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Solar Technology Laboratory (STL)

Our mission is to develop the science and technology that is required for transforming, \textit{at an industrial scale}, solar energy into chemical fuels with a thermochemical process that effects this conversion \textit{more competitively} than any other solar-to-fuel process.

concentrate — store — transport
Outline

- general motivation: solar fuels
- concentrated solar radiation
  - concepts
- thermochemical cycles
  - basics
  - energetics / efficiencies
- instrumentation: solar furnace / solar simulator

- example: Zn / ZnO cycle
  - carbon free
  - carbothermic
Electricity Consumption

12.8 TW

world wide

To be replaced
Solar Radiation

- annual energy consumption = 150'000 TWh
- annual solar input = 2300 kWh/m²
- energetic efficiency (solar to electricity) = 20%
- land use factor = 25%

area used: ca. 1000 km x 1000 km
Concentrated Solar Radiation: High Temperatures

Stagnation Temperature

<table>
<thead>
<tr>
<th>C</th>
<th>$T_s$ [K]</th>
<th>$T_s$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>364</td>
<td>91</td>
</tr>
<tr>
<td>10</td>
<td>648</td>
<td>375</td>
</tr>
<tr>
<td>100</td>
<td>1152</td>
<td>879</td>
</tr>
<tr>
<td>1'000</td>
<td>2049</td>
<td>1776</td>
</tr>
<tr>
<td>5'000</td>
<td>3064</td>
<td>2791</td>
</tr>
<tr>
<td>10'000</td>
<td>3644</td>
<td>3371</td>
</tr>
</tbody>
</table>

$T_s = \left( \frac{C \cdot I}{\sigma} \right)^{1/4}$

$\sigma = 5.67 \times 10^{-8}$ J s$^{-1}$ m$^{-2}$ K$^{-4}$

Irradiation: $I = 1$ kW/m$^2$ (1 Sun)  \hspace{1cm} C = 1
Concentrated Solar Radiation: High Efficiency

\[ \eta_{\text{max}} = \eta_{\text{abs}} \eta_{\text{Carnot}} = \left( 1 - \frac{\sigma T^4}{C I} \right) \left( 1 - \frac{T_L}{T} \right) \]

peak efficiency (maximum power point)

\( T = 1500 \text{K}, \quad C = 5000 \quad \eta_{\text{max}} = 0.75 \)

\[ \eta_{\text{Carnot}} = 1 - \frac{T_L}{T} \]

\[ \eta_{\text{abs}} = \frac{P_{\text{abs}} - P_{\text{rerad}}}{Q_{\text{solar}}} \]

\[ \eta_{\text{abs}} = 1 - \frac{\sigma T^4}{C I} \]
Instrumentation:

Solar Furnace

maximum power (60 mm aperture): $10 \text{ kW}_{th}$
peak concentration: $5'000 \text{ kW/m}^2$ (5000 suns)
Instrumentation:

Solar Simulator

- **lamps:**
  - 10 Xe-arc lamps (water-cooled)
  - power: 15 kW\textsubscript{el} per lamp

- **feeds:**
  - 10 rectifiers
  - air and water cooling unit

- **Lambertian target:**
  - flux measurement

- **plattform:**
  - 3-axis stage
  - maximum: 500 kg

- **experiment at secondary focus:**
  - maximum power (60 mm aperture):
    - 20 kW\textsubscript{th}
  - peak concentration:
    - > 10’000 kW/m\textsuperscript{2} (suns)

- **reflectors:**
  - ellipsoidal reflectors
  - coated Al layer
Solar Fuels

- Zn / ZnO cycle
  - hydrogen
  - syngas

- ceria cycle
  - syngas

- thermo-chemical cycles
- solar thermal gasification

- gasification of biomas
  \[ C + H_2O \rightarrow H_2 + CO \]

- gasification of carbonaceous waste
  \[ C + H_2O \rightarrow H_2 + CO \]

- cracking of hydrocarbons
  \[ C_xH_y \rightarrow C + H_2 \]

- steam reforming
  \[ CH_4 + H_2O \rightarrow CO + 3H_2 \]
  \[ (CO + H_2O \rightarrow CO_2 + H_2) \]
Thermochemical Cycles: Hydrogen from Water in Two Steps

- **Oxygen**
- **Zinc**
- **Zinc Oxide**
- **Water**
- **Hydrogen**

**Metal:**
- Base Metals
- Noble Metals

(oxide is more stable than water)

(\textit{low reduction temperature of oxide})

**Other candidates:**
- Fe / Ce / Sn
Thermochemical Cycles: Variations

**carbothermal**
- (only) solar process heat
+ lower temperature
+- syngas

**syngas direct**
+ “one pot” reaction
+ simple / cheap

**zinc / air battery**
- electricity
- transport (Zn / ZnO)

- carbon monoxide
- zinc
- coal
- zinc oxide

- zinc
- Water / CO₂

- oxygen
- zinc oxide
- zinc

- syngas
Thermochemical Cycles: Black Box

water splitting reaction:  \[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \]

CO\(_2\) reduction:  \[ \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2 \]
Energetics:

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 \]

Concentrated Solar Energy

**SOLAR REACTOR**

\[ \text{ZnO} \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 \]

\( \Delta H = 557 \text{ kJ/mol, } T = 2000 \text{ K} \)

**HYDROLYSER**

\[ \text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2 \]

\( \Delta H = -62 \text{ kJ/mol, } T = 700 \text{ K} \)

Fuel cell

ZnO \text{ recycle}
Solar to Fuel Efficiency: 2nd Law Analysis

\[ \eta_{\text{solar-to-chemical}} = \frac{W_{\text{FC}}}{Q_{\text{solar}}} = \begin{cases} 39\% & \text{ZnO/Zn-cycle} \\ 29\% & \text{Fe}_3\text{O}_4/\text{FeO-cycle} \end{cases} \]

Process efficiency will be lower: optical efficiency, support, ...

Quenching with inert gas to separate Zn\(_{(g)}\)/O\(_2\)
Zn / ZnO Cycle: 10 kW Solar Reactor

1. ZnO
2. Zn / O₂
3. sintered ZnO or Al₂O₃
4. 20% SiO₂ - Al₂O₃

- Concentrated solar radiation
- Water-cooled front
- Aperture
- Cavity
- Rotary joint
- Feeder
- Rotary feeds gas / water
- Insulation
- Window
Zn / ZnO Cycle: 10 kW Solar Reactor

Thermal Dissociation

- ZnO thermal dissociation
- purge gas
- transport of Zn\(_{(g)}\) / O\(_2\)
- quench sepn. Zn / O\(_2\)
- feeder retraced
- Zn\(_{(s)}\) / O\(_2\)
Zn / ZnO Cycle: 10 kW Solar Reactor

Feeding

screw feeder rotates

fresh ZnO
Zn / ZnO Cycle: 10 kW Solar Reactor

- ZnO container
- rotary joint
- ZnO feeder
- data acquisition
- ZnO-tile cavity
- porous Al₂O₃ insulation
- water-cooled reactor front
- Al₂O₃ CMC front cone
- Ar nozzles
- water-cooled Cu aperture
- lateral front wall
Zn / ZnO Cycle: 10 kW Solar Reactor

feed: 120 g ZnO (each)

Solar power

Temperature behind ZnO tiles (K)

Solar power input (W)

Time (s)

O$_2$ rate (mol · s$^{-1}$ · 10$^{-4}$)

O$_2$ from ZnO dissociation

mass balances
heat transfer analysis
“efficiencies” $\rightarrow$ models
Quench:

Pure Zinc

- Pure Zinc
- Quench:
  - Nucleation sets in
  - Surface is made available
  - Condensation starts
  - Net rate becomes zero: $(p - p_s = 0; \ S = 1)$

- Condensation rate > quench rate
- Small slope
- System follows phase boundary
Quench: \( \text{Zn} / \text{O}_2 \) (Quench Rate)

- Oxidation continues \((p_{s,\text{Zn}} = p_{s,\text{O}_2} = 0.0)\) (gas)
- Increased quench rate results in increased nucleation super saturation and nucleation rate:
  - More surface is created
  - All surface reactions become faster (slopes do not vary a lot)
- Condensation and oxidation evaporation and oxidation (evaporation not included)

Avoid leaving region \(\text{Zn}_{\text{liquid}}\) (or \(\text{Zn}_{\text{solid}}\))
Quench:  

Zn / O₂  

(Initial Dilution)

parallel curves
- same rates

increased dilution delays nucleation
- reaction(s) occur at lower $p_{Zn}$ and $T$
- smaller slope of vapor pressure curve at lower $T$
- system remains longer within liquid phase

even more favorable: resublimation
Quench: Comparison Model ↔ Experiment

$p_{\text{tot}} = 100\text{kPa}$
stoichiometric mixture
66 kPa Zn / 33 kPa $O_2$

model explains experimental observations on a qualitative level
large amounts of inert gas to be recycled (solar process?)
Zn / ZnO Cycle: Scale Up to 100 kW

- front cone
- cavity receiver
- quartz window
- concentrated solar radiation
- insulation
- rotary joint
- outlet tube
- rear panel
- quench unit
- center casing
- front cap
- front shield
- Zn + ½ O₂
- ZnO
- Zn / ZnO Cycle
Zn / ZnO Cycle: Scale Up to 100 kW

- screw feeder
- ZnO container
- mixer motor
- screw motor
- filter
- product gas outlet
- data acquisition system
- movable carriage
- motorized wheels for cavity rotation
- support for radiation shield
- bosch profile
- screw feeder
- ZnO container
- mixer motor
- screw motor
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- data acquisition system
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- motorized wheels for cavity rotation
- support for radiation shield
- bosch profile
Zn / ZnO Cycle: Scale Up to 100 kW

MWSF: PROMES-CNRS Font Romeu Odeillo

63 heliostats (2835 m²)

1 MW (80 cm aperture)
peak concentration: 10'000 suns
Zn / ZnO Cycle: Scale Up to 100 kW

no results yet:
- installation completed
- start up / initial testing under way
- experimenting starts soon
Carbothermic Reduction of ZnO

ZnO is stable in presence of

\[ \text{CH}_4 \rightarrow \text{C} \]

\[ \text{ZnO} + \text{CH}_4 \rightarrow \text{CO} + 2\text{H}_2 \]

\[ \text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO} \]

- carbon free
  - \( \text{ZnO} \rightarrow \text{Zn} + \frac{1}{2}\text{O}_2 \)

- minimum carbon
  - \( \text{ZnO} + \frac{1}{4}\text{CH}_4 \rightarrow \text{Zn} + \frac{1}{4}\text{CO}_2 + \frac{1}{2}\text{H}_2\text{O} \)

- ideal syngas
  - \( \text{ZnO} + \frac{1}{2}\text{C} \rightarrow \text{Zn} + \text{CO}_2 \)

- scale up
  - 300 kW\(_{th}\)}
Carbothermic Reduction: Beam Down Concept

SRFU: Weizmann Institute of Science

- Hyperboloidal mirror (70 m²)
- 64 heliostats (3584 m²)
- Aperture of experiment: 0.5 MW (0.5 m aperture)
  4000 suns

Secondary concentrator
Carbothermic Reduction: 300 kW\textsubscript{th} pilot reactor

- **upper part (stationary)**
- **lower part**
- **carrier gas inlet**
- **quartz window**
- **offgas pipe with heater**
- **ZnO/C batch**
- **≤ 300 KW solar power input**
- **140 cm**
- **Zn(g) + CO**

**principle:**
- “2-cavity” reactor
- fixed bed of ZnO/C-mixture
- 1 batch per day

**features:**
- \(D_{rxn-chamber} = 1.4 \text{ m}\)
- \(H_{bed} ≤ 0.5 \text{ m}\)
- capacity ≤ 500 kg ZnO/C
- lining: SiC plates
- insulation: \(\text{Al}_2\text{O}_3\)-\(\text{SiO}_2\)
- separation plates: graphite, SiC on graphite
- lower part easy to lift down for refilling
Carbothermic Reduction: 300 kW\textsubscript{th} pilot plant

Impressions
Carbothermic Reduction: 300 kW<sub>th</sub> pilot plant

100 Kg ZnO / 16 Kg beech char coal

Temperature separation plates

Bed bottom temperature

Temperature reaction chamber side wall

kg Zn/h

CO

CO<sub>2</sub>
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