Solar Steam Reforming of Natural Gas
presented by Stephan Möller
H2-production pathways extracted from SRA and amended

This route has a high potential for sunny regions.

On-site production (centralised or decentralised).

HT process heat using concentrated solar energy
Solar Thermal Processes for Hydrogen Production

Fossil fuels or biogas
- Reforming
- Gasification/Partial Oxidation
- Splitting

Metal oxide
- Open Thermo-Chemical Process

Biomass
- Pyrolysis

Water
- Splitting
- Thermo-Chemical-Cycle
- Steam Electrolysis
- Electrolysis

(+$Electricity$)

$+$ Electricity + heat
$+$ Electricity

$\rightarrow H_2$

Electricity from solar thermal power plants or photovoltaic plants.
Solar Thermal Processes for Hydrogen Production
Projects coordinated by DLR or involved as a partner

- **Fossil fuels or biogas**
  - Reforming
  - Gasification/Partial Oxidation
  - Splitting

- **Metal oxide**
  - Open Thermo-Chemical-Process

- **Biomass**
  - Pyrolysis

- **Water**
  - Splitting
  - Thermo-Chemical-Cycle
  - Steam Electrolysis
  - Electrolysis

**Projects**
- **SOLREF, SOLASYS, SCR, ASTERIX**
- **SOLHYCARB**
- **HYDROSOL 1+2; HYTEHC**
- **HI2HY**
- **HYSOLAR**
HYDROSOL (EU FP5 -10/2005)

- 2 Step redox thermochemical cycle using mixed iron oxides:

- 1. Endothermal Step (1000-1200°C)
  \[ MO_{\text{ox}} \leftrightarrow MO_{\text{red}} + \frac{1}{2} O_2 \]

- 2. Splitting (700 - 1000°C)
  \[ MO_{\text{red}} + H_2O \leftrightarrow MO_{\text{ox}} + H_2 \]

- System: e.g. \( MO = (Zn,Y)Fe_2O_4 \)
  \( Y = \) Ni oder Mn

- costs: 10-20 ct/kWh [DLR]
THE HYDROSOL-II PARTNERSHIP

- APTL/CERTH/CPERI - Aerosol & Particle Technology Laboratory (Coordinator) (RES) - advanced material synthesis, reactor design

- DLR - Deutsches Zentrum für Luft- und Raumfahrt (RES) – solar reactor engineering, solar field/plant design and operation

- CIEMAT - Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (RES) – owner/operator of PSA solar platform

- JOHNSON MATTHEY (IND) - catalyst supplier and manufacturer-Fuel cells developer/producer

- STC (SME) - Producer of advanced ceramics

**DURATION:** 01/11/05-31/10/09; **Total cost:** 4,297,400 €; **EU funding:** 2,182,700 €
HYTHEC
Sulphur-Iodine and Westinghouse Cycle

- EU FP6 STREP
- Solarisation of $\text{H}_2\text{SO}_4$ Splitting
- Improvement of the process and its efficiency
- Design study for the co-generation of H2 and electricity
- Evaluation of solar nuclear und hybrid plant concepts
- Partners: DLR, CEA, EA, Uni Sheffield, Uni Roma Tre, ProSim
SOLHYCARB – Hydrogen from solar thermal energy

- High temperature reactor for the co-production of hydrogen and carbon black by cracking of natural gas
- Partner
  CNRS/PROMES (FR) - coordinator, ETH, PSI (CH), WIS (IL), CERTH/CPERI (EL), DLR (DE), TIMCAL (BE), SOLUCAR (SP), CREED (FR), N-GHY (FR)
- Start: 1.4.2006
SOLREF

Past: SOLASYS

Future: 1 MW<sub>th</sub> Prototype Plant

- Catalysis
- Reformer
- Operation
- Pre-design of 1MW plant
- Conceptual layout of 50 MW plant
- Studies
SOLREF – The project

- FP 6 project – Sustainable Energy Systems
- Contract no.: SES-CT-2004-502829
- Title: Solar Steam Reforming of Methane Rich Gas for Synthesis Gas Production
- Seven participants from seven countries
- Duration: April 2004 – December 2007
- Total budget: 3.5 M€
- Requested EC contribution: 2.1 M€

Swiss Federal Institute of Technology Zurich

Johnson Matthey Fuel Cells

HYGEAR

SHAP

Solar Heat And Power S.p.A.
### Assessment of relevant H$_2$ pathways until 2020

Taken from DS including NG Solar-SMR and TC-cycle for comparison issues

<table>
<thead>
<tr>
<th></th>
<th>NG SMR</th>
<th>NG Solar-SMR</th>
<th>Grid Electricity electrolysis</th>
<th>Wind electrolysis</th>
<th>Biomass</th>
<th>TC-Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H$_2$ production cost</strong></td>
<td>7-8* €/GJ</td>
<td>12-14* €/GJ</td>
<td>31 €/GJ</td>
<td>50-67 €/GJ</td>
<td>25-33 €/GJ</td>
<td>28-56 €/GJ</td>
</tr>
<tr>
<td><strong>Positive impact on security of energy supply</strong></td>
<td>modest</td>
<td>high</td>
<td>high</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td><strong>Positive impact on GHG emission reduction</strong></td>
<td>neutral - modest</td>
<td>modest - high</td>
<td>negative - neutral</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
</tbody>
</table>

*assuming a NG price of 4€/GJ$_{NG}$; NG Solar-SMR: expected cost for large scale, solar-only
*assuming a NG price of 12€/GJ$_{NG}$ including sequestration cost
Partly-Solar Hydrogen  
Increase of the LHV/HHV – Savings of Natural Gas

Assuming that from 1 mole methane 4 mole H₂ can be produced via reforming, WGS and recycling of the off-gas to the feedstock after removal of CO₂ and H₂.

\[ \text{LHV: 17\% / 83\%} \]
\[ \text{HHV: 22\% / 78\%} \]
SOLREF – Motivation
Why solar steam reforming?

- The process heat provided by combustion of fossil fuels in the conventional case can be provided completely by concentrated solar energy using solar-thermal concentrating systems.
  - Saving of (fossil) fuels up to 40% (based on LHV and reforming efficiency of 75%), because fossil fuels can be used up to 100% only for chemical issues.
    - High level policy objective regarding security of energy supply
  - Reduction of CO$_2$-Emissions.
    - High level policy objective regarding reduction of GHG emissions
Solar Steam Reforming – Different Routes

a) separated/allothermal

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

b) indirect and e.g. tubular

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

C) integrated direct and volumetric

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

Source: DLR
Some examples of Solar Reformers

Process schematic

- 20-50 kW\textsubscript{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

Inside receiver
Some examples of Solar Reformers

- 10 kW<sub>th</sub> reformer (DIAPRRRef)
- Integrated concept
- Ongoing research at WIS, Israel
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).
SOLREF – Solar Reformer

- Insulation
- Catalytic Ceramic Absorber
- Quartz-Window
- Vessel
- Inlet
- Outlet

"sun"
SOLREF – Solar Reformer
State-of-the-art (SOLASYS)

This reformer, a direct irradiated volumetric reactor receiver, was realised in the EU-project SOLASYS (duration 1998 bis 2002).

Results:
- In the gas absorbed power: 100 to 220 kW_{th} (more power was not available)
- Reforming temperature: 700 to 765°C
- Operation pressure: 4 to 9 bar_{a}
- Conversion of methane: max. 78% (close to theoretical equilibrium)
SOLREF

Past: SOLASYS

Future: 1 MW<sub>th</sub> Prototype Plant

- Pre-design of 1MW plant
- Conceptual layout of 50 MW plant
- Studies
- Reactor
- Operation
- Catalysis
SOLREF – Project main objectives

- Develop an advanced 400 kWth solar reformer
- Investigate various catalyst systems
- Simulate mass and heat transport and reaction in porous absorber
- Perform thermodynamic and thermochemical analyses to support the system design phase
- Operate the reformer with gas mixtures which represent the variety of possible feedstock on the solar tower at WIS, Israel, producing partly-solar hydrogen
SOLREF – Project main objectives

- Evaluate new operation strategies
- Pre-design of a 1 MWth prototype plant in Southern Italy
- Conceptual layout of a commercial 50 MWth reforming plant
- Assess on potential markets including cost estimation and environmental, socio-economic, and institutional impacts
SOLREF – Catalyst development

- Develop an advanced catalytically-active absorber featuring the following properties:
  - High catalytic activity with high resistance to coking.
  - Good absorption for thermal radiation.
  - Acceptable mechanical strength and thermal shock resistance.
  - High gas permeability together with high turbulence and mixing of the gases as well as low pressure drop.
  - Low costs.

- **Status:** The catalyst group of the consortium has selected the catalyst system and has applied to the absorber segments. The noble metal content could decreased by a factor of about five.
SOLREF – Reformer development

- Absorber holding structure
  - Smaller and lighter than the SOLASYS absorber
  - Max. temperature 1100°C
SOLREF – Reformer development

⇒ Vessel with flange and insulation
  ⇒ Smaller ⇒ less weight, but same power level (400 kW_{th})
  ⇒ Opt. pressure 10 bars
  ⇒ Reforming temperature of about 900°C
  ⇒ Steam protection

⇒ Status: The reformer is constructed and the manufacturing is about starting.
Perspectives for Solar Reforming in Sunny Regions

- **Installed capacity in MW<sub>th</sub>**
- **Years:**
  - **2007:** Short term
  - **2010:** Medium term
  - **2015:** Long term

- **SOLREF pilot plant**
- **Biomass or fossil, CO₂-lean production, CO₂ sequestration**
- **Fossil, CO₂-lean**

**Note:** CO₂-lean means significant CO₂ reduction

- Single site demonstration
- 1 MW
Solar Steam Reforming – Motivation

- The process heat provided by combustion of fossil fuels in the conventional case can be provided completely by concentrated solar energy. The energy content of the hydrogen is than partly-solar.
  - Saving of (fossil) fuels up to 40% (based on LHV and reformer efficiency).
  - Reduction of CO₂-Emissions.
- Production costs of partly-solar hydrogen with less than 5 ct€/kWh (based on the LHV of H₂) are possible and therefore near to profitability.
- The solar driven process reaches profitability when the assumed today’s price of NG (20ct€/Nm³) increases by a factor about two.

⇒ Solar Reforming is qualified outstandingly as a first step into a renewable hydrogen production.
Thank you for your attention!