From Solar Energy to Green Mobility

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Introduction

• Concentrating Solar Systems and Solar Thermal Power Plants (STPPs)

• From solar receivers to receivers/reactors.

• Solar fuels synthesis chemistries.

• Solar fuels technologies: current developments and state-of-the-art.

• Commonalities in materials requirements and reactor concepts among solar energy conversion, storage and transformation-related processes

• R&D needs and outlook.
Concentrated Solar Power (CSP) systems

Systems that **make use** of solar energy by first **concentrating** solar radiation and then converting it to **thermal energy**

- Uses:
  - Electricity (Solar Thermal Power)
  - Industrial Process Heat
  - Absorption cooling
  - Chemical processes
  - …
Solar Thermal Power Plants

Heat transfer fluid: thermal oil, air, steam, molten salt.
Temperature Levels of CSP Technologies

Paraboloid: “Dish”

- 3500°C
- 1500°C
- 390°C
- 150°C
- 50°C

Solar Tower (Central Receiver System)

Parabolic Trough / Linear Fresnel
Solar receivers- From solar electricity to solar chemicals

• In direct analogy with “conventional” catalytic applications, solar receivers can employ proper functional materials capable of performing/catalyzing a variety of high-temperature chemical reactions and thus be “transformed” to solar receiver/reactors where (endothermic) chemical reactions can take place.

• In this way absorbed radiation is converted from thermal to chemical form, storing solar energy in the chemical bonds of the reaction products (e.g. Hydrogen) rather than as thermal energy in a working fluid.
Energy densities of fuels

Fuel: any chemical compound that stores energy, which can be released by being oxidised to provide heat.

“Solar fuel”: any chemical compound that can react with oxygen to release energy, and was initially formed, at least partly, using energy from solar radiation.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Energy density (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>142,000</td>
</tr>
<tr>
<td>Gasoline</td>
<td>45,000</td>
</tr>
<tr>
<td>Coal</td>
<td>24,000</td>
</tr>
<tr>
<td>Sulfur</td>
<td>12,500</td>
</tr>
<tr>
<td>Cobalt oxide redox-cycle</td>
<td>850</td>
</tr>
<tr>
<td>Lithium-ion battery</td>
<td>580</td>
</tr>
<tr>
<td>Molten salt (phase change)</td>
<td>230</td>
</tr>
<tr>
<td>Molten salt (sensible)</td>
<td>155</td>
</tr>
<tr>
<td>Elevated water dam (100 m)</td>
<td>1</td>
</tr>
</tbody>
</table>
Political Drivers: Examples – EU Sustainable Energy Technology Plan (SET-Plan 2007) G7 Goals (2015)

- **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 CO₂ emissions than in 1990

- **G7 Goals, Elmau, Germany**
  - 100% Decarbonisation until 2100
  - 100 bln $/year for climate actions in developing countries, large share by industrial investment
Partial listing of various feedstocks and solar energy variances for solar liquid hydrocarbon fuels production

**Feedstocks**
- Natural Gas (CH₄)
- Biogas (CH₄, CO₂)
- Biomass (CH₄ + CO₂)
- Zero-Energy Chemicals (H₂O, CO₂)

**Solar (Plant) Energy Choices**
- Thermochemical
- Photochemical/Photobiological
- Electrochemical
  - Solar Heat: CSP
  - Direct use of solar photon energy
  - Solar Electricity: CSP or PV
  - Reforming
  - Gasification
  - Splitting Cycles
  - Electrolysis (H₂O, CO₂)

**Solar Fuels**
- Hydrogen (H₂)
- Synthetic Fuels (CₙH₂n+2)
Strategy and Approach on Solar Fuels in Germany

Goal in the Helmholtz Association
To demonstrate stand-alone, viable systems for the emission-free production of chemical fuels – especially **Hydrogen** - with sunlight.
DLR German Aerospace Center

- Research Institution
- Space Agency
- Project Management Agency

>8000 employees across 32 institutes and facilities at 16 sites.

DLR Institute of Solar Research

160 staff, 20 M€/a, 4 sites
DLR Philosophy of the Institute of Solar Research

“Leading competences in CSP systems world-wide”

Idea

Unique infrastructure

Excellent research

Partner for Academia and Industry

Product
From fundamentals to commercial viability

- **Power Plant**
  - 20kW$_{th}$
  - 50MW$_{el}$

- **Academia**
- **Industry**
- **Laboratory**

- Investigation of ceramic absorber structures at solar furnace
- Measurement of radiation and temperature
- Materials investigations
- Numeric simulations

Material and structure for safe absorber operation at high temperatures
From fundamentals to commercial viability

- Development of HiTRec-Receiver Structure
- safe and scalable receiver structure, safety for investments
From fundamentals to commercial viability

- Site selection
- Computer aided design
- Scientific support of operation

Flexible and robust plant design
From fundamentals to commercial viability
CSP-aided routes for the production of "solar syngas"

- **Carbonaceous feedstocks**
  - Gaseous feedstocks
    - Natural gas (CH₄)
    - Biogas (CH₄, CO₂)
  - Solid feedstocks
    - Pet Coke (C)
    - Biomass CₓHᵧO₂

- **Splitting**
  - Reforming (steam, CO₂)
  - (H₂O, CO₂)

- **Gasification**
  - H₂ + CO

Solar syngas from carbonaceous feedstocks

Solar (liquid) fuels from carbonaceous feedstocks
Solar (Fuels) Chemistry

Solar Steam/dry methane Reforming (SMR/DMR)

- \( \text{CH}_4 + \text{H}_2\text{O} + (\Delta H) \rightleftharpoons 3 \text{H}_2 + \text{CO} \)  
  \( (~850-950^\circ C) \)

- \( \text{CH}_4 + \text{CO}_2 + (\Delta H) \rightleftharpoons 2 \text{H}_2 + 2\text{CO} \)  
  \( (~850-950^\circ C) \)

Solar Gasification

- \( \text{CH}_4 + \text{H}_2\text{O} + (\Delta H) \rightleftharpoons 3 \text{H}_2 + \text{CO} \)  
  \( (~850-950^\circ C) \)

- \( \text{CH}_4 + \text{CO}_2 + (\Delta H) \rightleftharpoons 2 \text{H}_2 + 2\text{CO} \)  
  \( (~850-950^\circ C) \)

Solar Redox processes / Thermochemical (water splitting) cycles

“Net” reactions: \( \text{H}_2\text{O} + (\Delta H) \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2 \)

Sulfur-based

- \( \text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + \text{H}_2\text{O} \)  
  \( (~400^\circ C) \)

- \( \text{SO}_3 + (\Delta H) \rightleftharpoons \text{SO}_2 + \frac{1}{2} \text{O}_2 \)  
  \( (~850-950^\circ C) \)

- \( \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \)  
  \( (80-120^\circ C, \text{electrolysis}) \)

Redox-oxides based

- \( \text{MeO}_{\text{oxidized}} + (\Delta H) \rightarrow \text{MeO}_{\text{reduced}} + \frac{1}{2} \text{O}_2 \)  
  \( (~1100-1450^\circ C) \)

- \( \text{MeO}_{\text{reduced}} + \text{H}_2\text{O} (\text{g}) \rightarrow \text{MeO}_{\text{oxidized}} + \text{H}_2 + (\Delta H) \)  
  \( (~700^\circ C) \)
Steam and CO$_2$-Reforming of Natural Gas Reactions

Steam Reforming:

1. $CH_4 + H_2O \rightarrow 3H_2 + CO$ \hspace{1cm} \Delta h = 206$ kJ/mol
2. (WGS) $CO + H_2O \rightarrow H_2 + CO_2$ \hspace{1cm} \Delta h = -41$ kJ/mol
3. (1+2) $CH_4 + H_2O \rightarrow 4H_2 + CO_2$ \hspace{1cm} \Delta h = 165$ kJ/mol

Dry (CO$_2$) Reforming:

1. $CO_2 + CH_4 \rightarrow 2H_2 + 2CO$ \hspace{1cm} \Delta h = 247$ kJ/mol

- Reforming Product is Syngas – Mixture of H$_2$ and CO
- Highly endothermic $\rightarrow$ Favoured by high temperatures; $> 700 \, ^\circ C$ in industrial processes
- Increase in number of moles $\rightarrow$ Favoured by low pressures
- Reforming of mixtures of CO$_2$/H$_2$O is possible
- Use of syngas for methanol production: e.g. $2H_2 + CO \rightarrow CH_3COH$
- Both technologies can be driven by solar energy
(Water-splitting) Redox-oxide-based Thermochemical Cycles

- Series of chemical reactions with net result being H₂ & O₂ production from H₂O
- Why a series of reactions? The indirect H₂O splitting is necessary since thermolysis is feasible at impractical temperature ranges (>2200°C).

1st Step: Thermal reduction (Regeneration)

\[ \text{MO}_{\text{ox}} + \Delta H \rightarrow \text{MO}_{\text{red}} + \frac{1}{2} \text{O}_2 \]

2nd Step: H₂O / CO₂ Splitting WS /CDS

\[ \text{H}_2\text{O} + \text{MO}_{\text{red}} \rightarrow \text{MO}_{\text{ox}} + \text{H}_2 + (\Delta H) \]
\[ \text{CO}_2 + \text{MO}_{\text{red}} \rightarrow \text{MO}_{\text{ox}} + \text{CO} + (\Delta H) \]

Net reaction: H₂O \( \rightarrow \) H₂ + \( \frac{1}{2} \) O₂
Net reaction: CO₂ \( \rightarrow \) CO + \( \frac{1}{2} \) O₂

Net effect: Solar Q \( \rightarrow \) Solar Fuels

[Diagram of SOEC]
Solar Hydrogen

Solar Energy

Heat

Thermochemical Cycles

Metal oxide cycles: HYDROSOL (800-1200°C)

Other Thermochemical Cycles

Thermolysis >2000°C

Mechanical Energy

Biomass

Electricity

Conversion

Photolysis

Electrolysis

HYDROGEN
Principle of the solar thermal fuel production

Resources (Natural Gas) Water, CO₂

Heat
Heat + electricity

Chemical Reactor
Electrolyzer

H₂ CO + H₂

Industry Transportation

CH₄, CH₃OH, Fisher-Tropsch Fuels

Energy Converter Fuel Cell

Transportation Power Production

Clean Exhaust

Solar Tower

Heliosstats

Central Receiver

Solar Tower

Industry Transportation

Clean Exhaust

Power Production
Solar Hydrogen supply: Power to Gas/Liquid Technologies

Current such “benchmark” technology: solar-aided electrolysis with electricity supplied from PV or CSP sources.

- **Power-to-Gas (PtG):** Production of a high-energy density gas via the electrolysis of water. First intermediate product is hydrogen; may be converted to methane via methanation requiring CO₂ feed-in.

- **Power-to-Liquids (PtL):** Production of liquid carbon-based energy carriers from electricity via the electrolysis of water. Hydrogen is the intermediate product; is further converted to synthesis gas by adding CO₂ and to synthetic gasoline, Diesel or kerosene.
From “Reforming” to “Solar Reforming”

Hydrocarbons $\rightarrow$ reformer $\rightarrow$ Synthesis Gas (H$_2$/CO)

$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$

1 mole CH$_4$ e.g. NG $\rightarrow$ 4 mole H$_2$

Energy Reforming $\rightarrow$ Solar H$_2$

Heliostat field

20% 80%
Solar Methane Reforming– Reformer (heating) Technologies

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

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

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
Reforming vs. W/CD redox-oxides-“splitting” Chemistry

- Employs fossil fuel (CH₄) as reactant.
- Solid catalyst: Ni-based catalysts supported on CaAl₁₀O₁₆ or MgAl₃O₆; noble metals (Ru, Rh, Pd, Pt); Fe, Co.
- Temperature range: **700-850°C**.
- Gaseous reactants can be fed **continuously**.

- Employs CO₂ as a reactant; i.e. can “reuse/valorize” atmospheric CO₂.
- Solid redox–pair materials: ferrites (NiFe₂O₄, CoFe₂O₄), CeO₂-ZrO₂, perovskites (La₁₋ₓSrₓMn₁₋ₓAlₓO₃₋δ).
- Temperature range: **750-1500°C**.
- Solid is not a “catalyst” but a reactant, with non-negligible mass to be heated to the reaction temperature and progressively depleted during reaction, having to be replenished (reactions cannot be carried out continuously).

Reforming vs. W/CD “splitting” solar reactors

- “Structured” reactors.
- Solar heating: direct or indirect.

- Structured & non-structured (particle) reactors.
- Solar heating: only direct (required Ts too high for indirect heating).
Solar receiver/reactor types (particles vs. porous solids; moving vs. non-moving parts)

- Rotating cavity (powder)

- Spouted (powder) bed

- Moving powder bed

- Ceramic honeycombs
  - SOLAIR receiver (DLR), 2004.

- Ceramic foams
  - SOLREF reactor (DLR), 2004.

- CR5, rotating solid disks
Receiver/reactor technology evolution at DLR

From Materials to Processes

Materials  Components  Systems

TGA  Lab-scale furnace  Solar receivers  Solar tower
Directly heated volumetric receiver/reformers: SOLASYS, SOLREF

Solar Platform-WIS Israel

Directly heated volumetric receiver/reformers: SOLASYS, SOLREF

- 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)
H₂ production via CSP-water splitting

The HYDROSOL technology: Monolithic honeycombs capable to absorb concentrated solar irradiation coated with (or eventually made entirely of) redox water splitting materials

1st Step: H₂O Splitting (WS)
H₂O + MO_red → MO_oxidized + H₂ + (ΔH)

2nd Step: Thermal Reduction (TR/Regeneration)
MO_oxidized + ΔH → MO_red + ½ O₂
HYDROSOL Technology: Continuous (dual chamber) Solar Receiver/ Reactor scalability and evolution


Further scale-up: “Convergence” of reactor concepts

- “Domed” reactor chamber.
- Assembled of individual foam pieces.
- WS/CDS: “Redox-oxide-made” foams (from NiFe$_2$O$_4$ and CeO$_2$-ZrO$_2$); interchangable with catalyst-coated ones (SMR).
Hydrosol Plant - Design for CRS tower PSA, Spain

- European FCH-JU project
- Partners: APTL (GR), DLR (DE), HELPE (GR), CIEMAT (ES), HYGEAR (NL)
- 750 kW\textsubscript{th} demonstration of thermochemical water splitting
- Location: Plataforma Solar de Almería, Spain, 2017
- Reactor set-up on the CRS tower
- 3 Reactors: two work on regeneration step while the third on water splitting ($T = 1400-1100^\circ\text{C}$).
- Storage tanks and PSA on the ground.
CeO$_2$-made foam reactor (ETH)


Criteria for the selection of processes of solar thermal hydrogen production

- Operation temperature has to be feasible and practicable. Optimum Temperature is between 800 and 1600 K.
- Fast reactions are desirable.
- High availability of raw materials.
- High efficiency must be realisable.
- \( \text{H}_2 \) production costs must be acceptable.
- Reference: \( \text{H}_2 \) from electrolysis by „solar electricity“

“…You can't always get what you want, but if you try, sometimes you just might find, you get what you need…”

The Rolling Stones, 1969.
Summary and Outlook:

- **CSP-aided large scale production of solar fuels** will require the economies of scale offered by **heliostat fields with central tower receivers**, that can comfortably generate solar thermal fluxes in the MW capacity.
- CSP can be employed as the only energy source for the renewable thermochemical production of hydrogen and/or syngas from **water/carbon dioxide via solar redox processes**. Such a route has in principle the potential to culminate essentially to the **synthesis of liquid hydrocarbon fuels using only renewable/recyclable resources: solar energy, water and captured/recycled CO\textsubscript{2}**. However, further research efforts are needed for the achievement of these targets in practice.
- The two main research tasks are the improvement of solar interfaces and **integrated heat recovery schemes** in the one hand and solving the main materials-related issues and providing the right functional materials at **reasonable costs** in the other hand.
- Thus, at least for a transition period, **CSP-aided reforming of methane-containing gaseous feedstocks** with natural gas (NG) being the first choice, can offer a viable route for fossil fuel decarbonization and create a transition path towards a “solar hydrogen- solar fuels” economy.
Summary and Outlook:

- **Solar reforming**: directly heated reformers can reach higher operating temperatures, thus higher fuel conversion. Their limitations largely centre on the need for a transparent quartz window to allow concentrated solar radiation into the receiver whilst at the same time providing a gas seal for the reacting gases and products that in most cases are under pressure.

- Indirectly irradiated reformers eliminate the window need at the expense of having less efficient heat transfer - by conduction - through the walls of an opaque absorber. While not able to reach as high operating temperatures, do not have the size limitations associated with directly heated reformers.

- In this perspective, perhaps “technically simpler” concepts like, for instance, the tubular indirectly-heated (“allothermal”) reformers might be more attractive for large-scale implementation and demonstration of the technology.

- **CSP systems as electricity providers, can supply** - alternatively to photovoltaics/ PVs - the renewable electricity for electrolysis of steam or steam/CO$_2$ mixtures towards hydrogen/syngas production.

- **(Co-)Electrolysis shares common features with solar redox processes**: both involve the composition optimization and the development of bulk, porous oxide structures that perform cyclic redox operations for extended periods of time.
Thank you for your attention!