Solar thermal Hydrogen Production via Reforming and Thermo-Chemical-Cycles

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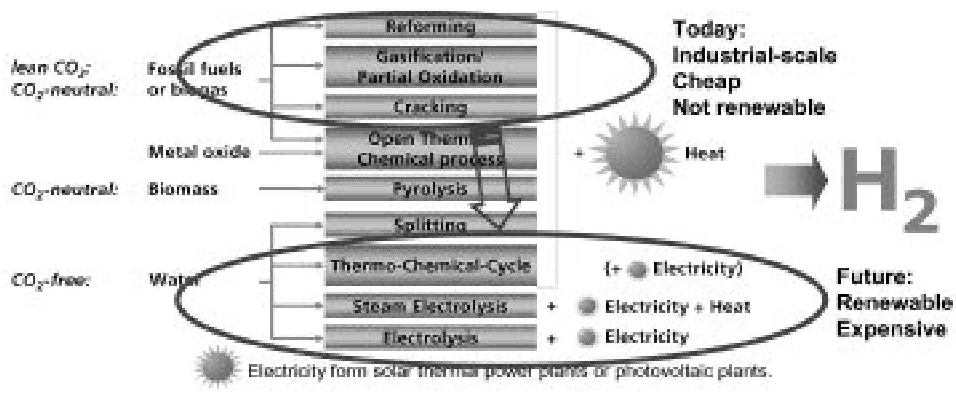
Produced from renewable energy, hydrogen is looked upon as a future secondary energy carrier, which has the potential to become an important substitute for fossil fuels for the next generations. If water and renewable energy, such as solar radiation, can be used for hydrogen production, then it is sustainable.

Apart from the still very costly procedure of electrolysing water by means of renewable electricity, the technologies needed for producing sustainable hydrogen are not yet ready for use. Researchers at DLR therefore dedicate their efforts on developing new ways of producing renewable hydrogen. Together with its European partners, DLR is involved in a number of very promising R&D projects, such as the solar-powered steam reforming of methane and the solar-driven thermochemical splitting of water.



Solar Thermal Processes for Hydrogen Production

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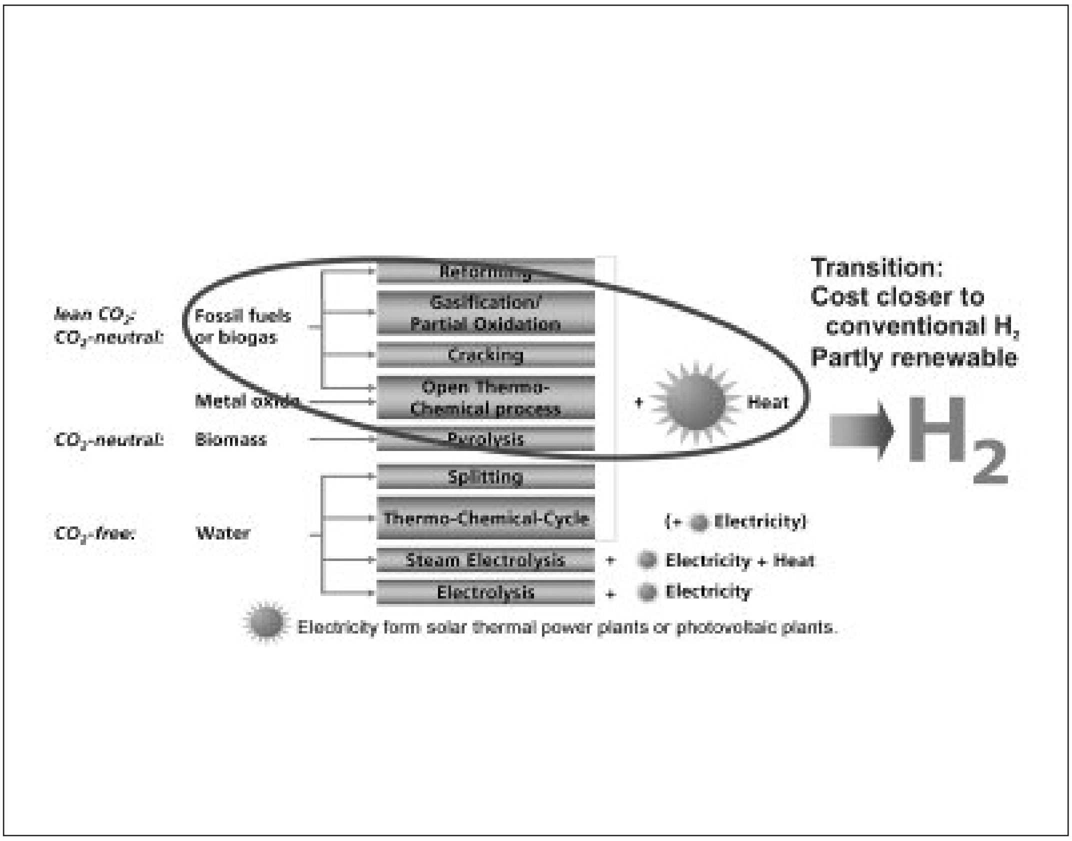
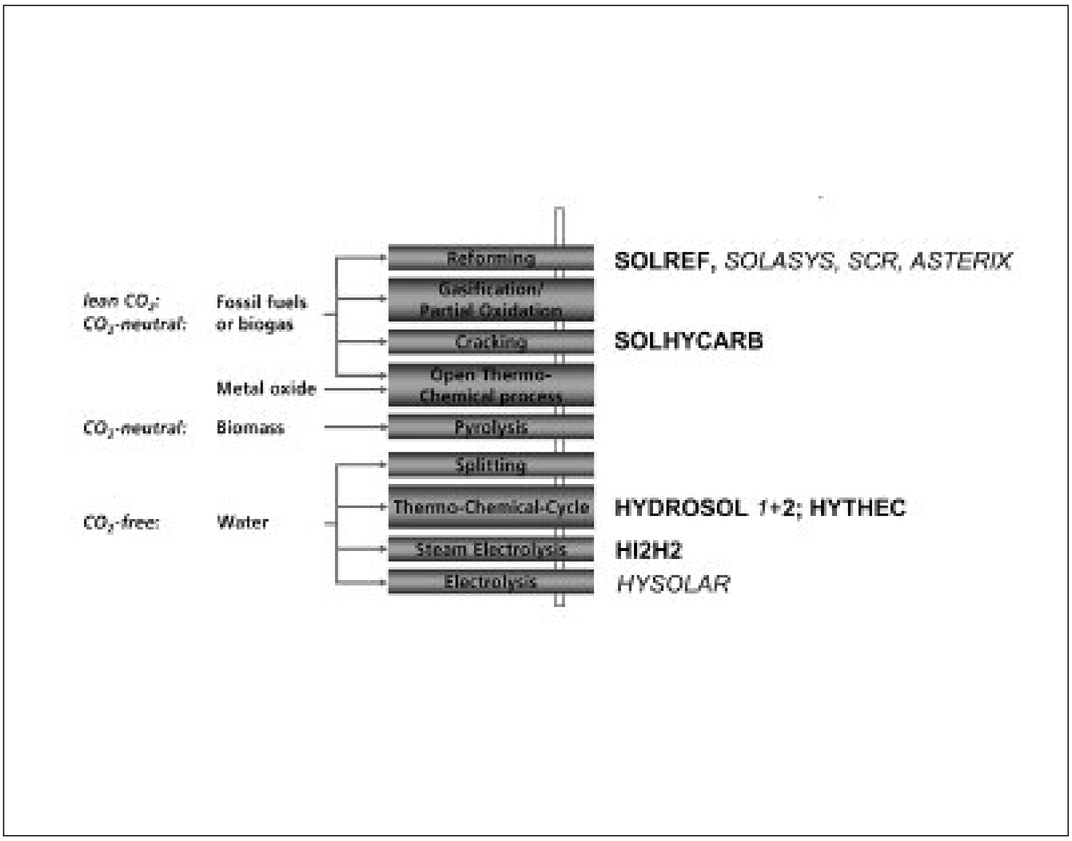
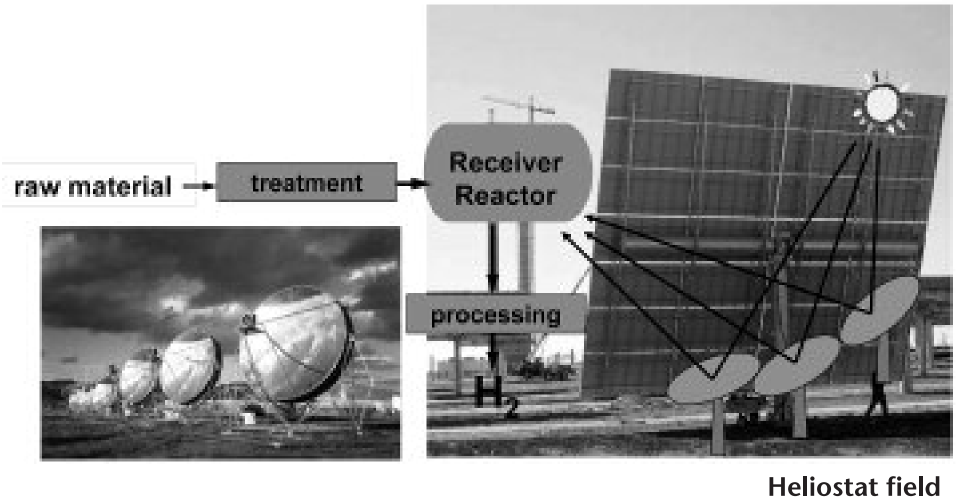


Projects coordinated by DLR or involved as a partner

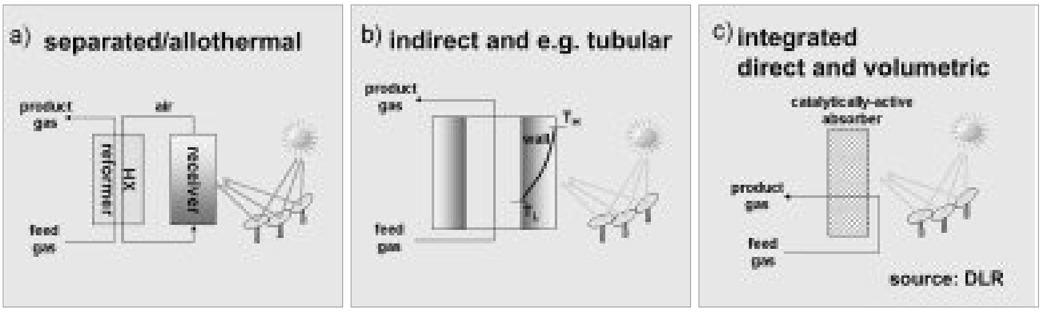




Scheme of a plant for solar thermal H_2 production

Transition pathway-merging fossil fuels with solar thermal energy

Solar Steam Reforming – Different Routes



- Reformer is externally heated. (700 bis 850°C)
- Heat storage operation is possible
- e.g. project Asterix (DLR, late eighties, begin nineties)

- Reformer wall is irradiated (up to 850°C)
- Approx. 70 % Reformer-η
- Ongoing research at CSIRO in Australia and in Japan; research in Germany and at WIS in Israel in the eighties and nineties

- Catalytically active ab-sorber is directly irradiated
- Approx. 90 % Reformer-η
- High flux densities
- Projects coord. by DLR: (SCR, SOLASYS, SOLREF); further research in Israel and Japan

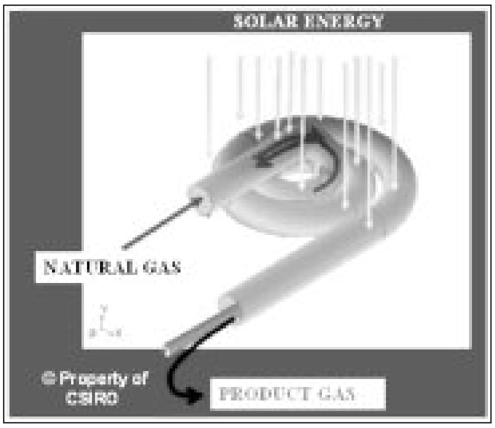
Solar Steam Reforming

Today approx. 95% of the produced hydrogen is made from carbonaceous raw materials, mainly from natural gas via processes based on steam refor-ming and partial oxidation respectively. A transition to a hydrogen economy would have to start with these applicable technologies that means with hydrogen produced from fossil fuels. In a next step the conventional processes must be substituted successively by renewable technologies. The first step could be the use of solar energy to provide the necessary heat for the steam reforming of methane.

By covering the heat demand of that process by solar energy the demand for fossil fuels and therefore CO_2-emissions can be reduced by up to 40% compared to the conventional steam reforming processes. The product is at first synthesis gas, a mixture of H_2 and CO, which can be further transformed to hydrogen and carbon dioxide by the catalytic water-gas shift reaction using additional steam. The solar steam reforming was successfully demonstrated at the solar field of the Weizmann Institute of Science/Israel within the scope of the EC-funded project SOLASYS. Significant advancements will be achieved in the ongoing follow-up project SOLREF. A pressurized volumetric receiver reactor at a few hundred kW level developed by DLR represents the core of the plant.

An economic study shows that hydrogen could be produced at cost below 5 ct €/kWhLHV by solar steam reforming of natural gas in a 50 MW plant. This is only 20% more expensive than the conventional production today. The solar driven process could reach profitability when the today's price of natural gas increases by a factor of about two. Therefore, the application of the solar driven reforming process opens the gate to the Hydrogen economy with less CO_2 emissions at an acceptable price.

Some examples of Solar Reformers



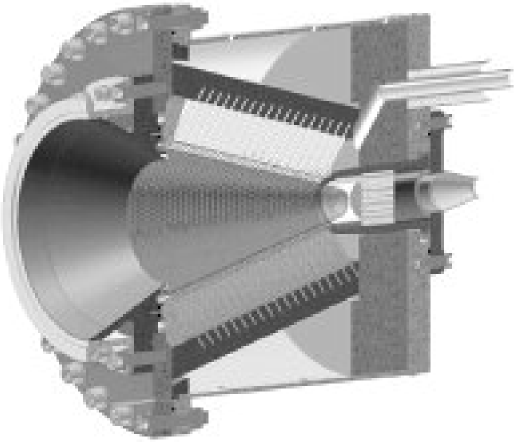
Process schematic

Inside receiver

- 20-50 kW_{th} reformer
- Tubular concept
- The catalyst is packed in between the inner and outer tubes; the inner tube is purely for countercurrent heating of the feed water stream
- Ongoing research at CSIRO, Australia

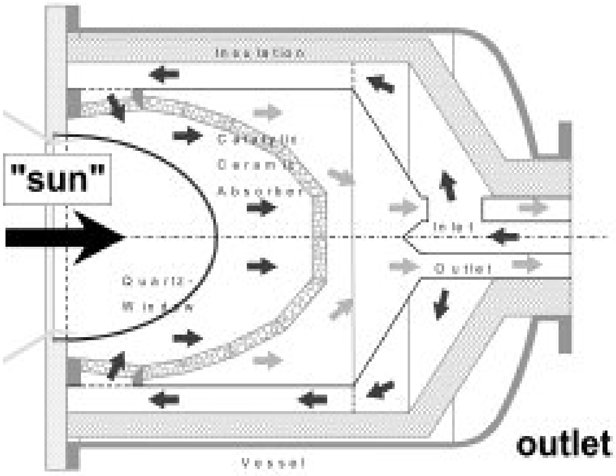
Some examples of Solar Reformers

- 10 kW_{th} reformer (DIAPRRef)
- Integrated concept
- Ongoing research at WIS, Israel

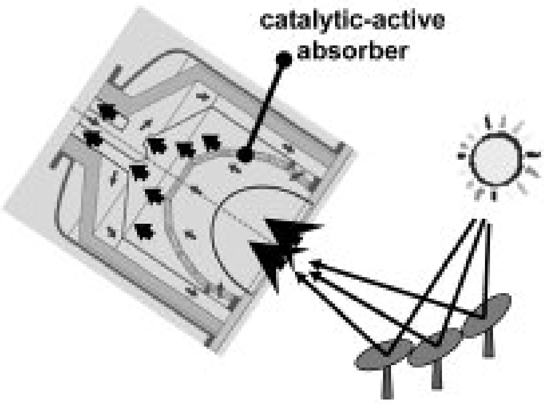


SOLREF –
Solar Reformer

The catalytically active absorber is directly heated by concentrated solar energy. Efficiencies above 90% can be achieved. (increase of sensible and chemical power of the gas mixture divided by the incoming solar power).



Solar steam reforming: project SOLREF - Improvements



- New construction of the reformer
- Enhanced catalysts
- Enhanced absorber (Material/ construction)
- Enhanced frontflange holding the window
- Reduced cost
- Solar power input: 400 kW_{th}
- Reforming temperature: 800-900°C
- Operation pressure, optimal: 10 bar.
- Study on a 1 MW test-plant and on an industrial 50 MW plant.

Future- Production of renewable H_2 from H_2O

- Long term necessary for the de-carbonised H_2 society
- Benchmark: Renewable electricity + electrolysis
- Challenging technologies

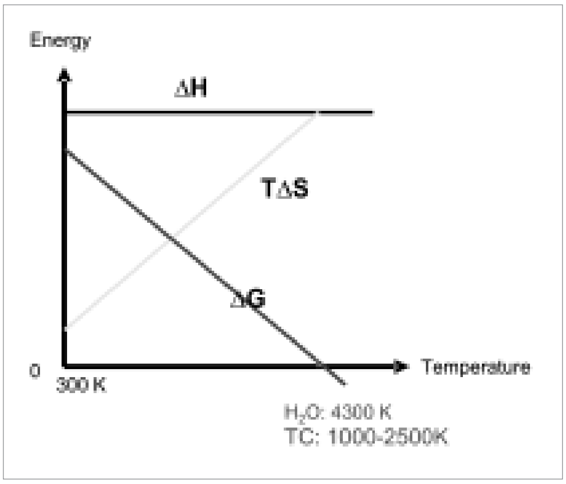
Solar thermal water splitting
$H_2O \leftrightarrow H_2 + ½O_2$ (> 2200°C)

Problems:

- High temperatures
- Materials
- Separation of the products

Solution:

- TC-Cycles
- Temperature decrease
- To achieve good h the number of steps should be low (<4).



Hydrogen Production by Thermo-chemical Cycles

Solar Thermo-chemical Cycles

By using water as feedstock and by applying solar energy as the driving energy for its decomposition, the production of hydrogen becomes free of emissions and free of the consumption of fossil fuels. A mature technology in that respect is the alkaline electrolysis of water, which is environmentally benign if „renewable" electricity is used, for example from photovoltaic and solar thermal power plants. A major disadvantage of this technology is the impact of high electricity/electrolyser costs.

The direct use of solar generated heat to split water has the potential to be less expensive. Direct thermal splitting of water is technologically difficult. Operating temperatures required to shift the equilibrium to the hydrogen side are far above 2.500°C posing high demands on materials and process conditions. To reduce the technical problems associated with those conditions the reaction can be replaced by two- or multi-step thermo-chemical cycles enabling the reduction of the maximum process temperature. In these cycles all the deployed chemicals apart from water that is converted into hydrogen and oxygen are regained and recycled.

A promising two-step water splitting process is investigated in the project HYDROSOL-2. Multivalence metal oxide redox materials are used to split the water in a temperature range between 700° - 1.200°C. These temperatures can be technically achieved by concentrated solar radiation.

The reaction is carried out as follows: during the first step a metal oxide (MO) is reduced by releasing oxygen. In the second step the reduced and therefore activated redox material is oxidized by taking the oxygen from water and releasing hydrogen.

Mixed iron oxides – doped with zinc, nickel or manganese – have proven to be suitable for this process. A solar thermal reactor was developed for operation in the Solar Furnace of DLR in Cologne. Hydrogen and oxygen production take place alternating at different temperature levels. An important breakthrough was achieved. For the first time water was thermally split by concentrated sunlight producing solar hydrogen. Also the regeneration step – the release of oxygen – was successfully demonstrated and repeated several times.

Three or more step thermo-chemical cycles have been developed mainly under the aspect of a potential coupling with a high temperature nuclear reactor working in a temperature range of 850°-900°C.

The Iodine-Sulphur (IS) cycle and the Westinghouse cycle are both sulphur based cycles. They have been developed in the US in the 1970s and 1980s turned out to be two of the most promising. The former comprises only thermochemical process steps. The latter combines a thermo-chemical and an electrolytic reaction step to split water offering the possibility to simplify the cycle.

In the project „Hydrogen Thermochemical Cycles - HYTHEC" both of these cycles are investigated with respect to solar and nuclear energy sources. The input of solar energy allows higher operation temperatures and therefore, the efficiency might be improved. The technical and economic feasibility is investigated by experimental methods using the DLR solar furnace in Cologne as well as by simulation and process design methods.

DLR has developed a solar test reactor which directly absorbs concentrated sunlight to use it as process heat for the decomposition of sulphuric acid. The higher temperatures allow splitting of sulphuric acid even without any catalyst.

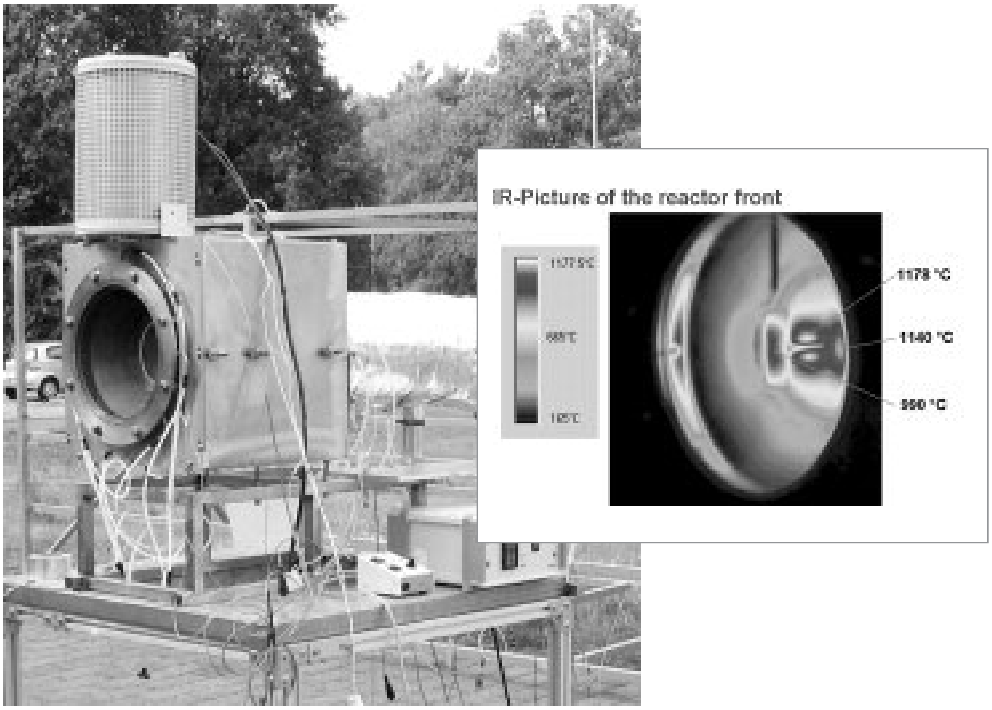
HYTHEC and HYDROSOL are both accomplished with cooperation of different European partners and funded by the European Commission within the scope of research into sustainable energy systems.

The integration of concentrating solar radiation in reaction systems able to split water might provoke an important impact on the energy economy worldwide. The mentioned projects concern key technologies for using solar heat to provide large amounts of sustainable hydrogen on the road to commercialization in the future.

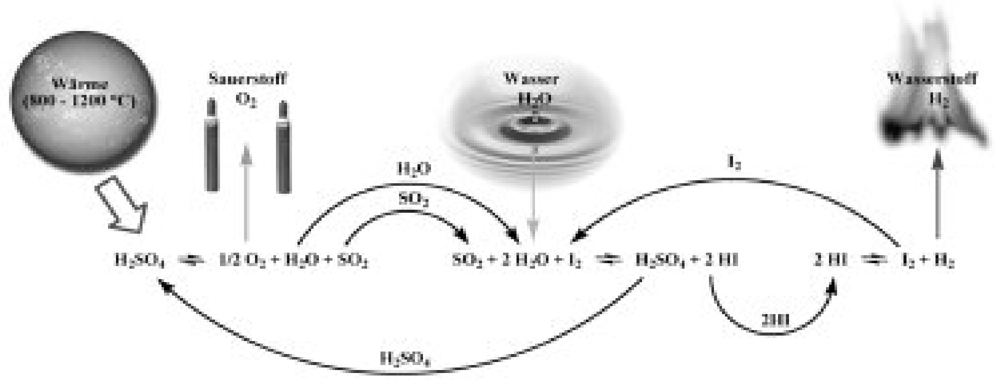
Hydrogen Production by Thermo-chemical Cycles

- Several hundred TCCs were invented during the last 40 years
- Originally developed to use nuclear heat and power for fuel production (General Atomics, Westinghouse, …)
- Today very much in the focus again because:
  - CO_2 free
  - No dependency on fossil fuels
- Today research on renewable TCCs (D, CH, USA, F, E, I, …) and nuclear TCCs (F, JPN, USA …)
- Most promising today:
  - Metal/Metaloxide: Fe, Zn, Mn, Ce … (?)
  - Salts: UT3, CuCl, … (?)
  - Sulfur: Westinghouse, Sulfur-Iodine (General Atomics)
- Carbon (CO/CO_2)

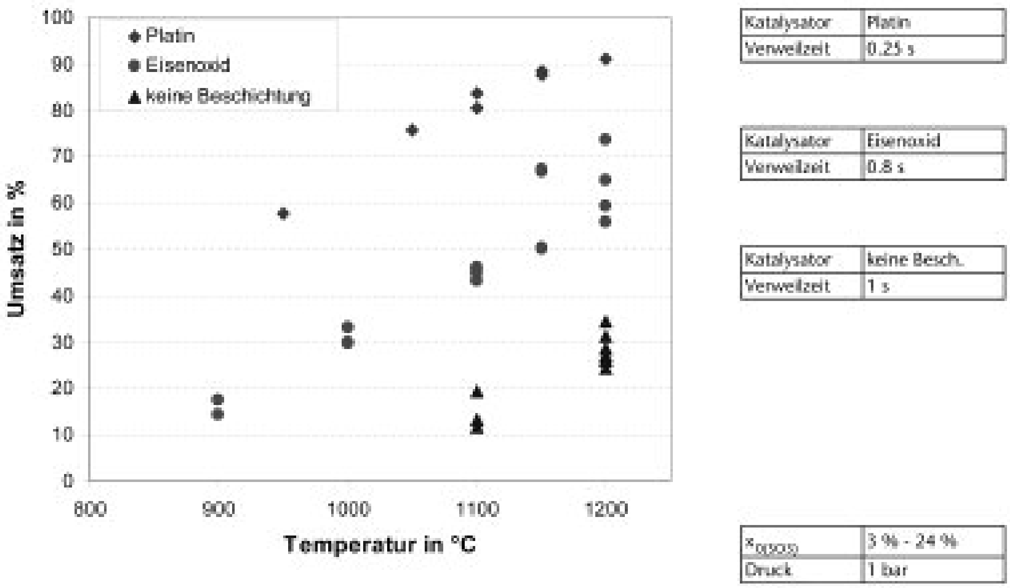
*HYTHEC **Hy**drogen Production by **The**rmo-chemical **C**ycles*

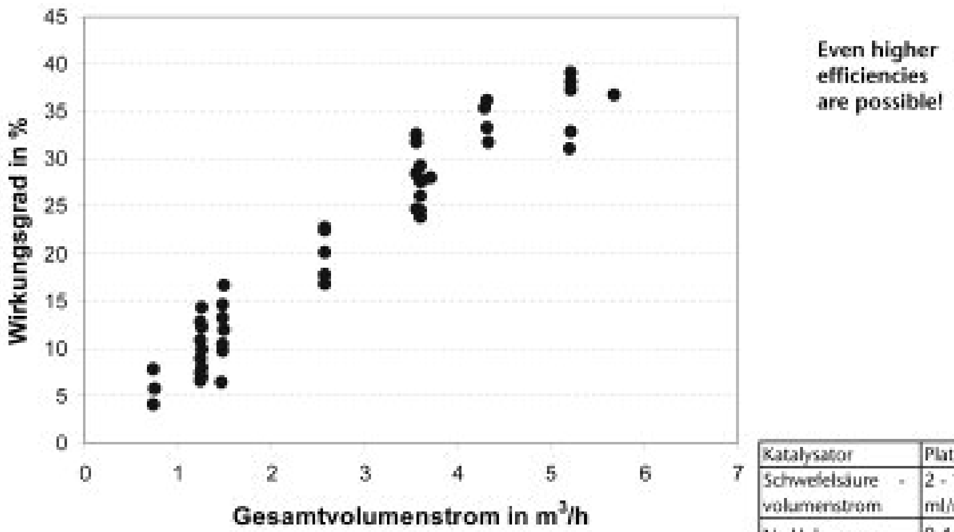


HYTHEC:
Sulphur-Iodine Process



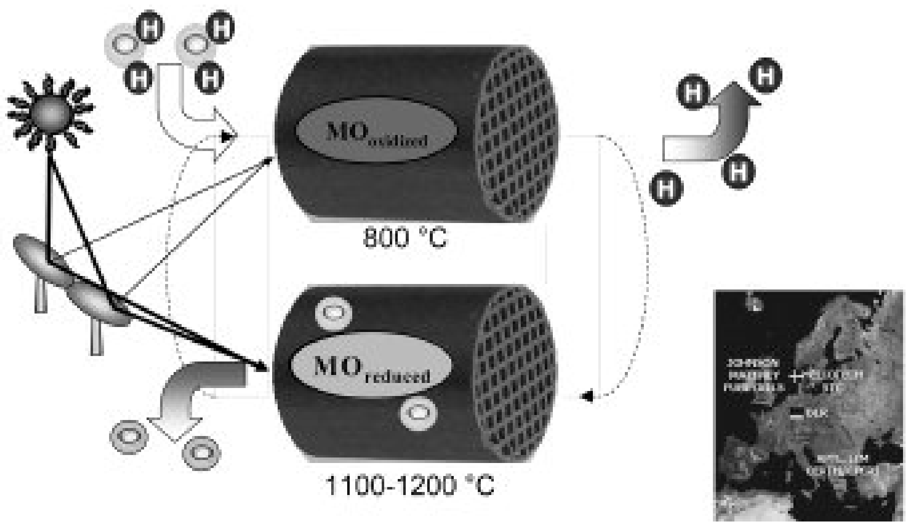
HYTHEC:
Comparison of
catalyst behaviour





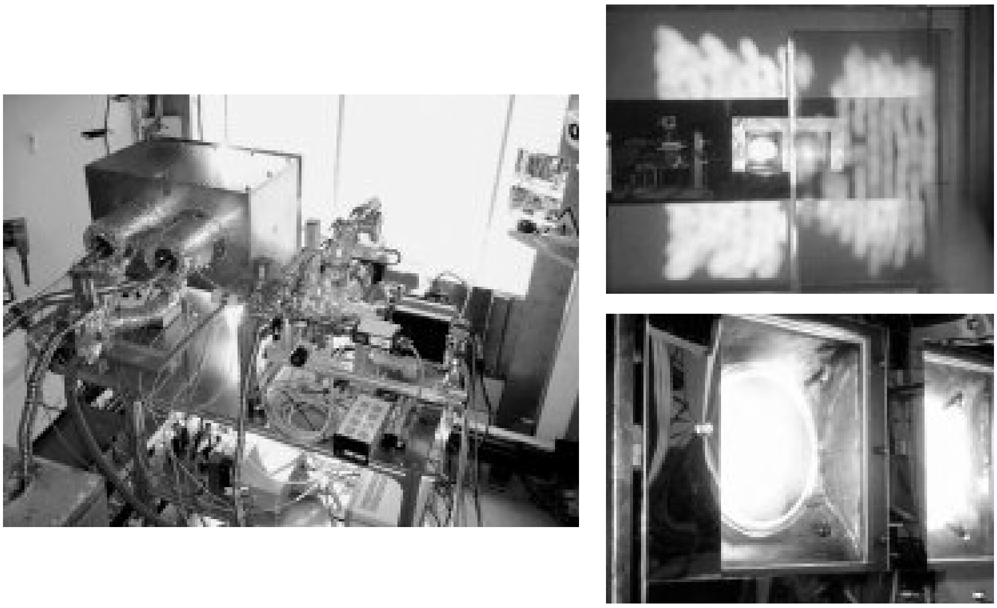
Katalysator	Platin
Schwefelsäure - volumenstrom	2 - 10 ml/min
N_2-Volumen-strom	0,4 - 3,6 m³/h

HYTHEC:
Efficiency depending on total volume flow



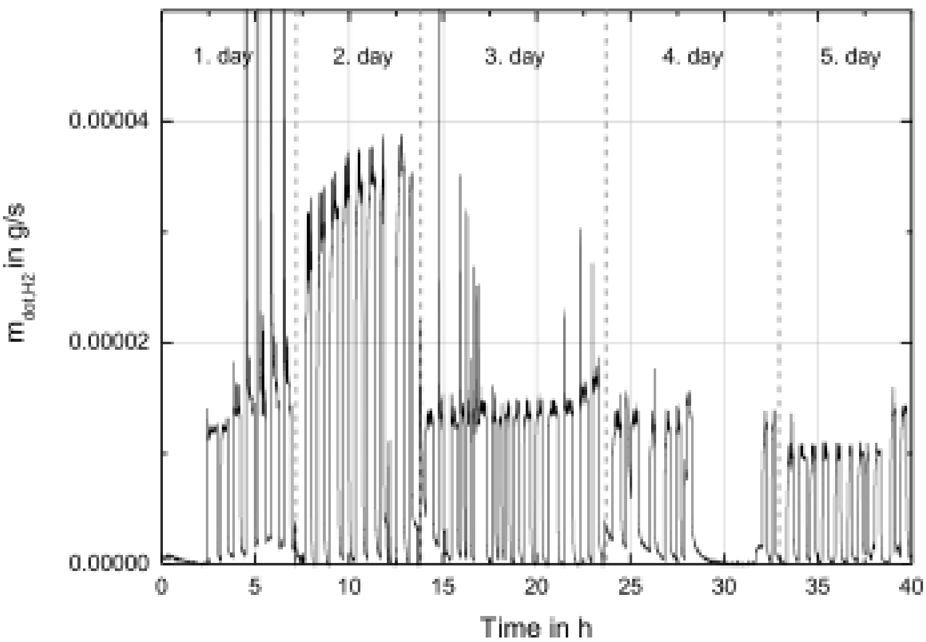
HYDROSOL:
2-Step redox cycle with mixed iron oxides - Principle of Operation

HYDROSOL: Continously operating reactor during exposure to sunlight



HYDROSOL: Long-term test

Hydrogen generation for 53 cycles performed with one sample



HYDROSOL: Start of installation at the PSA

- Scale-up from solar furnace-scale of few kW to 100kW thermal energy input

Conclusion and Outlook

- For the EU H_2 is the Energy carrier of the future especially for mobile applications
- Thermal H_2 production is besides electrolysis the technology for bulk production of H_2
- The market introduction in Europe is planned to be done by carbon containing processes.
- In the USA only carbon free processes will be developed (solar, nuclear, biomass)
- The solar research of DLR will continue its work on reforming und cracking because of the medium term chances of these technologies
- Thermochemical cycles are for long term use
  - Three main problems have to be solved:
  - Heat provision
  - Material properties of components and reactants
- Product separation
- The aim is to produce renewable hydrogen under ecologically and economically reasonable conditions

Acknowledgement

The Projects

HYDROSOL, HYDROSOL- II; HYTHEC, SCR, SOLASYS, SOLREF, Hi2H2, and INNOHYP-CA

have been co-funded by the European Commission.

HYDROSOL was awarded

- Eco Tech Award Expo 2005, Tokyo
- IPHE Technical Achievement Award 2006
- Descartes Research Price 2006

Forschungsbedarf im Bereich solarer Reformierung

- Pilotanlagen und Demonstration (Langzeittests)
- Entwicklung von Regelungsstrategien und Prozeduren für den Betrieb von optimierten Solar-Reformierungsanlagen
- Neuentwicklung von Solarreformern für die H_2-Erzeugung
- Fertigung und Qualifizierung von Prototypen (Receiver, Spaltreaktoren, Separatoren, Wärmeübertrager)
- Materialentwicklung und -tests für Hochtemperaturanwendungen und korrosive Medien
- Prozessdesign und Simulation
- Modellierung von Schlüsselkomponenten

Forschungsbedarf im Bereich solarer TCC

- Fertigung und Qualifizierung von Prototypen (Receiver, Spaltreaktoren, Separatoren, Wärmeübertrager)
- Materialentwicklung und -tests für Hochtemperaturanwendungen und korrosive Medien
- Hardware für Hochtemperaturwärmetransport
- Prozessdesign und Simulation
- Ausbeuteoptimierung, Optimierung von Reaktionsgeschwindigkeiten, Katalysatorentwicklung
- Grundsatzuntersuchungen zu Mechanismen der H_2O-Spaltung an Metalloxiden
- Entwicklung von Regelungsstrategien und Prozeduren für solche solar-chemischen Prozesse
- Modellierung von Schlüsselkomponenten
- Pilotanlagen und Demonstration!!!