Solar Cracking and Solar Reforming

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Established High Temperature Industrial Processes

Cracking of natural gas to produce
- Hydrogen
- Carbon black

Goal: Two valuable products, easy storable solid (really?)

Gasification (see Dr. Meiers talk) and reforming of carbonaceous feedstock for the production of synthesis gas
- Natural gas
- Coal
- Pet coke
- Waste
- Biomass

Goal: Fuels with reduced CO₂ emissions for power production but also for air, land, and sea transportation
H₂-Production by Solar Cracking of Hydrocarbons

Decarbonisation of Methane $\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$

- Temperature up to 1600° C
- Ambient pressure.
- Conversion 70%.
- Theoretical system efficiency: 30%
- EU Project SOLHYCARB 2006 - 2010
- Partner CNRS/PROMES (FR) - ETH, PSI (CH), WIS (IL), CERTH/CPERI (EL), DLR (DE), TIMCAL

Source: Hirsch et al.
CO₂ Reduction by solar heating of state of the art processes like steam methane reforming and coal gasification

CO₂ Reduction 20 – 50%
Steam and CO₂-Reforming of Natural Gas

Steam reforming: \( \text{H}_2\text{O} + \text{CH}_4 \rightarrow 3 \text{H}_2 + 1 \text{CO} \)

CO₂ Reforming (Dry): \( \text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{H}_2 + 2 \text{CO} \)

Reforming of mixtures of CO₂/H₂O is possible and common

Use of syngas for methanol production:

e.g. \( 2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{COH} \) (Methanol)

Both technologies can be driven by solar energy as shown in the projects: CAESAR, ASTERIX, SOLASYS, SOLREF…
Solar Methane Reforming – Technologies

a) **decoupled/allothermal**
- Reformer heated externally (700 to 850°C)
- Optional heat storage (up to 24/7)
- E.g. **ASTERIX** project

b) **indirect (tube reactor)**
- Irradiated reformer tubes (up to 850°C), temperature gradient
- Approx. 70 % Reformer-h
- Development: Australia, Japan; Research in Germany and Israel

c) **Integrated, direct, volumetric**
- Catalytic active direct irradiated absorber
- Approx. 90 % Reformer-h
- High solar flux, works only by direct solar radiation
- DLR coordinated projects: **SOLASYS, SOLREF**; Research in Israel, Japan

Source: DLR
SANDIA-WIS’s sodium reflux heat pipe solar receiver-reformer (1983-1984)
ASTERIX: Allothermal Steam Reforming of Methane

- 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
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\textsubscript{th} and 400 kW\textsubscript{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)
Central Receiver Plants: Pressurized air receiver

- **Receiver heat transfer fluid:**
  - Air (10-16 bar)

- **Hybrid system:**
  - The maximum temperature achievable in solar operation is currently limited to 1000° C.
  - Therefore natural gas firing is always needed for operation.

- **Technology Status**
  - 250 kWe (6.5 bar) demonstration at Plataforma Solar de Almeria

- **Companies:**
  - DLR
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).
Receiver Lay-out
- Nominal layout data for the SOLASYS receiver-reactor:
- Absorbed power: 400 kW
- Methane conversion level: 80%
- Operating pressure: 10 bar
- Fluid inlet temperature: appr. 500°C
- Syngas outlet temperature: appr. 850°C
Receiver Unit

Heliotstat Field

Secondary

Receiver

Outlet

Inlet
Outlet gas composition at $p_{\text{receiver}} = 4.9$ bar

Inlet gas composition: 22.7 mole-% $\text{CH}_4$, 7.6 mole-% $\text{CO}_2$, 0.0 mole-% $\text{CO}$, 59.3 mole-% $\text{H}_2\text{O}$, 10.3 mole-% $\text{H}_2$

$T_{\text{reaction}} = 716^\circ \text{C}$

Temperature in °C
SOLASYS - Test Plant in Operation
SOLASYS Economic Analysis (2006)

Comparison of hydrogen production cost by conventional and solar reforming of natural gas (NG) depending on the NG price reported in 2004 by “www.oilenergy.com”
SOLREF Solar Steam Reforming (SES6-CT-2004-502829)

SOLASYS

SOLREF

Catalysis
Reformer
Operation

Pre-design of 1MW plant
Conceptual layout of 50 MW plant
Studies

1 MW_{\text{th}} Prototype Plant e.g. in Southern Italy
Motivation & Consortium

- Production costs of partly-solar hydrogen with less than 5 ct€/kWh or 1.7 €/kg H₂ (large scale, solar-only) are possible.
- The solar driven process reaches profitability when the price of NG increases to about 40 ct€/Nm³
- Eight participants from seven countries:
  - DLR, coordinator Germany
  - APTL/CERTH/CPERI, Greece
  - Weizmann Institute of Science, Israel
  - ETH Zurich, Switzerland
  - Johnson Matthey Fuel Cell Ltd, UK
  - HyGear B.V., The Netherlands
  - SHAP S.p.A., Italy
  - Region Basilicata, Italy
Project main objectives

- Develop an advanced 400 kW
- 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
- Evaluate new operation strategies
- Pre-design of a 1 MW prototype plant in Southern Italy
- Conceptual layout of a commercial 50 MW reforming plant
- Assess on potential markets including cost estimation and environmental, socio-economic, and institutional impacts
Solar Reformer - Improvements

SOLREF Reformer:

- Absorbed power: app. 400 kW_{th}
- Feed-temperature: app. 450° C
- Outlet-temperature: app. 900° C
- Absorber temp.: max. 1100° C
- Operation pressure: optimal pressure 10 bars; max. 15 bars_{a}
- Mass flow: 0.12 kg/s
Future Steps

-Areas for market introduction

  -Addition of “solar upgraded fuel” into large scale CC power plants with mixing rate 5 -10 %
  -Dual fuel operation
  -Solar reforming of biogas or landfill gas

-Further research is directed to

  -Flexible feed gas composition
  -Modified process parameters including CO₂ separation and reforming

-Next step towards market introduction

  -Pre-commercial solar reforming plant of 1-5 MW size adapted to the specific fuel and process conditions
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