# Solar Energy Conversion Devices and Plants

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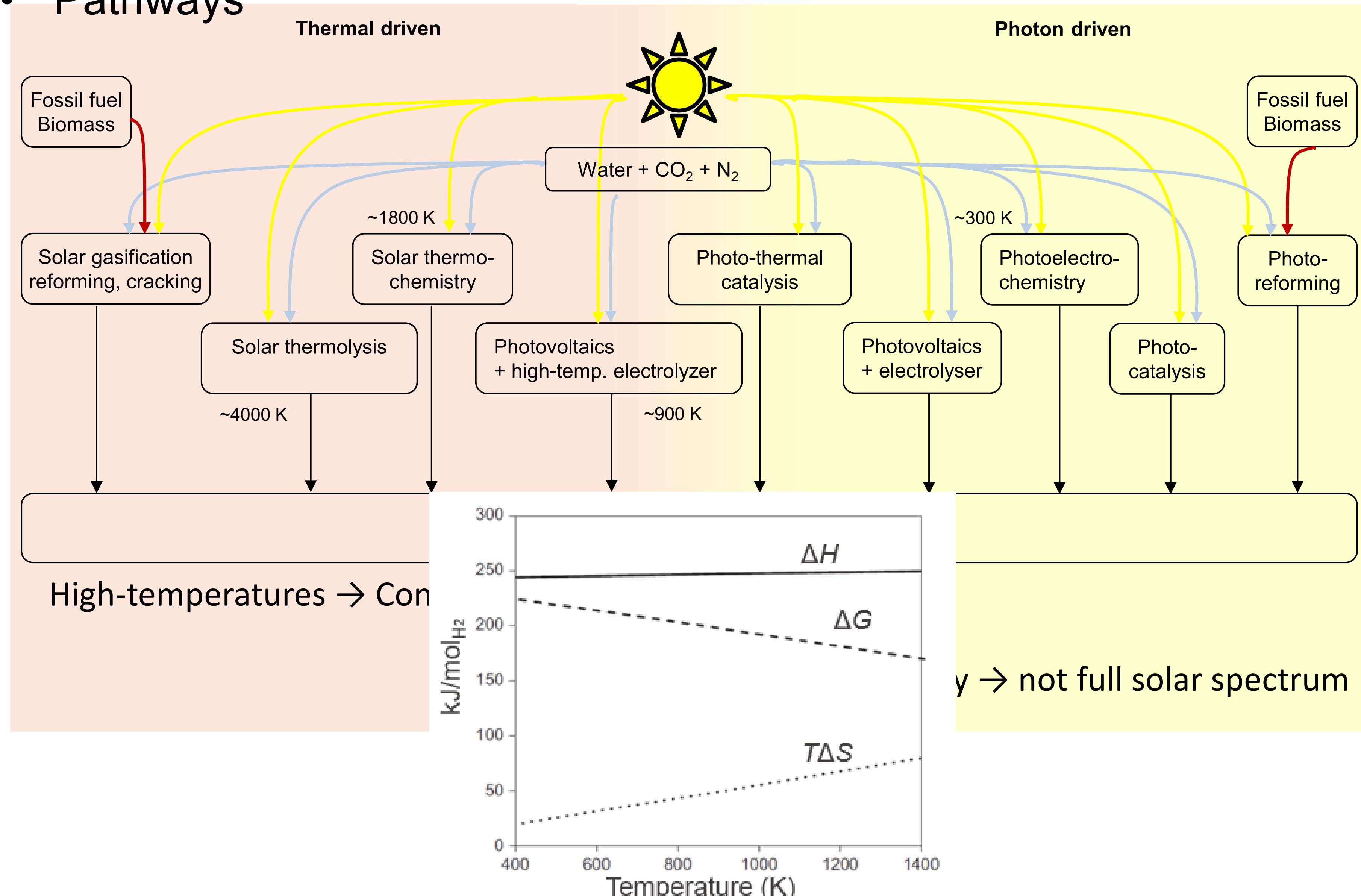
Laboratory of Renewable Energy Science and Engineering

# Outline

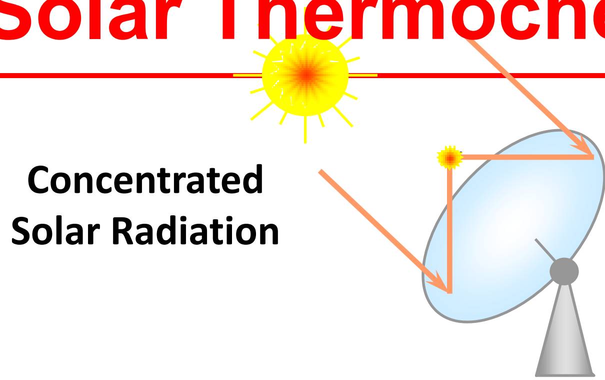
- Solar-driven thermochemistry
  - Solar thermolysis
  - Solar thermochemical redox cycles
  - Hybrid approaches:
    - Solar reforming
    - Solar cracking
    - Solar gasification

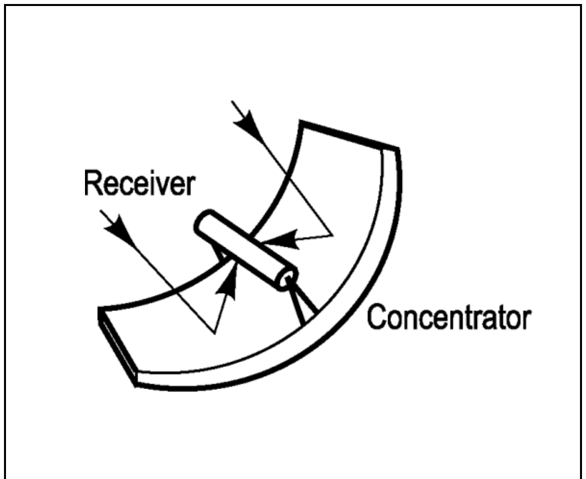
# Solar Fuels

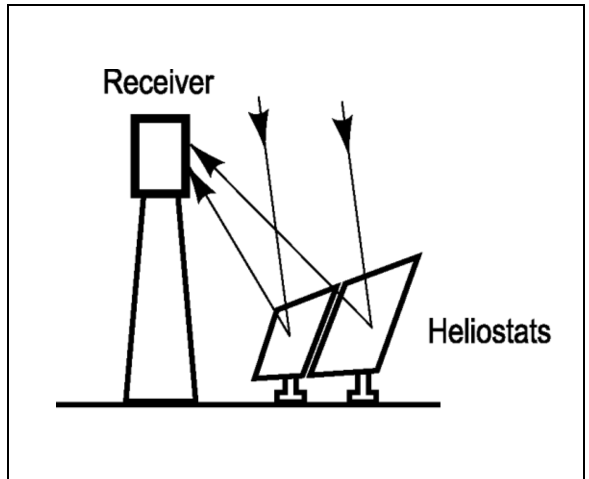
- Pathways

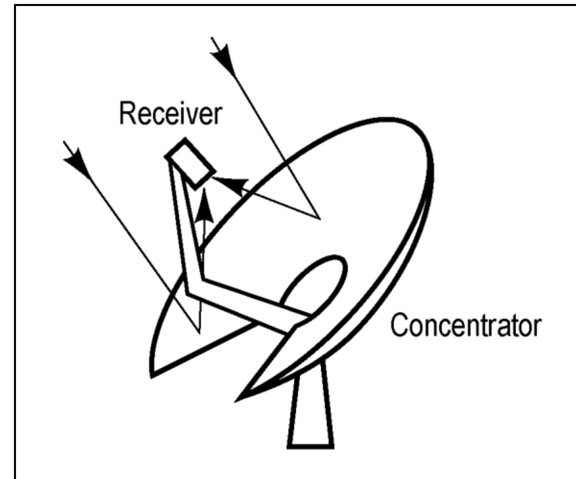


# Solar Thermochemical Conversion

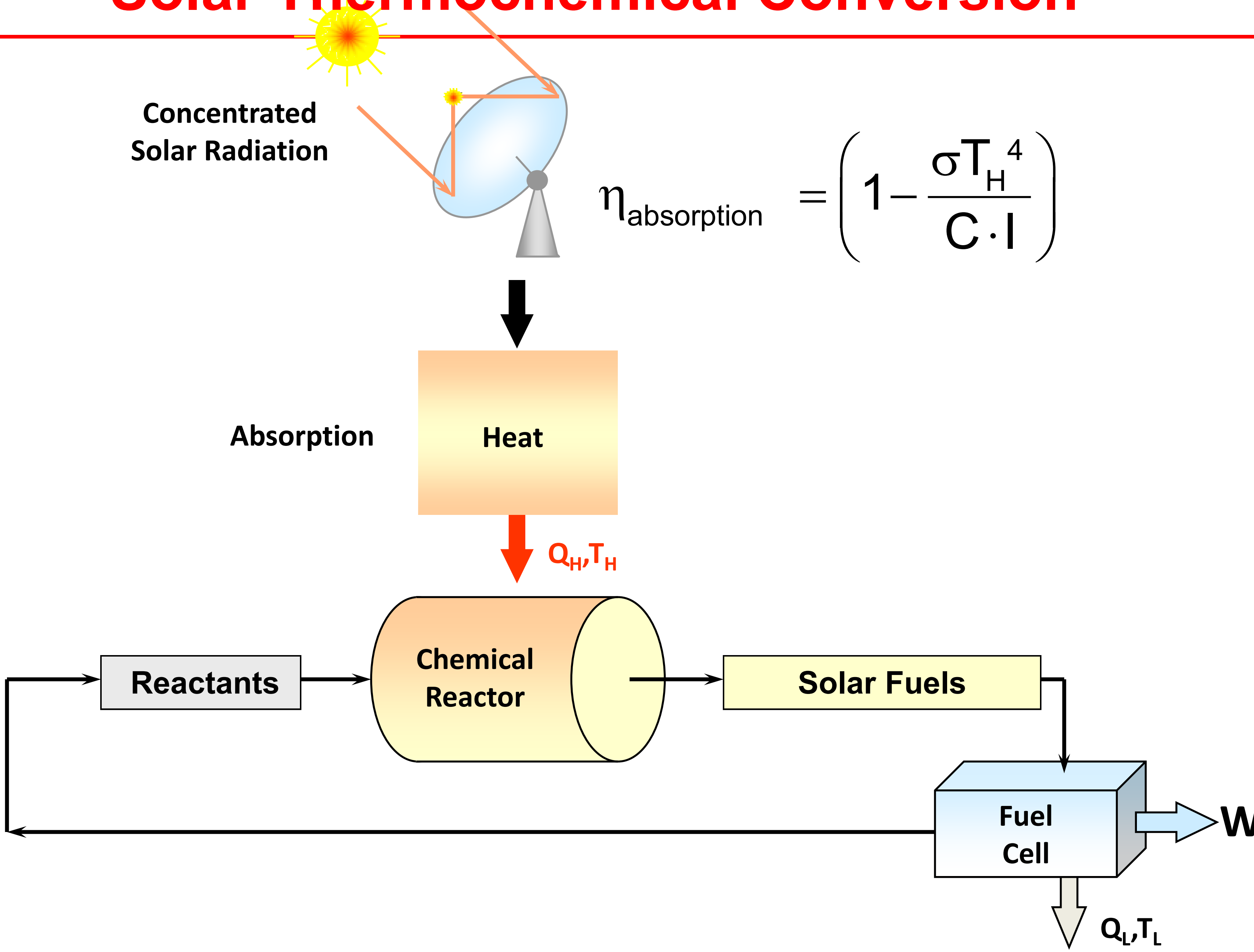


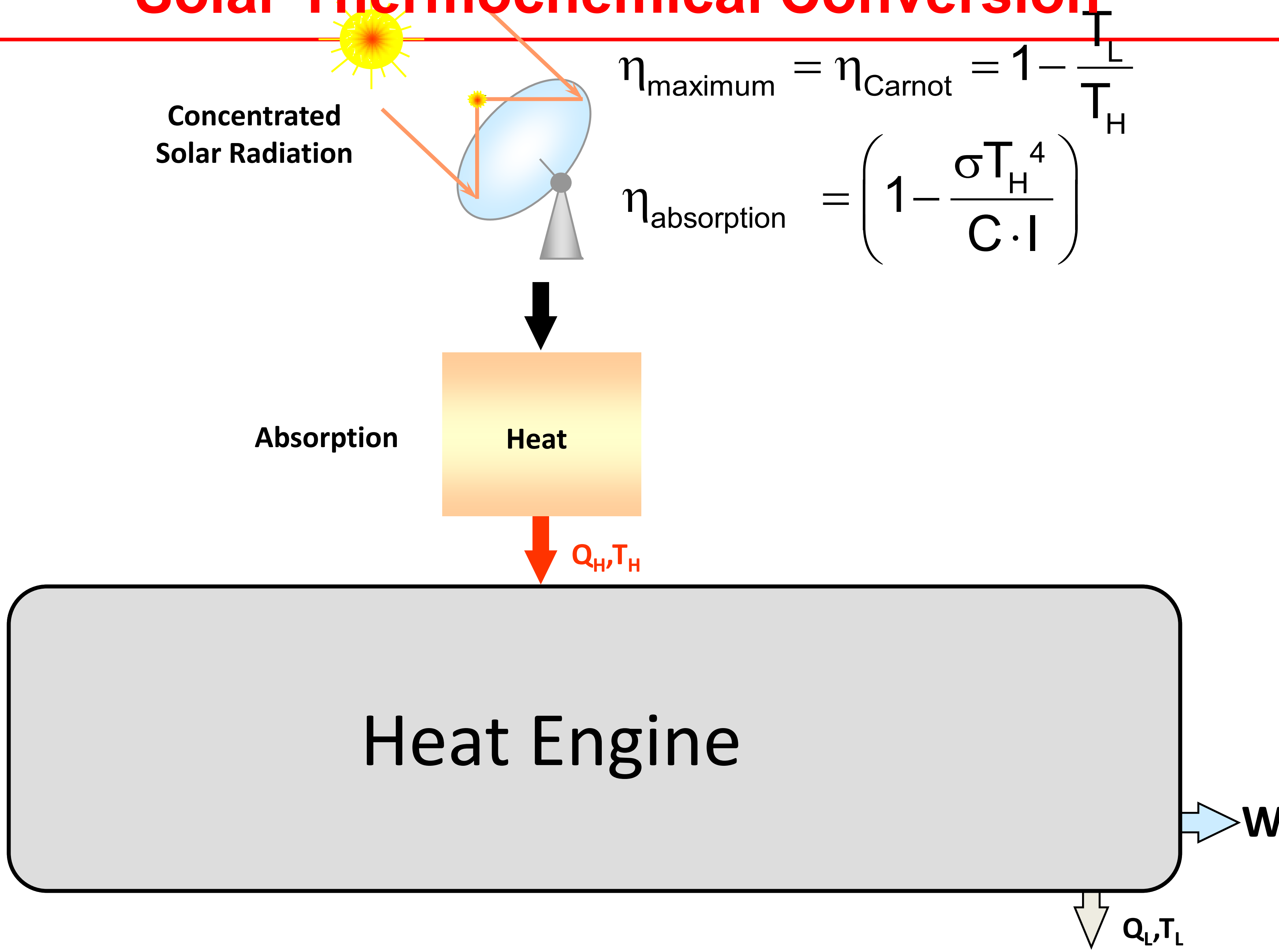

# Solar Thermochemical Conversion



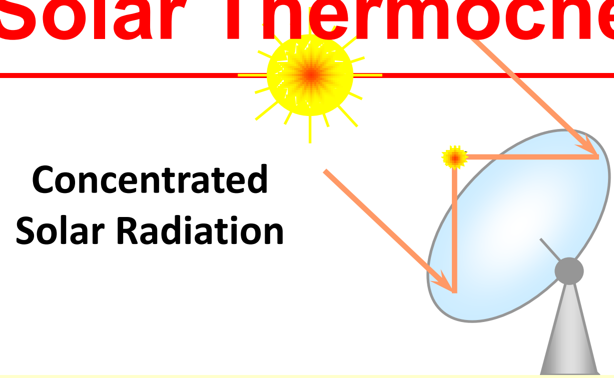
# Solar Thermochemical Conversion

$$\eta_{maximum} = \eta_{Carnot} = 1 - \frac{T_L}{T_H}$$

$$\eta_{absorption} = \left(1 - \frac{\sigma T_H^4}{C \cdot I}\right)$$



# Solar Thermochemical Conversion

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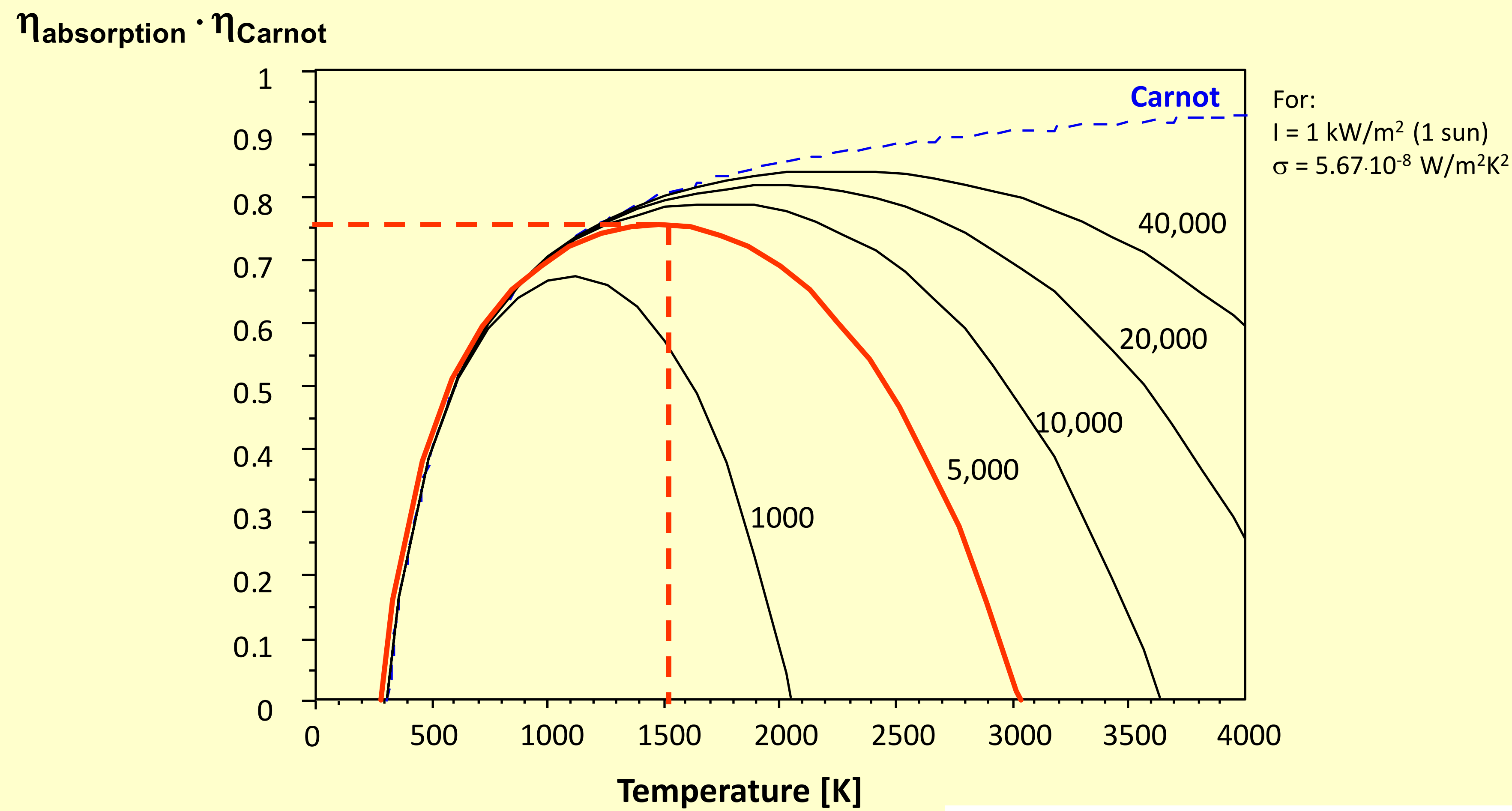
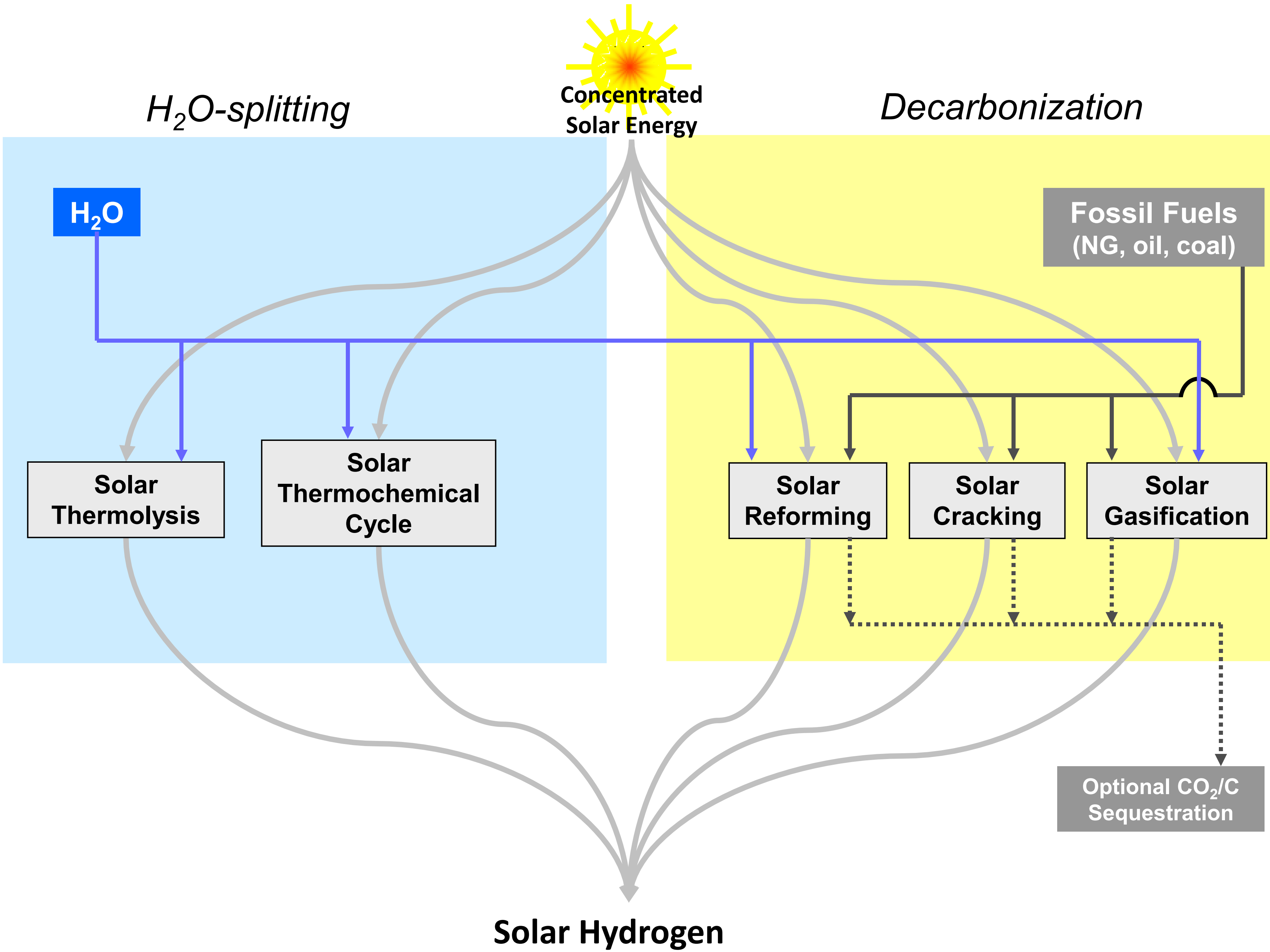
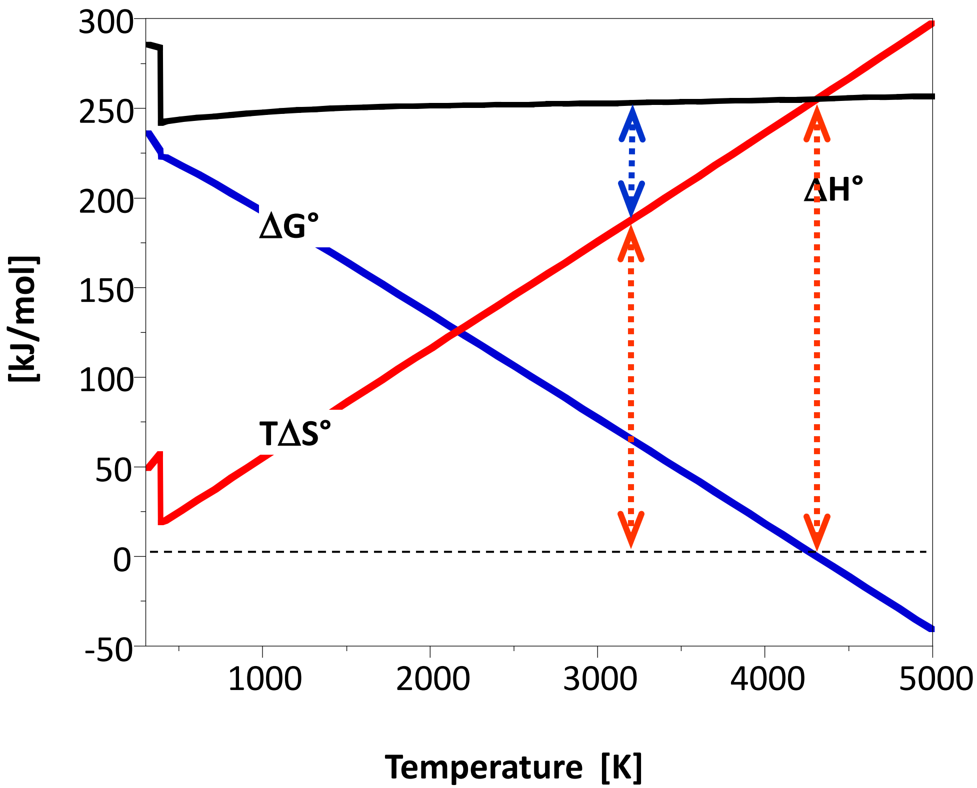



Fletcher and Moen, *Science* 197, 1050-1056, 1977.

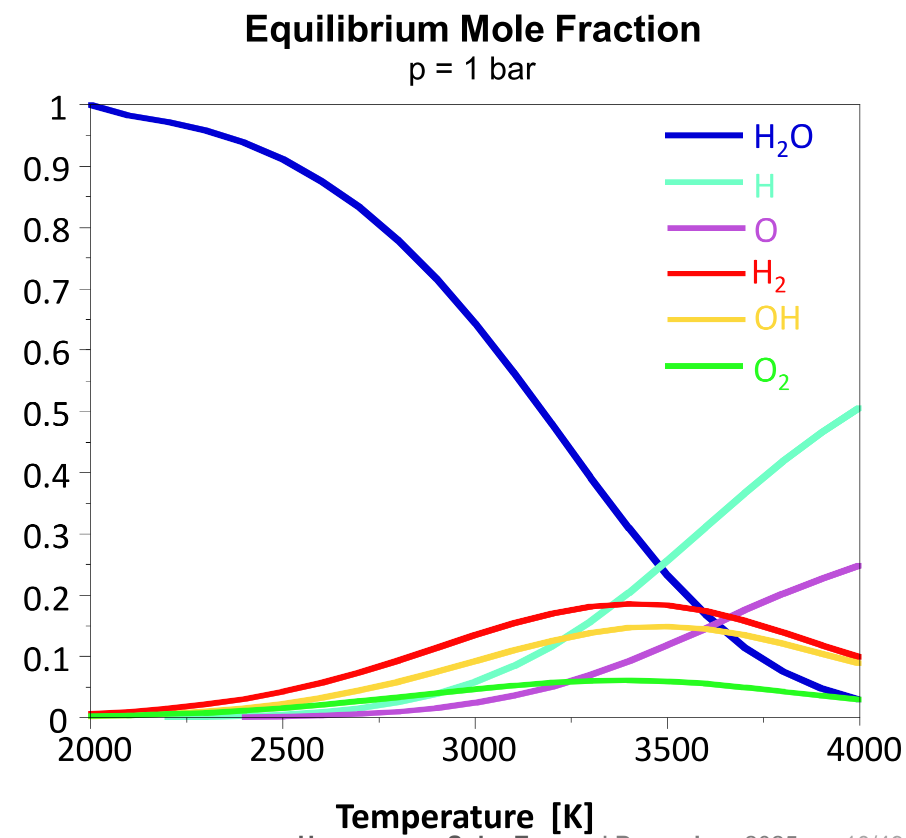

Concentrated
Solar Energy
$H_2O$-splitting
Decarbonization
$H_2O$
Fossil Fuels
(NG, oil, coal)
Solar
Thermolysis
Solar
Thermochemical
Cycle
Solar
Reforming
Solar
Cracking
Solar
Gasification
Optional $CO_2$/C
Sequestration
Solar Hydrogen

# Solar Thermolysis

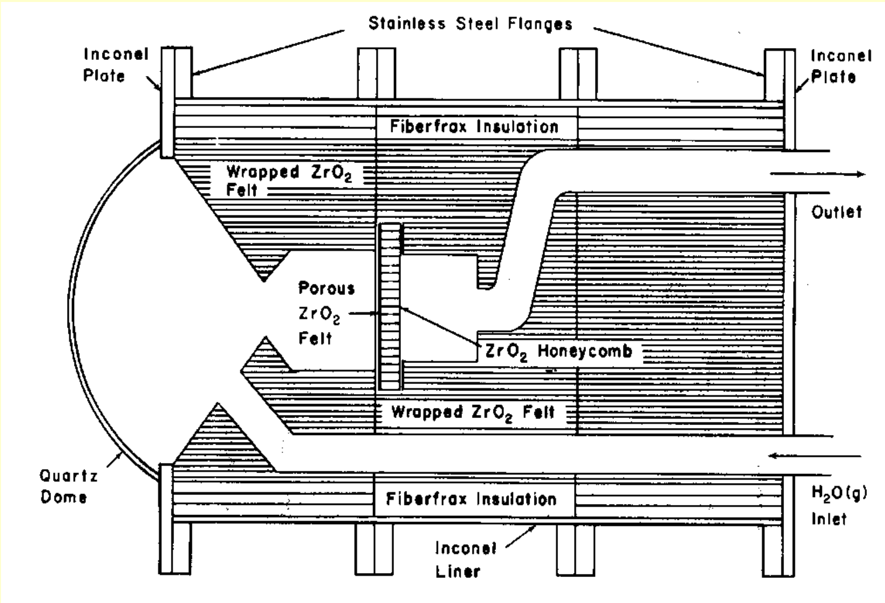
# Solar Thermolysis



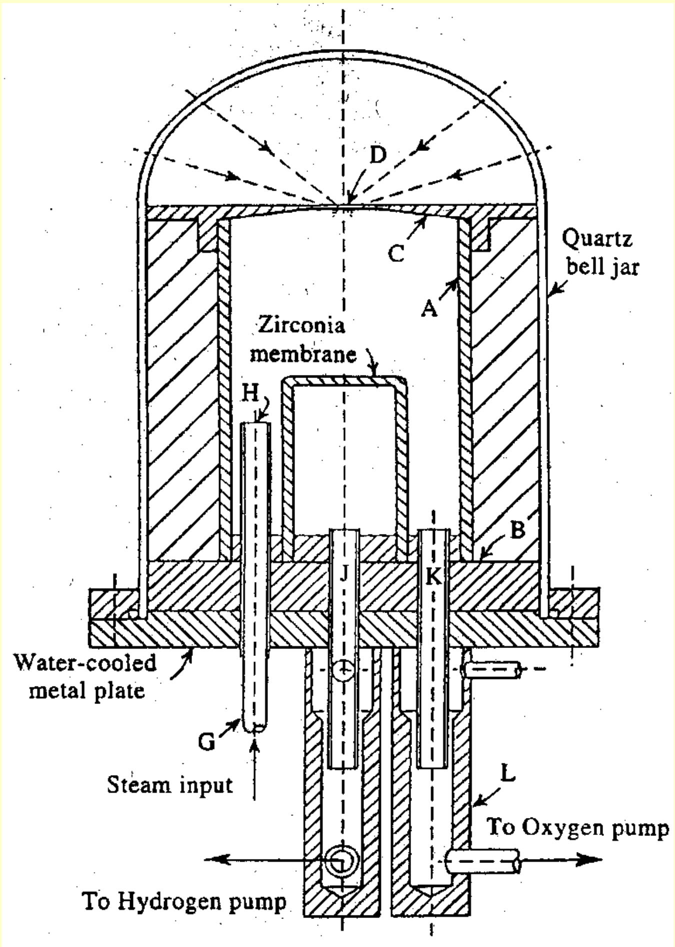

Thermal Dissociation: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$



# Solar Thermolysis

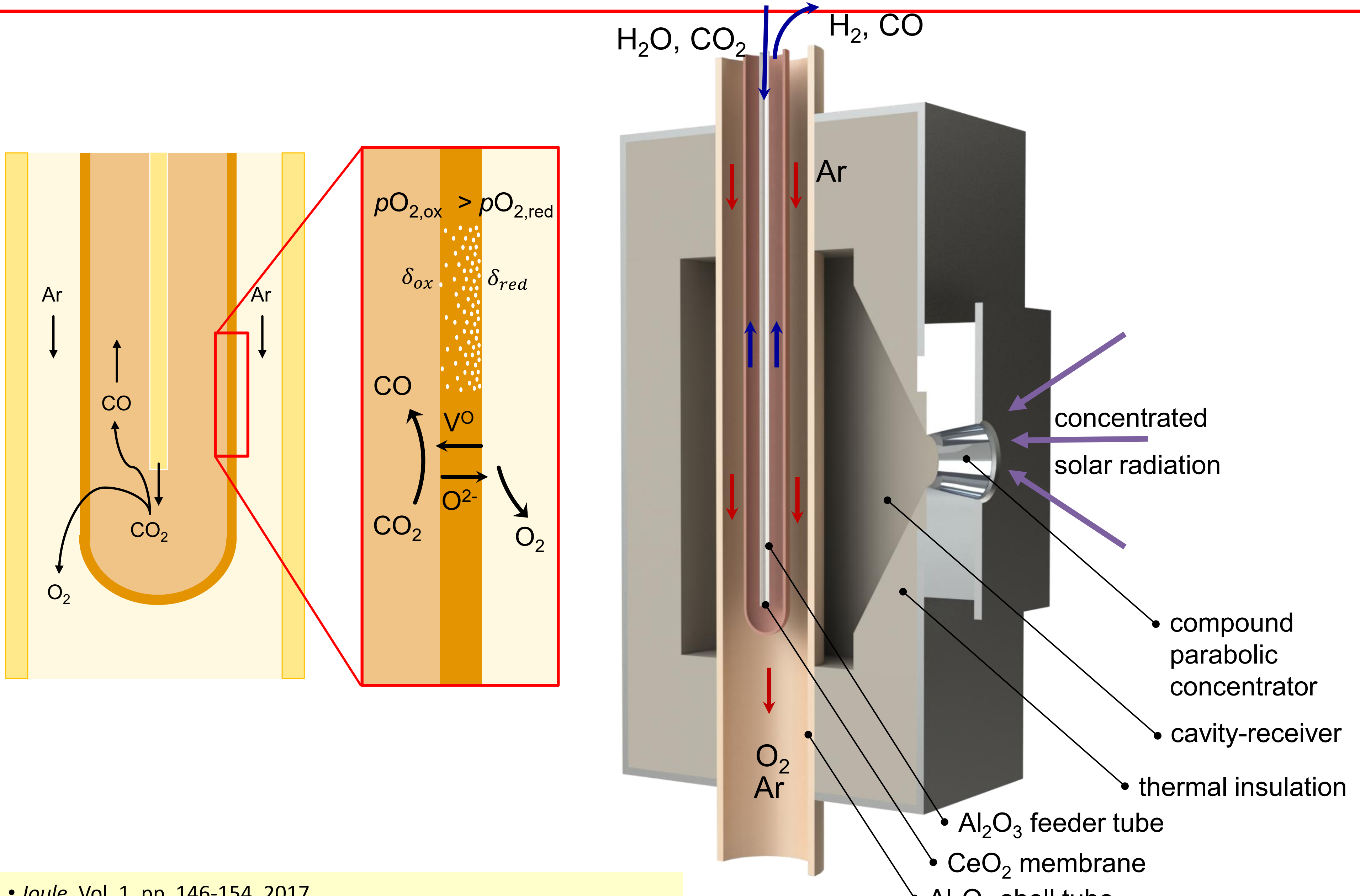



- Fletcher E., *J. Solar Energy Engineering* **123**, 63-74, 2001.




- Kogan et al., *Int. J. Hydrogen Energy* **23**, 89-98, 1998.

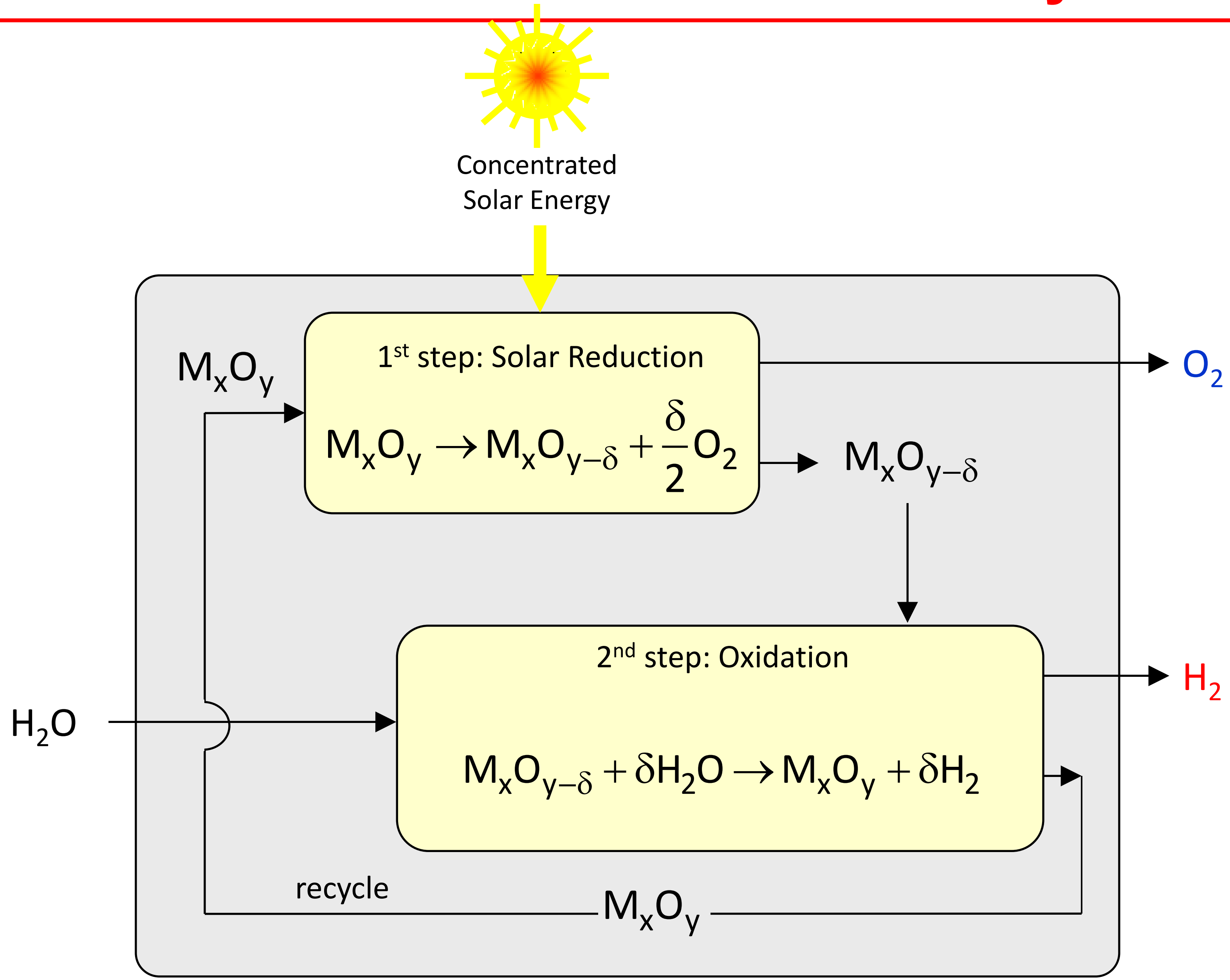
# Solar Thermolysis



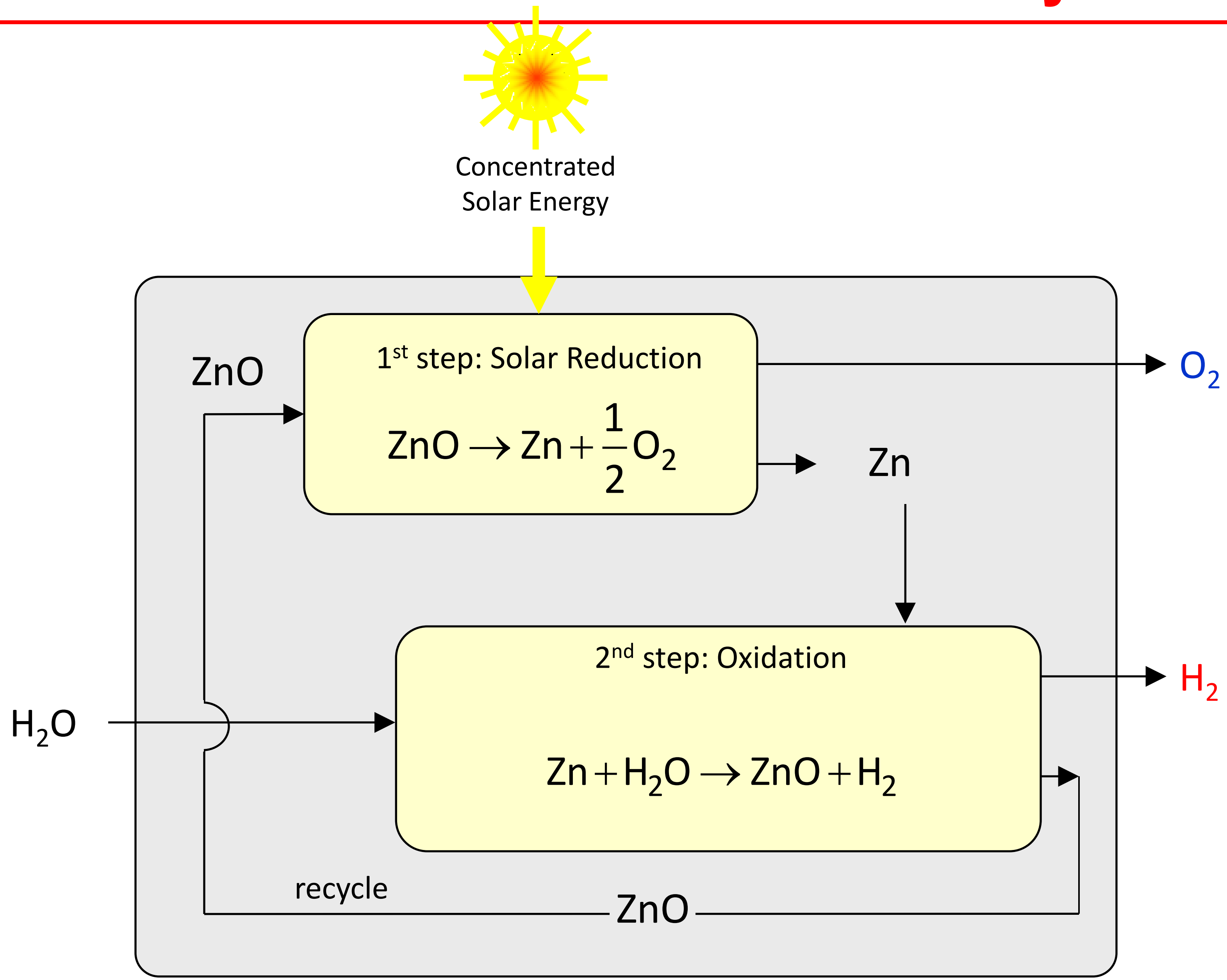

- *Joule*, Vol. 1, pp. 146-154, 2017
- *Reaction Chemistry & Engineering*, Vol. 4, pp. 1431–1438, 2019

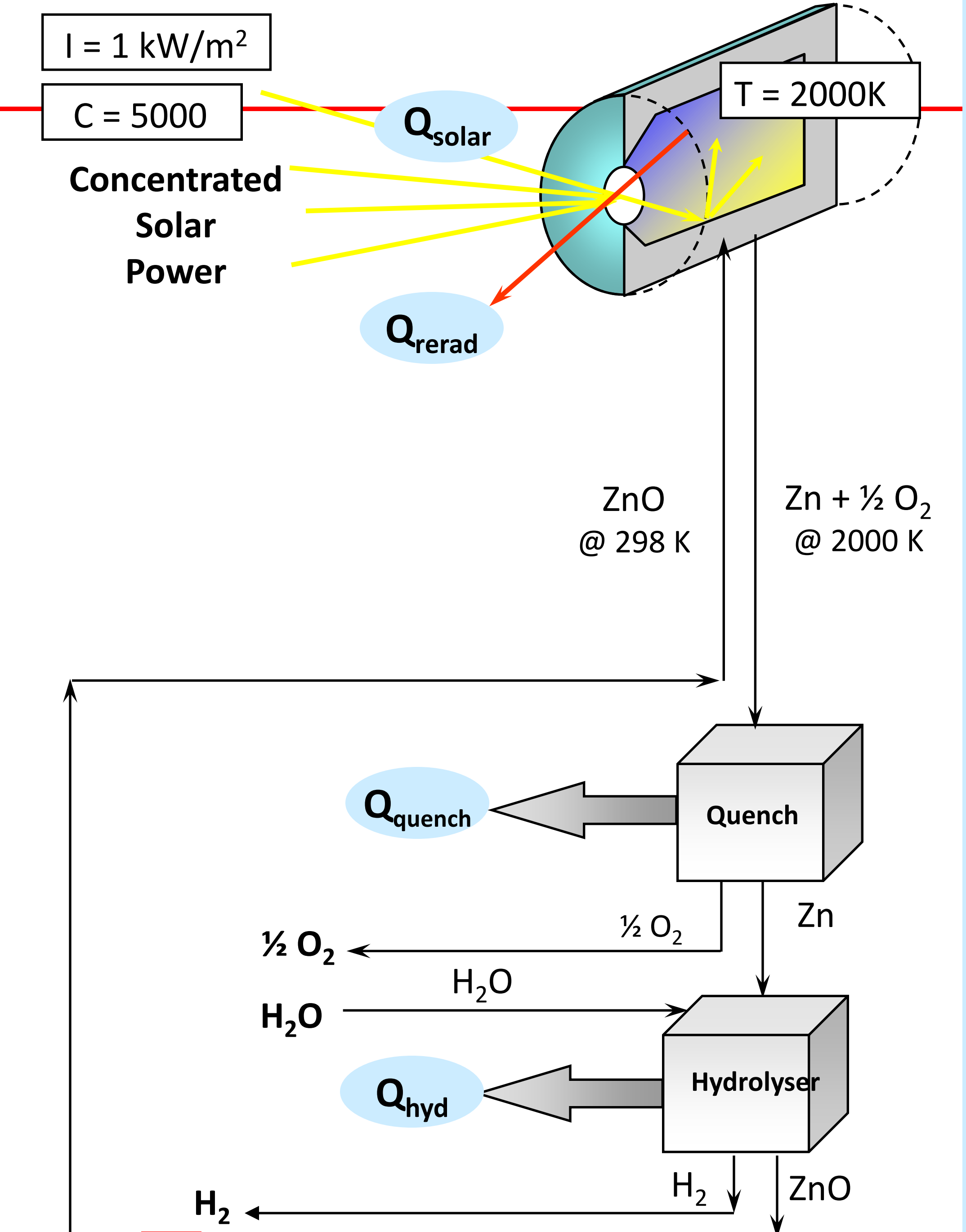
# Solar Thermochemical Cycles

# Solar Thermochemical Redox Cycle



# Solar Thermochemical Redox Cycle






$$\Delta H_{ZnO\ @\ 300K \rightarrow Zn + ½O_2\ @\ 2000K} = 557\ \text{kJ/mol}$$

---

$$\eta_{absorption} = \frac{\Delta H_{rxn}}{Q_{solar}} = 1 - \frac{\sigma T^4}{I \times C} = 82\%$$

$Q_{solar} = 680$ kJ/mol

$Q_{rerad} = 123$ kJ/mol

---

$$Q_{quench} = \Delta H_{Zn + ½ O_2\ @\ 2000K \rightarrow Zn + ½ O_2\ @\ 300K}$$

$$= -209\ \text{kJ/mol}$$

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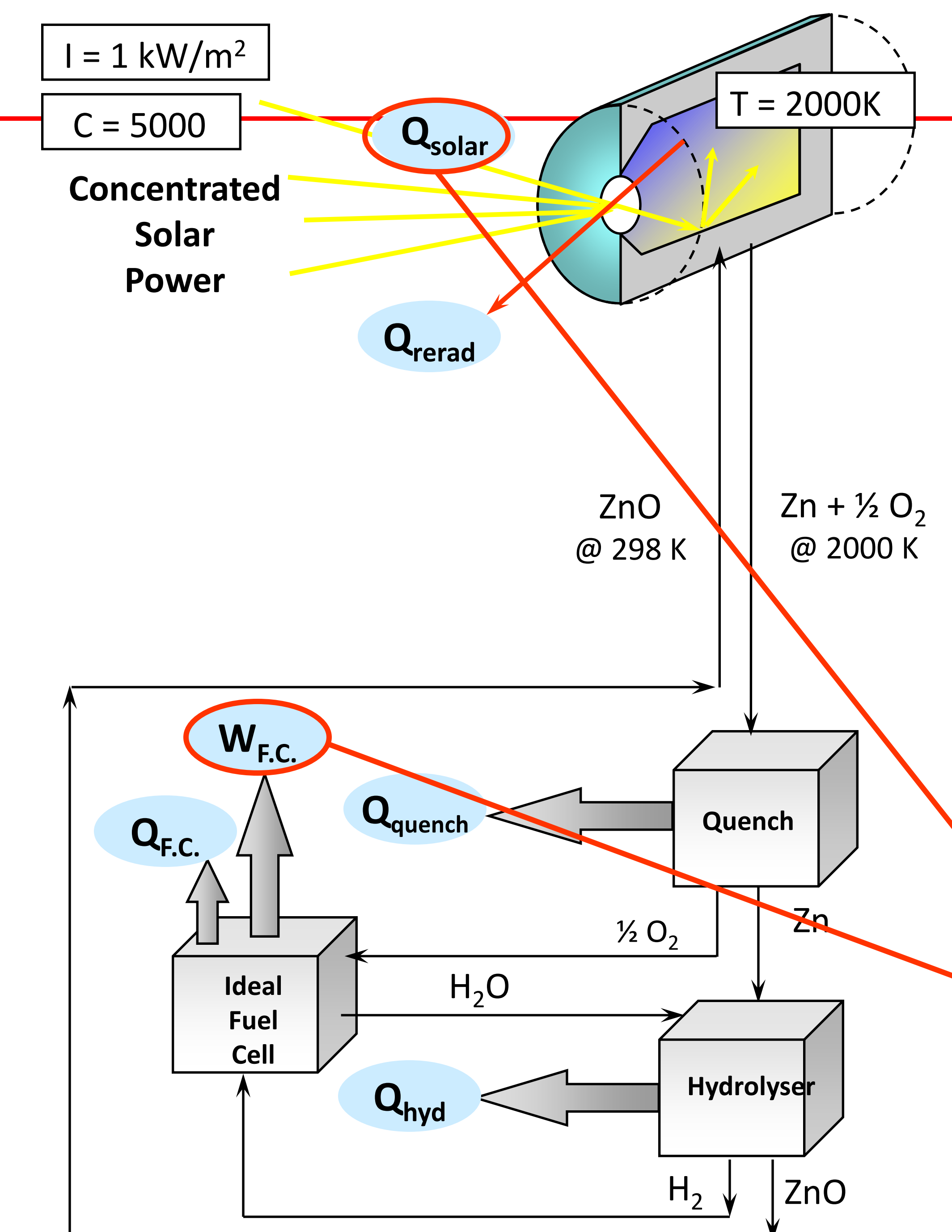
$$Q_{hydrolyser} = \Delta H_{Zn + H_2O \rightarrow ZnO + H_2} = -62\ \text{kJ/mol}$$

---




$\Delta H_{ZnO\ @\ 300K \rightarrow Zn + \frac{1}{2}O_2\ @\ 2000K} = 557$ kJ/mol

---

$$\eta_{absorption} = \frac{\Delta H_{rxn}}{Q_{solar}} = 1 - \frac{\sigma T^4}{I \times C} = 82\%$$

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---

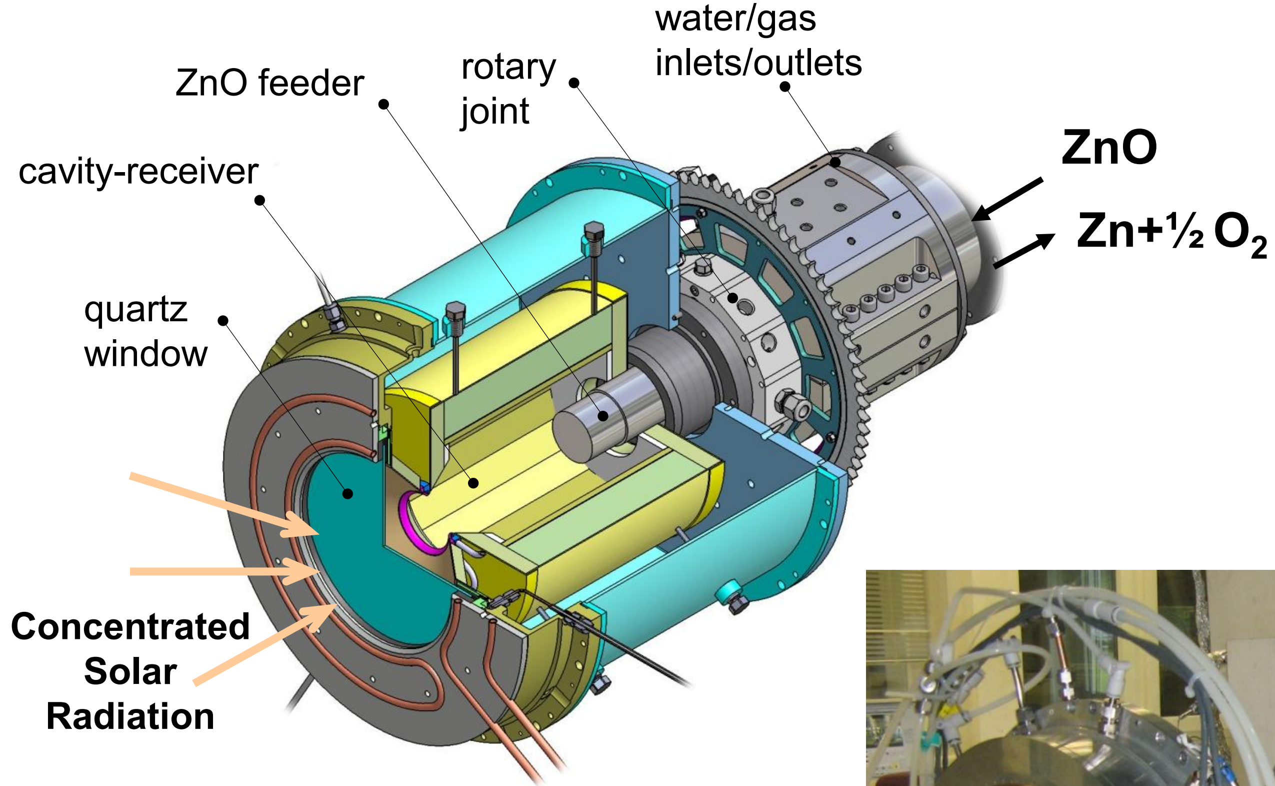
$W_{F.C} = -\Delta G_{H_2 + \frac{1}{2} O_2 \rightarrow H_2O\ @\ 300K} = 237$ kJ/mol

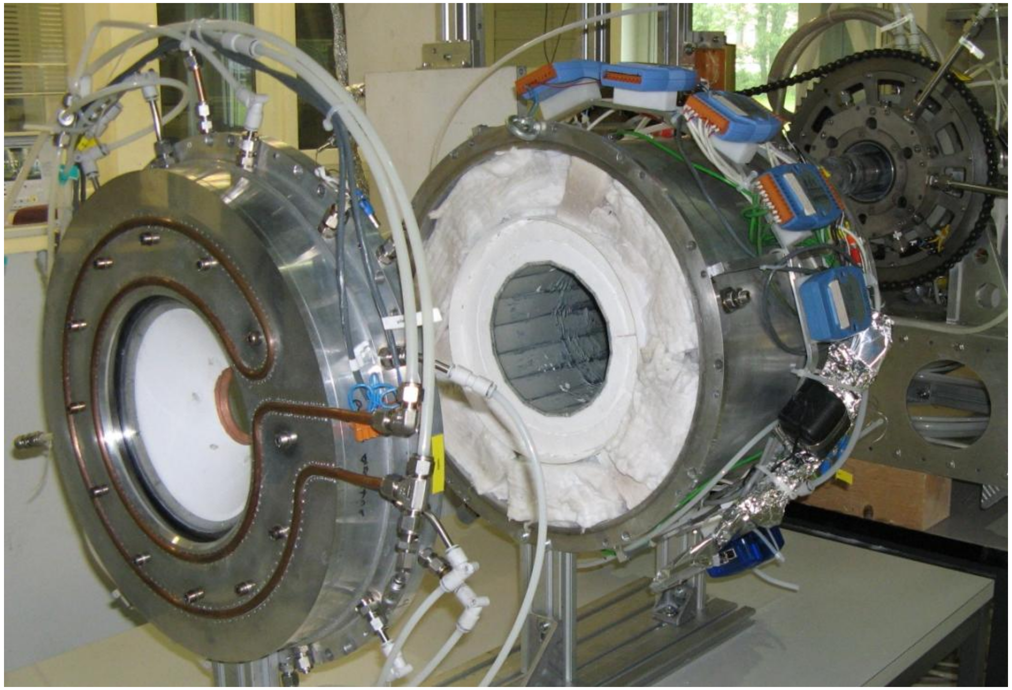
$Q_{F.C} = (\Delta H - \Delta G) = -49$ kJ/mol

---

$$\eta = \frac{W_{F.C.}}{Q_{solar}} = \begin{cases} 35\% & \text{no h.r.} \\ 58\% & \text{with h.r.} \end{cases}$$

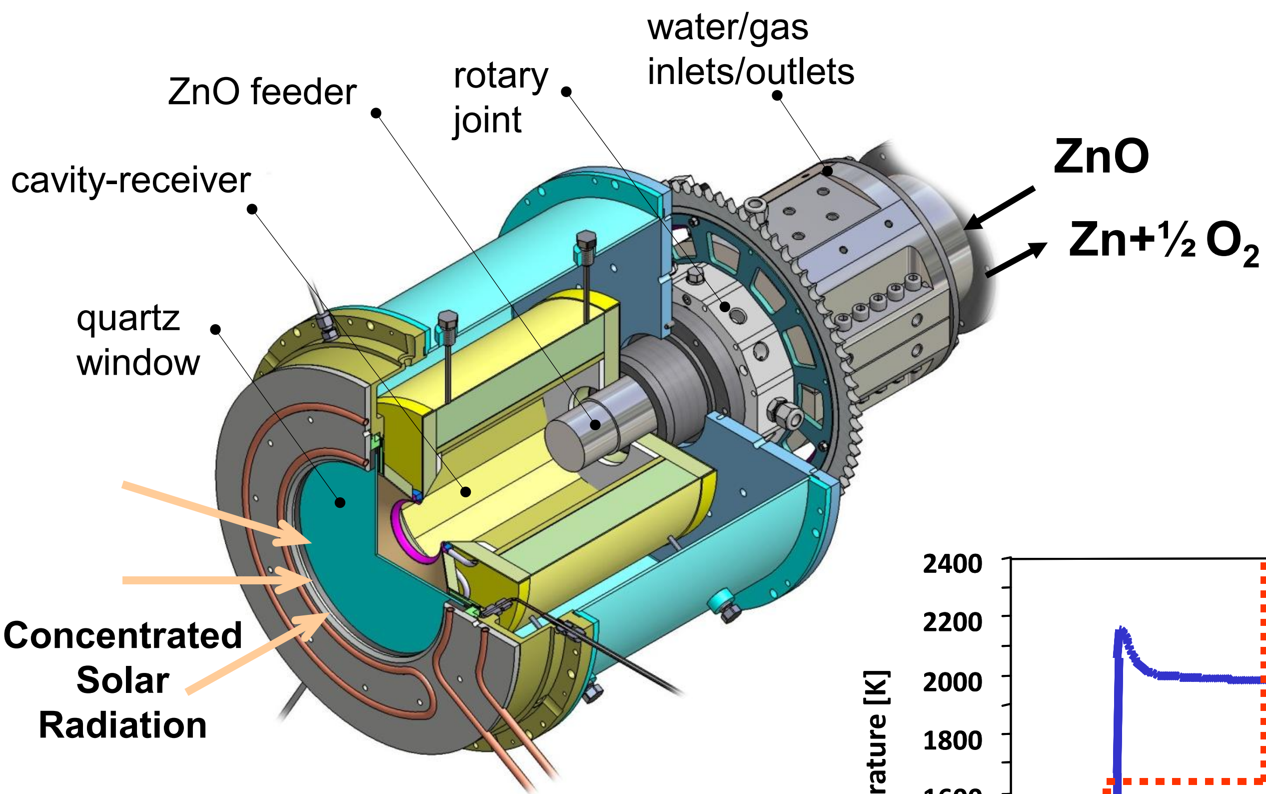
# ZnO/Zn Cycle

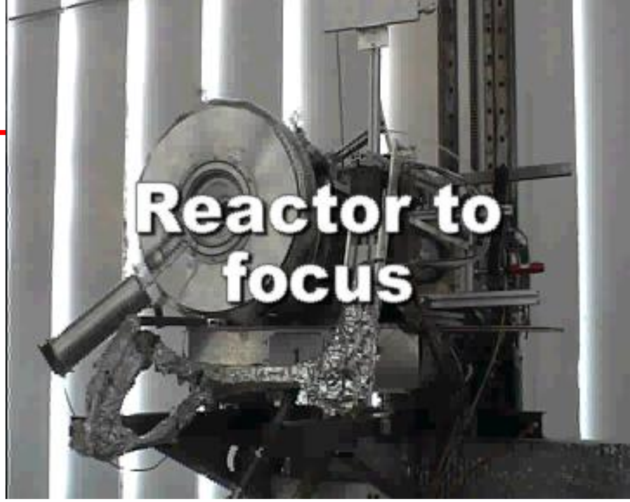


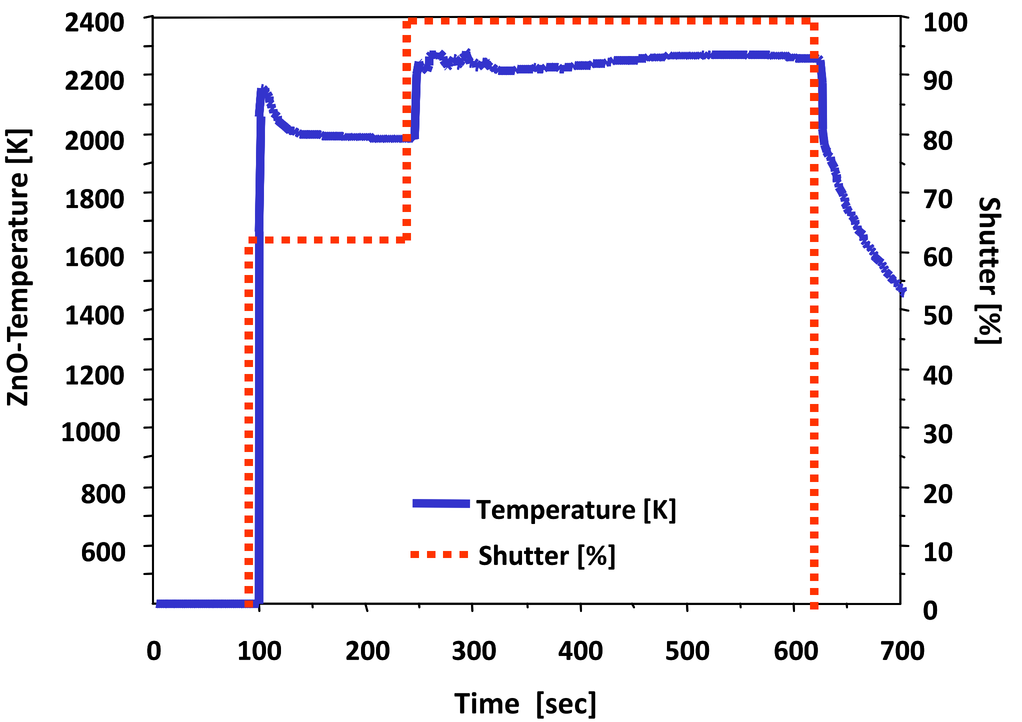
- *AIChE J.* 55, 1497-1504, 2009.
- *Chem. Eng. J.* 150, 502-508, 2009.
- *Int. J. Heat Mass Transfer* 52, 2444-2452, 2009.

# ZnO/Zn Cycle



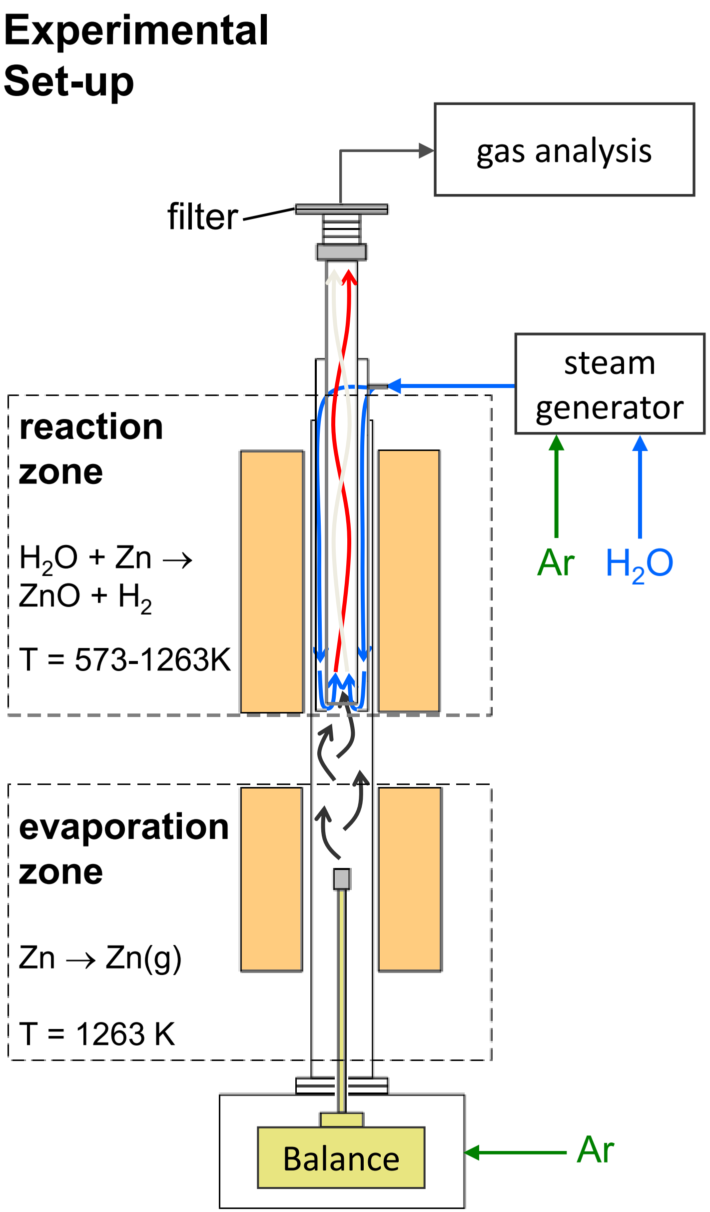



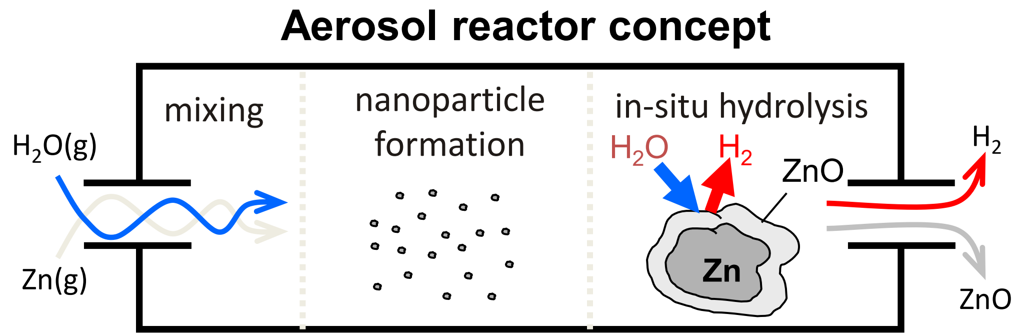

- $T_{reactor}$ = 2000 K
- $Q_{solar}$ = 10 kW
- $C_{peak}$ = 5880 suns
- $m_{ZnO}$ = 11 g/min
- Zn yield = 50 – 95 %

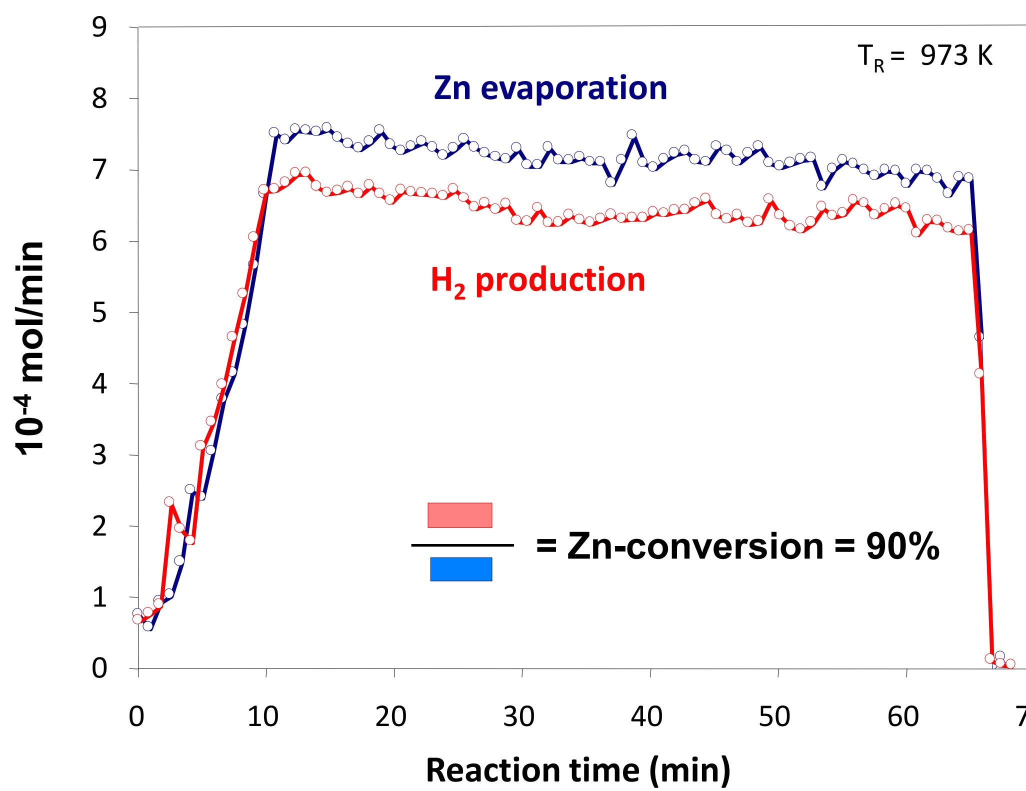



- *AIChE J.* 55, 1497-1504, 2009.
- *Chem. Eng. J.* 150, 502-508, 2009.
- *Int. J. Heat Mass Transfer* 52, 2444-2452, 2009.

# Zn Hydrolysis



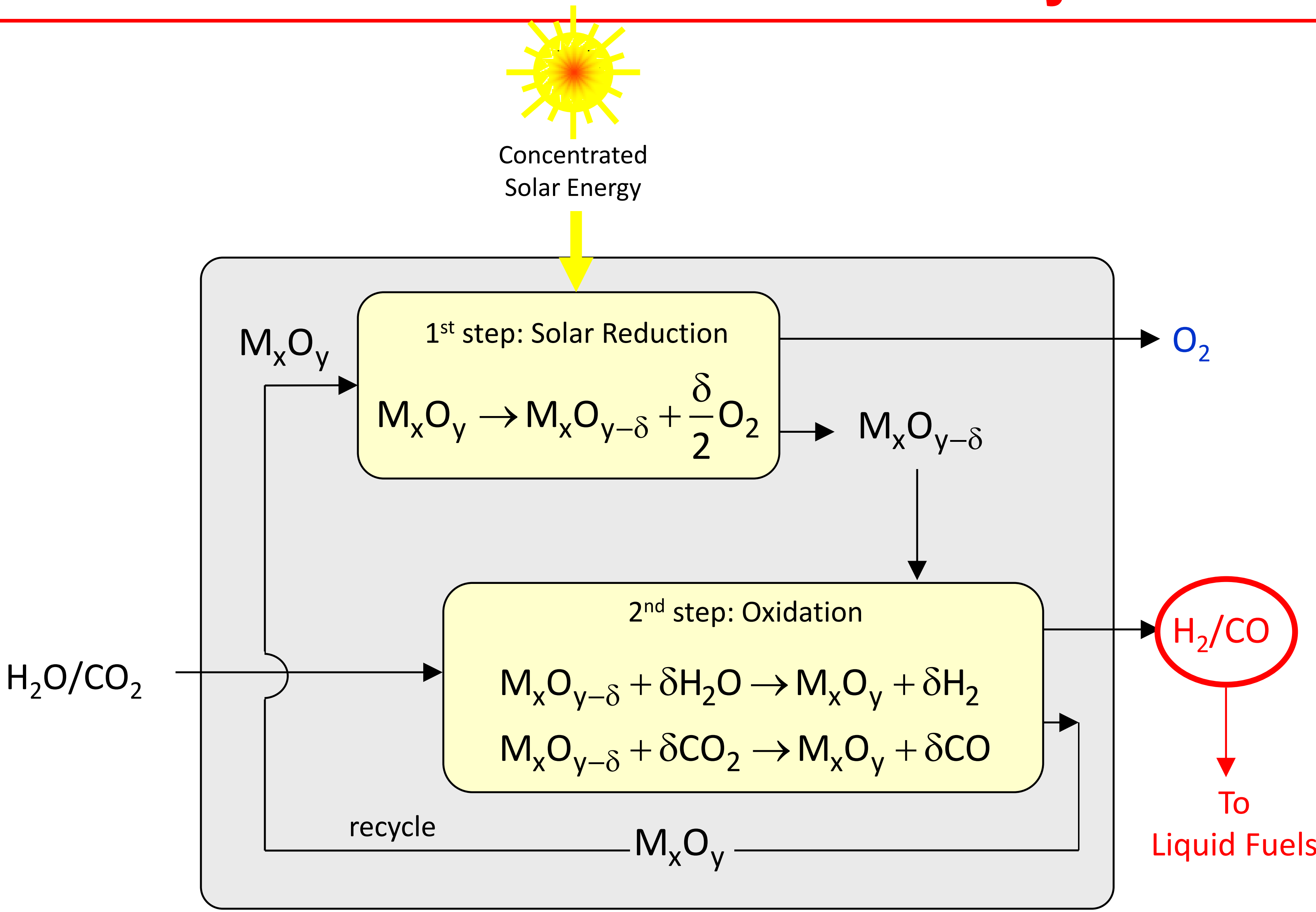



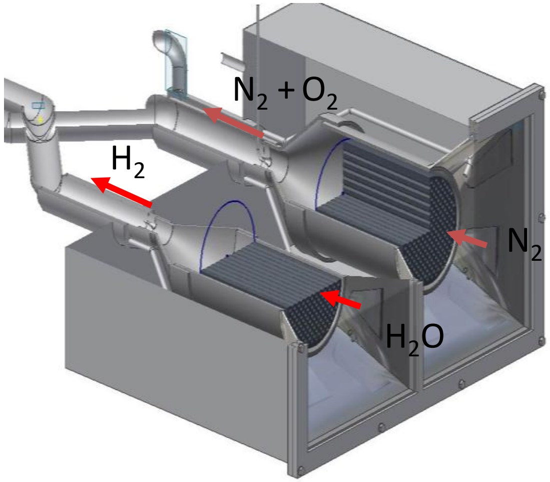


- *AIChE J.* 52, 3297-3303, 2006.
- *Chem. Eng. Sc.* 64, 1095-1101, 2009.

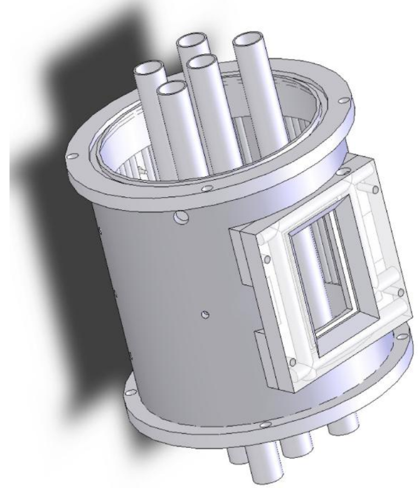
# Solar Thermochemical Redox Cycle



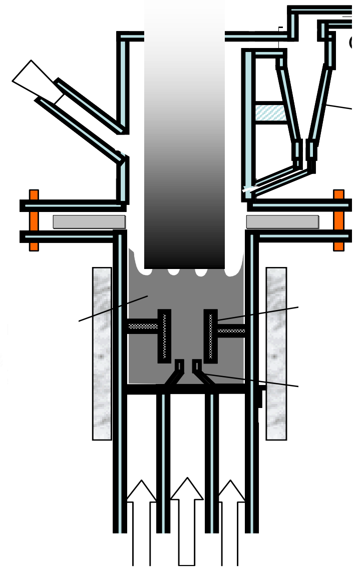
DLR, Germany
$ZnFe_2O_4$



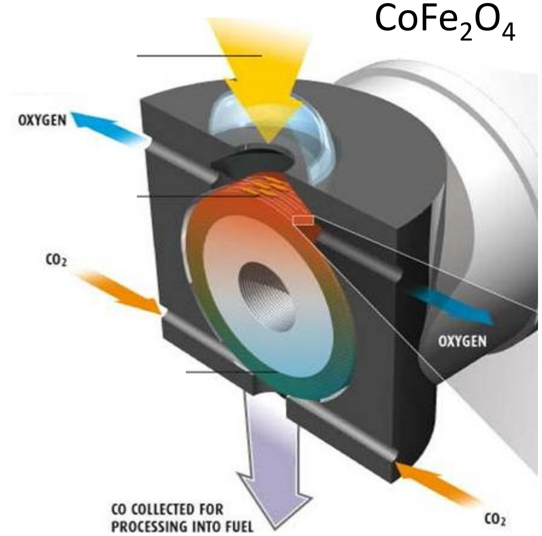

U. of CO, USA
$NiFe_2O_4$



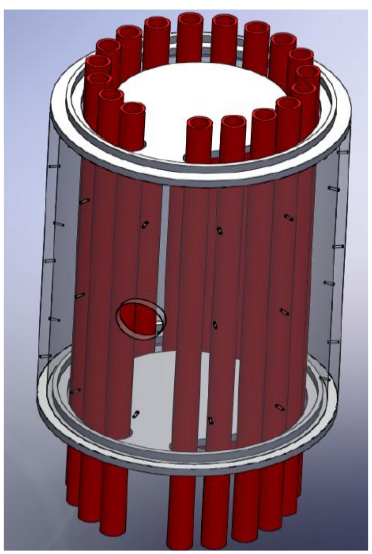
Niigata U., Japan
$NiFe_2O_4$



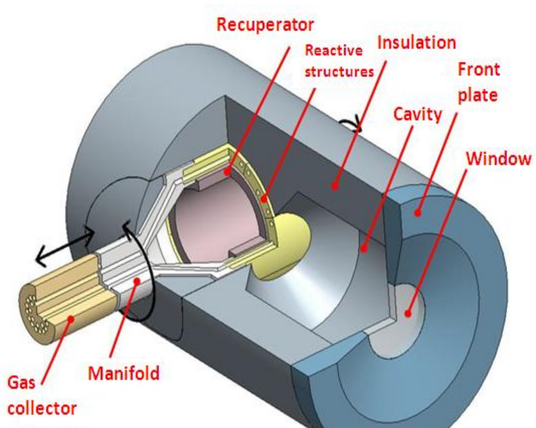
SNL, USA
$CoFe_2O_4$



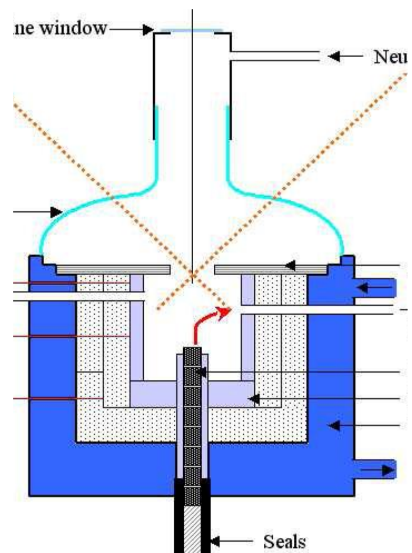

U. of FL, USA
$CoFe_2O_4$



U. of MN, USA
$CeO_2$

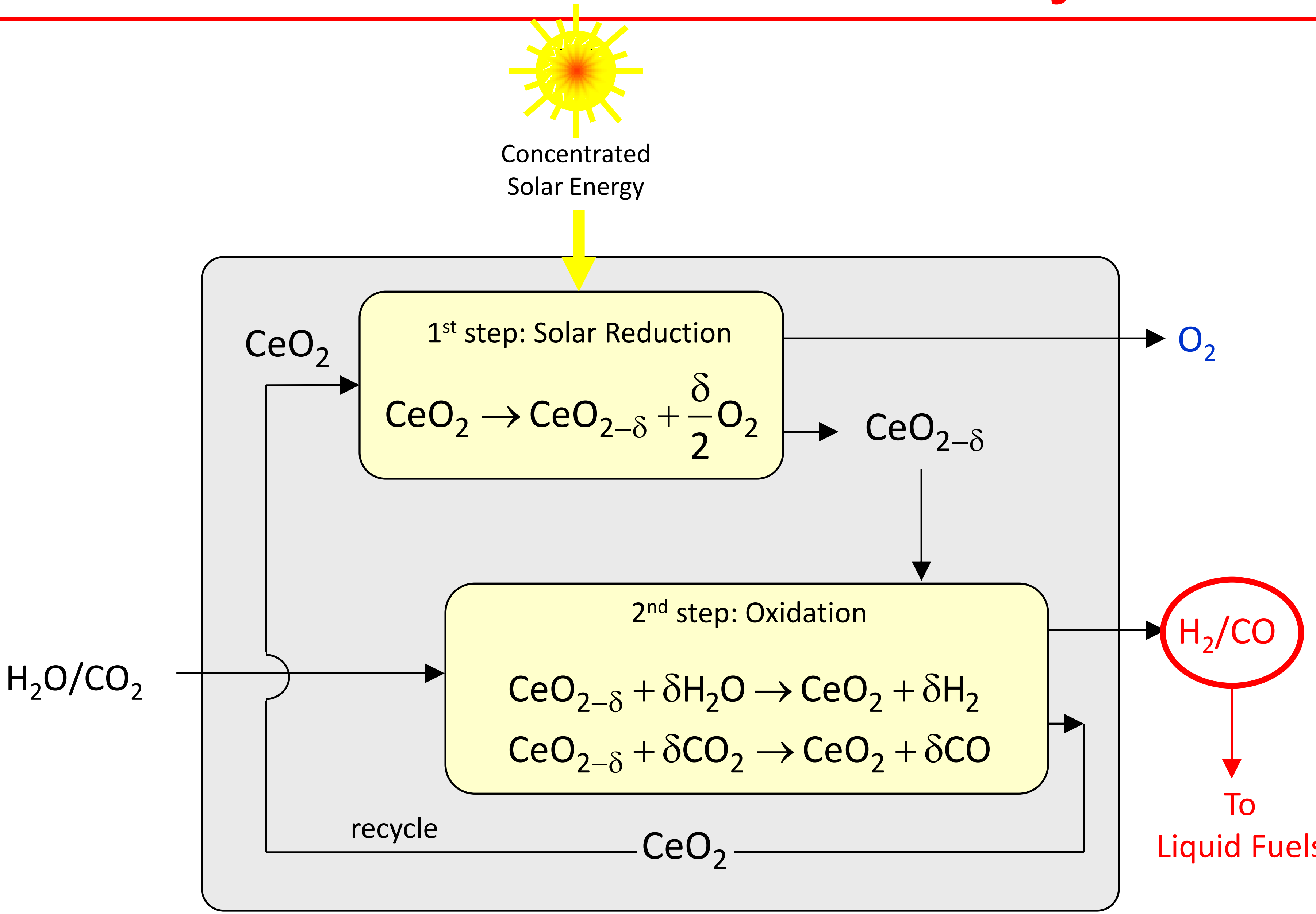



CNRS, France
$ZnO$, $SnO_2$




SNL, USA
$CeO_2$

# Solar Thermochemical Redox Cycle



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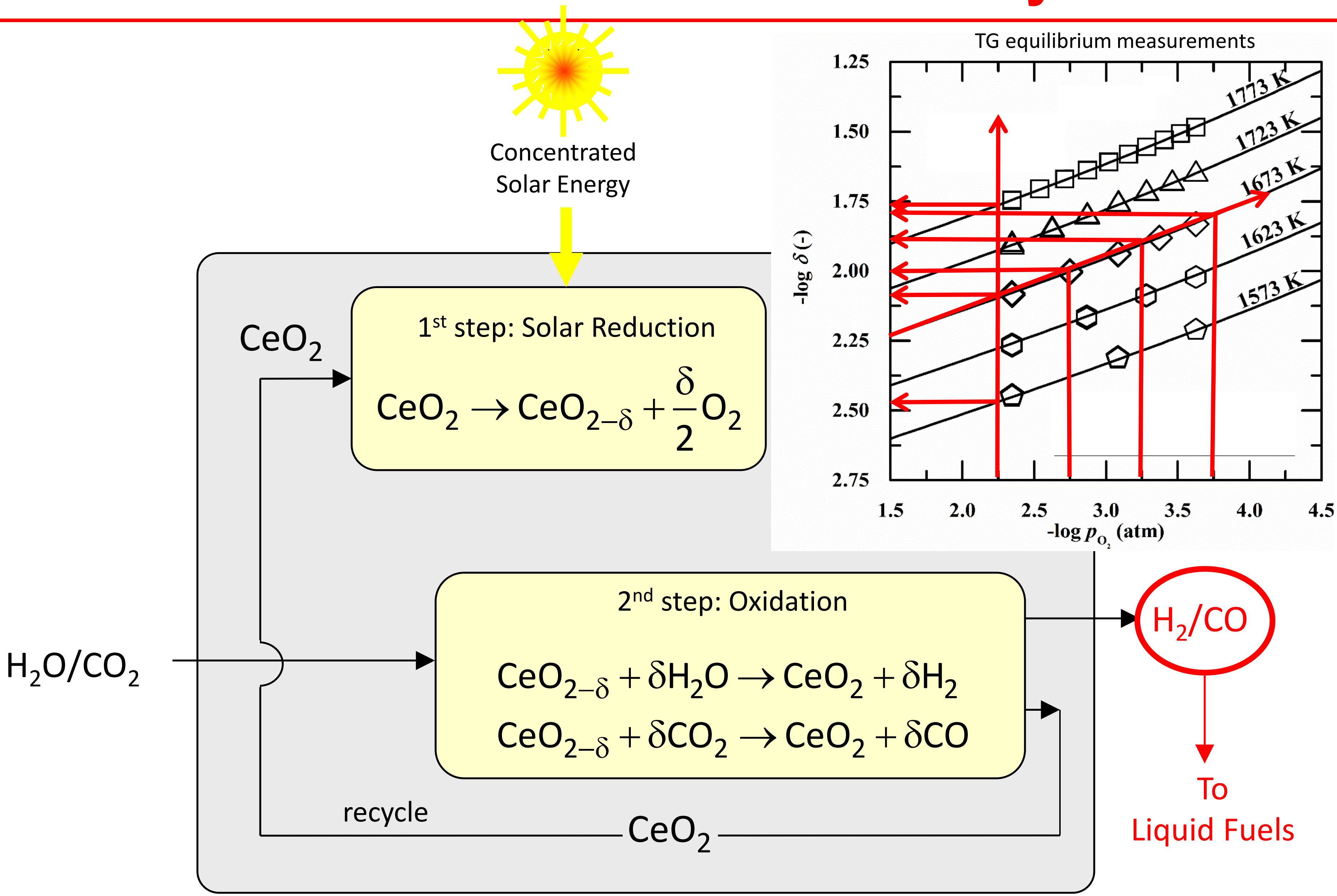
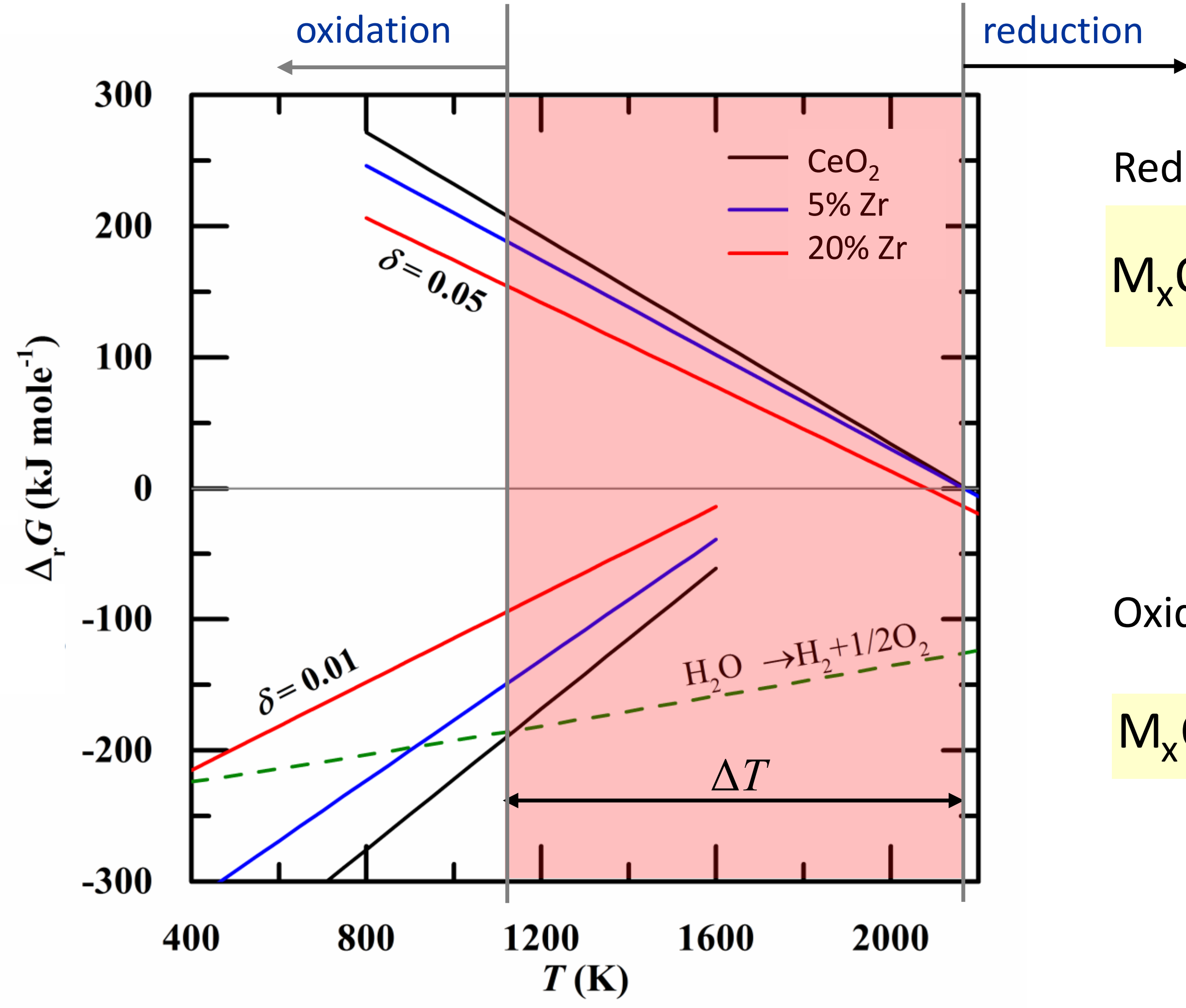



• Physical Chemistry Chemical Physics, 17, 7813-7822, 2015.

# Redox Material

- Ellingham Diagrams




Reduction

$$M_xO_y \rightarrow M_xO_{y-\delta} + \frac{\delta}{2}O_2$$

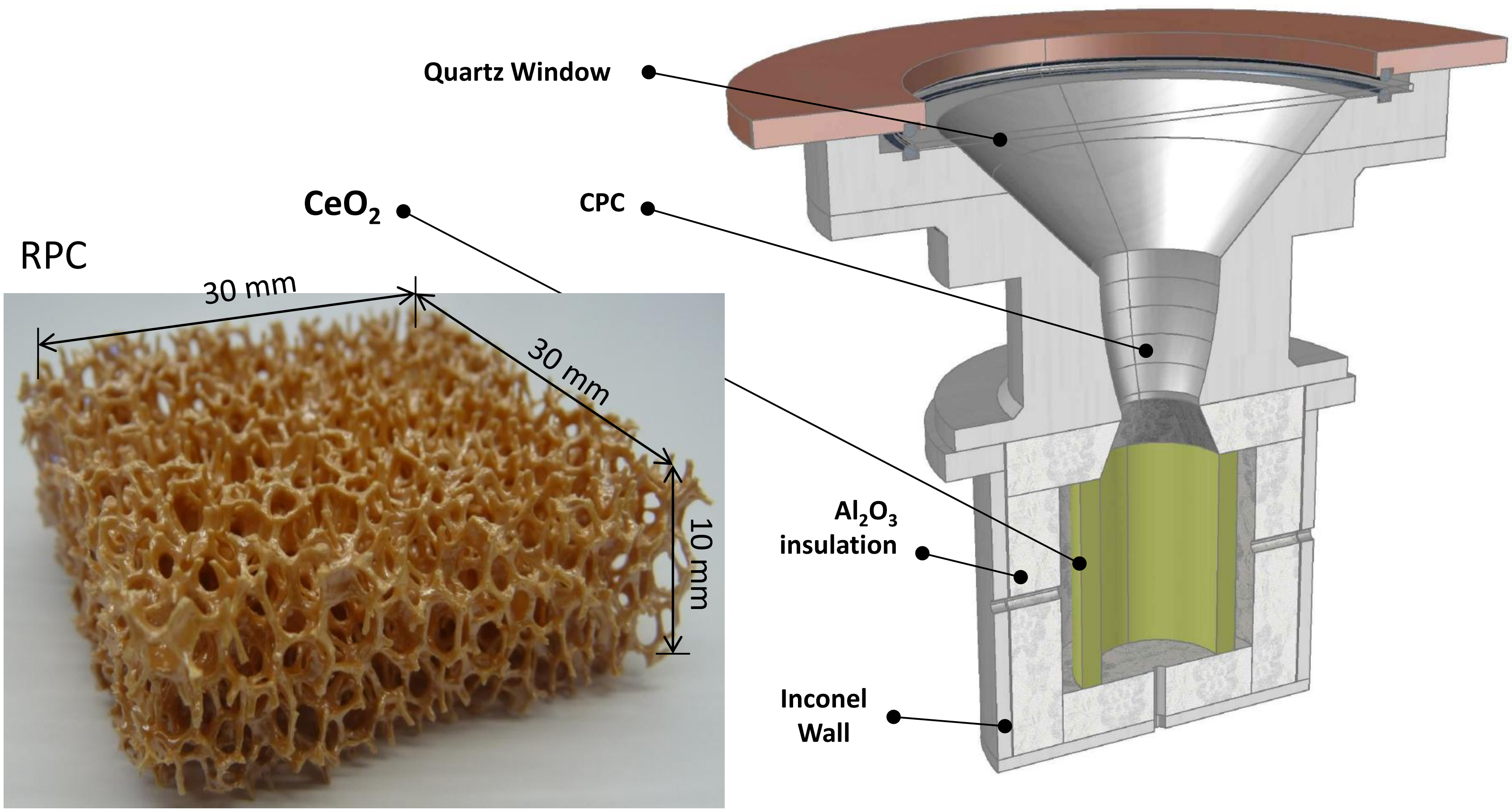
Oxidation

$$M_xO_{y-\delta} + \delta H_2O \rightarrow M_xO_y + \delta H_2$$

- Phys Chem Chem Physics 17, 7813-7822, 2015.
- Acta Materialia 103, pp. 700-710, 2016.

# Solar Reactor Technology

EMPA




- Science 330, 1797-1801, 2010.
- *Energy & Env. Science* 5, 6098-6103, 2012.
- Energy & Fuels 26, 7051–7059, 2012.

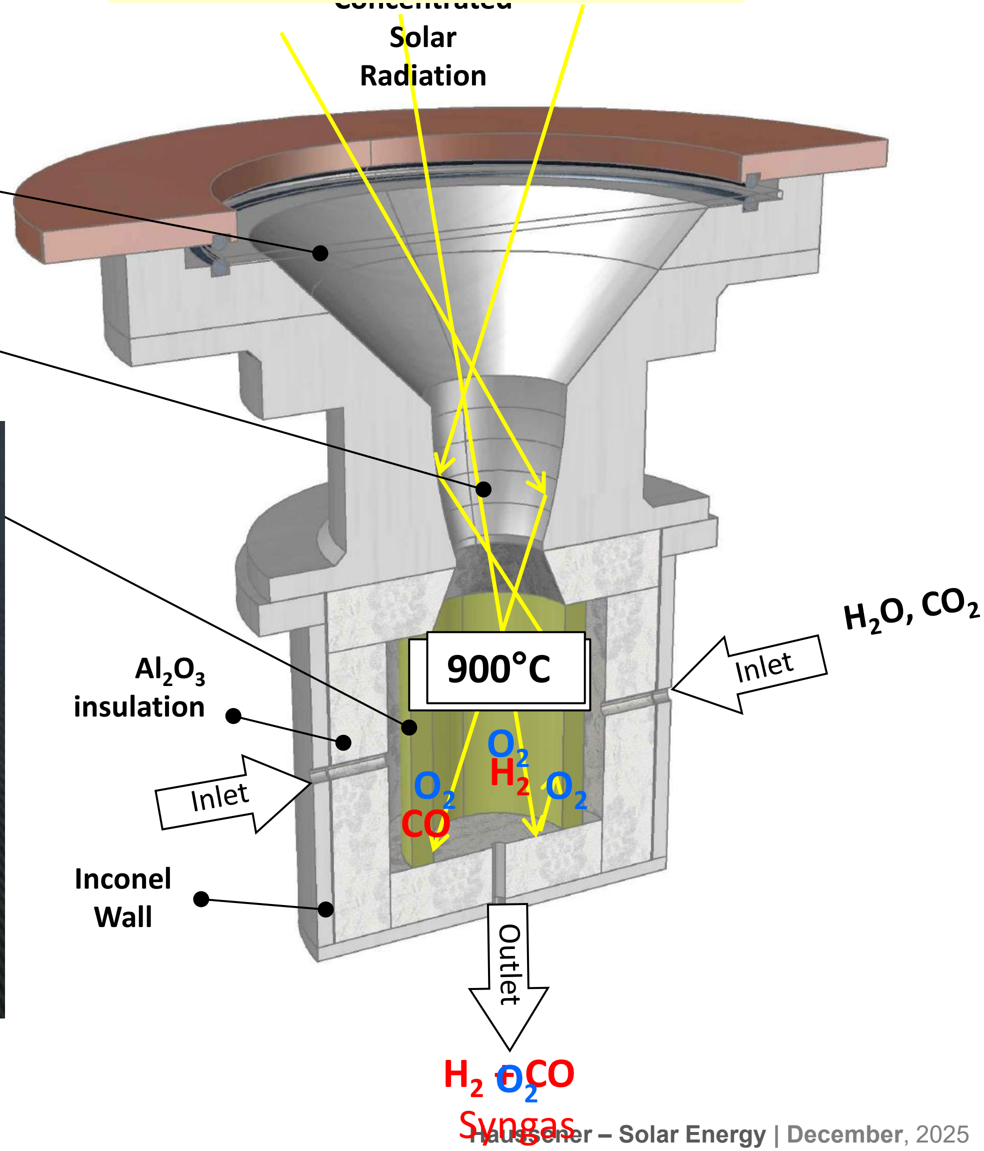
# Solar Reactor Technology

2[nd] step: Oxidation

$$CeO_{2-\delta} + \delta H_2O \rightarrow CeO_2 + \delta H_2$$

$$CeO_{2-\delta} + \delta CO_2 \rightarrow CeO_2 + \delta CO$$

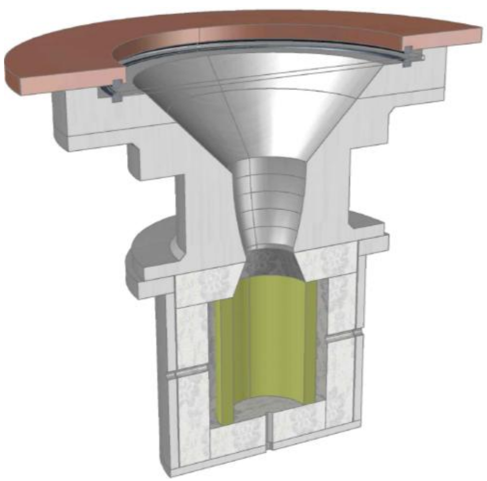
RPC



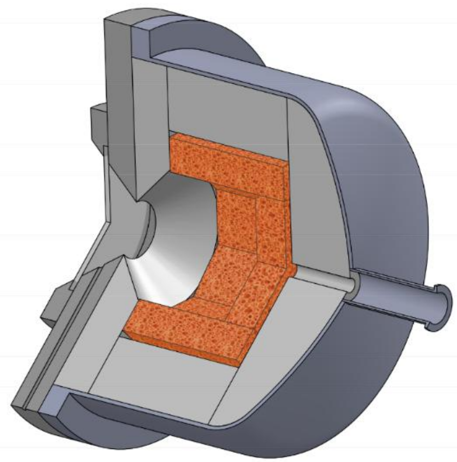

- Science 330, 1797-1801, 2010.
- *Energy & Env. Science* 5, 6098-6103, 2012.
- Energy & Fuels 26, 7051–7059, 2012.

# Solar Reactor Technology

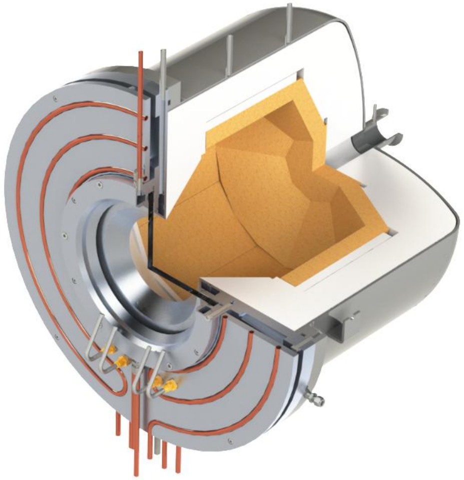
Generation 0
2 kW Lab-scale
Monoliths



Generation 1
4 kW Lab-scale
RPC



Generation 2
50 kW Pilot-scale
RPC

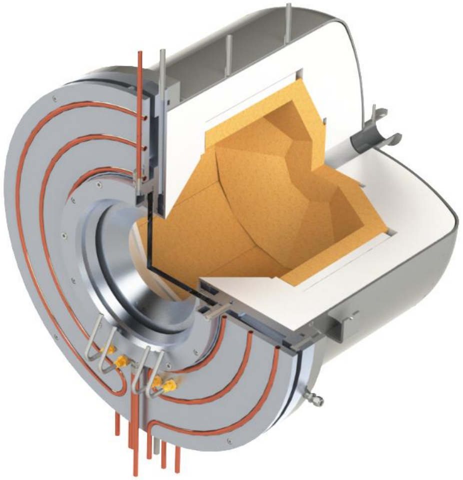


- Science 330, 1797-1801, 2010.
- Energy & Env. Science 10;1142-1149, 2017.

# Solar Reactor Technology

## EU Sun-to-Liquid Project

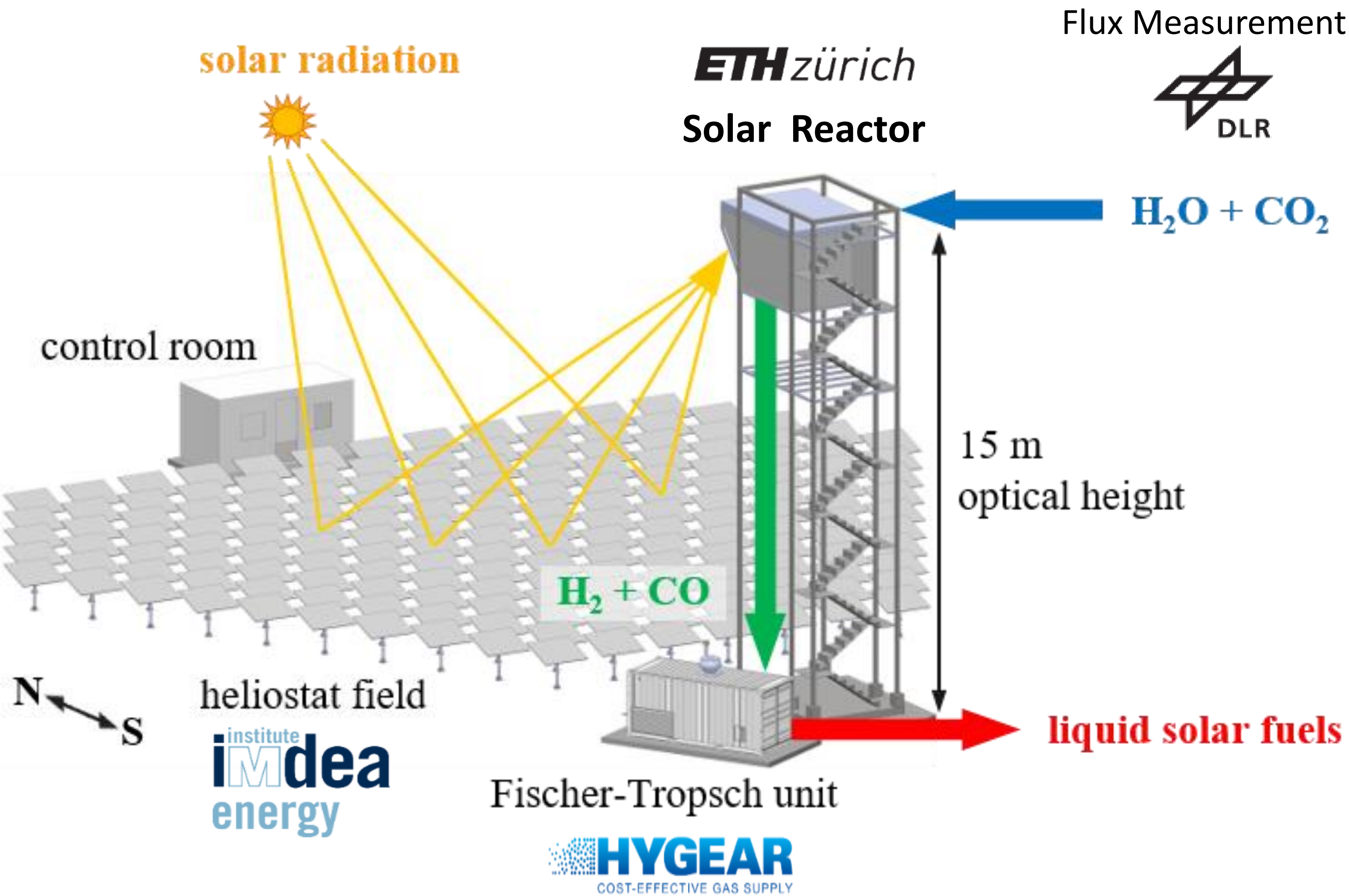
Generation 2
50 kW Pilot-scale
RPC



SUN to LIQUID
Fuels from concentrated sunlight

www.sun-to-liquid.eu

# EU Sun-to-Liquid Project

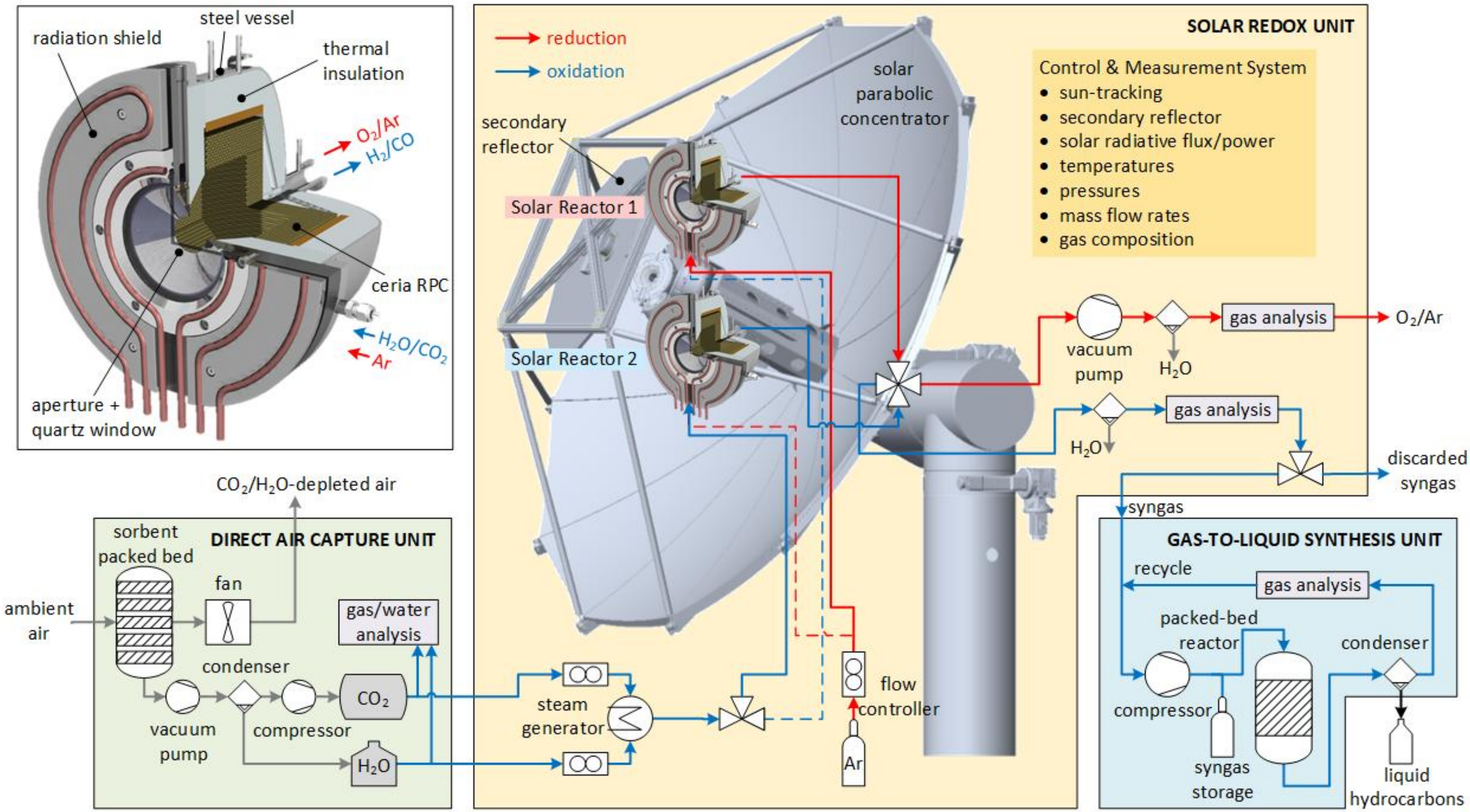


# Fuels from Sunlight and Air

$1^{st}$-ever production of carbon-neutral hydrocarbon fuels from sunlight and air
13-6-2019

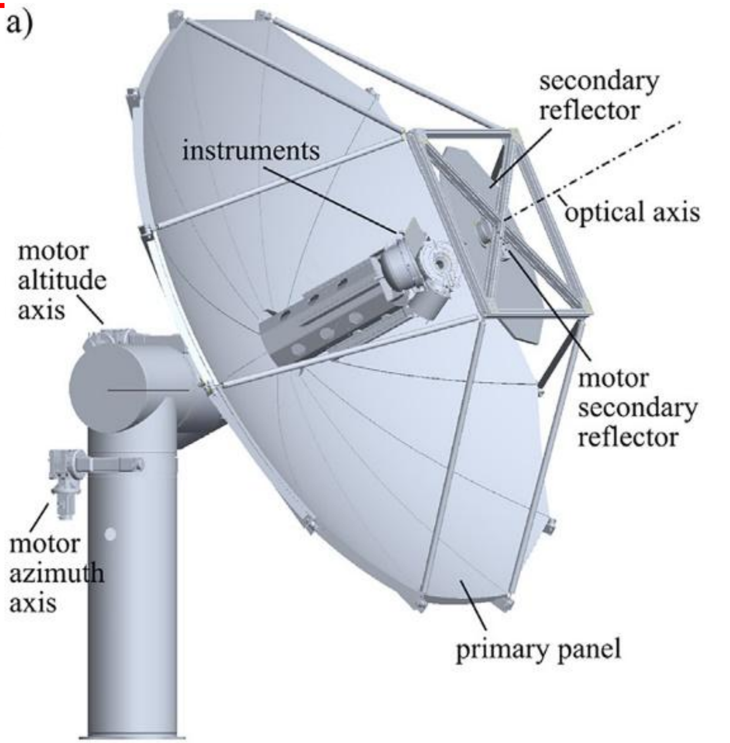
# Fuels from Sunlight and Air

## Solar Mini-Refinery @ ETH

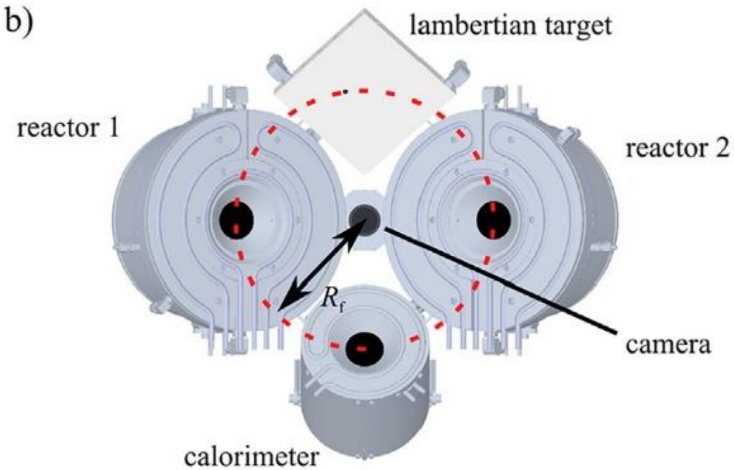


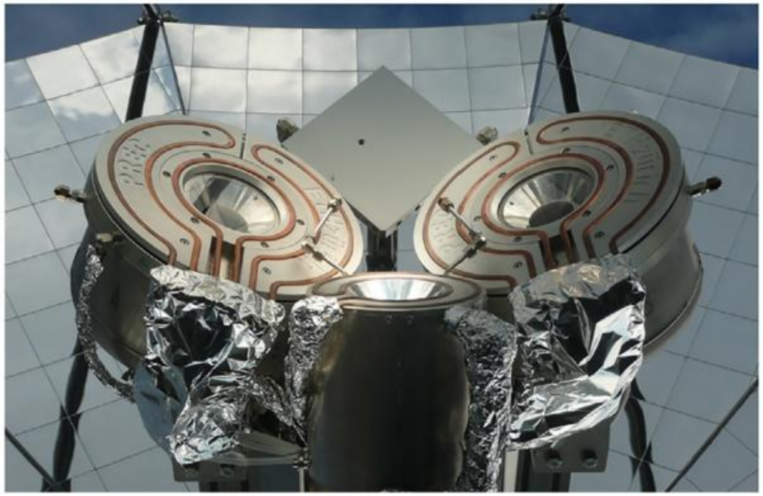
# Fuels from Sunlight and Air

a)




b)





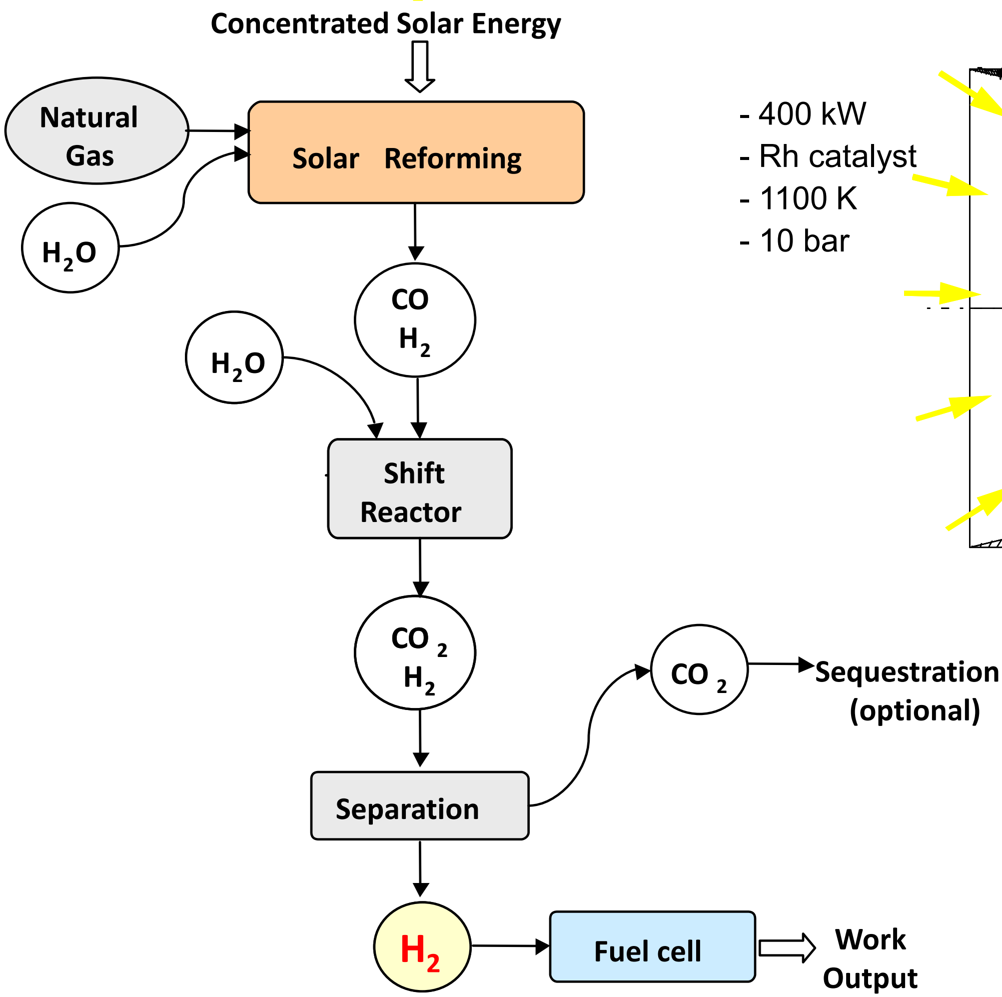
• Solar Energy 170, pp. 568-575, 2018.

# Solar Reforming

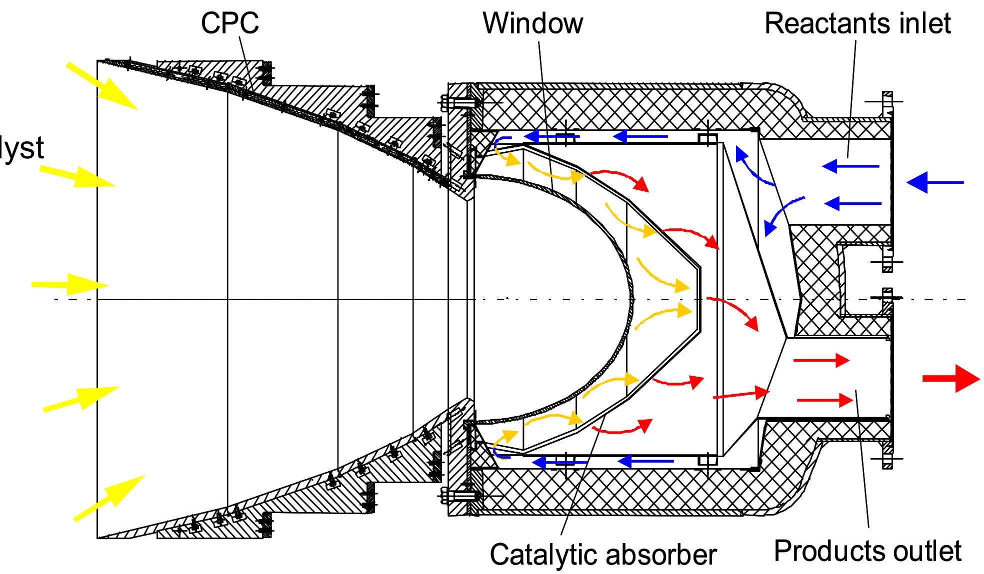
# Solar Reforming

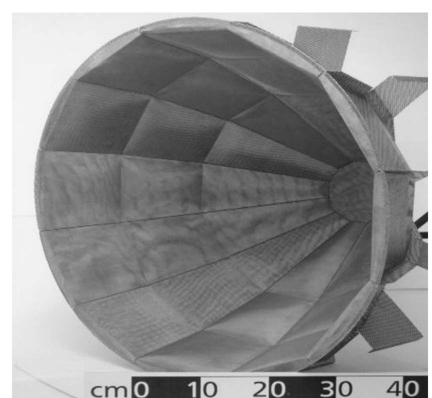
**EU-Project SOLREF**: DLR (D), WIS (IL), Hexion (NE), JM (UK), CERTH (GR), ESCO (I), ETH/PSI (CH)

$$C_xH_y + xH_2O = \left(\frac{y}{2} + x\right)H_2 + xCO$$



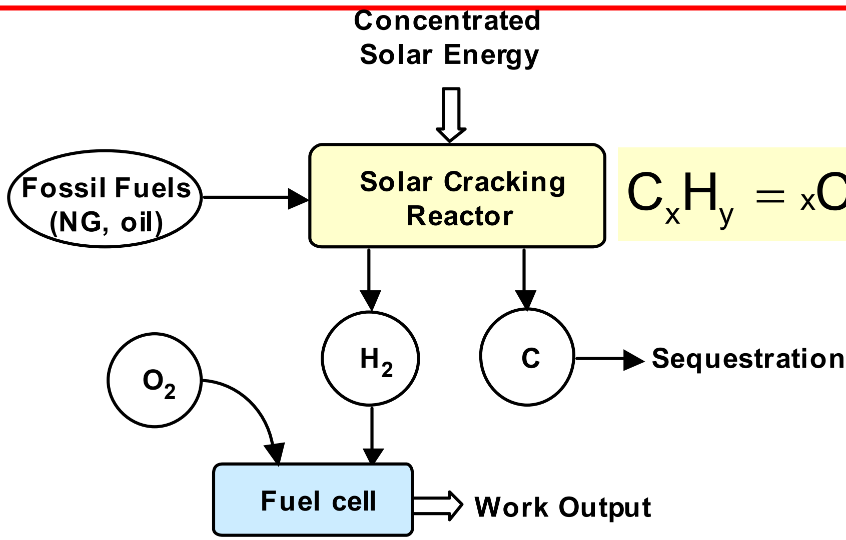

- 400 kW
- Rh catalyst
- 1100 K
- 10 bar



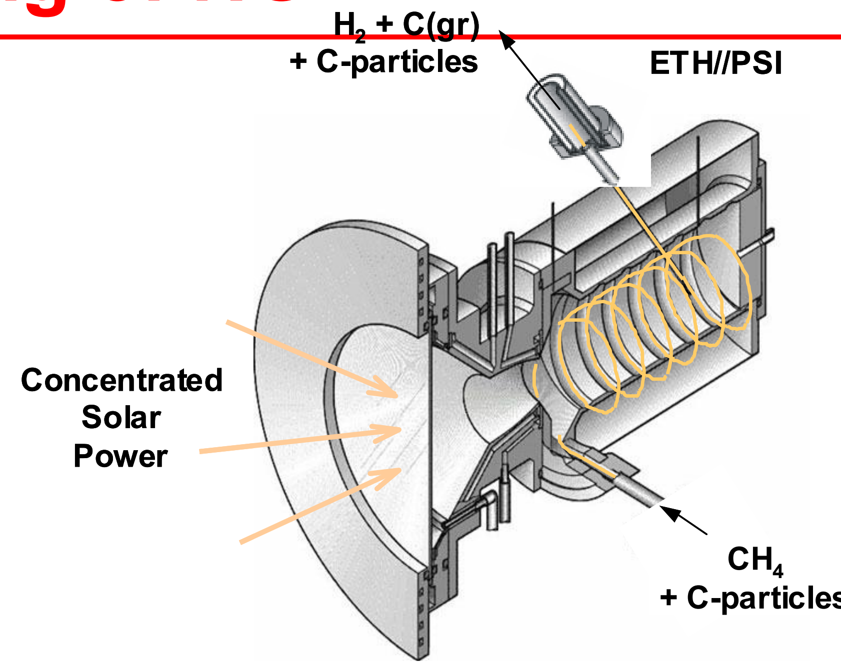



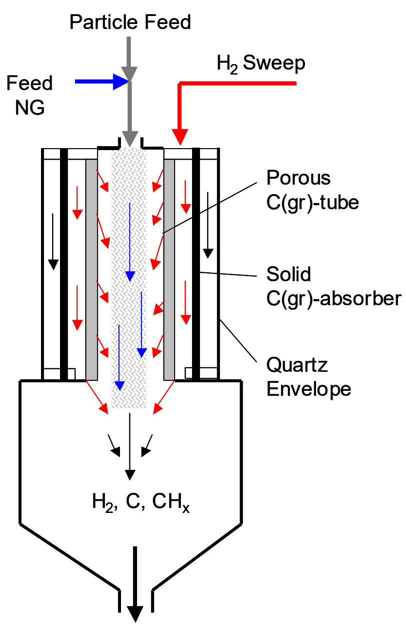

# Solar Cracking

# Solar Cracking of NG

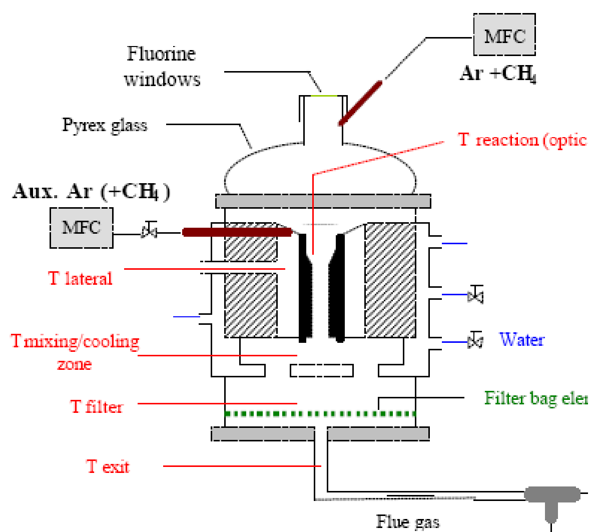



$$C_xH_y = xC + \frac{y}{2}H_2$$

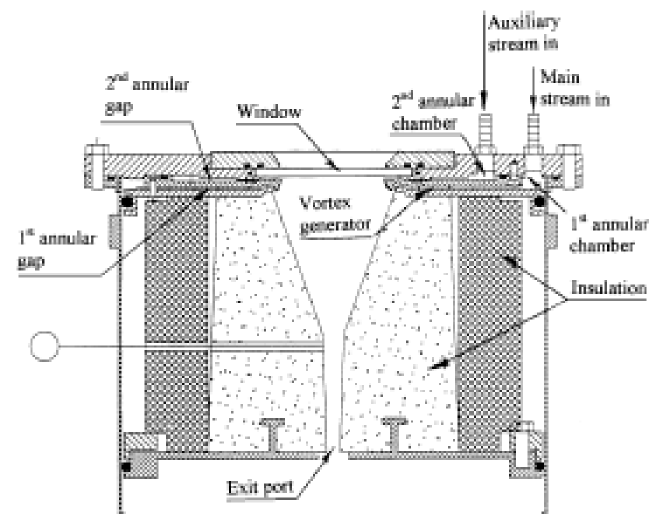



NREL//UC




CNRS



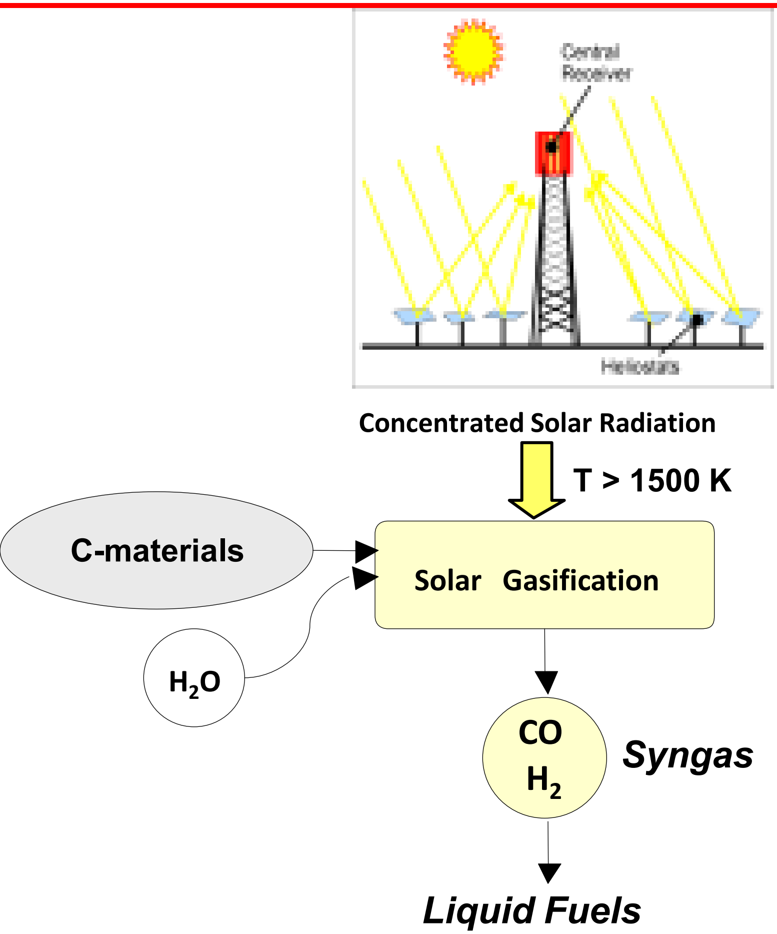

WIS



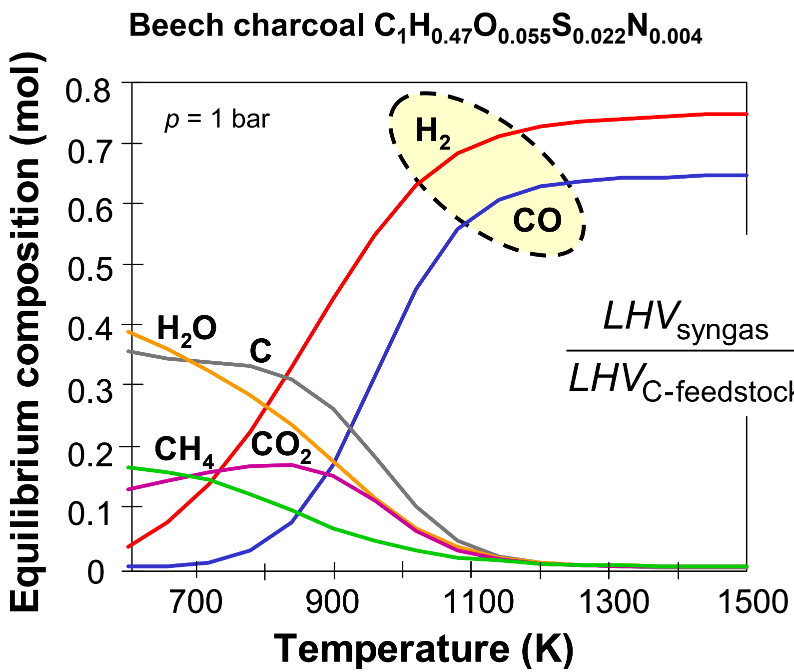
*Int. J. Hydrogen Energy* 34, 7676-7685, 2009.

# Solar Gasification

# Solar Gasification




$$C_1H_xO_y + (1-y)H_2O = \left(\frac{x}{2} + 1 - y\right)H_2 + CO$$




$$\frac{LHV_{syngas}}{LHV_{C\text{-}feedstock}} = 1.33$$

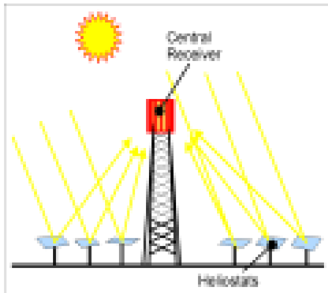
Vis-à-vis autothermal:

- Syngas with higher calorific value and lower $CO_2$ intensity
- Higher syngas output per unit of feedstock
- Higher quality of the syngas produced
- Elimination of air-separation unit



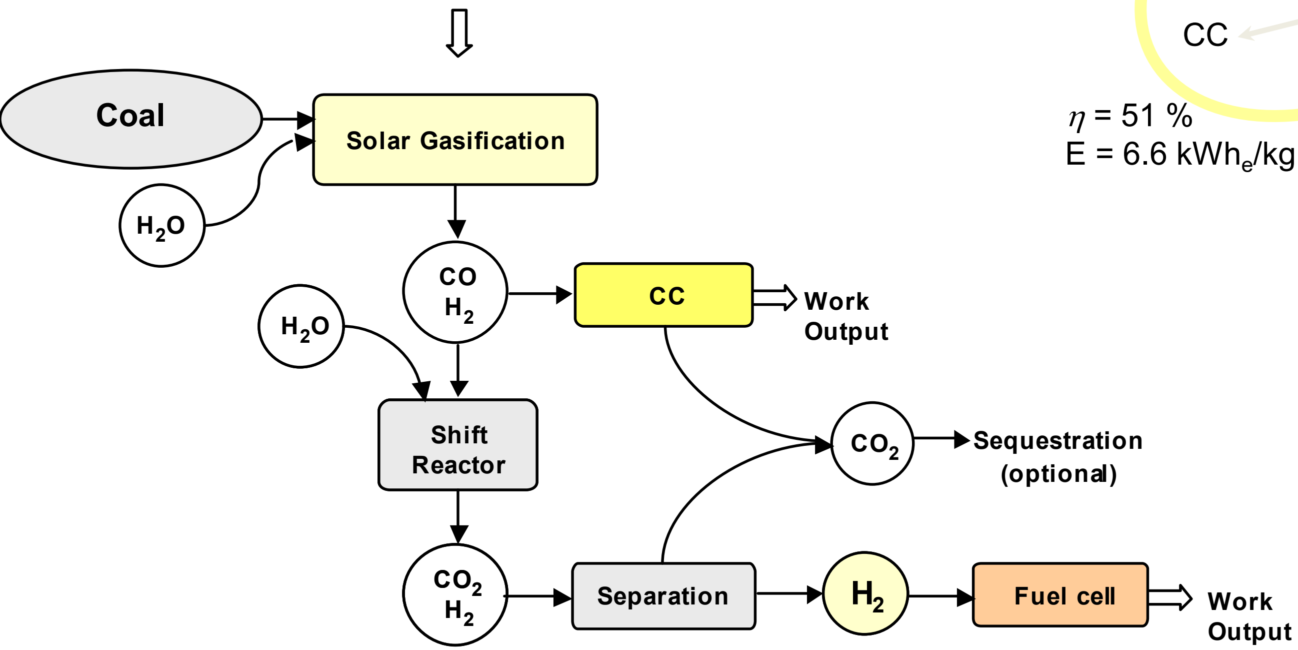
• *Energy & Env. Science* 4, 73-82, 2011.

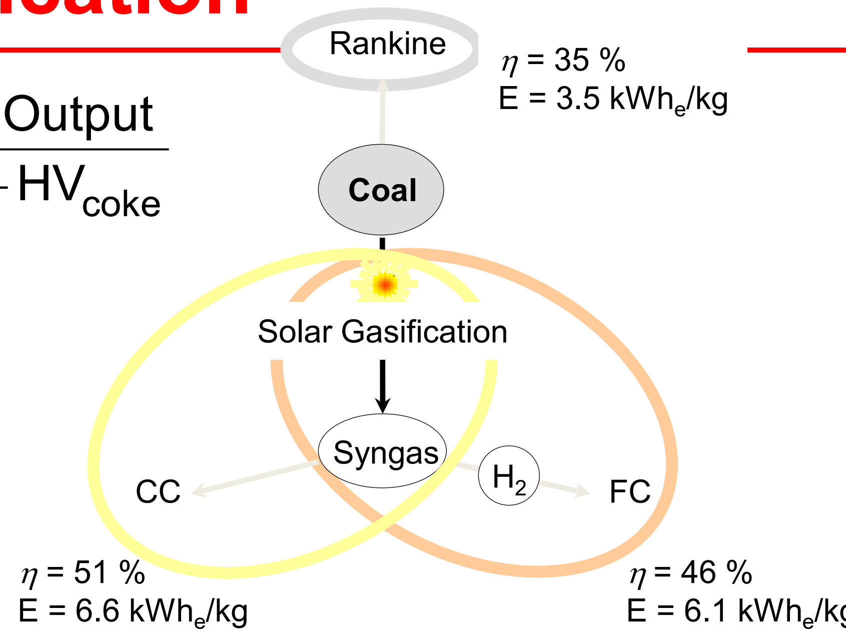
# Solar Gasification

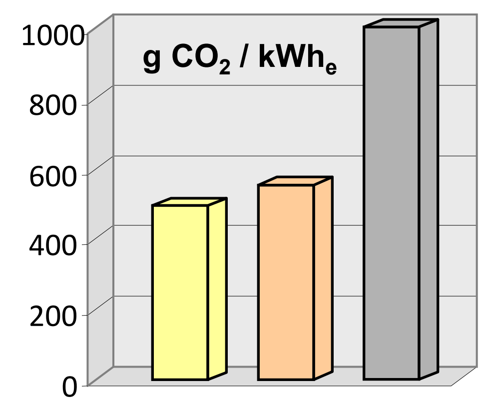



Concentrated Solar Power

$$\eta = \frac{\text{Work Output}}{Q_{solar} + HV_{coke}}$$




Coal-gasification to syngas + 55%-η CC

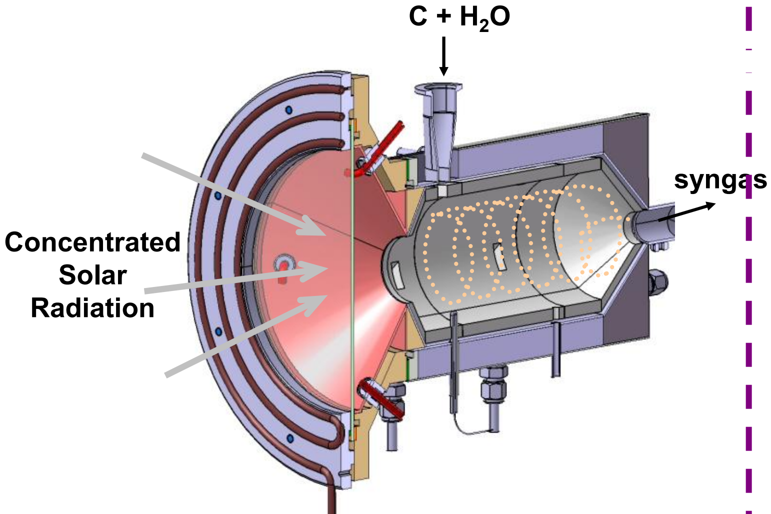
Coal-gasification to $H_2$ + 60%-η fuel cell

Coal-combustion + 35%-η Rankine cycle

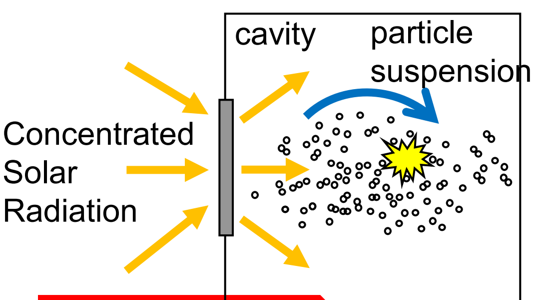
• v. Zedtwitz, Steinfeld, *Energy* 28, 441-456, 2003.

# Solar Reactor Concepts

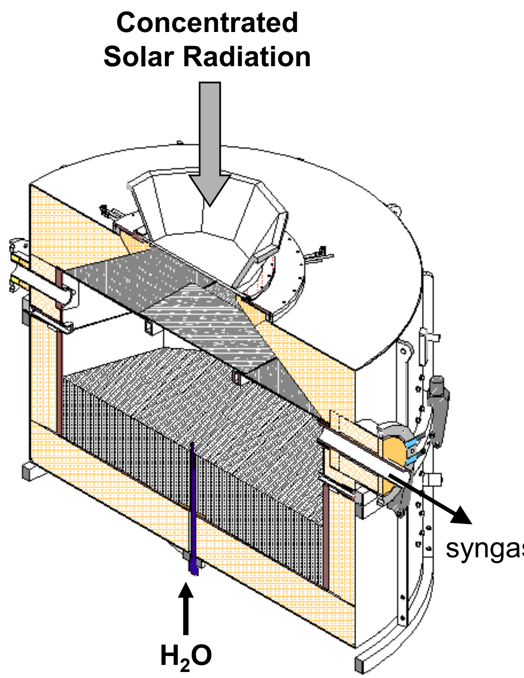
## Direct-irradiation

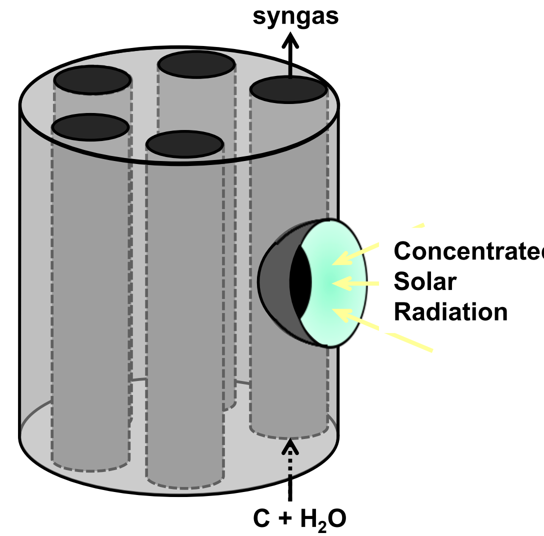


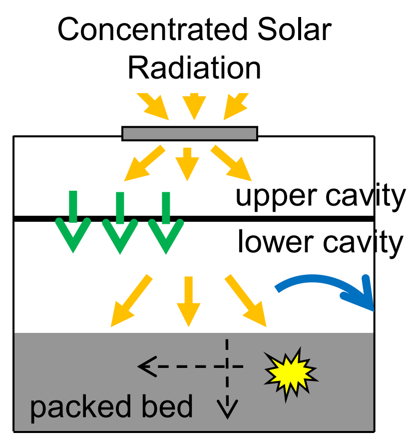

convective heat transfer
conductive heat transfer
radiative heat transfer
chemical reaction

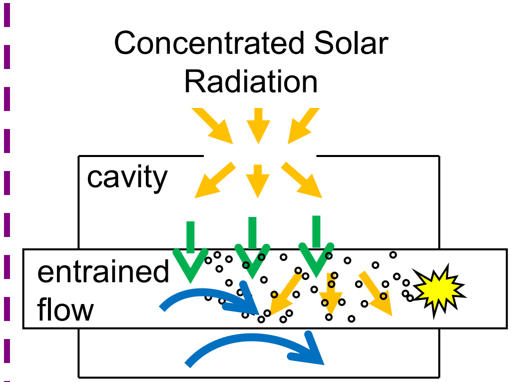



## Indirect-irradiation



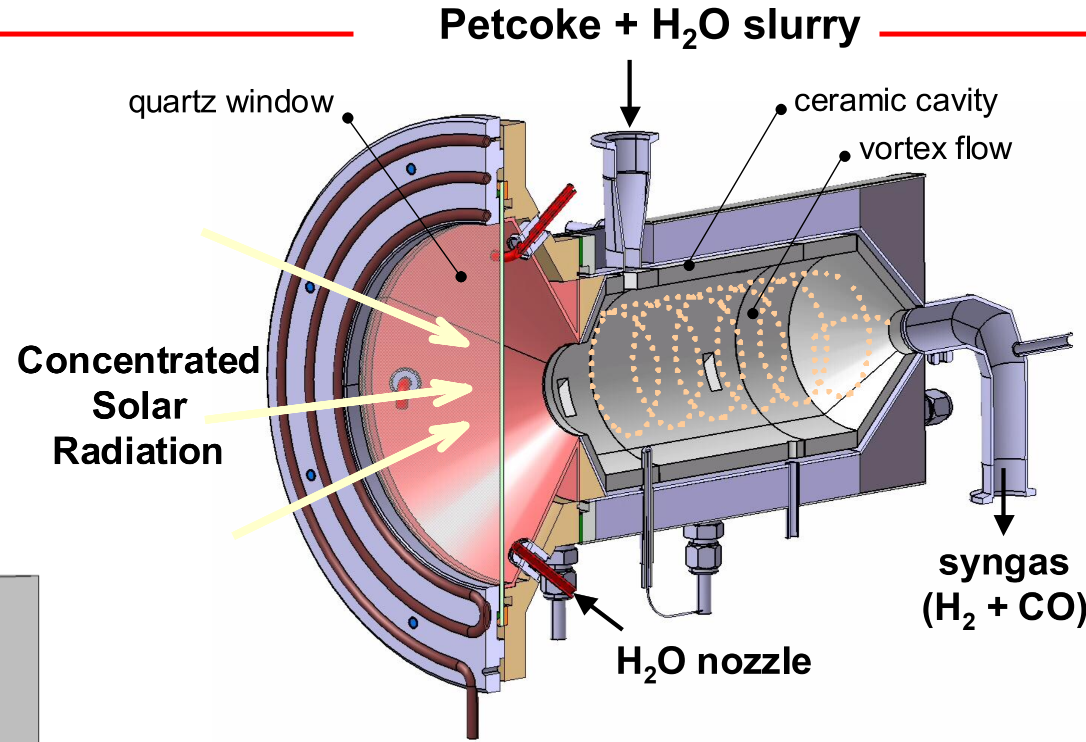



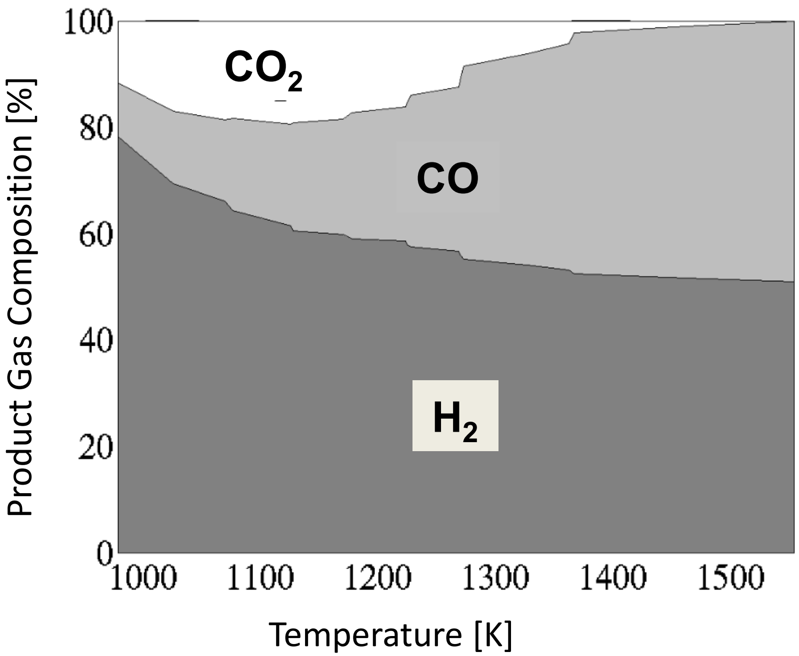



• *Energy & Env. Science* 4, 73-82, 2011

# Solar Vortex Reactor

- $Q_{solar}$ = 5 kW
- $C$ = 3000 suns
- $m_C$ = 4 g/min
- $T_{reactor}$ = 1600 K
- $x_C$ = 87 %
- $\eta_{thermal}$ = 19 %

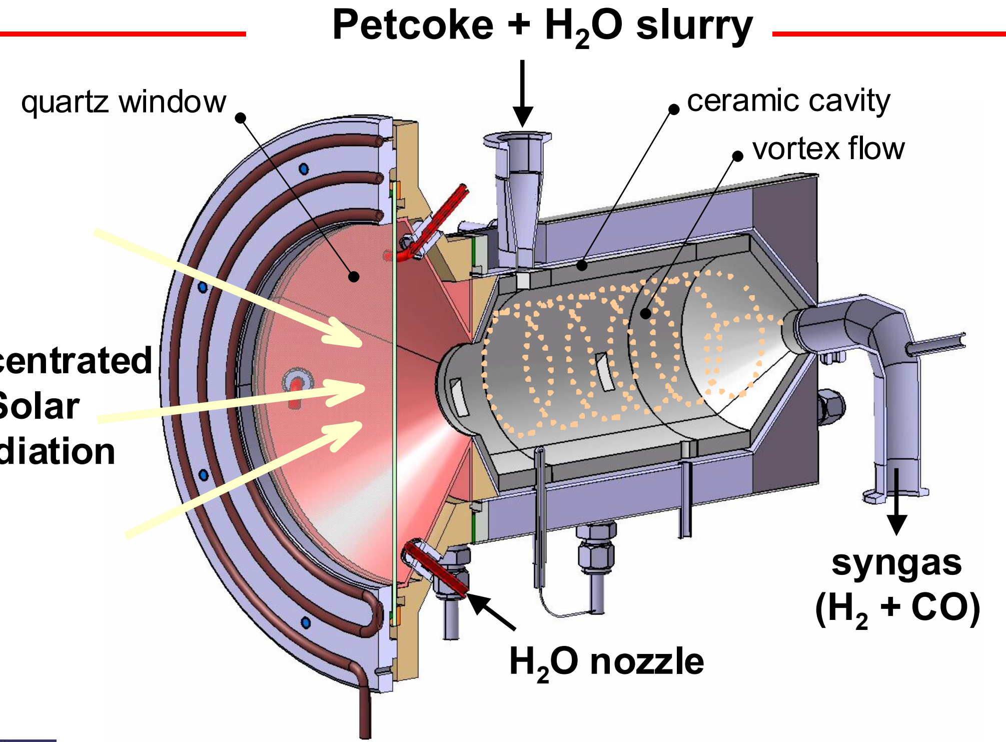


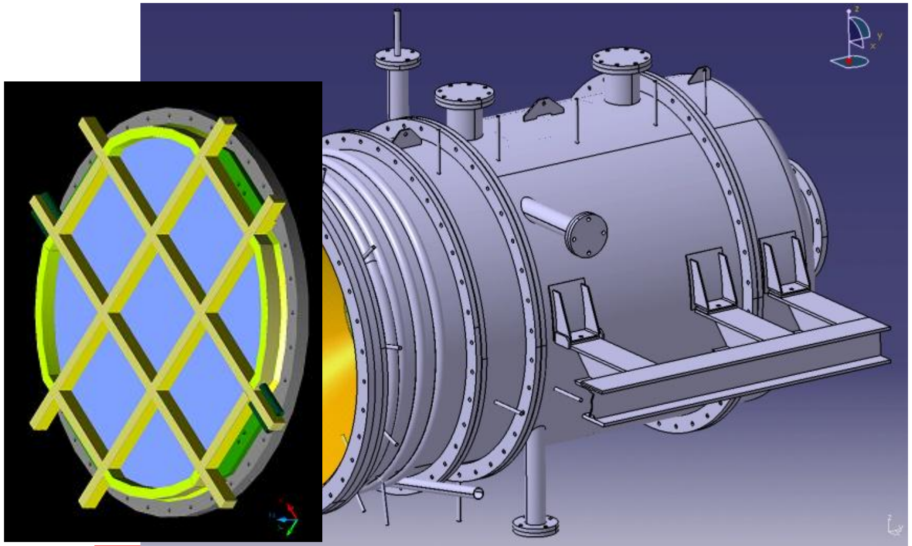




- *Energy & Fuels* 22, 2043-2052, 2008.
- *Int. J. Hydrogen Energy* 33, 679-684, 2008

# Solar Vortex Reactor – 500 kW

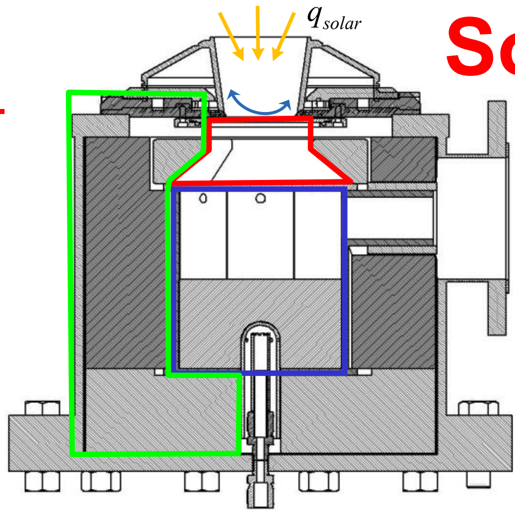
- Reaction temperature:
  - T = 1400-1700 K
- Material flows:
  - $m_{petcoke}$ = 30-50 kg/h
  - $m_{water}$ = 60-100 kg/h
- Syngas production:
  - $m_{syngas}$ = 100-180 $Nm^3/h$



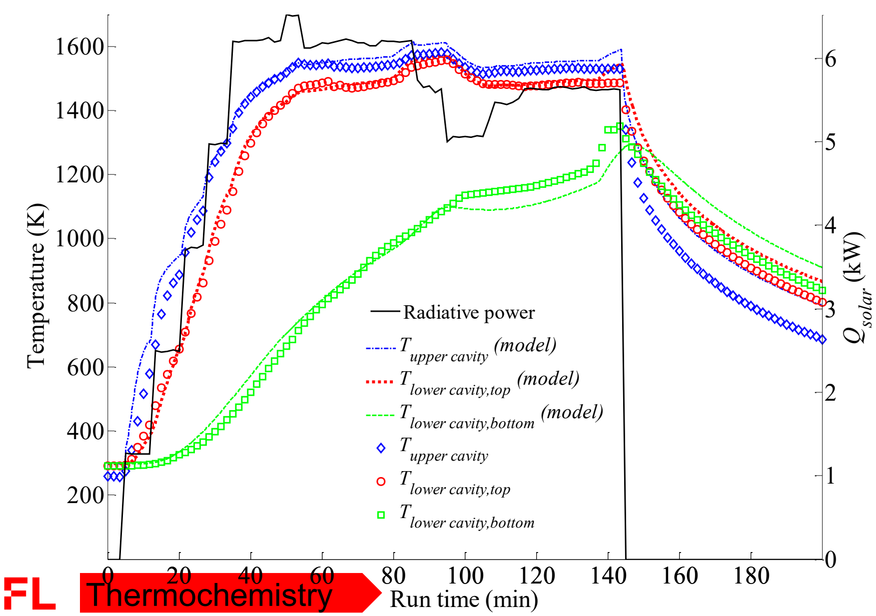
PSA

# Solar Two-Cavity Reactor

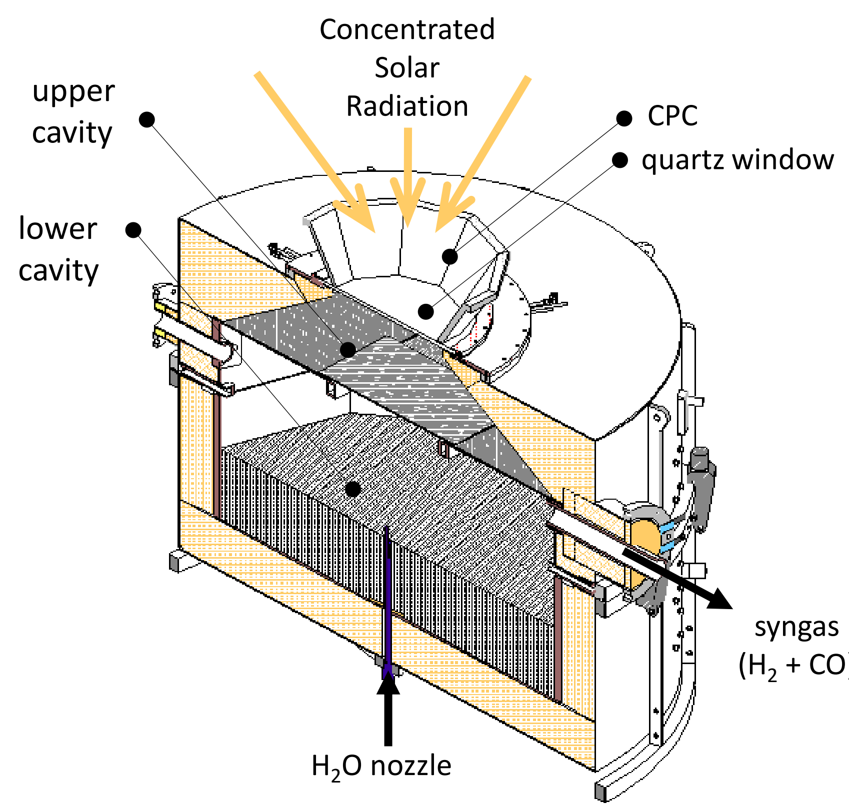



$$\rho c_p \frac{\partial T}{\partial t} = \underbrace{\nabla\left(k_{\text{eff}} \nabla T\right)}_{\text{heat transfer}} - \underbrace{k_0\, e^{-\frac{E_A}{RT}} \cdot \Delta H_r(T)}_{\text{chemistry}}$$

**Beech charcoal**

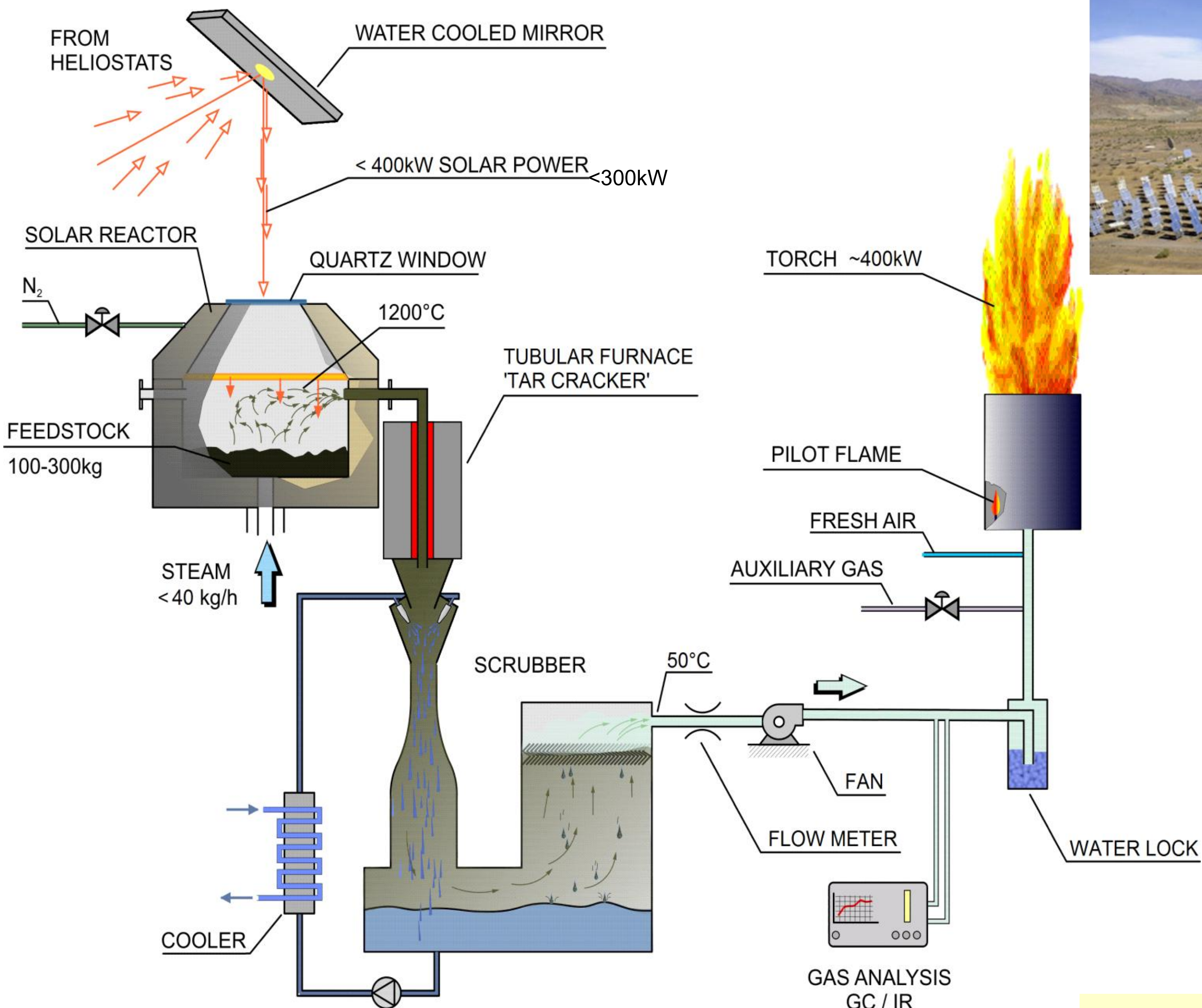



***Solar Reactor Technology***




- Fuel 89, 1133–1140, 2010.
- AIChE Journal 57, 3522-3533, 2011.

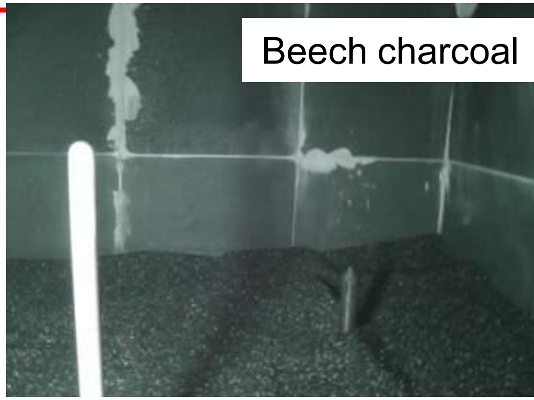
# Solar Two-Cavity Reactor – 250 kW




• *Energy & Fuels 27*, 4770-4776, 2013.

# Solar Gasification Pilot Plant

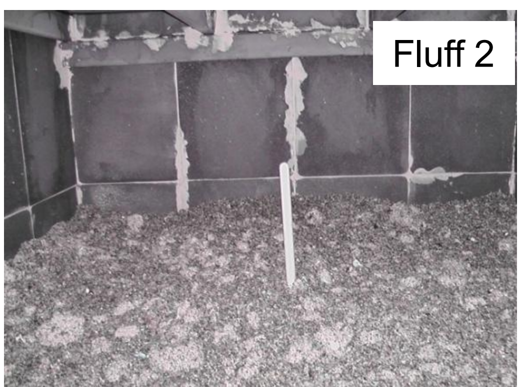
Holcim









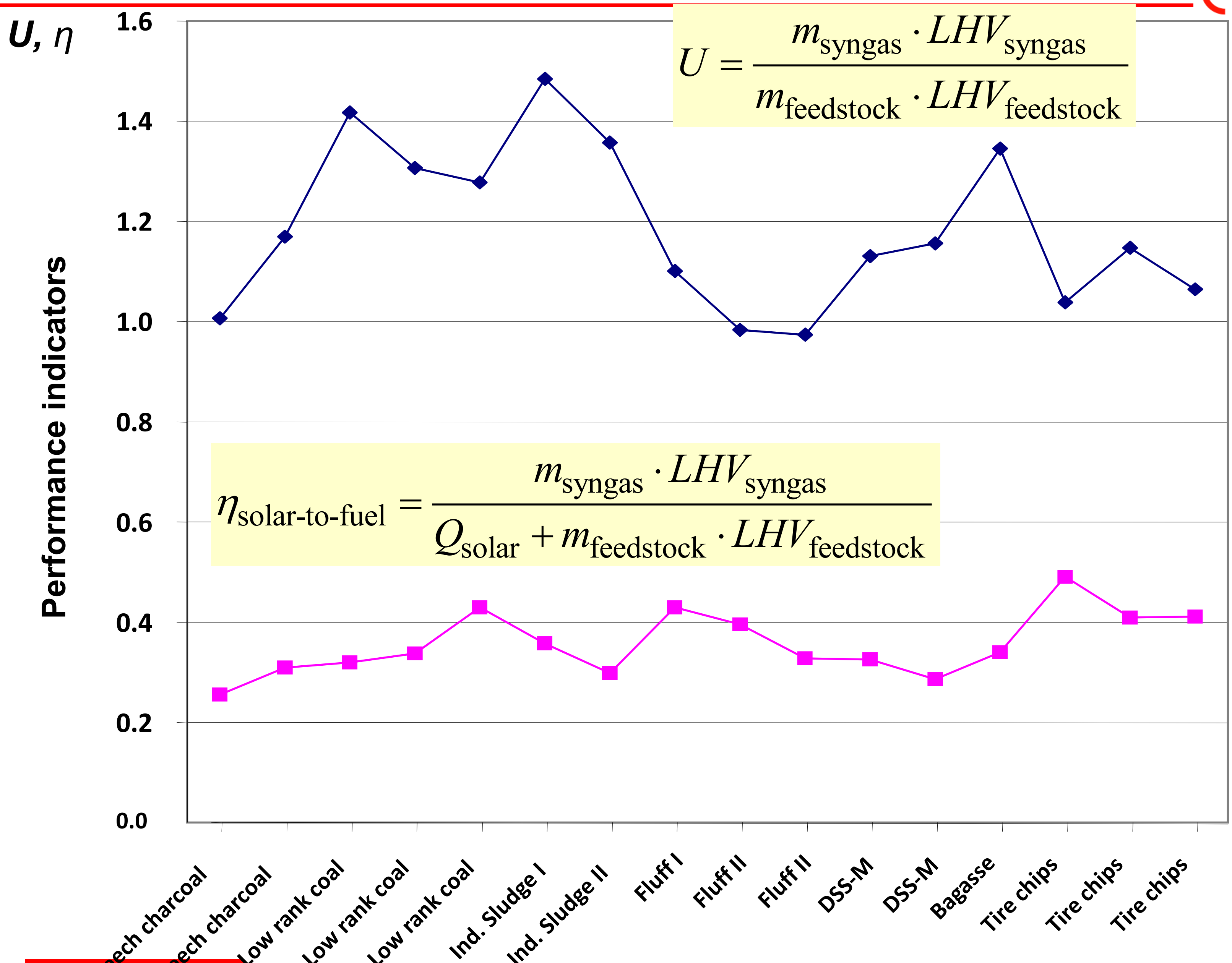







Hau • *Energy & Fuels 27*, 4770-4776, 2013.

# Solar Gasification Pilot Plant




Holcim



Hau • *Energy & Fuels 27*, 4770-4776, 2013.