Redox oxides-based solar thermochemistry and its materialization to reactor/heat exchanger concepts for efficient solar energy harvesting, transformation and storage

Christos Agrafiotis, Martin Roeb, Christian Sattler

Institute of Solar Research
DLR/ Deutsches Zentrum für Luft- und Raumfahrt/
German Aerospace Center
Linder Höhe, 51147 Köln, Germany
Introduction

• Solar fuels production from Concentrating Solar Systems and Solar Thermal Power Plants (STPPs)

• Solar fuels chemistries and reactors

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

• Outlook, needs and ideas for the future.
Partial listing of various feedstocks and solar energy variances for solar liquid hydrocarbon fuels production

**Feedstocks**
- Hydrogen (H₂)
- Synthetic Fuels (CₙH₂ₙ₊₂)
- 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

**Solar Fuels**
- Hydrogen (H₂)
- Synthetic Fuels (CₙH₂ₙ₊₂)

**Processes**
- Reforming
- Gasification
- Splitting Cycles
- Electrolysis (H₂O, CO₂)
Solar Methane Reforming– Reformer (heating) Technologies

**a) decoupled/allothermal**

Reformer heated externally (700 to 850°C)
E.g. **ASTERIX** project

**b) indirect (tube reactor)**

Irradiated reformer tubes (up to 850°C), temperature gradient
Development: Australia, Japan; Research in Germany and Israel

**c) Integrated, direct, volumetric**

Catalytic active direct irradiated absorber
DLR coordinated projects: **SOLASYS, SOLREF**; Research in Israel, Japan

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

- Employs fossil fuel (CH₄) as reactant.
- Solid catalyst: Ni-based catalysts supported on CaAl₆O₁₀ or MgAl₂O₄; 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₋ₓSrₓMnₓAl₁₋ₙO₃₋₅).
- 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).
Principle of the solar thermal fuel production

Solar Tower

Resources (Natural Gas)
Water, CO₂

Heat + electricity

Electrolyzer

CH₄, CH₃OH, Fisher-Tropsch Fuels

Industry Transportation

Chemical Reactor

H₂, CO + H₂

Energy Converter Fuel Cell

Transportation

Power Production

Clean Exhaust
Redox-oxide-based thermochemical cycles - structured receiver/reactors / heat exchangers

1st Step: Thermal reduction (Regeneration)

2nd Step: H₂O / CO₂ Splitting WS /CDS

\[
\begin{align*}
\text{H}_2\text{O} + \text{MO}_{\text{red}} & \rightarrow \text{MO}_{\text{ox}} + \text{H}_2 + (\Delta H) \\
\text{CO}_2 + \text{MO}_{\text{red}} & \rightarrow \text{MO}_{\text{ox}} + \text{CO} + (\Delta H)
\end{align*}
\]

Net reaction: \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \)

Net reaction: \( \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \)

Net effect: Solar Q \( \rightarrow \) Solar Fuels (H₂, syngas)

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

2nd Step: (Air) Oxidation (AO)

\[
\begin{align*}
\text{MO}_{\text{red}} + \frac{1}{2} \text{O}_2 & \rightarrow \text{MO}_{\text{ox}} + \Delta H \\
\text{TR} \text{ aided by electrical energy: (high T) Solid Oxide (co)electrolysis Cell (SOEC) for WS/CDS to H}_2/\text{CO. }
\end{align*}
\]

Net effect: Solar Q \( \rightarrow \) \( \Delta H \) \( \rightarrow \) Q non-solar Thermochemical storage
Solar receiver/reactor types (particles vs. **porous solids**; moving vs. **non-moving parts**)

- Rotating cavity (powder)  

- Spouted (powder) bed  

- Ceramic foams  
  SOLREF reactor (DLR), 2004.

- Moving powder bed  
Solar fuels: Solar receiver/reactors based on coated honeycombs:


From active-material-coated “inert” structural supports to structures made entirely of the active material:

Further scale-up: “Convergence” of reactor concepts

Directly heated receiver/reformers (SOLASYS, SOLREF, 1998-2009)

- Domed reactor chamber.
- Assembled of individual foam pieces.
- WS/CDS: “Redox-oxide-made” foams (from NiFe$_2$O$_4$ and CeO$_2$-ZrO$_2$); interchangeable with catalyst-coated ones (SMR).

Directly heated WS/CDS reactors (HYDROSOL-PLANT, 2012-2017)

Solar Platform-WIS Israel
HYDROSOL Technology: Continuous (dual chamber) Solar Receiver/ Reactor scalability and evolution


From WS/CDS to TCS
(or from direct heating to allothermal heating)
RESTRUCTURE/ STOLARFOAM technology: TCS reactor/ heat exchanger scalability and evolution

Lab-scale Co$_3$O$_4$-made and coated objects

$m_{\text{Co}_3\text{O}_4} = 10-150$ g

$m_{\text{Co}_3\text{O}_4} = 200$ mg


Pilot-scale Co$_3$O$_4$ coated cordierite honeycombs
$m_{\text{Co}_3\text{O}_4} = 88$ kg

Powders, mini Co$_3$O$_4$ made and coated objects 100 cycles; all Co$_3$O$_4$ exploited, no activity loss

m$_{\text{Co}_3\text{O}_4} =$ 88 kg
Properties of merit required for redox oxide pairs

<table>
<thead>
<tr>
<th>WS/CDS</th>
<th>TCS</th>
<th>SOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Reduction of oxidized oxide state at “reasonable” temperatures</td>
<td>• High $\Delta H$ of air oxidation; reversibility</td>
<td>• High ionic (oxygen) and electronic conductivity</td>
</tr>
<tr>
<td>Under low $P_{O_2}$</td>
<td>• High volumetric energy storage density</td>
<td>• Reactivity with $H_2O$ and/or $CO_2$</td>
</tr>
<tr>
<td>• Reactivity of reduced oxide with $H_2O/CO_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• High volumetric/gravimetric $H_2$, $CO$ yield</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Long-term cycling chemical, mechanical, thermal and dimensional stability</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**WS/ CDS materials**
- **Ferrites** $(Ni, Co)Fe_2O_4-\delta_{ox}$
- **Ceria** $CeO_{2-\delta_{ox}}$
- **Perovskites**: $La_{1-x}Sr_xAlO_3-\delta_{ox}$
  - $T \approx 1500-700^\circ C$

**TCS materials**
- **$Co_3O_4$** $T_{eq}=870^\circ C$
- **$(Fe,Mn)_2O_3$** $T_{eq}=970-920^\circ C$
- **Perovskites**: $CaMn_{1-y}B_yO_3-\delta_{ox}$
  - $T_{eq} \geq 470^\circ C$

**$O_2$ electrode materials**
- **LSM-YSZ**
- **Perovskites**: LSCF
- **$La_{1-x}Sr_xCo_yFe_{1-y}O_3-\delta_{ox}$**
  - $T \approx 1000-500^\circ C$
Criteria for solar thermal materials/processes selection?

“...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.

Want !

CSP-carbon-neutral solar fuels from sun, H₂O and CO₂ but “...the reactions involved are on the edge of being feasible and practicable...”.

CSP-reactors with high theoretical efficiency.

Redox pair material compositions that can be thermally reduced and split H₂O / CO₂.

Need ?

Hybrid options exploiting similar materials and reactors yet realizable under milder conditions, as a transition path from fossil fuel-based solar-fuels to such produced only by renewable resources?

Technically simpler, viable, pragmatic CSP-reactor concepts attractive for large-scale implementation and demonstration?

Bulk, robust, porous oxide structures from inexpensive raw materials, that can perform cyclic redox operations for extended periods of time? (WS/CDS, TCS, Membranes, SOECs)?
Thank you for your attention!