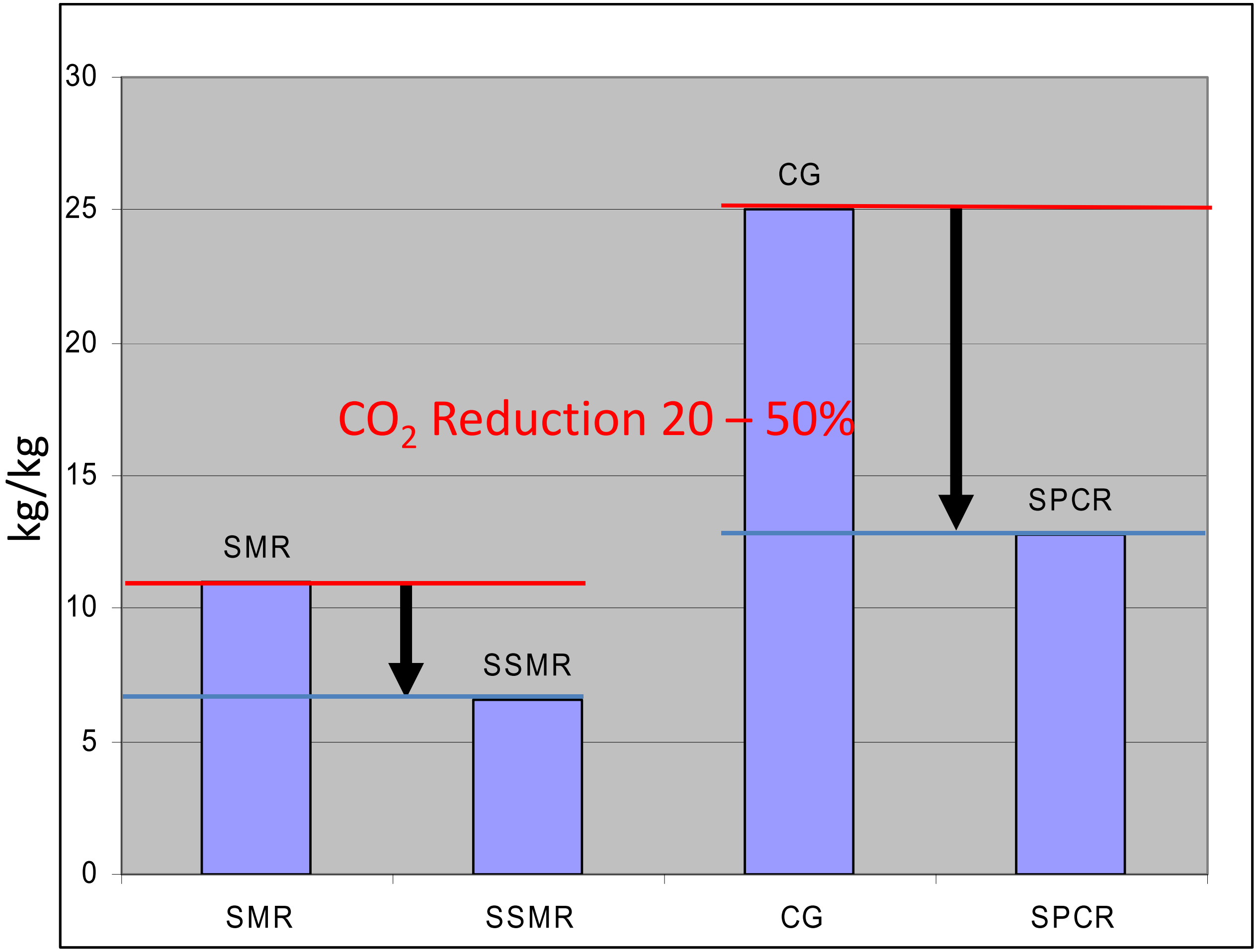
CO_2 Reforming: $CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$

Reforming of mixtures of CO_2/H_2O is possible and common

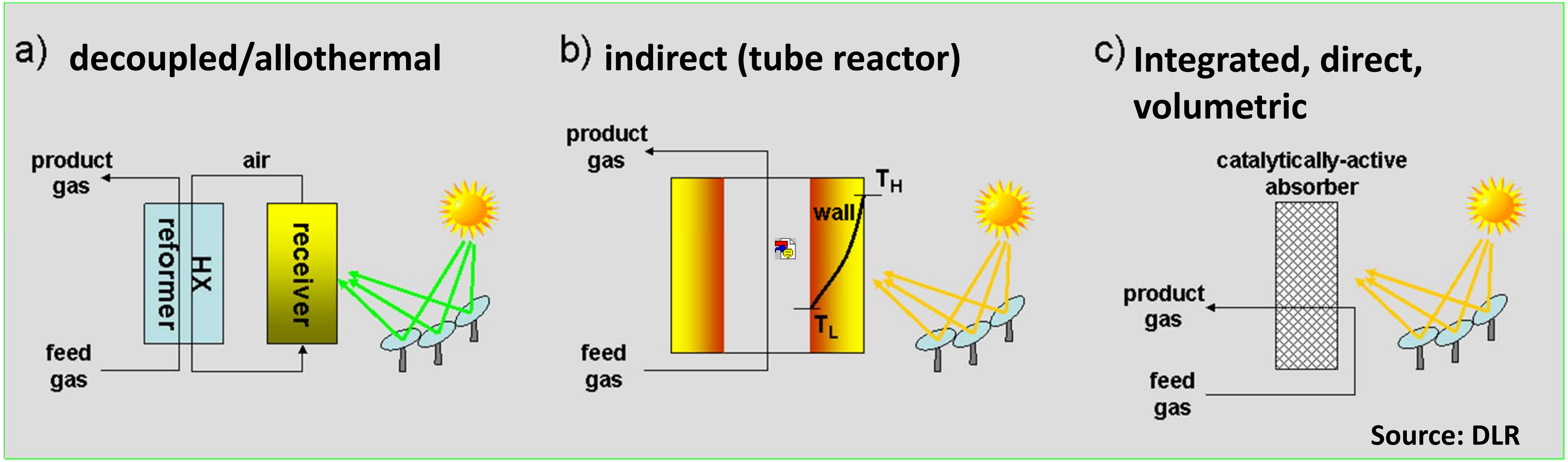
Use of CO_2 for methanol production:

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

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



Solar Methane Reforming – Technologies



Reformer heated externally (700 to 850°C)

Optional heat storage (up to 24/7)

Development: Australia, Germany, Israel, Spain, USA

E.g. ASTERIX project

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,

Presentation this morning by UMN,

Afternoon by Niigata University

Catalytic active direct irradiated absorber

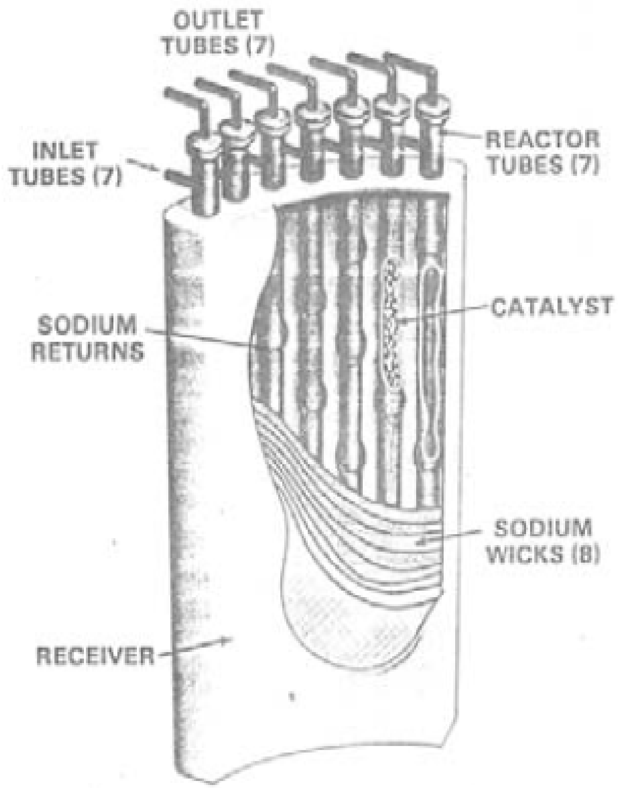
Approx. 90 % Reformer-h

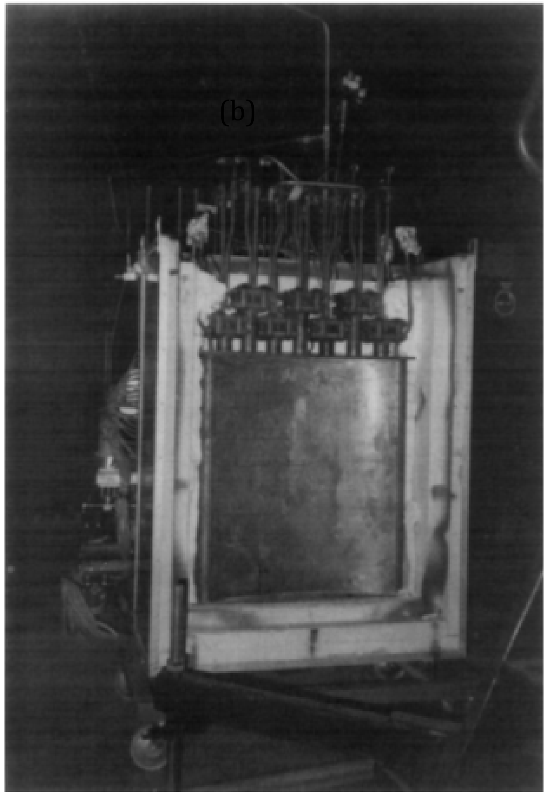
High solar flux, works only by direct solar radiation

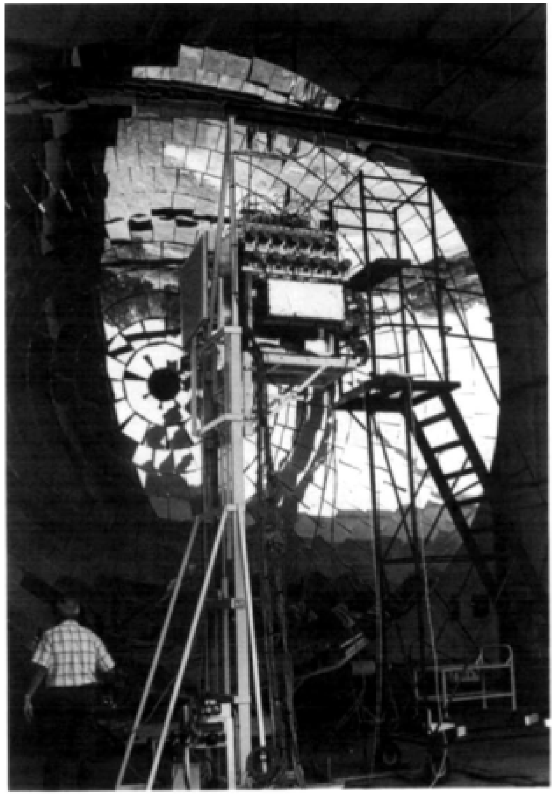
Development: Germany, Israel, Japan

e.g. SOLREF project

SANDIA-WIS's sodium reflux heat pipe solar receiver-reformer (1983-1984)



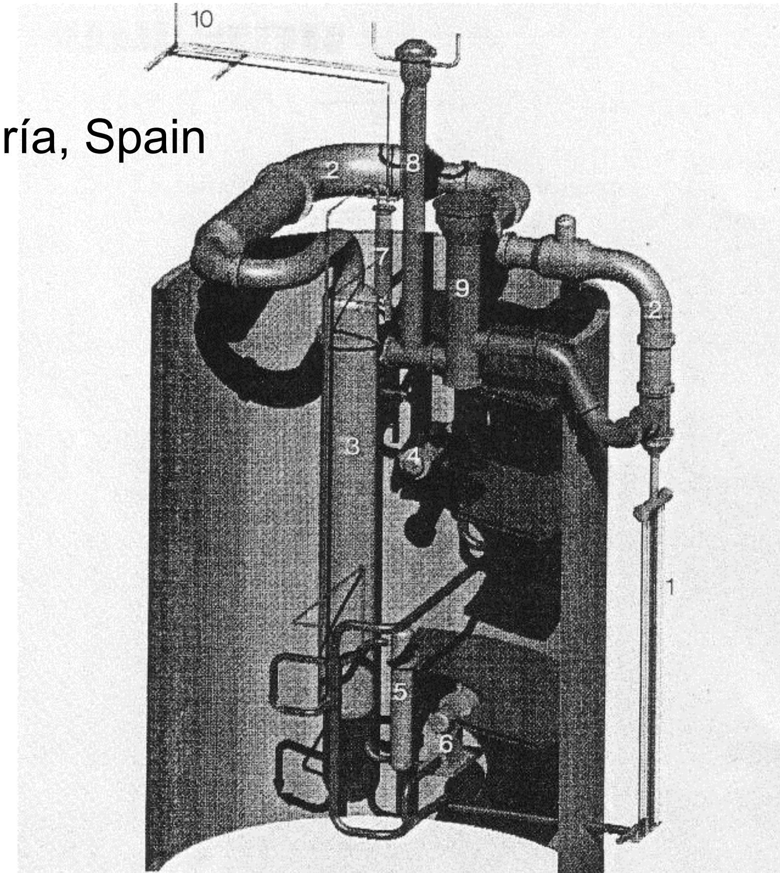




Project Asterix: Allothermal Steam Reforming of Methan

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


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



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

Pilot Scale Solar Chemical Reactors - SolarGas

Experimental set-up of the 200 kW SolarGas reactor, scale-up to 600 kW

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

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

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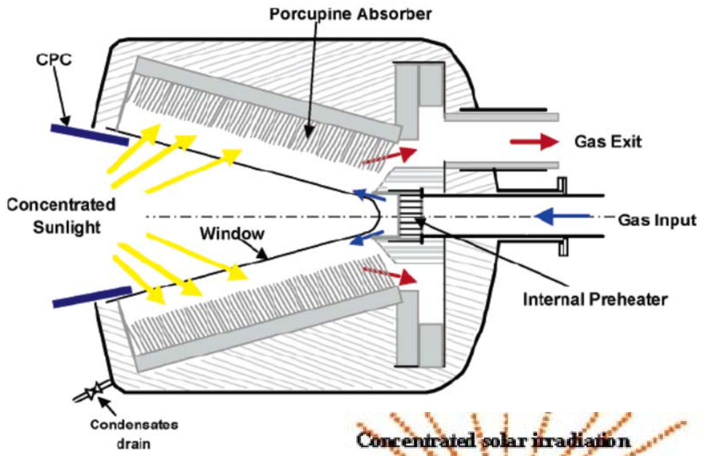
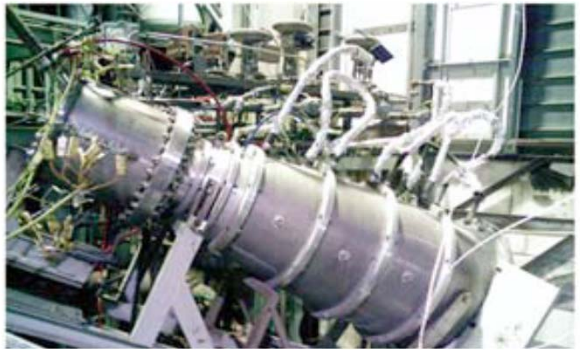
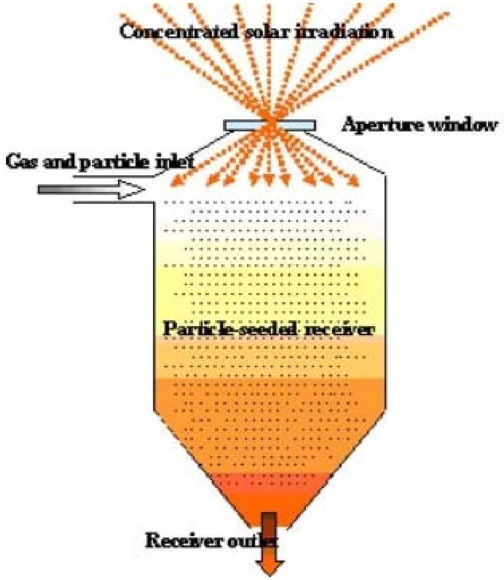
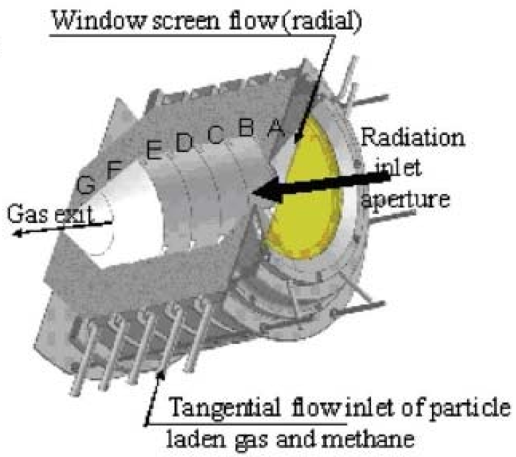
„Porcupine“ and „Particle“ Receivcer, WIS









The metallic-foam-based 5-kW_{th} absorber/reactor of Inha University, Korea

- CO_2 reforming of methane on the Solar Dish System

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)

Solar Fuels

Water or CO_2 splitting processes

New High Temperature Industrial Processes

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

Goals:

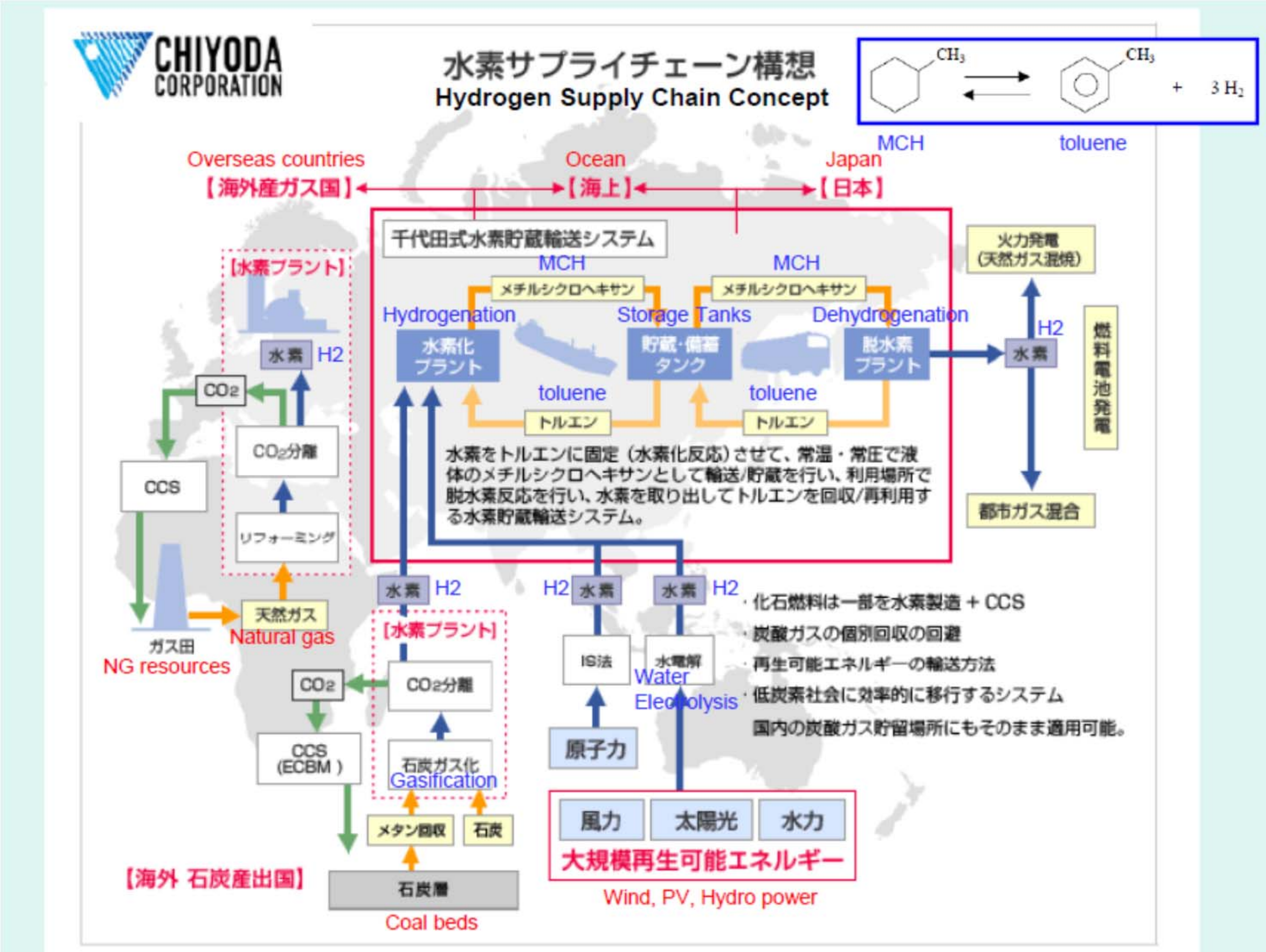
  - Production of hydrogen for power generation and transportation (land, sea, and air?)
  - Upgrade of fossil recourses (oil sands, coal, natural gas)

- 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

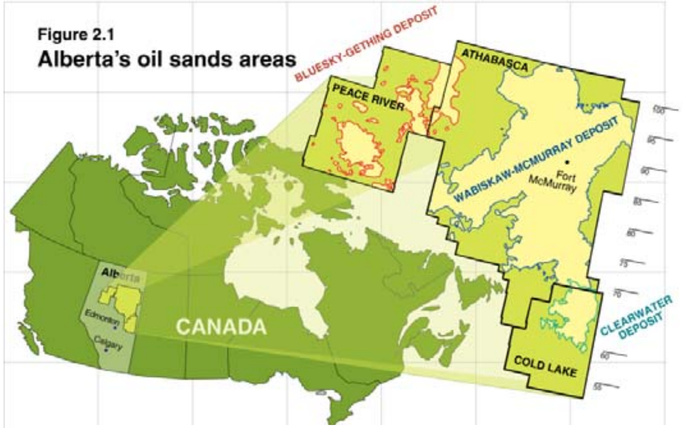
Hydrogen Vision by the CHIYODA Corporation

- 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

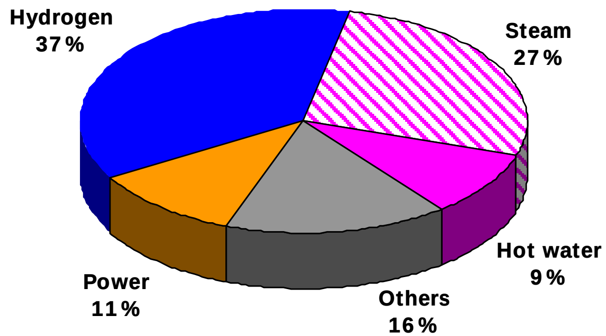


Canadian Oil Sands – Vision by Alberta Innovates

- 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
Poster at SolarPACES 2013

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.

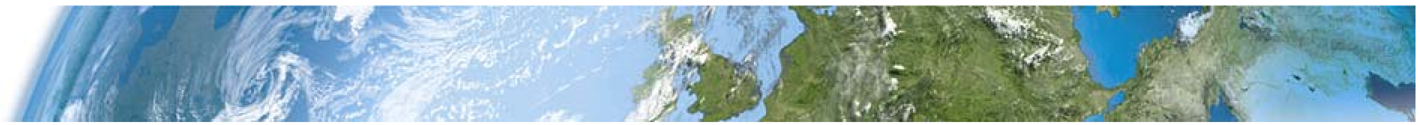
Hydrogen Planes?

- 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

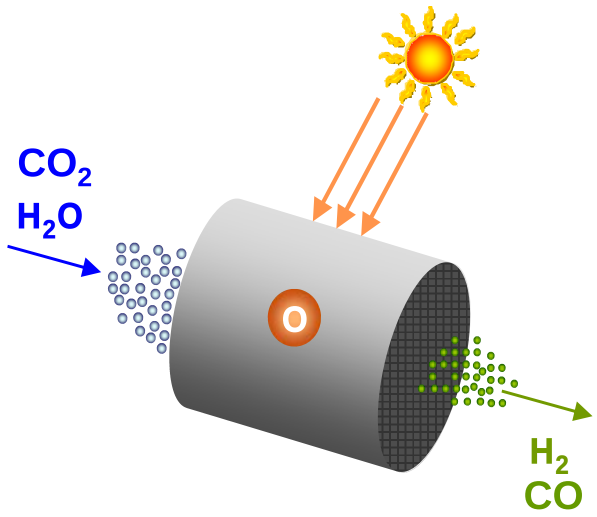
Need for liquid fuels with very high quality and reduced carbon foot print - Solar Jet Fuels!

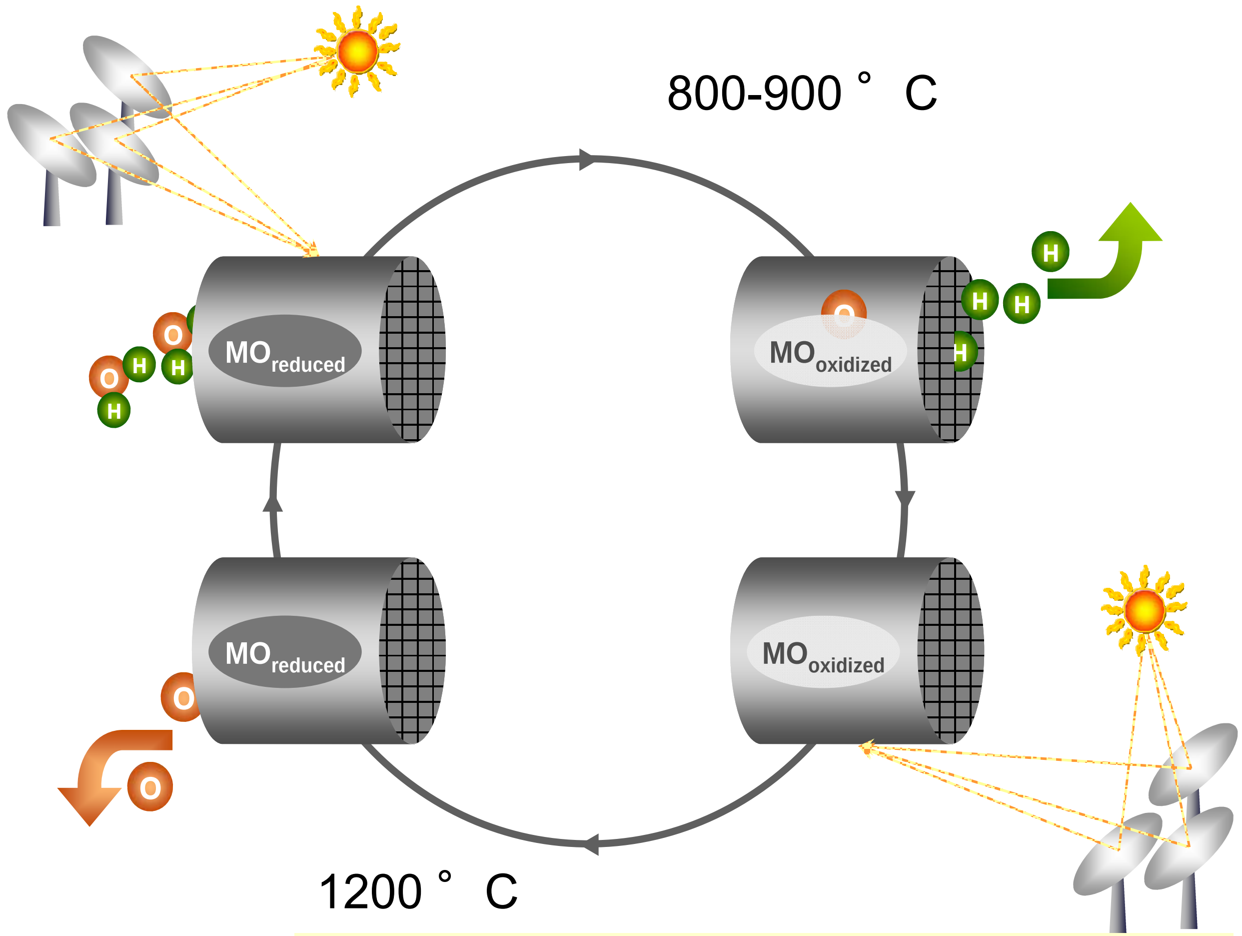
Well researched Thermochemical Cycles

	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 an example for Solar Fuel Production

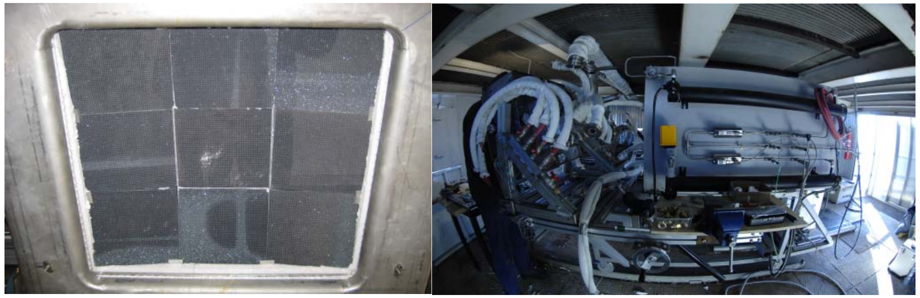




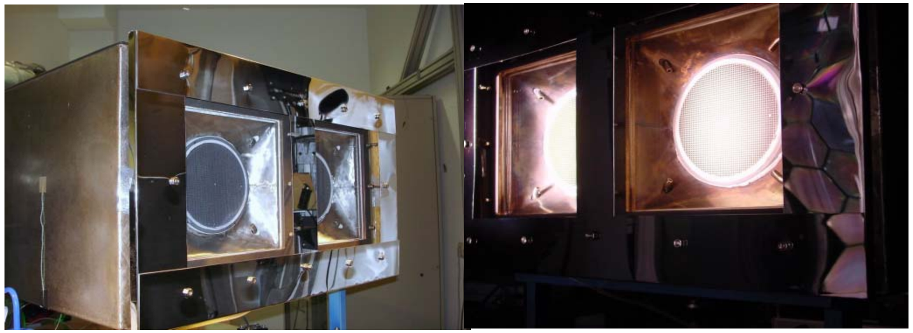
DLR: Roeb, Müller-Steinhagen, *Science*, Aug. 2010

HYDROSOL as a technology scale-up example

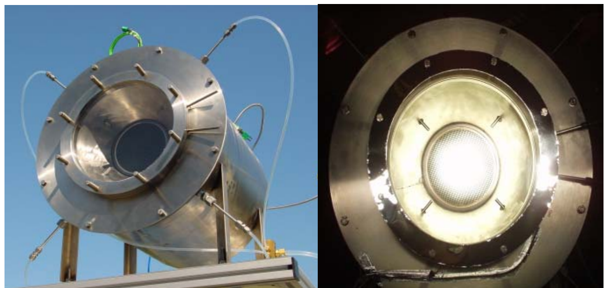
PSA solar tower



2008:
Pilot reactor (100 kW)



2005:
Continuous H_2 production



2004:
First solar thermochemical
H_2 production

DLR solar furnace

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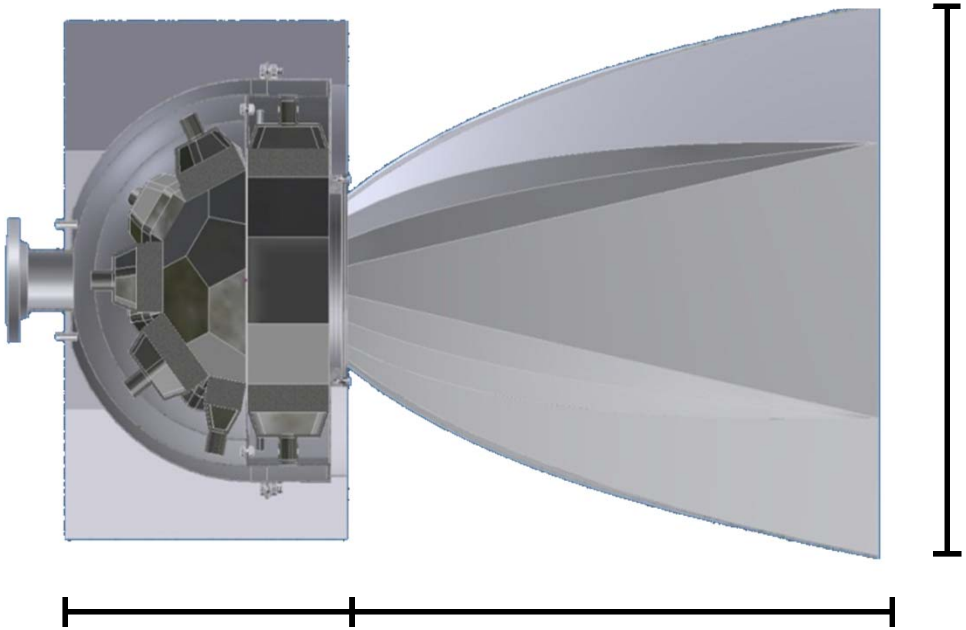
2012: HYDROSOL 3D: 1 MW Pilot Plant Designs

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



Compact 1 MW Receiver Design

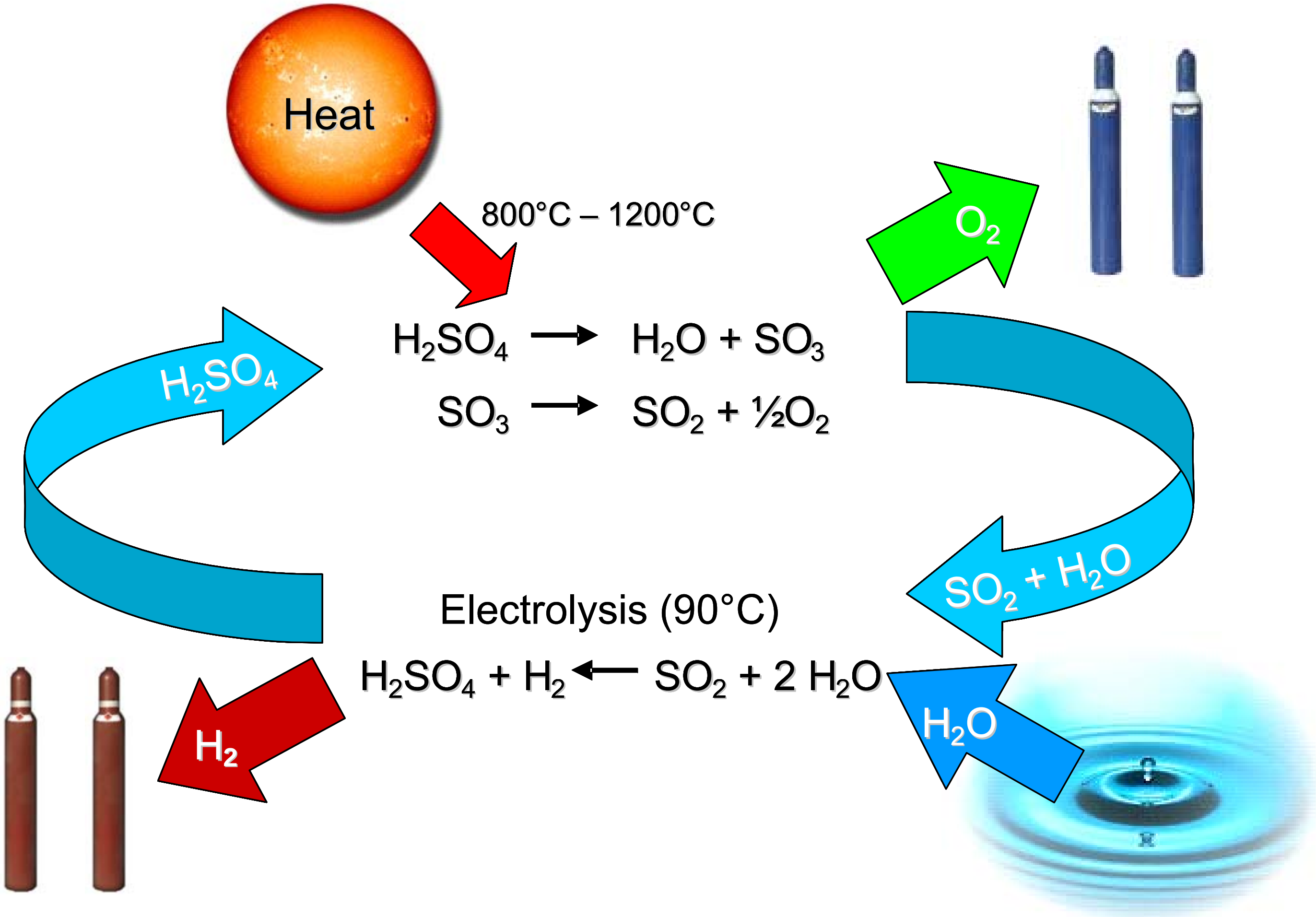
Important Recent Improvements

- 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
    - Two presentations by SANDIA this morning, three by APTL, KIER, and Niigata University this afternoon
  - 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

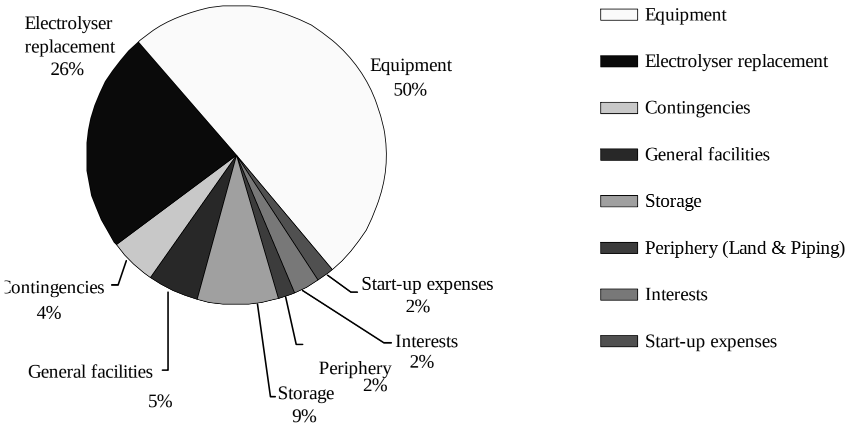
2014: Start of the next project „HYDROSOL Plant“

- Demonstration of a thermochemical cycle based on metal oxides
- A lot was learned over the last ten years which has to be implemented
- In all projects we could realise improvements and scale-up
- It is not perfect yet and also the demonstration will not be!
- The chance to do continous work on a technology is the important advantage of a program like HYDROSOL

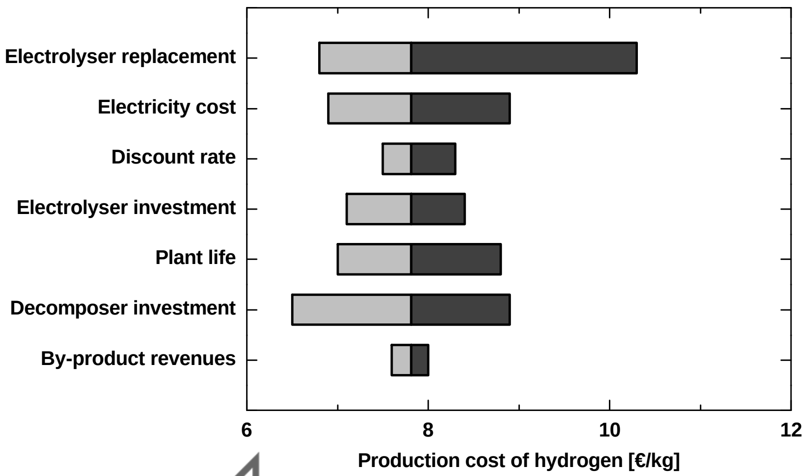
Hybrid Sulphur Cycle



Two concecutive European Projects: HyThec and HyCycleS: Techno-economic analysis

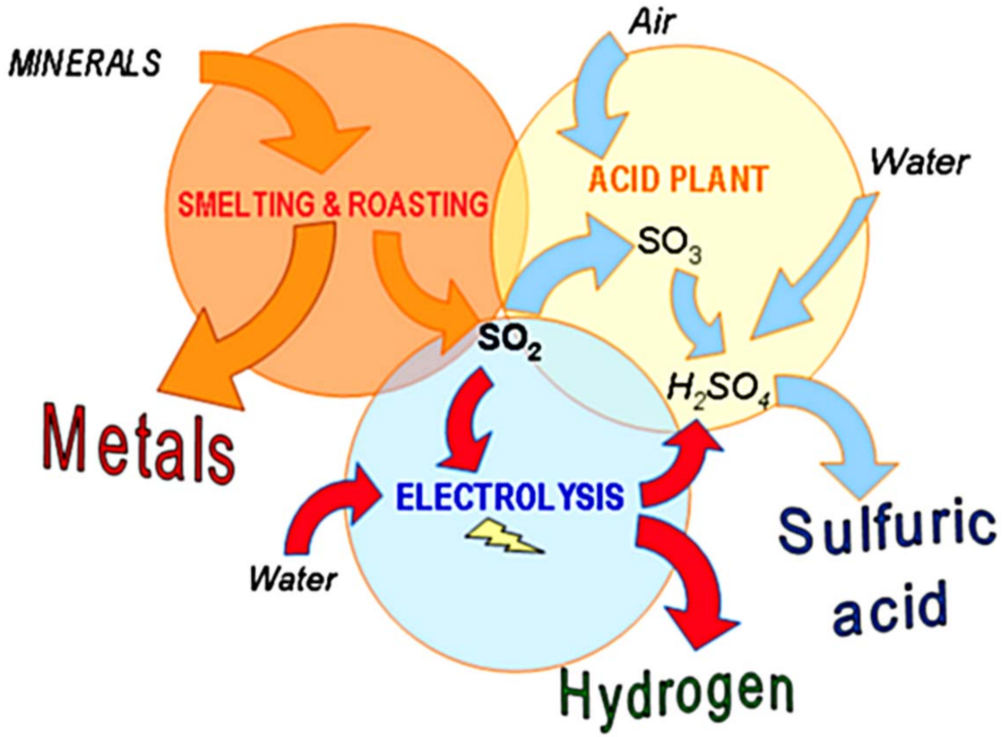


Lebros et et al, IJHE 2010



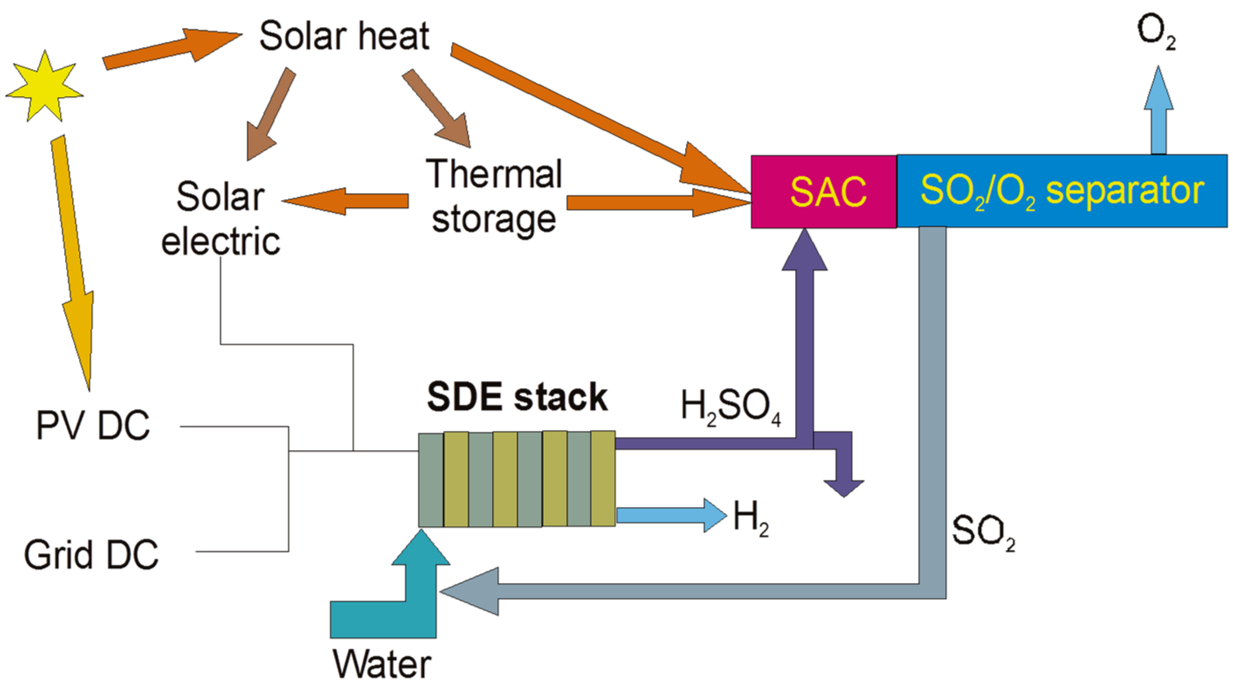
- Flowsheet for solar HyS process refined and completed
- All Components including the solar field were sized for a nuclear HyS and SI process and a solar HyS process
- Investment, O&M cost, production cost were analysed
  → 6-7 €/kg(H_2) for HyS
  → scenarios lead to 3.5 €/kg(H_2)
- 50 MW solar tower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

Outotec^{TM} Open Cycle (OOC)



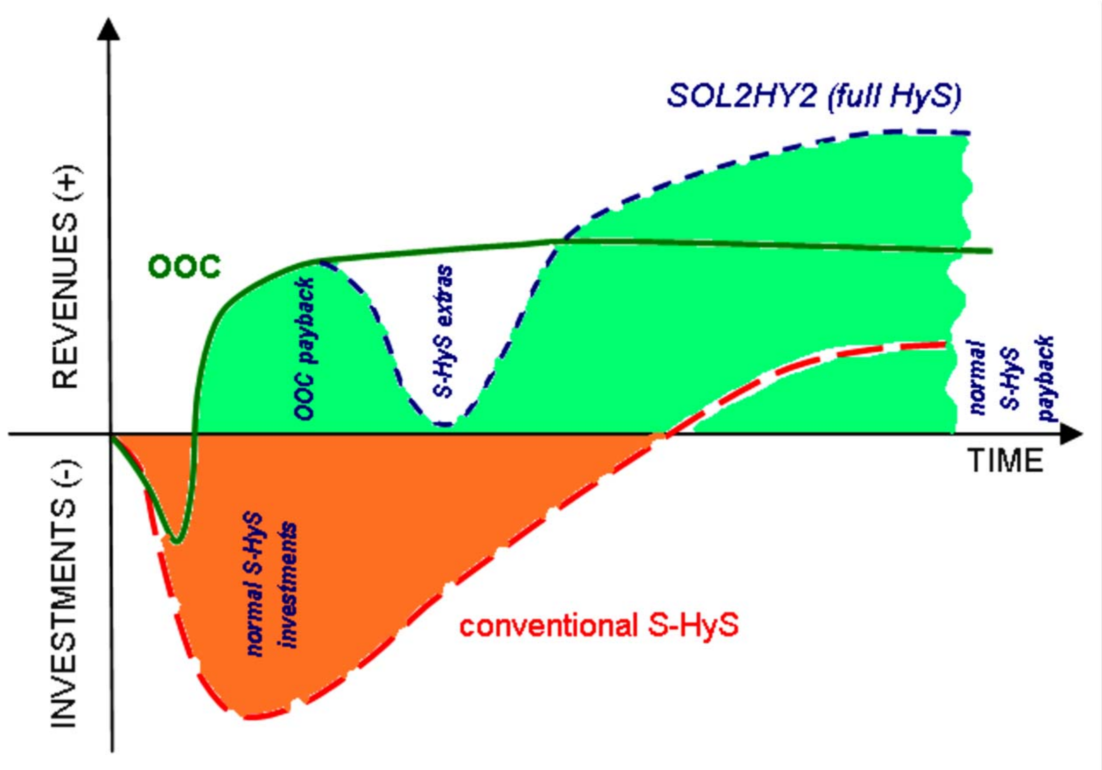
- Utilization of waste SO_2 from fossil sources
- Co-production of hydrogen and sulphuric acid
- Hybridization by usage of renewable energy for electrolysis

SOL2HY2 process strategy concept



- Development in 3 phases
  1. OOC: fossil SO_2 + fossil electricity
  2. solar-OOC: fossil SO_2 + solar electricity
  3. solar-HyS: solar heat + solar electricity

Investments vs. revenues



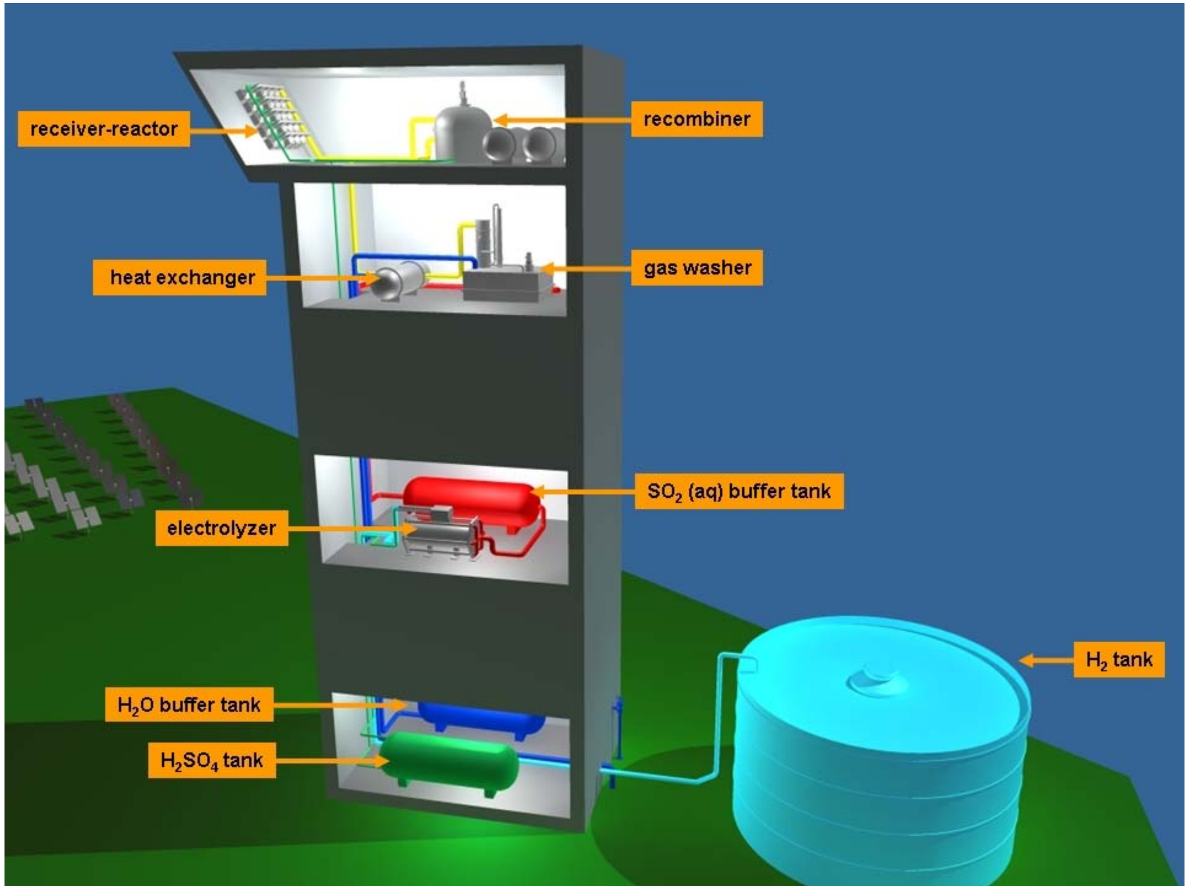
- Reduction of initial investments
- Financing of HyS development by payback of OOC
- Increase of total revenues

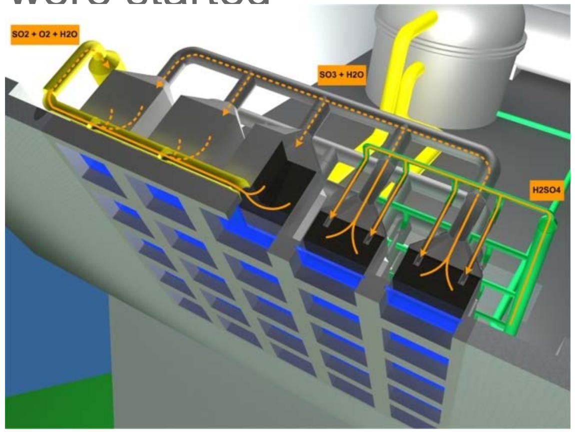
MW Scale-up

of volumetric receiver-reactor for decomposition of H_2SO_4 – Start May 2013

Next step would be the coupling of Savannah River National Lab‘s SO_2 electrolyzer to the solar sulfuric acid splitter at DLR

Plan exists since 2005 when joint efforts under the IPHE were started

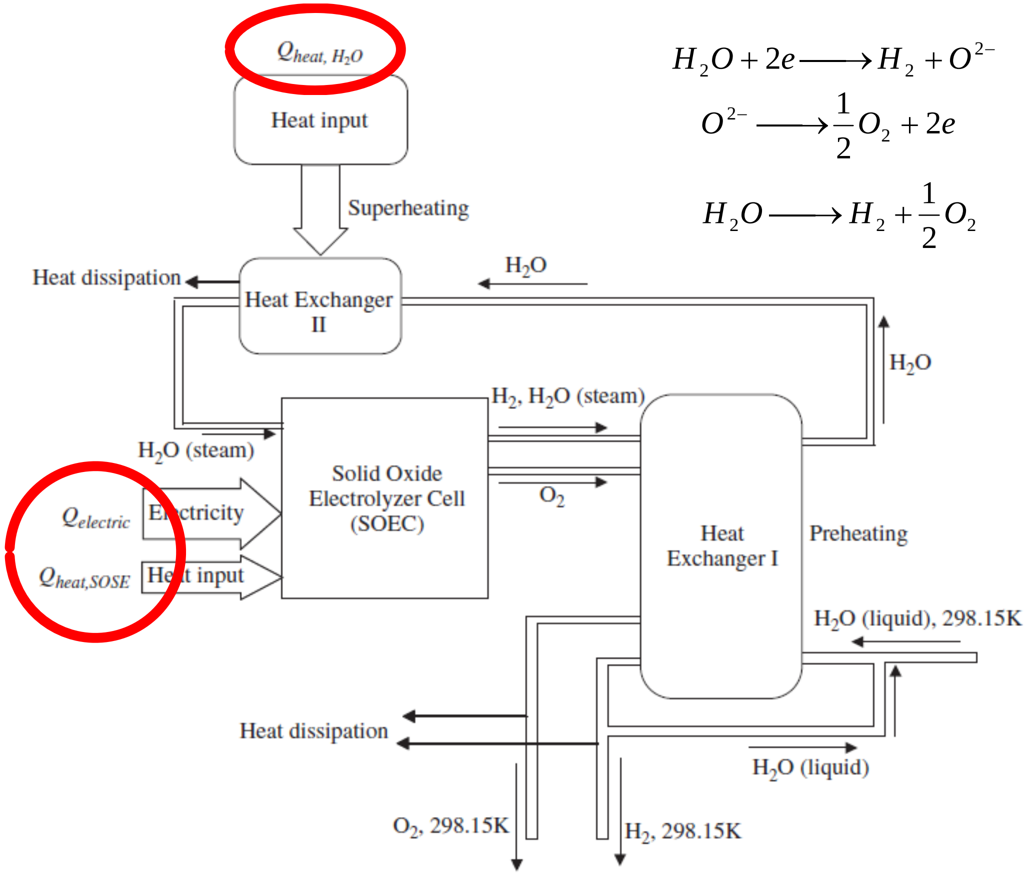




Solar tower Jülich

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.

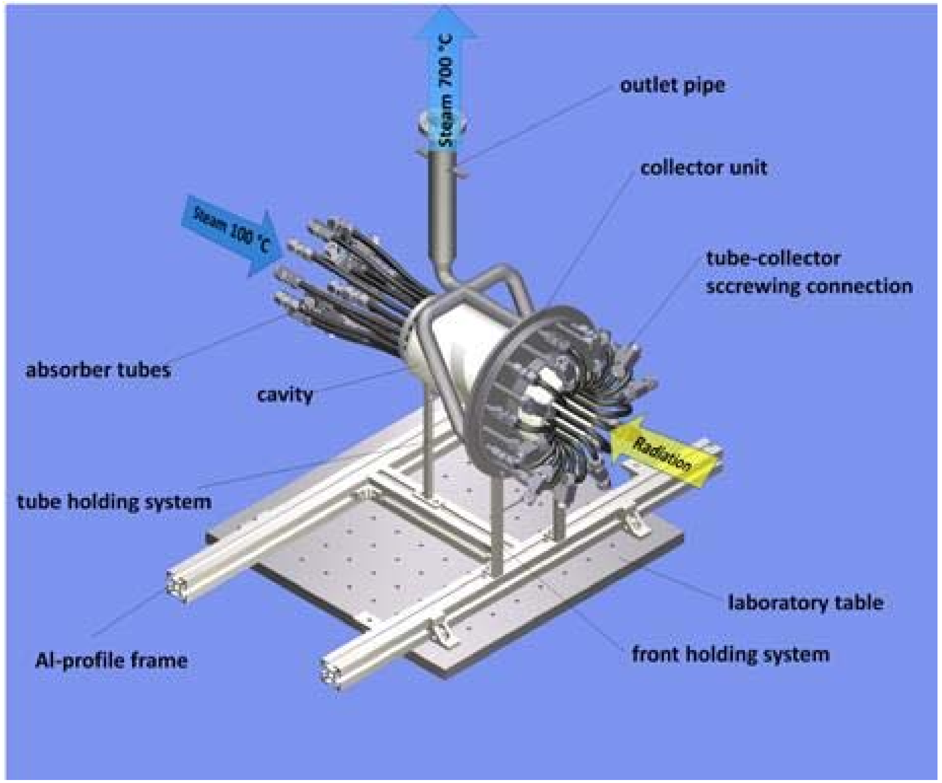


$$H_2O + 2e \longrightarrow H_2 + O^{2-}$$

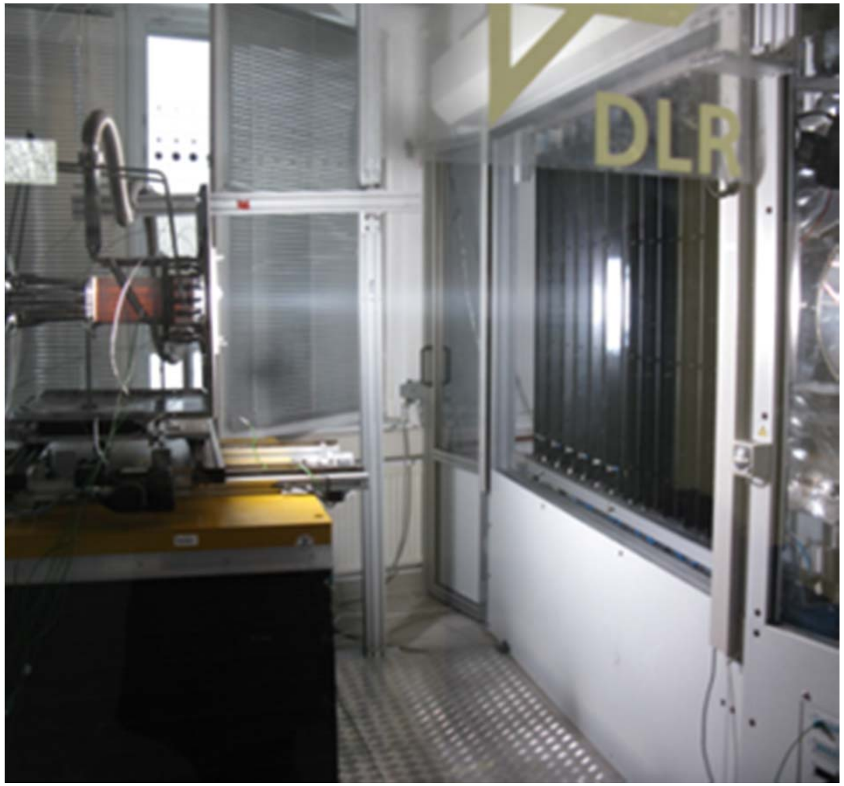
$$O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e$$

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

Solar Superheated Steam Generator for SOEC



3D Design



Operation in the solar simulator providing 5 kg/h steam at 700 °C

Source: Houaijia et al., DLR, Germany

Poster by Thomey et al. at SolarPACES

Business Possibilities for CSP and Components Industry

- Heliostat fields, towers, and Dishes
    - High temperature reactions like reforming, water or CO_2 splitting
- Linear Fresnel and parabolic troughs
    - Steam generation (process heat and feed for electrolyzer)
    - Concentrated photo(electrochemical) processes to reduce the reactor volume
- Innovative gas turbines for heat and solar fuel conversion
- Storage systems for keeping reaction conditions constant

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Conclusion and Outlook

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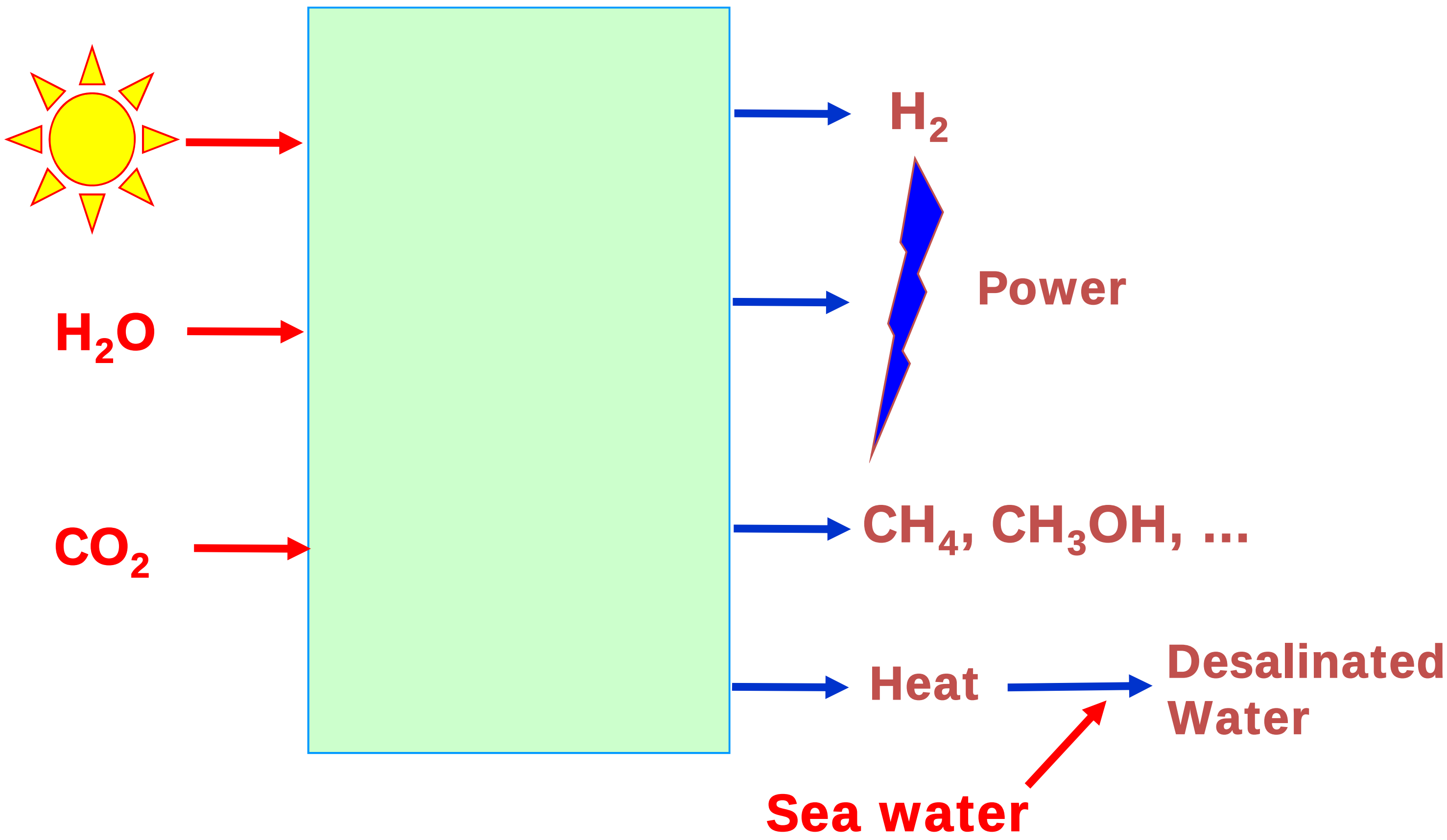
Future Concentrated Solar Plants – more than power!

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



Acknowledgement

- Thanks to all agencies funding the development of solar fuel technologies
- 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!

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Thank you very much for your attention!

Don’t miss the posters and presentations!

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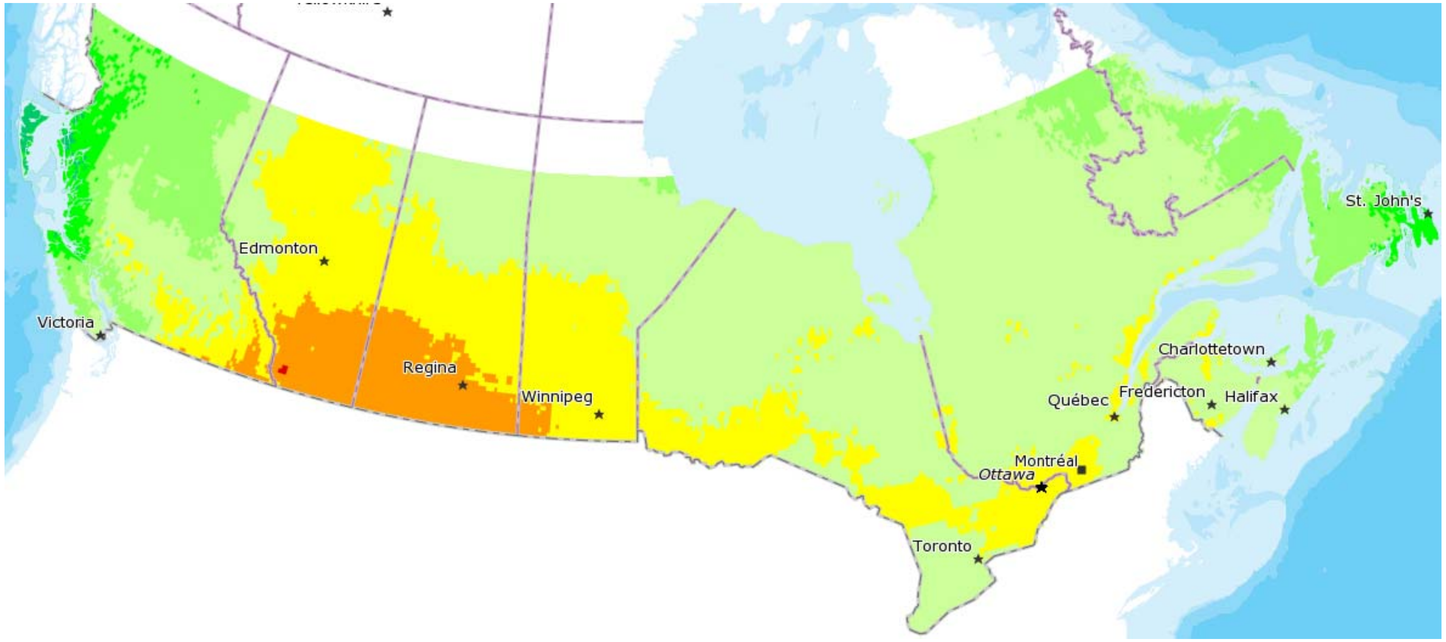
Canada DNI map (kWh/m²/y)



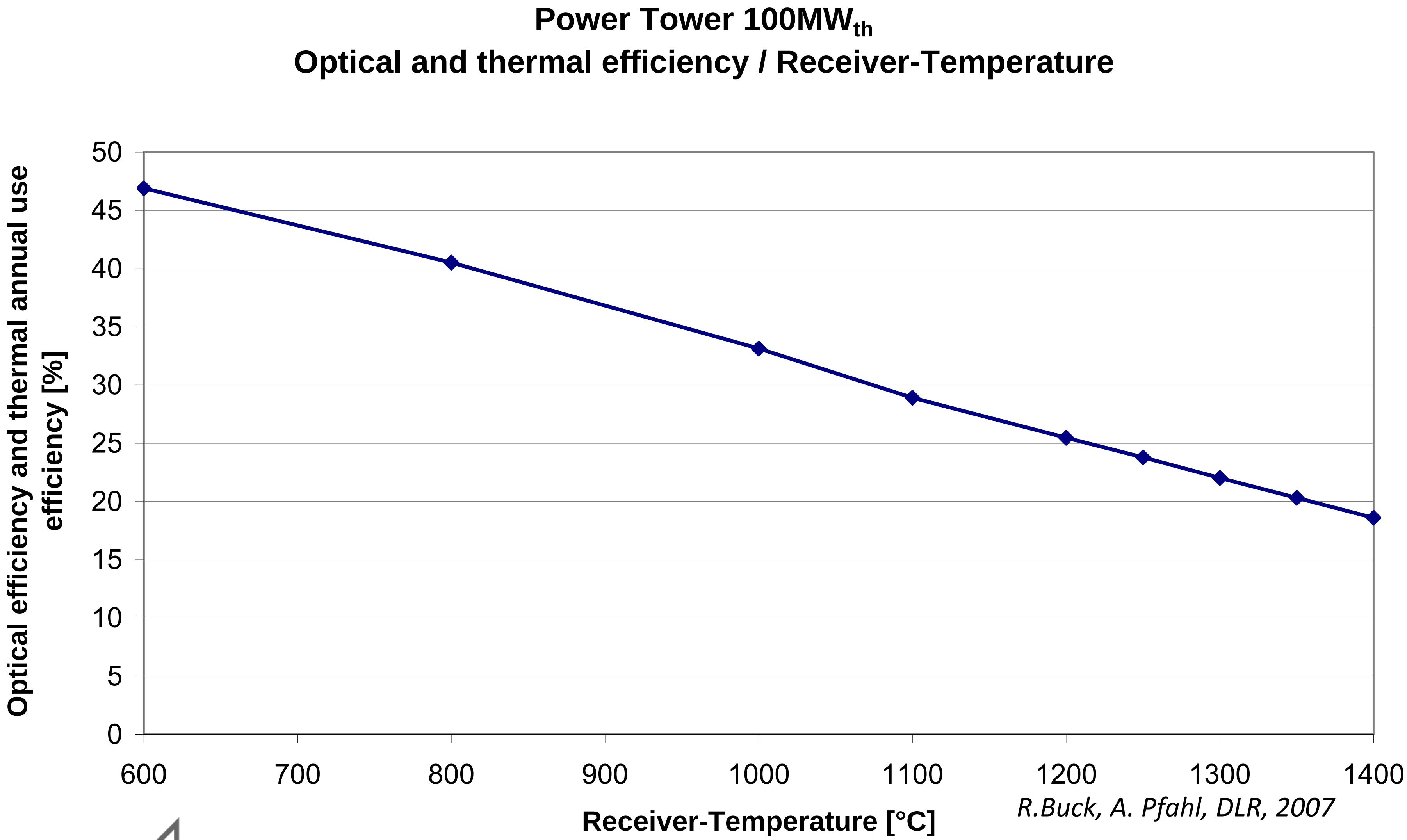
DNI annual average

- 700 - 900
- 901 - 1100
- 1101 - 1300
- 1301 - 1500
- 1501 - 1700
- 1701 - 1900
- > 1900

Source: NRCAN/CANMET

- Western Canada (Alberta and Saskatchewan) are home to Canada's top DNI solar resource

Annual Efficiency of Solar Power Towers



R.Buck, A. Pfahl, DLR, 2007

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Solar Tower Jülich

Receiver 22.7m²

(Intratec, Saint-Gobain)

Tower 60m

(Züblin)

2150 Heliostats á 8.2 m²

(SHP/AUSRA)

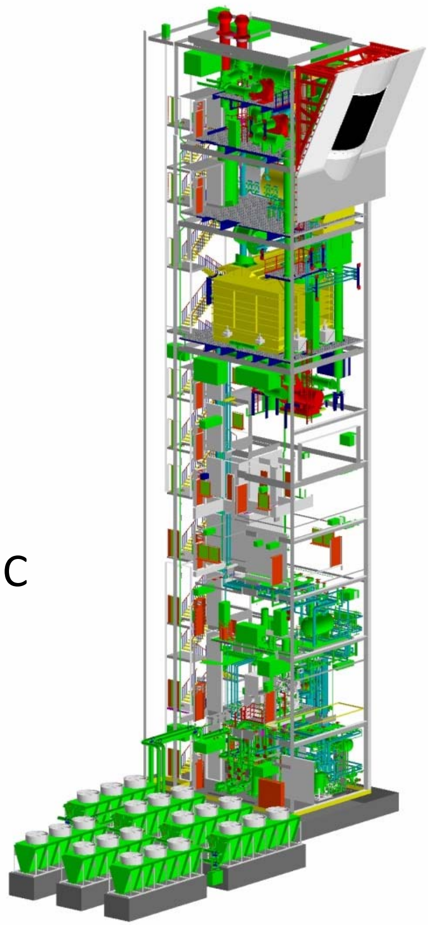
Vessel 9t/h, 30 bar/500°C

(VKK-Standardkessel)

Thermal storage 1h

Turbine 1.5 MWe

(KKK-Siemens)



Potential Solar sites