# Renewable Energy

- Outline:

    – Conversion pathways solar-to-fuel

    – Hybrid pathways

    – Solar thermochemistry

    – Photochemistry

Learning outcomes of todays lecture

- Solar fuels:
  - How can solar energy be converted into fuels?
  - What is a hybrid pathway?
  - Why using fossil fuels together with solar energy?
  - What is solar thermochemistry and how can it be used for solar fuel processing?
  - Why is solar water-splitting via multi-step water splitting cycles preferred compared to direct thermolysis?
  - What is photoelectrochemistry and how can it be used for solar fuel processing?
  - What other chemical commodities or materials can be processed using solar energy?
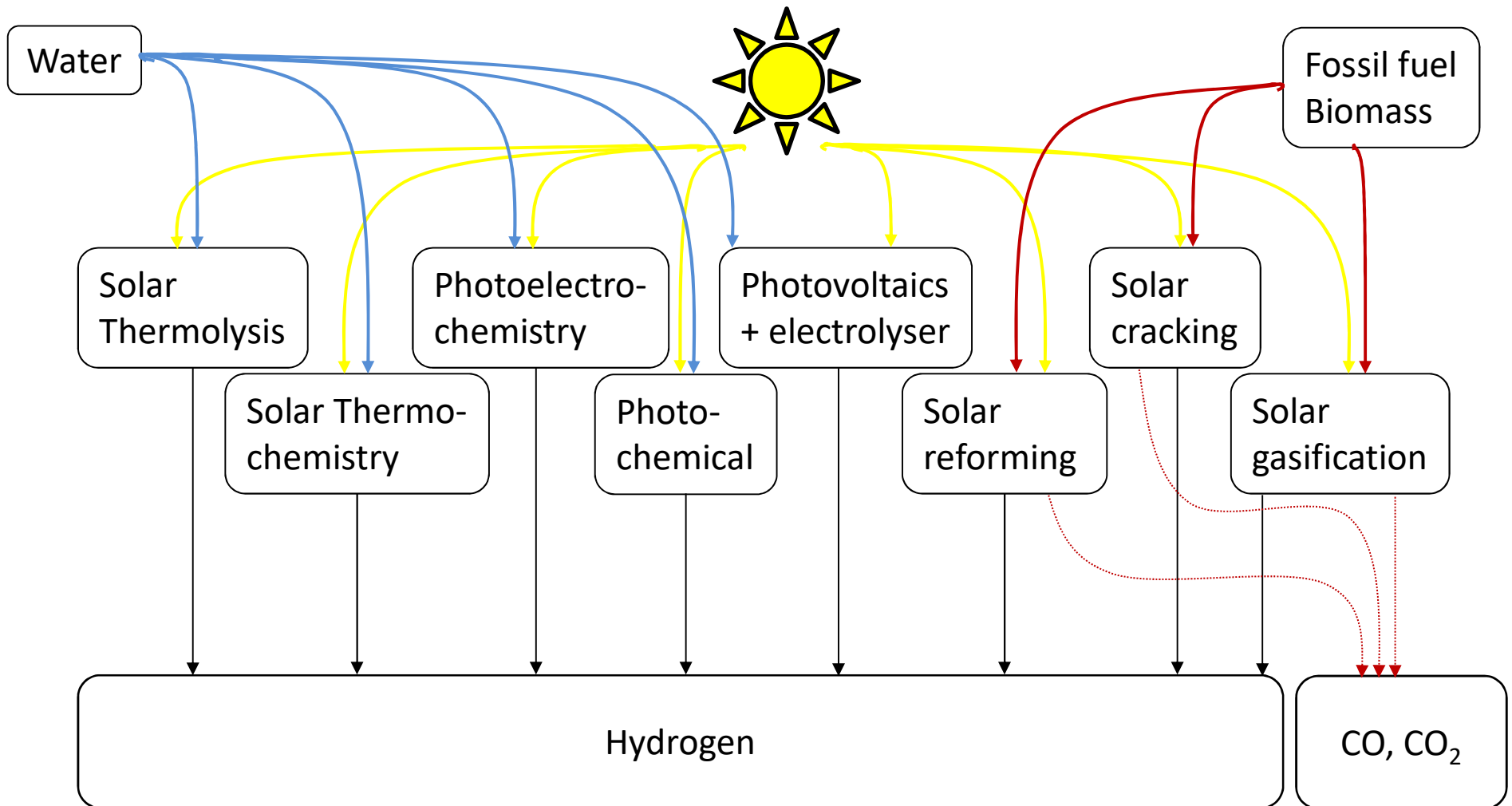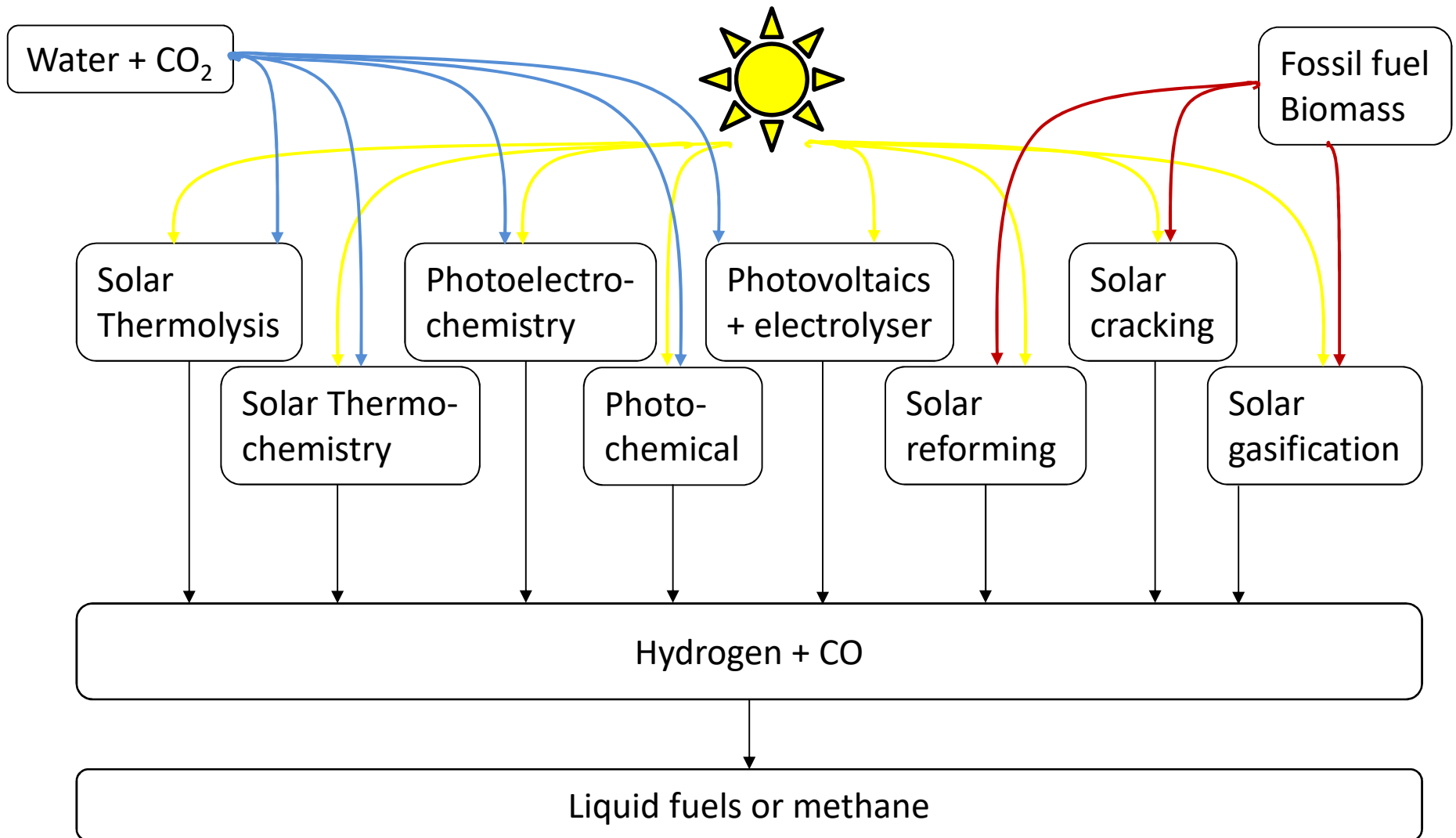
Conversion pathways

- Solar to fuels:
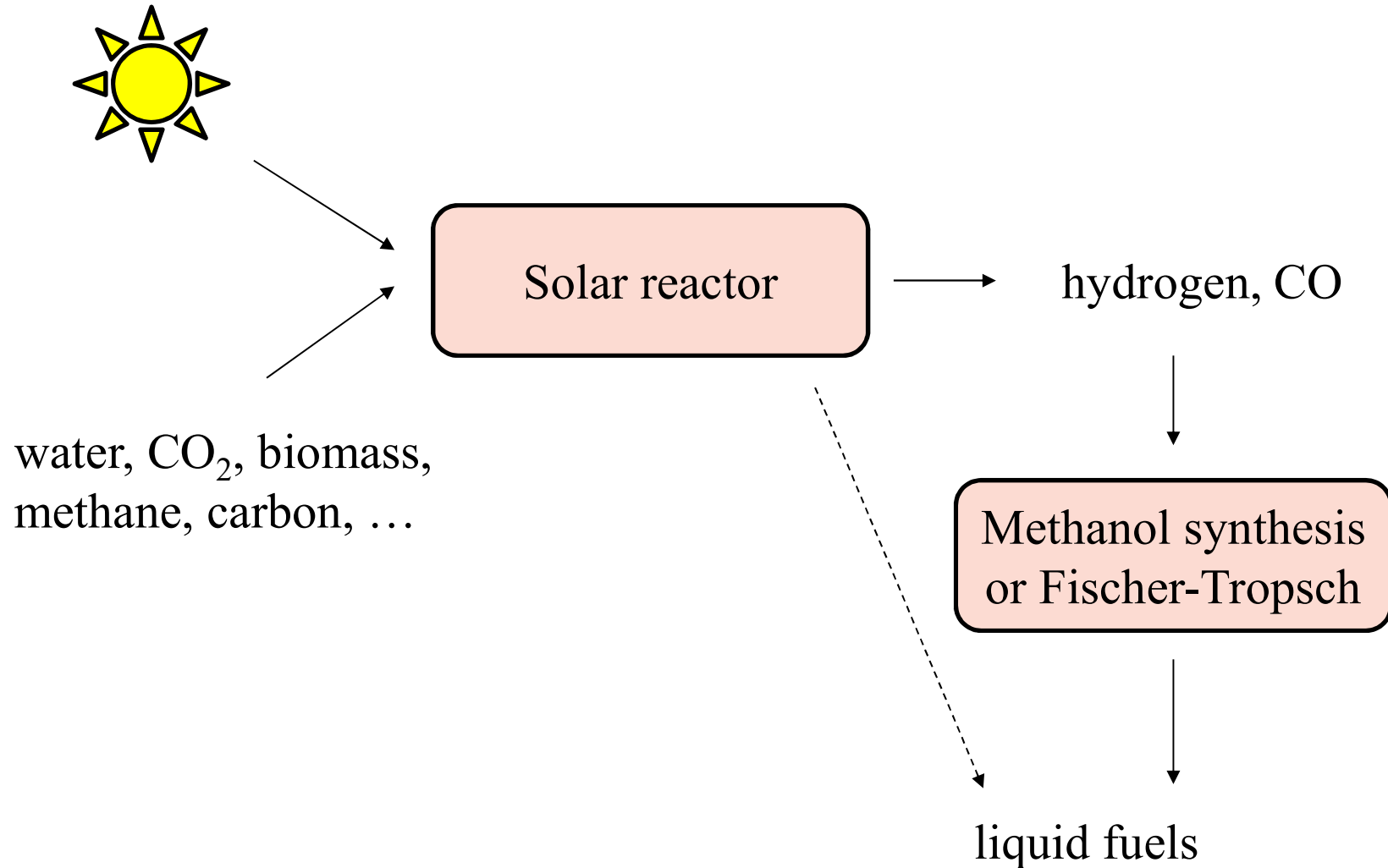
Conversion pathways

- Solar to hydrogen:
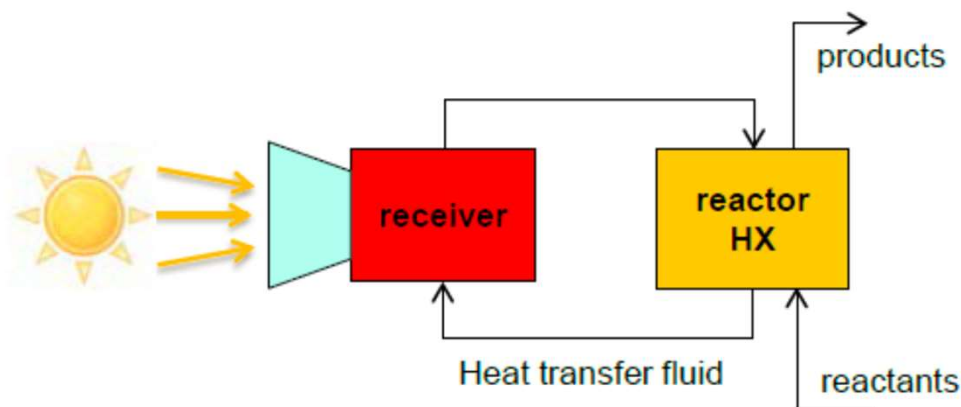
Conversion pathways

- Solar to synthesis gas (H_2+CO):

Conversion pathways

- General considerations:
  - What solar radiation concentration technology can be used (if needed)?
  - What solar reactor can be used and what are the requirements?
  - How can the sun be coupled into the process?
  - What can the reactor look like?

- Reactor concepts:

Decoupled receiver+reactor
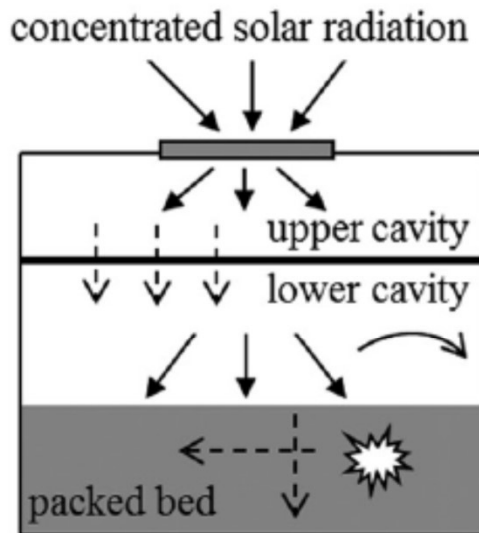Possibly with high-temperature storage
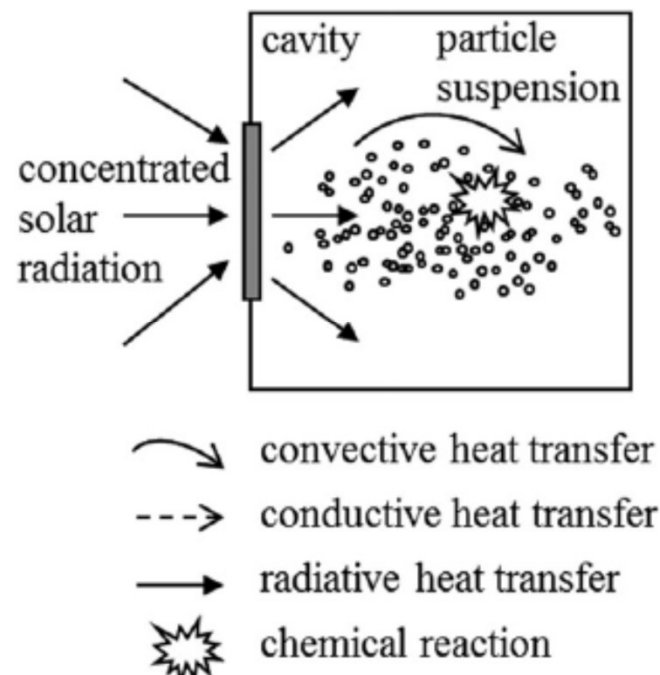
Coupled receiver-reactor
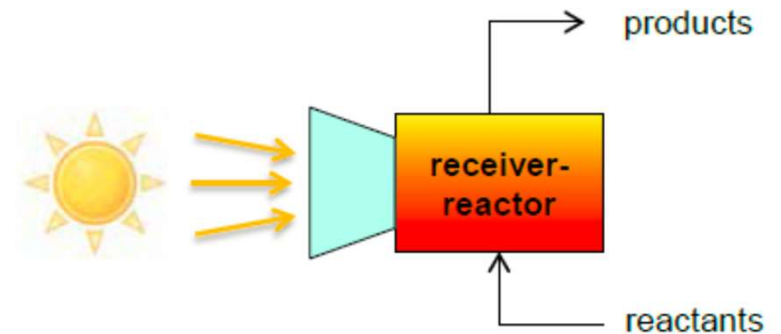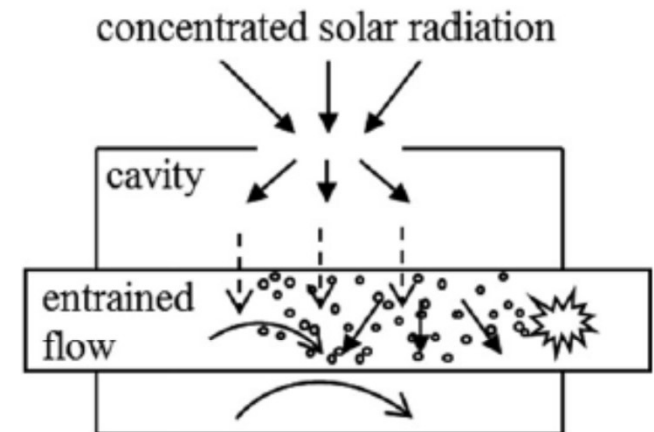
Conversion pathways

- Reactor concepts:

indirectly irradiated
packed-bed

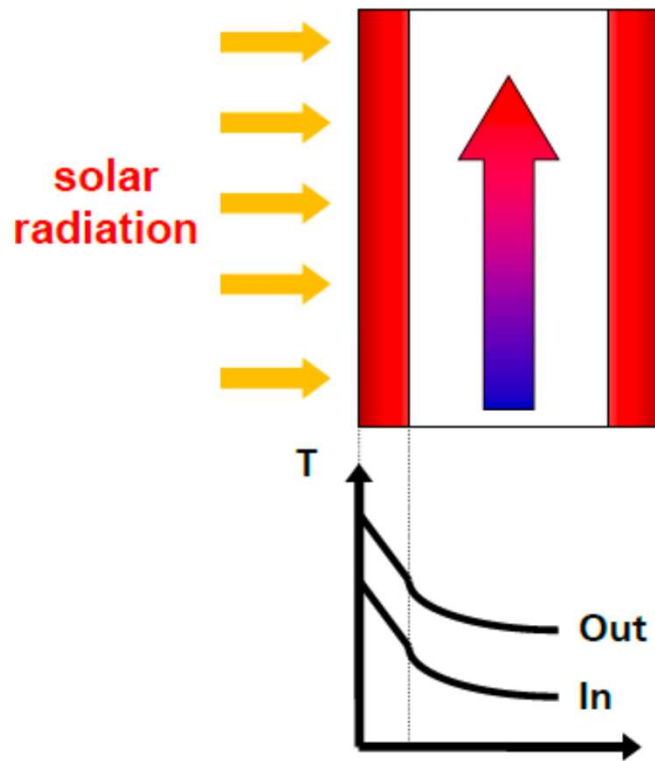directly irradiated
vortex-flow
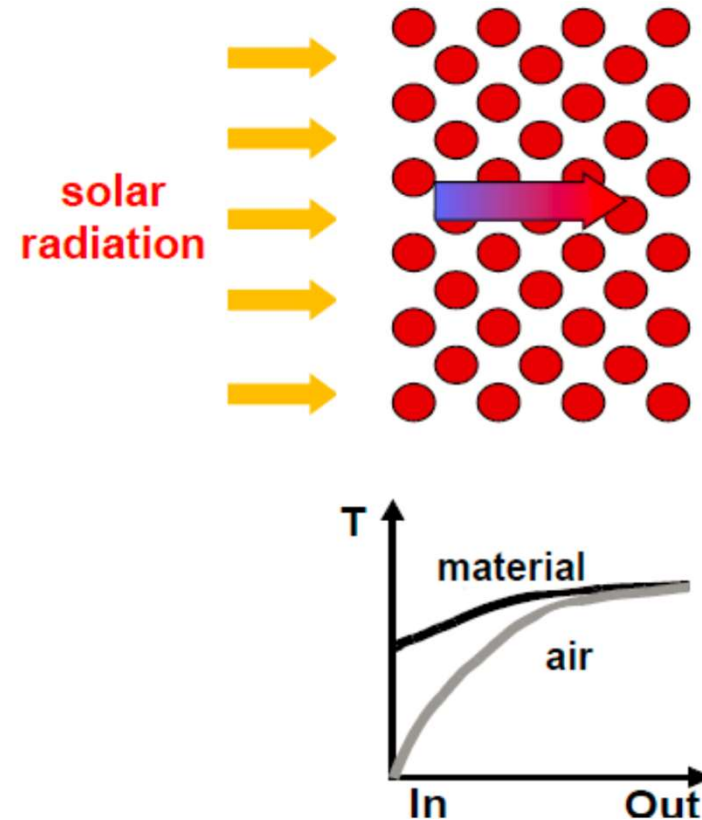
indirectly irradiated
entrained flow

Conversion pathways
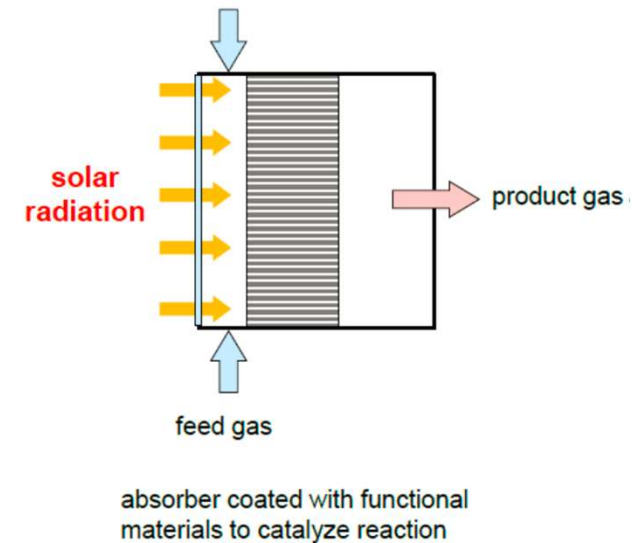
- Reactor concepts:

Tube receiver

Volumetric receiver

- Also: open versus closed systems

Conversion pathways

- Reactor concepts:
    - Stationary

product gas

solar radiation

catalyst

feed gas

solar radiation

product gas

feed gas

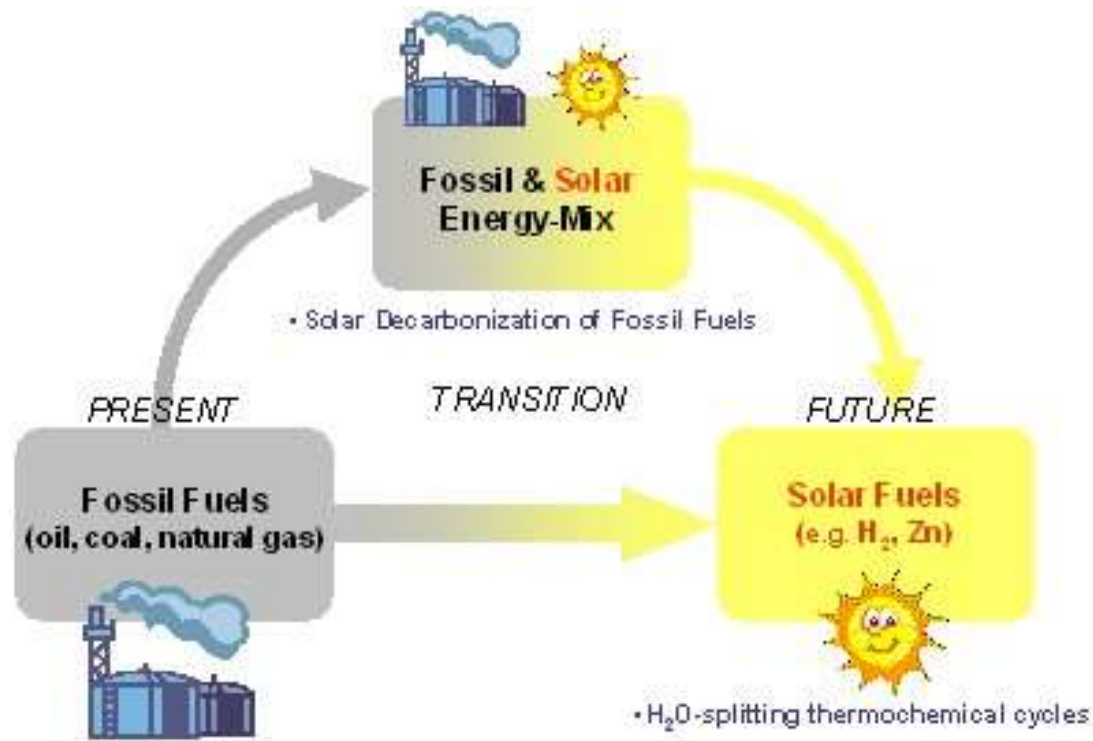absorber coated with functional materials to catalyze reaction
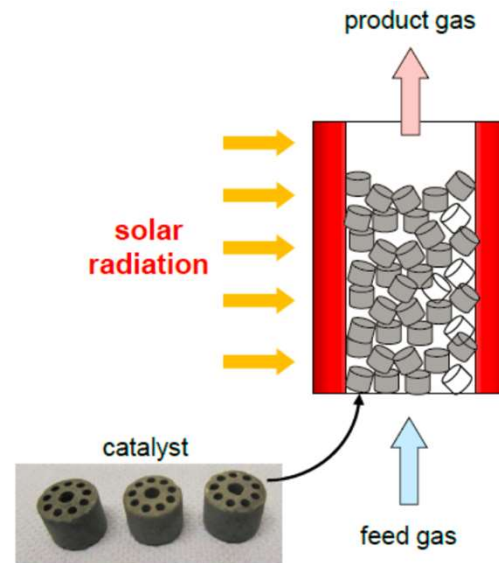
    - Moving:
        - Fluidized particle bed
        - Falling particle film
        - Rotating kiln
        - Moving particle bed

Hybrid solar conversion

- In the transition to a renewable future, hybrid pathways using fossil fuels exclusively as chemical source for the fuel production and solar energy as the process heat
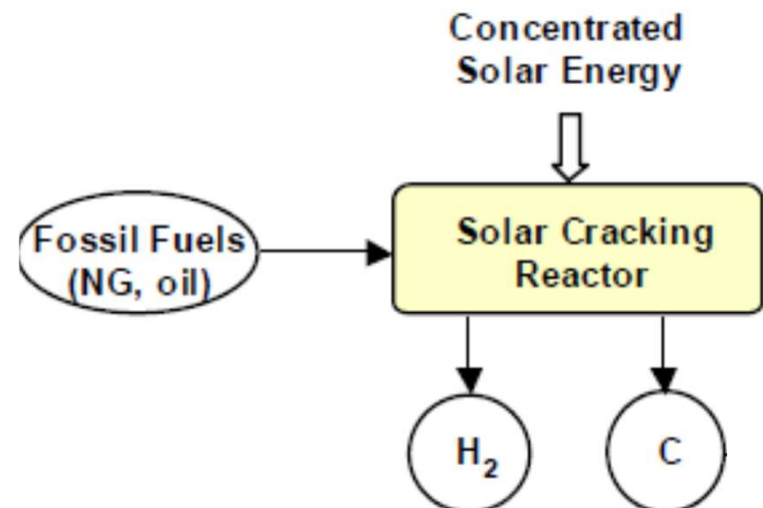
Hybrid solar conversion

- **Thermal cracking**: complex organic molecules such as heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors at high temperatures and by using catalysts
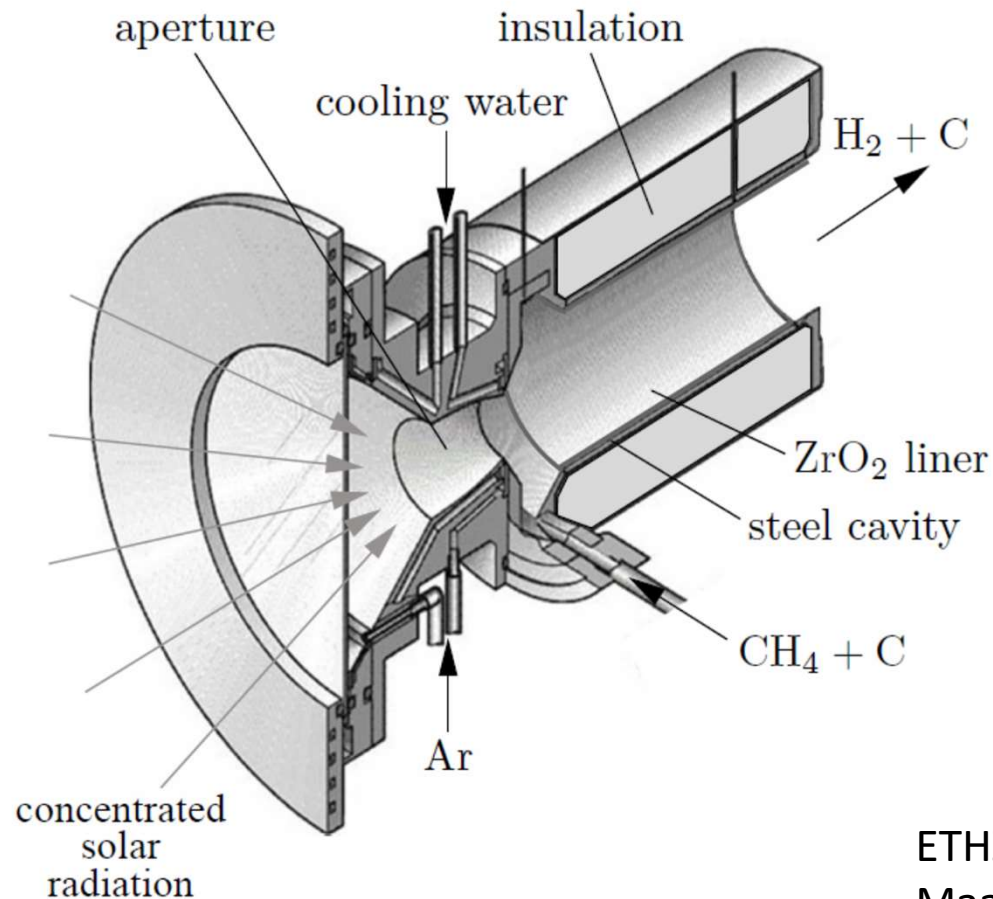
$$CH_4 \rightarrow C + 2H_2 \ (\Delta H = 74.85 \ kJ/mol)$$

- General:

$$C_nH_m \rightarrow nC + (m/2)H_2$$

Hybrid solar conversion

- Solar reactors developed for thermal cracking:

ETHZ and PSI
Maag et al., 2010.

Hybrid solar conversion

- Solar reactors developed for thermal cracking: CU Boulder
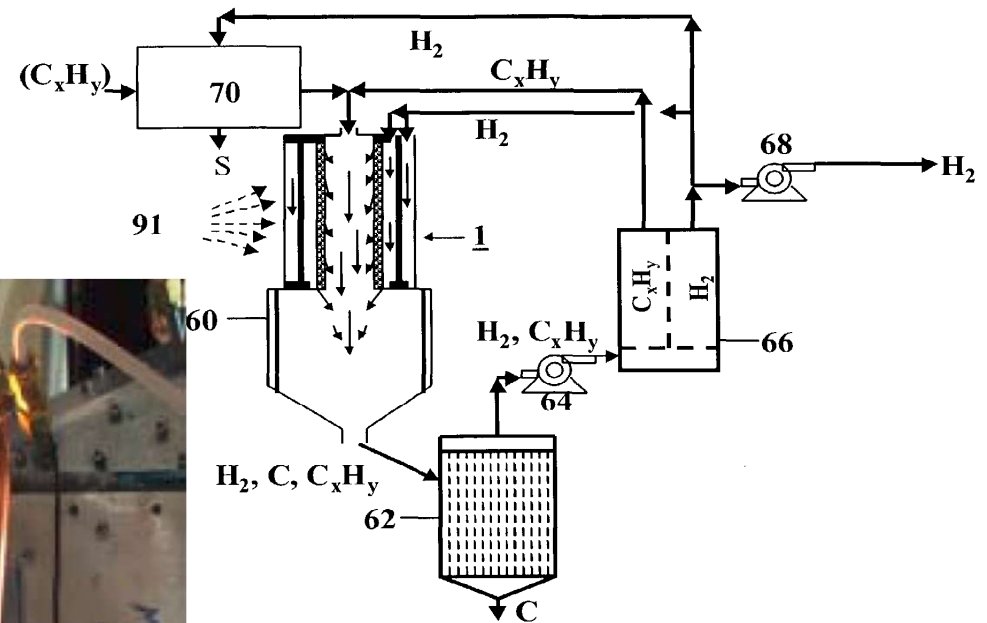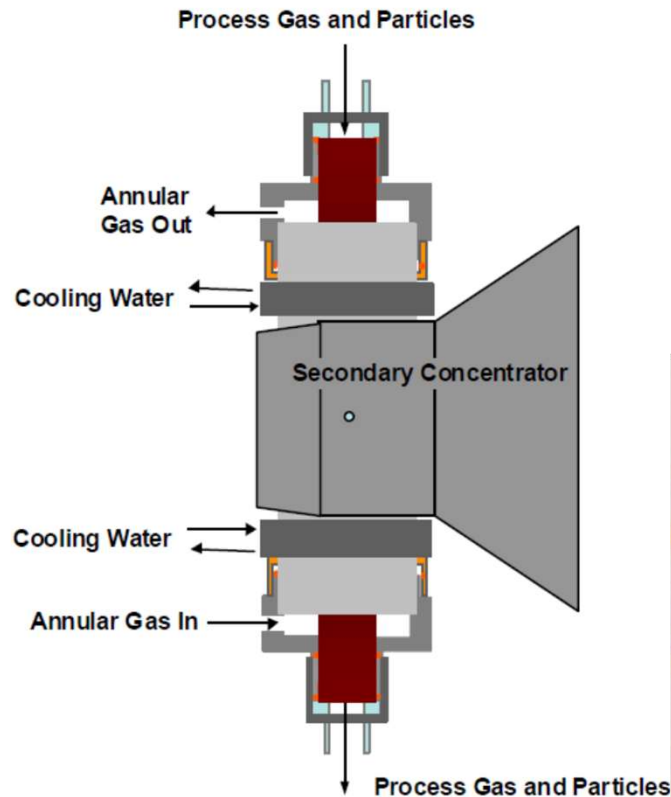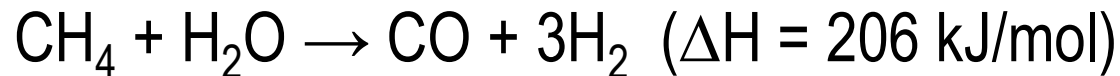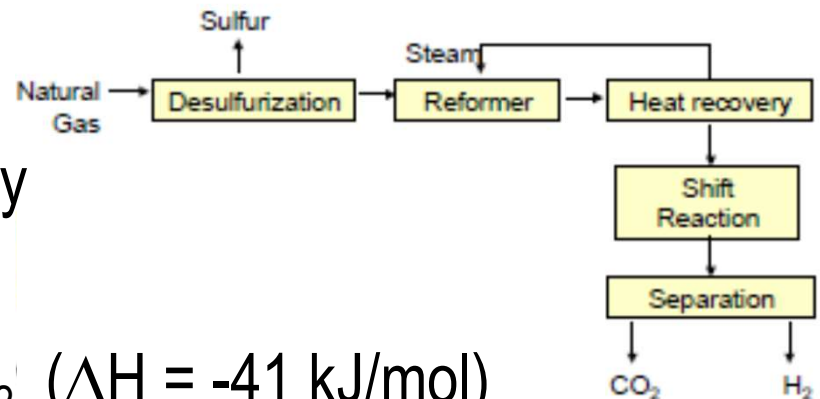 Dahl and Weimer et al., 2004.

Figure 4

Hybrid solar conversion

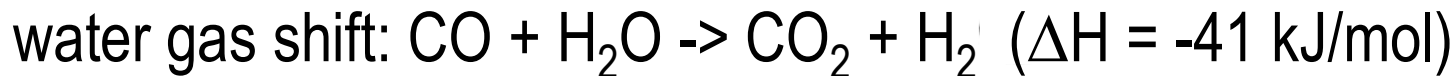- **Steam reforming**: uses light hydrocarbon feedstock, usually methane, reacts it at elevated temperatures with steam and catalytically converts the feed into hydrogen

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H = 206 \text{ kJ/mol})$$

- Operates around 700 – 925°C
- Can achieve 65 – 75% efficiency

water gas shift: $CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H = -41 \text{ kJ/mol})$
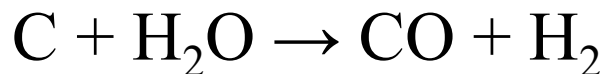
Hybrid solar conversion

- Solar reactors developed for steam reforming
  Solar gasification of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$), DLR
  SOLREF project

- 400 kW
- Rh catalyst
- 1100 K
- 10 bar
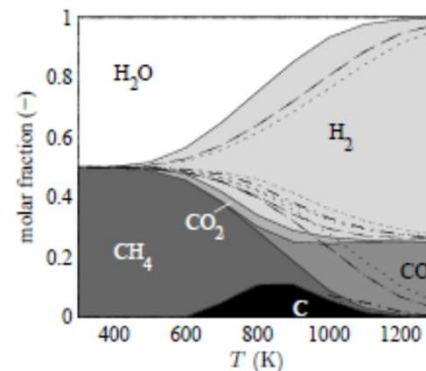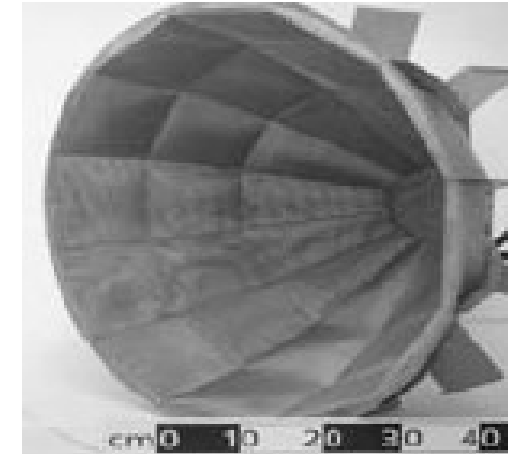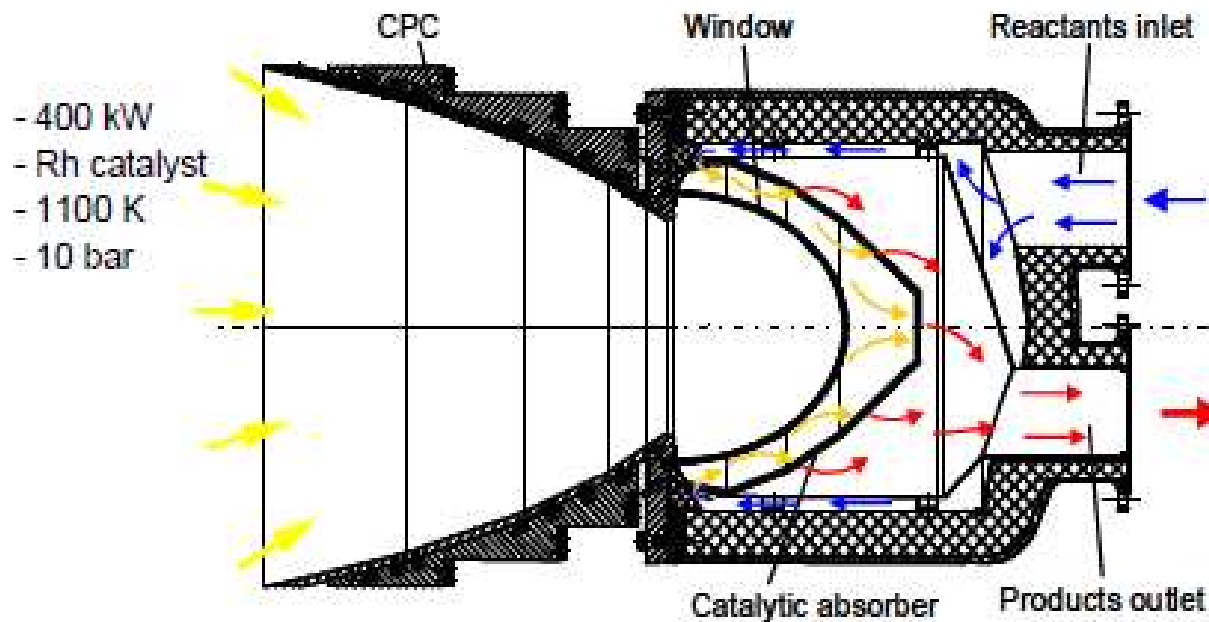
Hybrid solar conversion

- **Gasification**: uses carbonaceous materials, reacts it at high temperatures (>700 °C), without combustion, with a controlled amount of steam, oxygen, and/or CO_2. Results in CO, H_2, and CO_2.

- E.g. for coal, or C-sources

$$C + H_2O \rightarrow CO + H_2$$

- More realistic (especially for biomass, or C-waste):

$$CH_xO_yS_zN_u + (1-y)H_2O = \frac{1}{2}(x + 2(1-y) - 2z)H_2 + CO + zH_2S + \frac{1}{2}uN_2$$
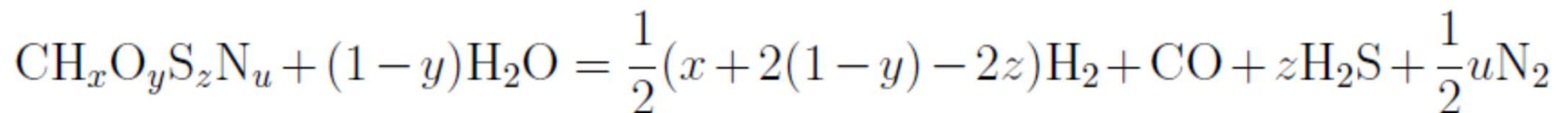
Hybrid solar conversion

- Consists of (sequential or simultaneous):

  - Dehydration

  - Pyrolysis (thermal decomposition in the absence of O_2, devolatilization)

  - Gasification (heterogeneous gas-soild reaction of pyrolysis residue with reactive gas)

  - Combustion
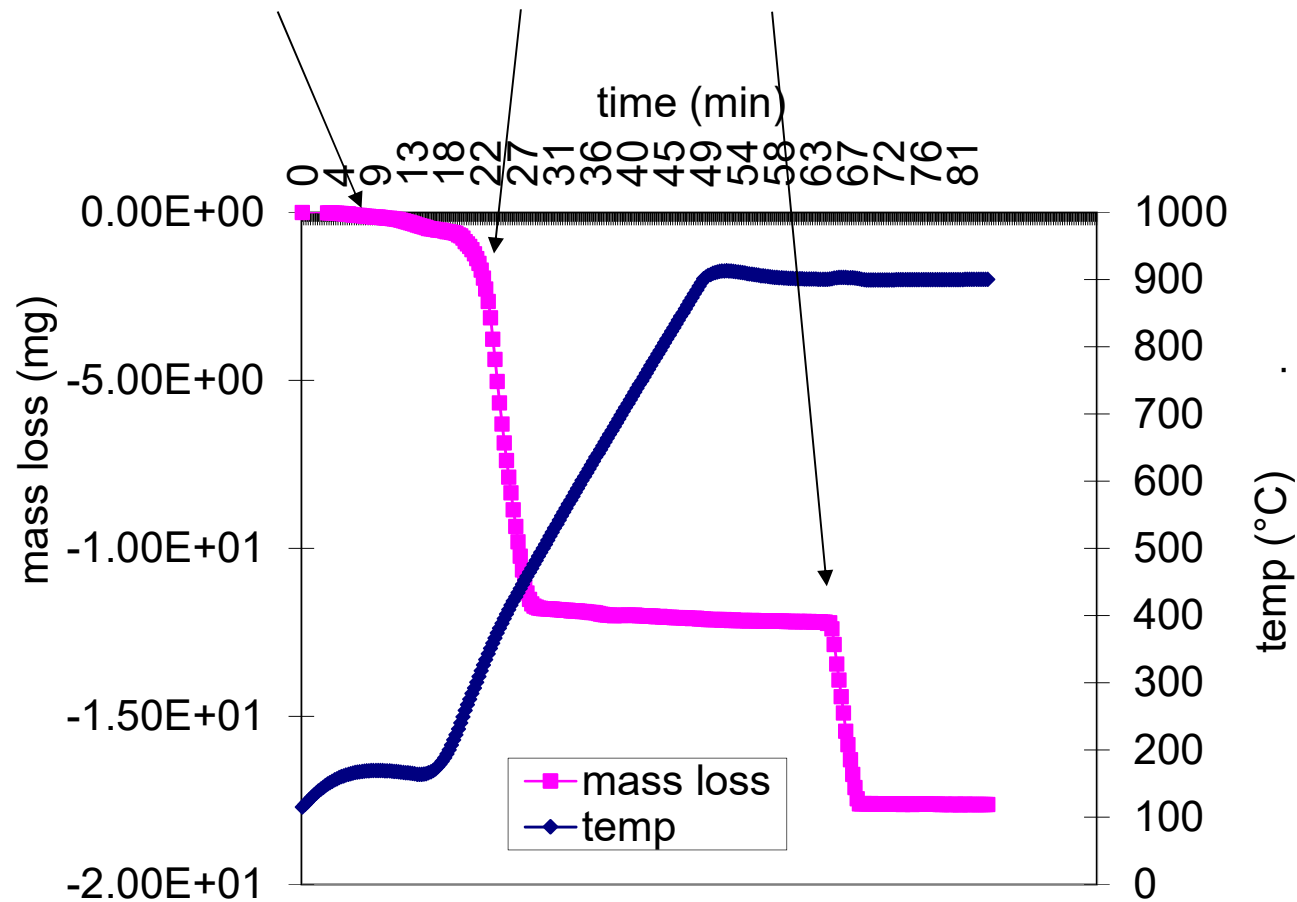
  - Water-gas-shift
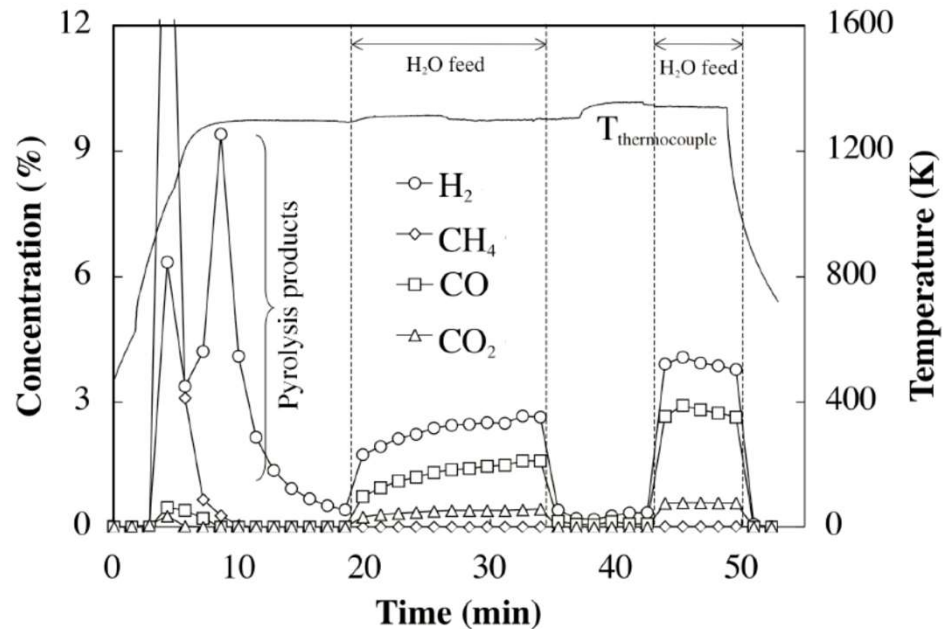
Trommer, Diss ETH, 2006.

Hybrid solar conversion

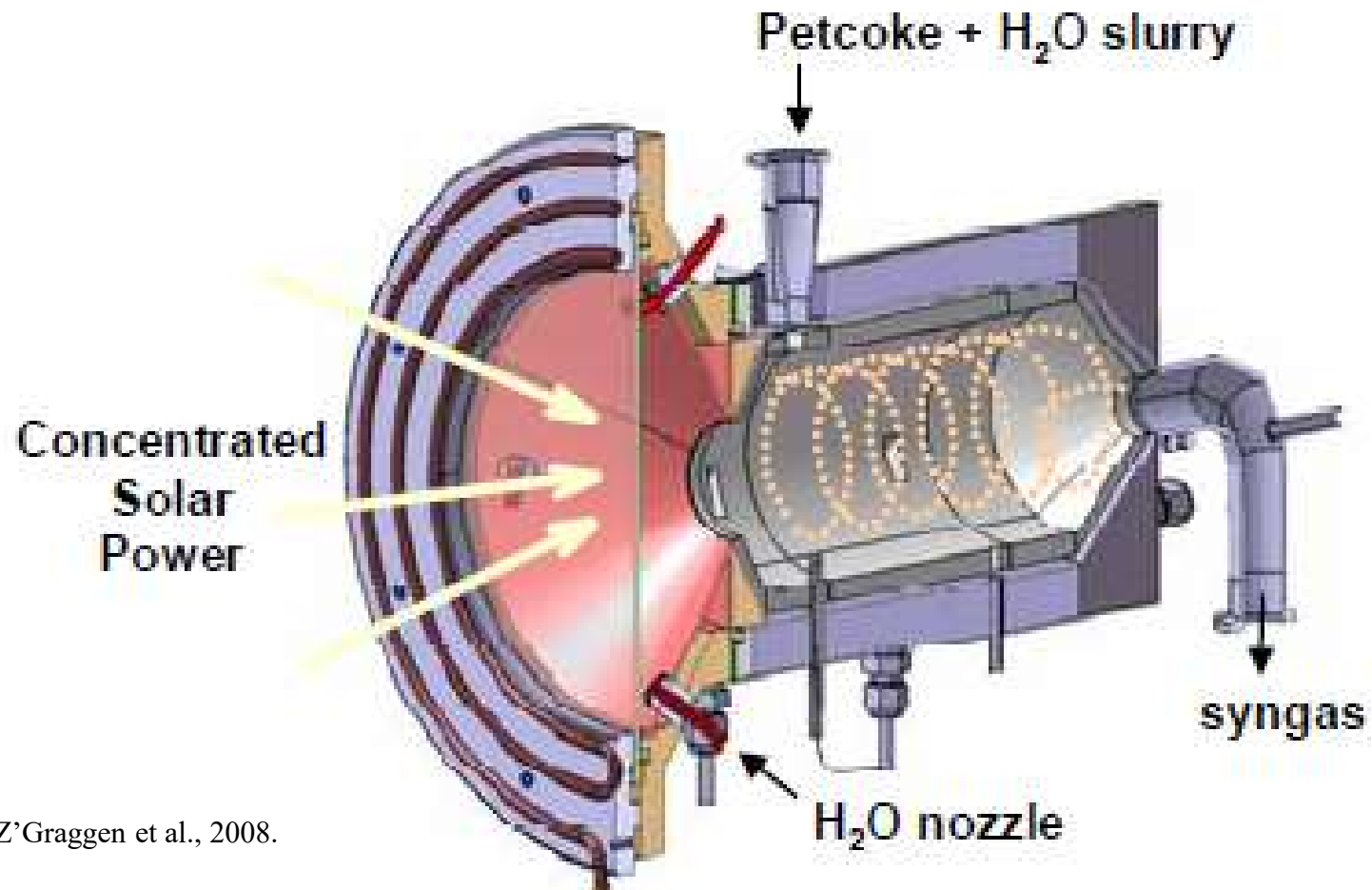- Gasification (thermographimetric experiment):

Dehydration, Pyrolysis, Gasification
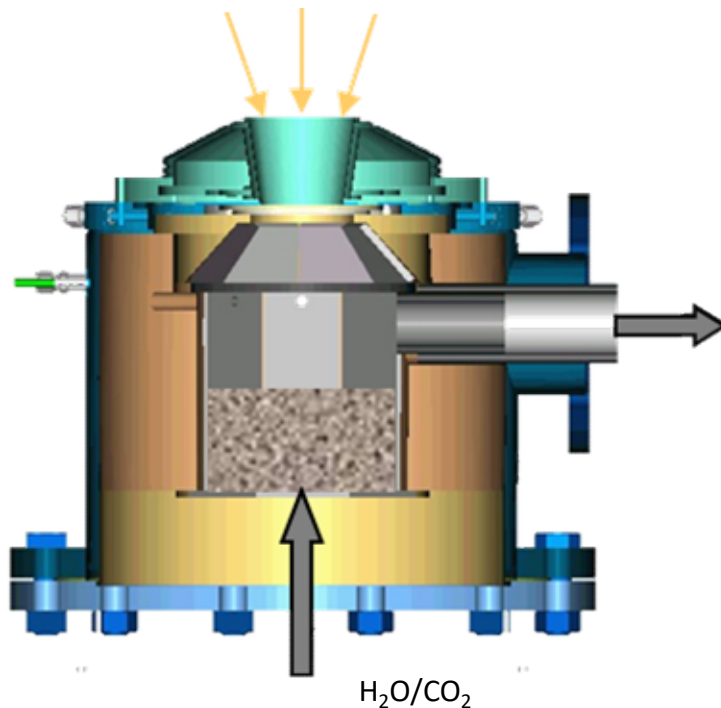
Hybrid solar conversion

- Solar reactors developed for gasification:
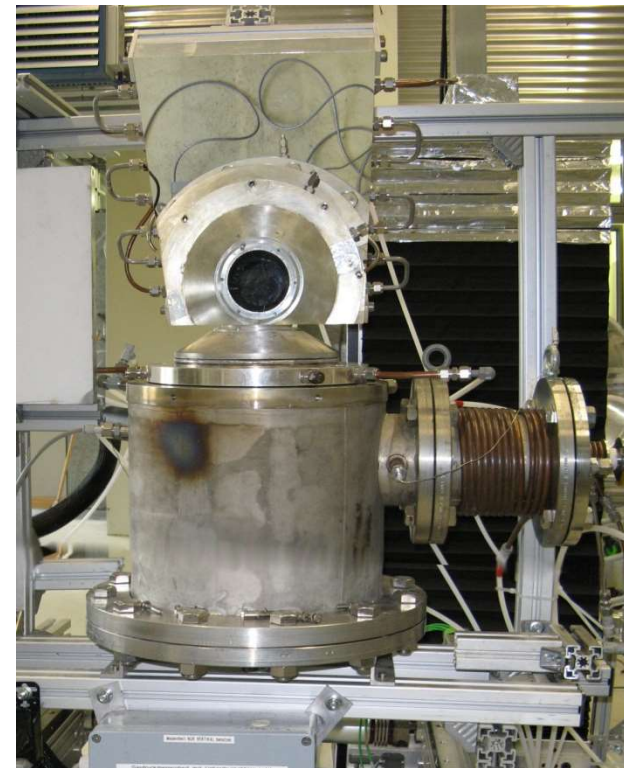   - Steam gasification of petcoke, ETH

Z'Graggen et al., 2008.

Hybrid solar conversion

- Solar reactors developed for gasification:
  - Steam gasification of carbonaceous waste material (ETH, PSI)

H_2O/CO_2

Piatkowski et al., 2010.

Hybrid solar conversion

- Hydrogen derived from fossil fuels has many impurities:
  - ~~From combustion: CO_2, CO, N_2~~
  - From the feedstock: sulfur

- Purification:
  - Desulfurization for gaseous feedstock: calcium-based slurries (SO_2 to sulfites and sulfates)
  - Desulfurization from solid/liquid feedstock: via catalysts into H_2S
  - ~~CO_2 removal:~~
    - ~~temperature swing adsorption (solubility variation of CO_2 with temperature)~~
    - pressure swing adsorption (pressure dependent absorption of e.g. zeolites)
    - special membranes (cellulose)
  - CO removal from H_2 mixture: Hydrogen-permeable membranes made of metals (palladium)

Hybrid solar conversion

- Hybrid solar conversion
  - Advantage of hybrid process vs. conventional autothermal processes:
    - the gaseous products are not contaminated by combustion's by-products
    - the discharge of pollutants to the environment is reduced
    - the calorific value of the feedstock is upgraded
    - the fuel is decarbonized
   - there is no need for energy-intensive processing of pure oxygen
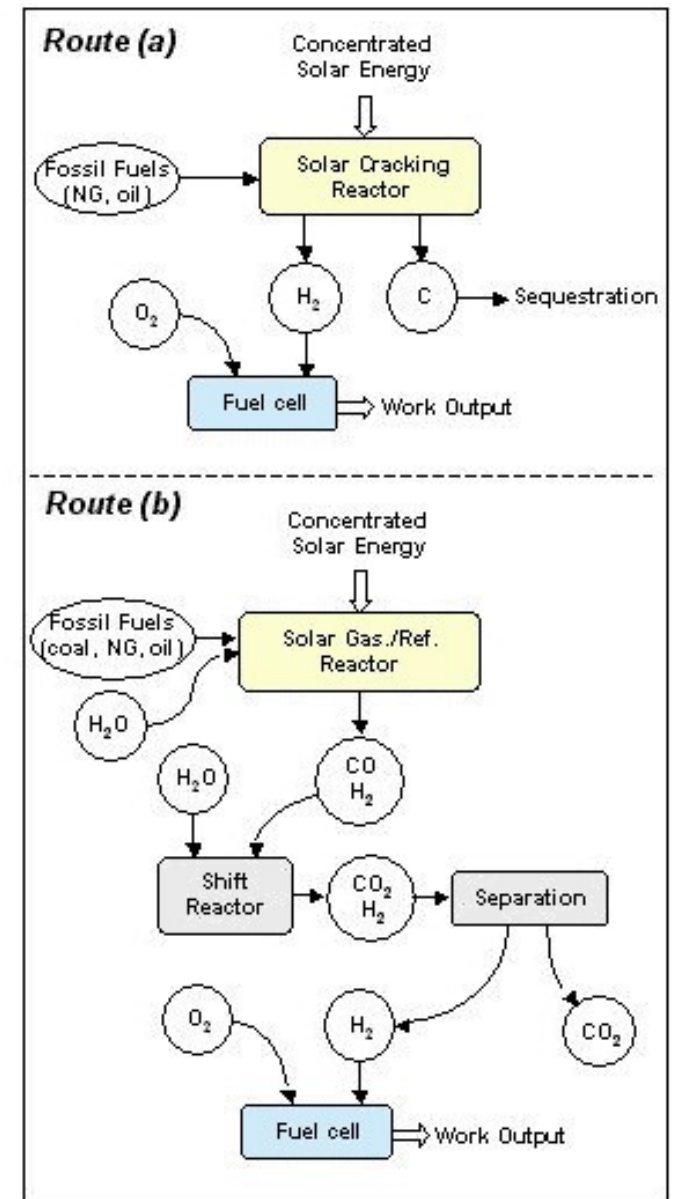
Renewable Energy

- Outline:

  - Conversion pathways solar-to-fuel

  - Hybrid pathways

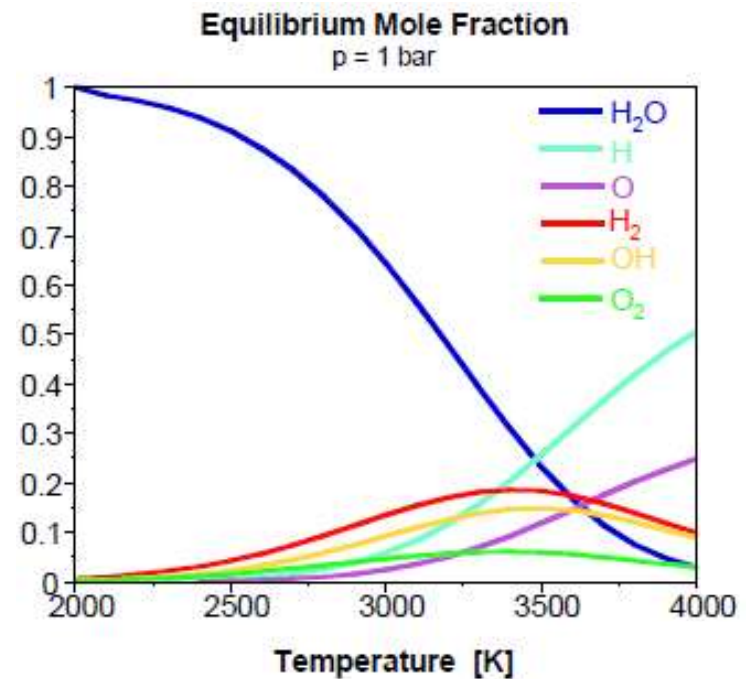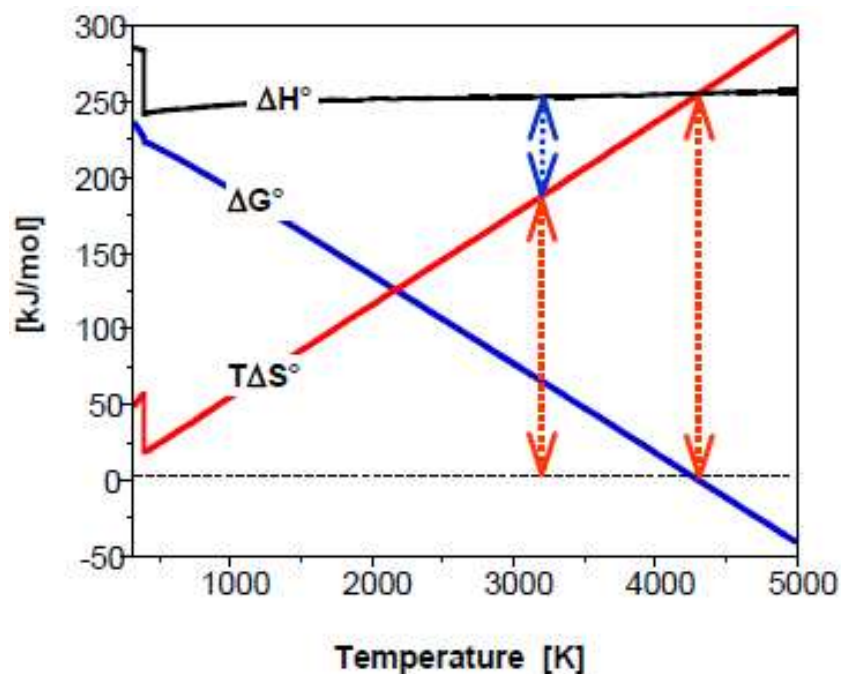 - Solar thermochemistry

  - Photochemistry

Solar thermolysis and thermochemistry

- In the transition to a renewable future, hybrid pathways using fossil fuels exclusively as chemical source for the fuel production and solar energy as the process heat
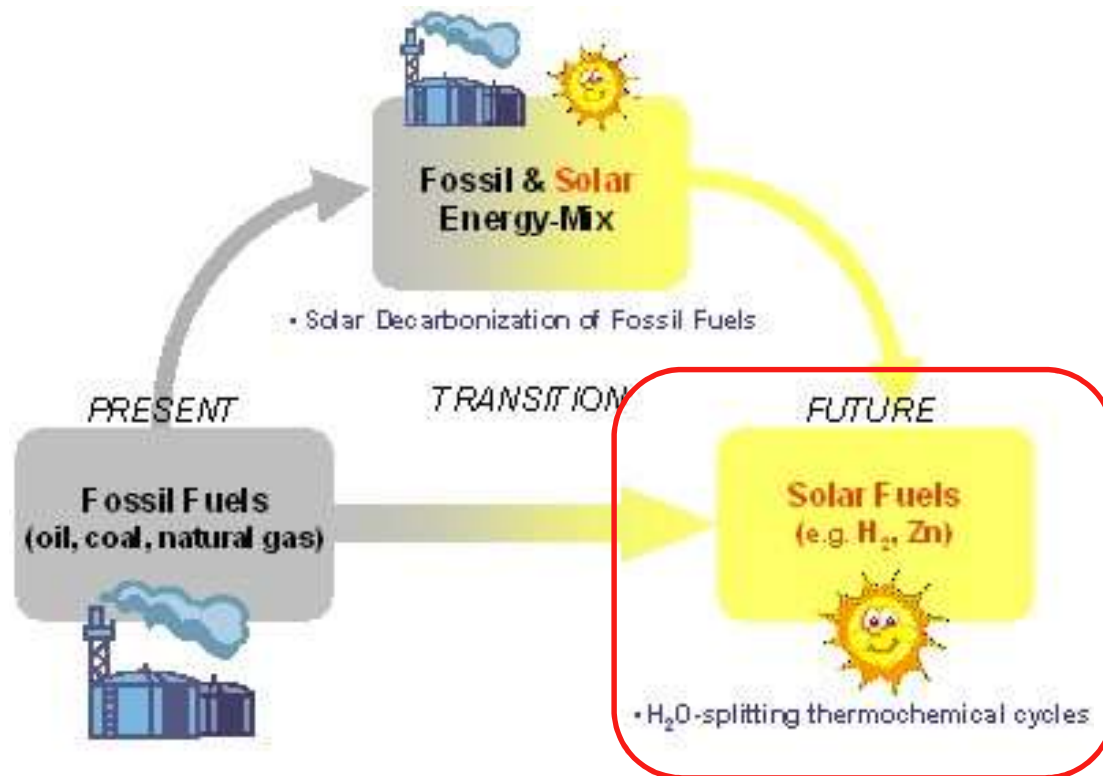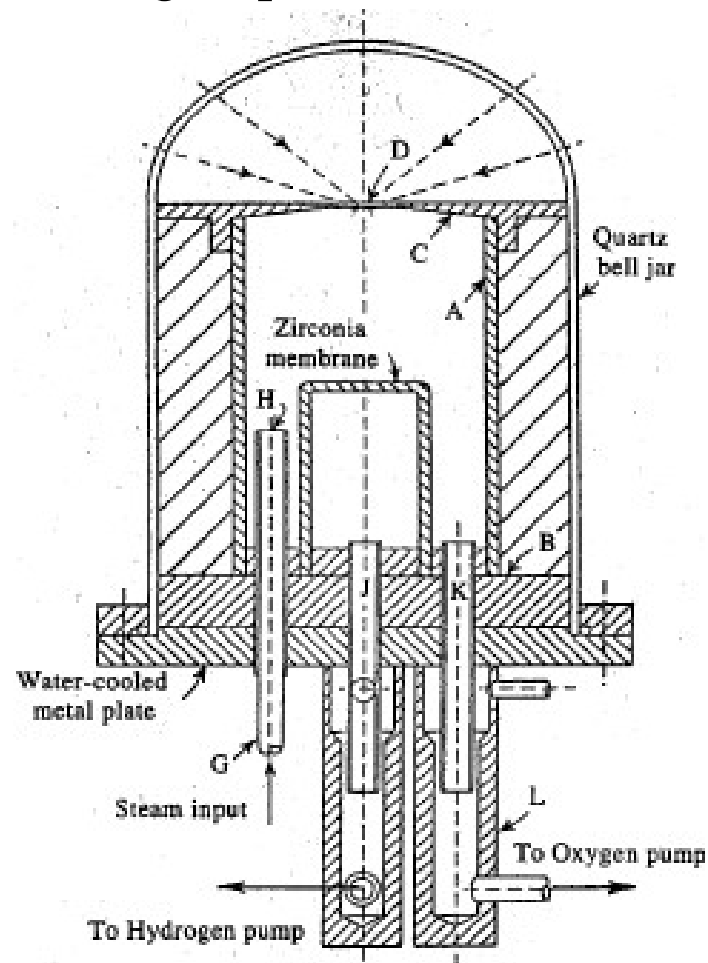
Solar thermolysis

- Solar **thermolysis**
  - Solar energy is used as process heat of chemical reaction
  - Direct thermolysis of water: $H_2O \rightarrow 1/2O_2 + H_2$
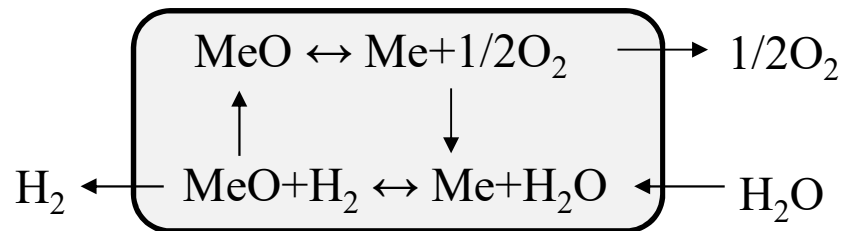
Solar thermolysis

- Reactor concept for solar thermolysis
  - Product separation by:
    - High temperature membranes
   - Rapid quenching of products

Kogan et al., 1998.

Solar thermochemistry

- Solar **thermochemical** cycles
  - Solar energy is used as process heat of chemical reaction
  - Multi-step water-splitting reactions:

$$MeO \leftrightarrow Me + 1/2\,O_2 \longrightarrow 1/2\,O_2$$

$$H_2 \longleftarrow MeO + H_2 \leftrightarrow Me + H_2O \longleftarrow H_2O$$

  - Omit explosive hydrogen and oxygen mixture since produced in separate steps
  - Requires lower temperatures
  - Possible redox pairs (Me/MeO):
   - Fe_2O_4/FeO
    - Ce_2O_3/CeO_2,
    - ZnO/Zn
    - SnO/SnO_2 …
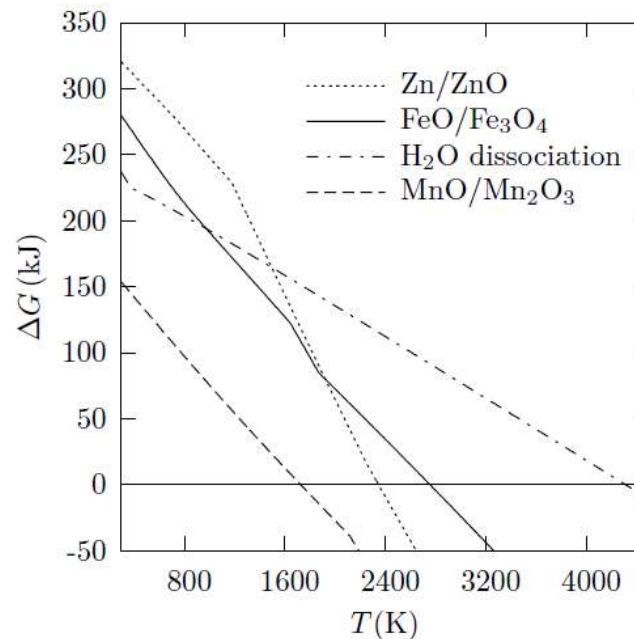
Solar thermochemistry

- Possible redox pairs for two-step cycles:

Cycle	Reactions
Zn/ZnO	$ZnO \rightarrow Zn + O_2$ $Zn + H_2O \rightarrow ZnO + H_2$
Fe_3O_4/FeO	$Fe_3O_4 \rightarrow 3\ FeO + \frac{1}{2}\ O_2$ $3\ FeO + H_2O \rightarrow Fe_3O_4 + H_2$
In_2O_3/In_2O	$In_2O_3 \rightarrow In_2O + 1/2\ O_2$ $In_2O + 2H_2O \rightarrow In_2O_3 + 2H_2$
SnO_2/Sn	$SnO_2 \rightarrow Sn + O_2$ $Sn + 2H_2O \rightarrow SnO2 + 2H_2$
MnO/$MnSO_4$	$MnSO_4 \rightarrow MnO + SO_2 + 1/2O_2$ $MnO + H_2O + SO_2 \rightarrow MnSO_4 + H_2$
FeO/$FeSo_4$	$FeSO_4 \rightarrow FeO + SO_2 + 1/2O_2$ $FeO + H_2O + SO_2 \rightarrow FeSO_4 + H_2$
CoO/$CoSO_4$	$CoSO_4 \rightarrow CoO + SO_2 + 1/2O_2$ $CoO + H_2O + SO_2 \rightarrow CoSO_4 + H_2$
Fe_3O_4/$FeCl_2$	$Fe_3O_4 + 6HCl \rightarrow 3FeCl_2 + 3H_2O + 1/2O_2$ $3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$
Mo/Mo_2	$MoO_2 \rightarrow Mo + O_2$ $Mo + 2H_2O \rightarrow MoO_2 + 2H_2$

| Cycle	Reactions
SoO_2/SiO	$SiO_2 \rightarrow SiO + 1/2\ O_2$ $SiO + H_2O \rightarrow SiO_2 + H_2$
W/WO_3	$WO_3 \rightarrow W + 3/2\ O_2$ $W + 3H_2O \rightarrow WO_3 + 3H_2$
Hg/HgO	$Hg + H_2O \rightarrow HgO + H_2$ $HgO \rightarrow Hg + 1/2O_2$
Cd/CdO	$Cd + H_2O \rightarrow CdO + H_2$ $CdO \rightarrow Cd + 1/2O_2$
CO/CO_2	$CO + H_2O \rightarrow CO_2 + H_2$ $CO_2 \rightarrow CO + 1/2O_2$
Ce_2O_3/CeO_2	$CeO_2 \rightarrow Ce_2O_3$ $Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2$
Mg/MgO	$MgO \rightarrow Mg + 1/2O_2$ $Mg + H_2O \rightarrow MgO + H_2$
SnO/SnO2	$SnO_2 \rightarrow SnO + 1/2O_2$ $SnO + H_2O \rightarrow SnO_2 + H_2$

Solar thermochemistry

- Three-step water-splitting cycles, e.g. sulfur-iodine:
  - further lower temperatures
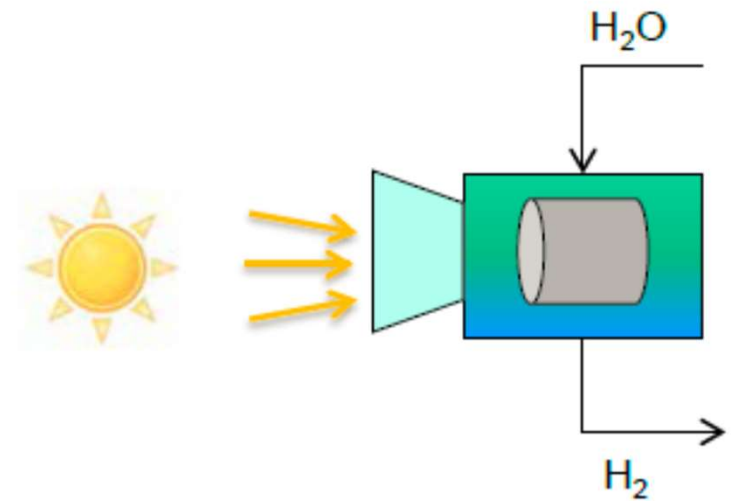 - but run in corrosive environment
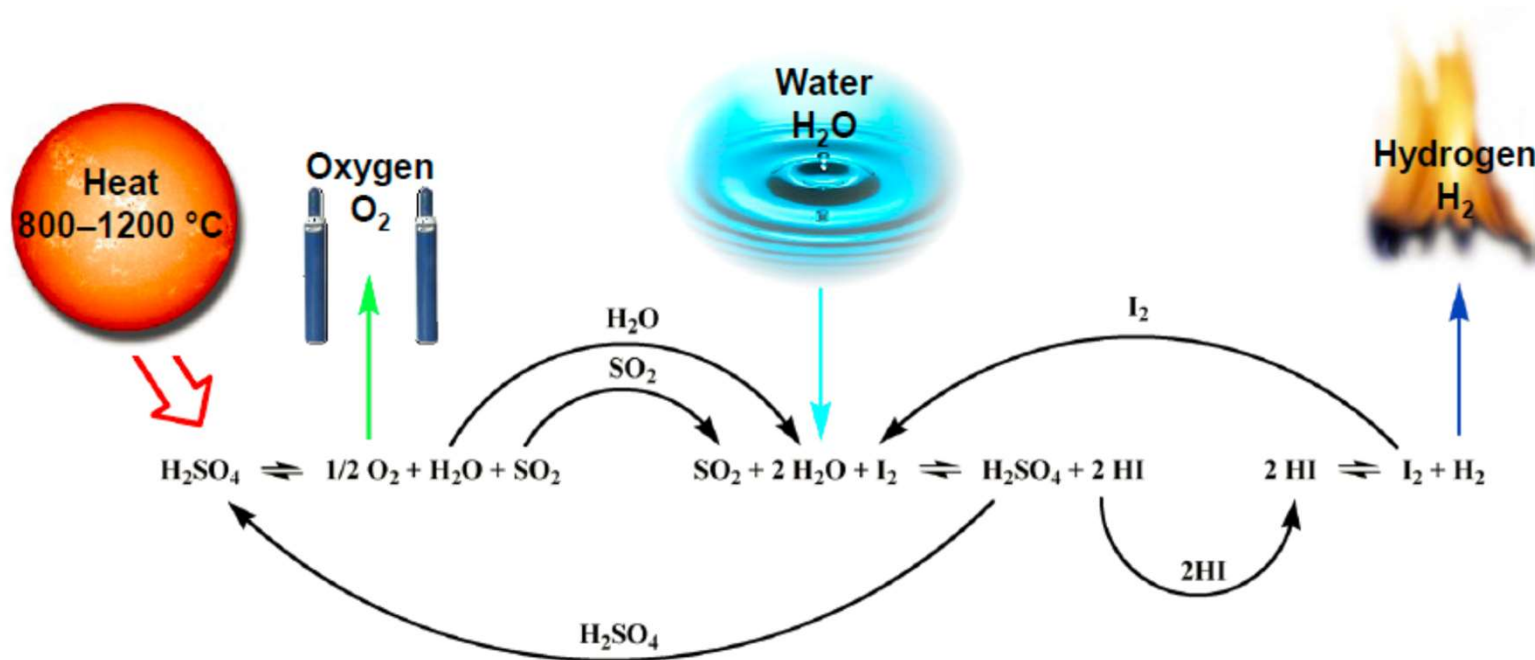
Solar thermochemistry

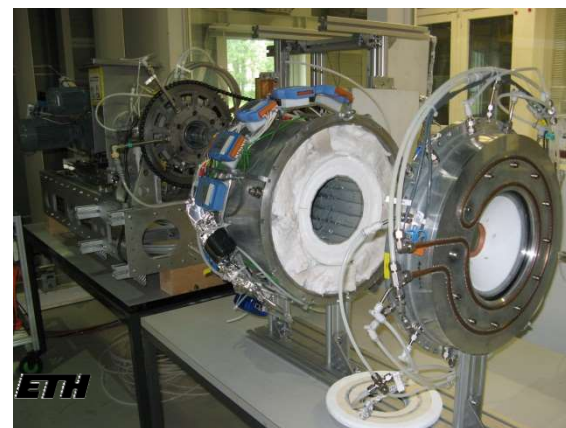- Reactor concepts: two-step cycles
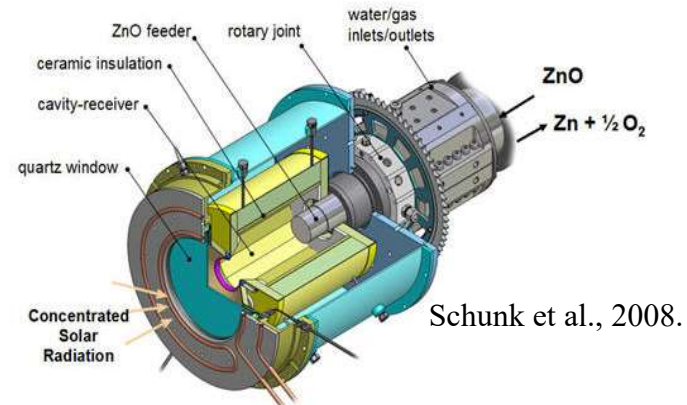
Moving material
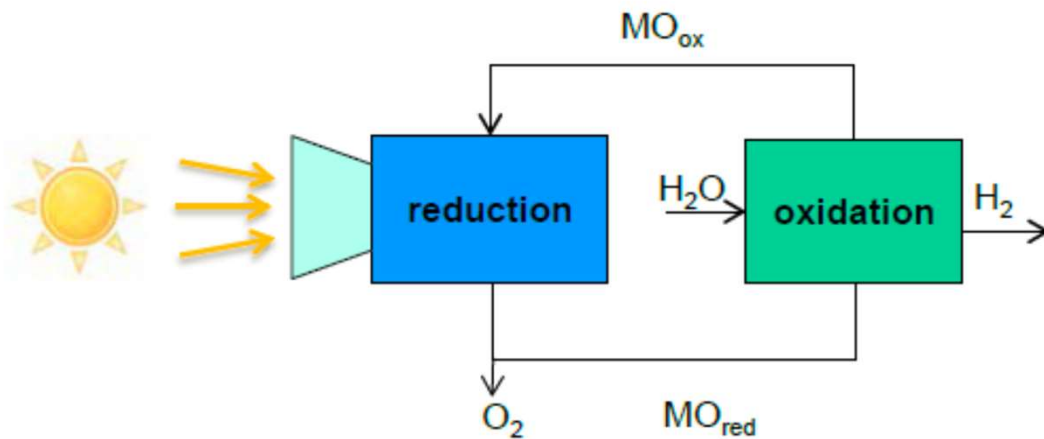
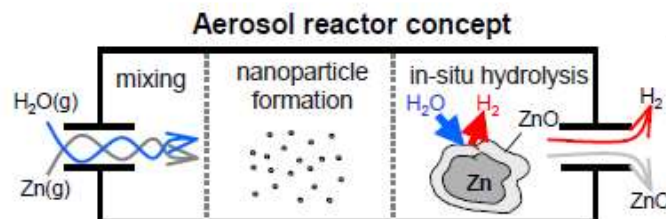Stationary material

Solar thermochemistry

- Zn/ZnO-based proposed reactors, e.g. at ETH Zürich and PSI:

  - High-temperature reactor

    – 10 kW reactor

    – Reactor temperature: 2000 K

    – Peak concentration: 5800 suns

  - Hydrolysis reactor:

    – Reactor temperature: 1263 K
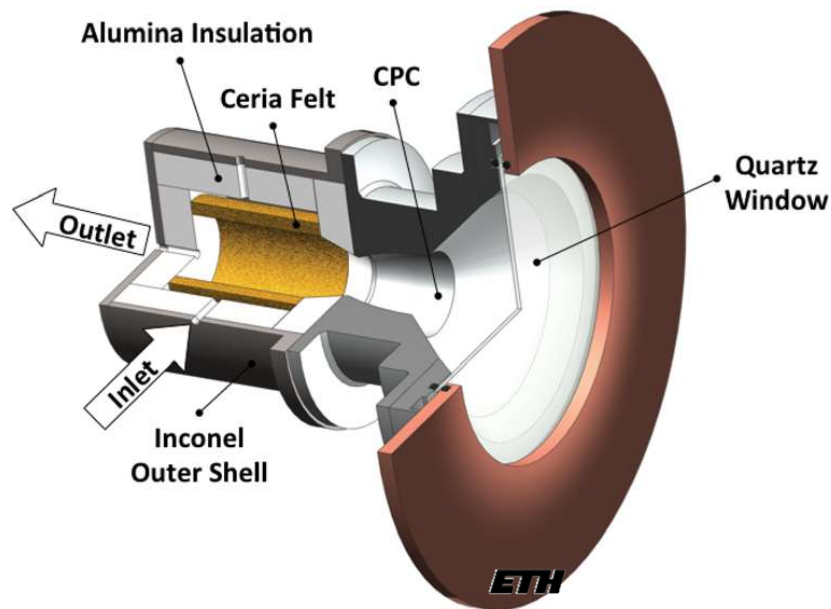

Schunk et al., 2008.

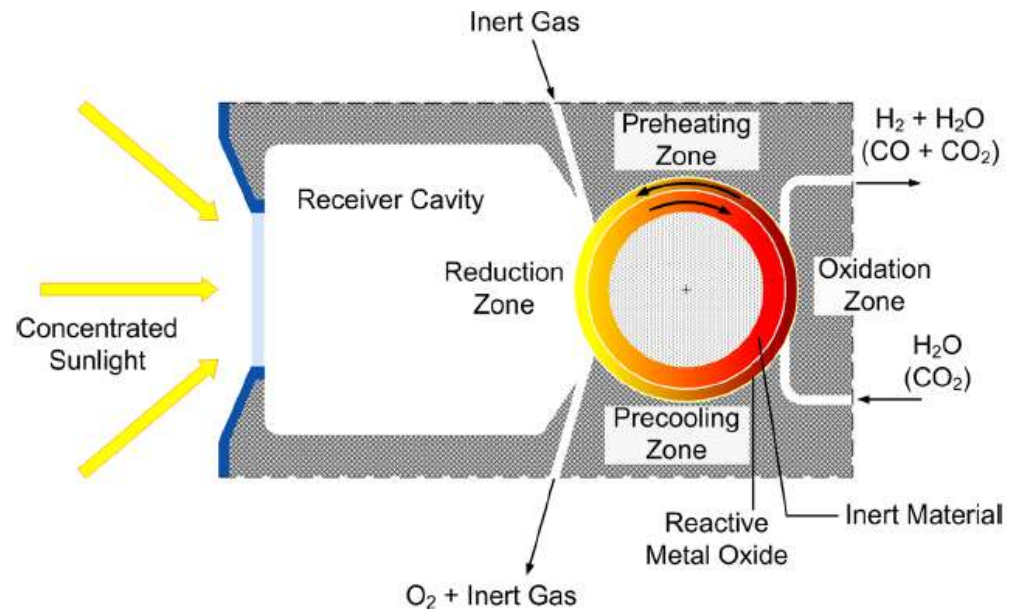
Melchior et al., 2009.

Solar thermochemistry

- Ceria-based proposed reactors, e.g.:

ETH Zürich

University of Minnesota
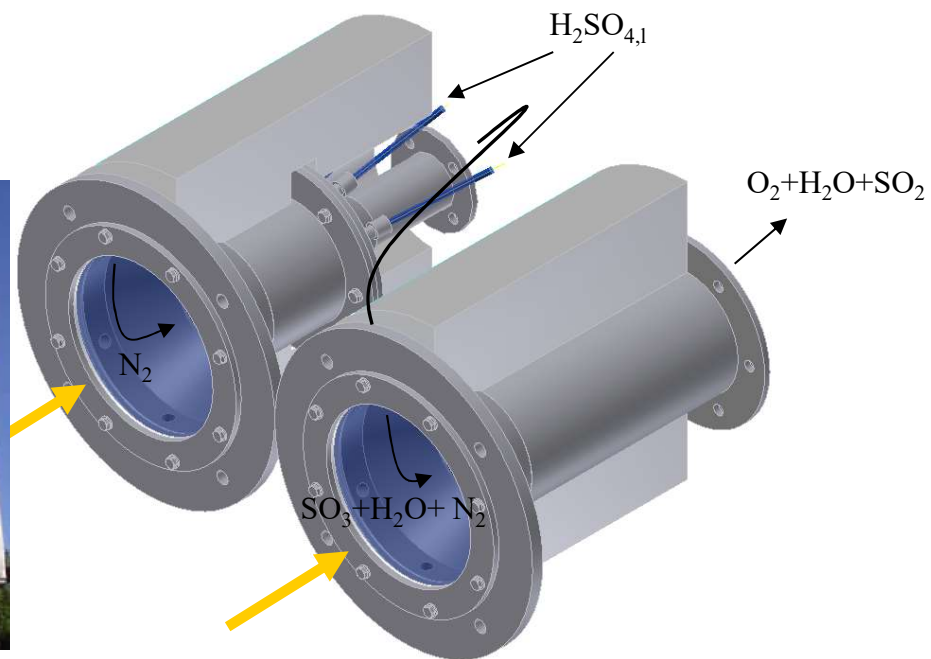

Temperature in reduction reaction: ~ 1800 K

Temperature in oxidation reaction: ~ 1200 K

Solar thermochemistry

- SI-cycle, DLR Germany
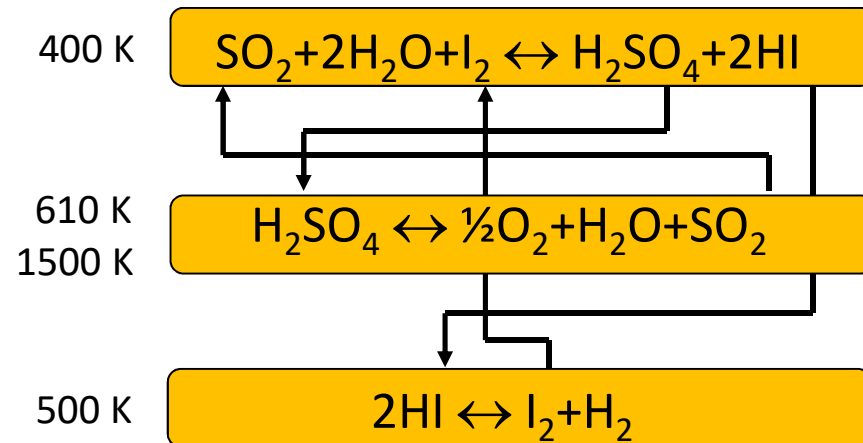
400 K $\quad SO_2 + 2H_2O + I_2 \leftrightarrow H_2SO_4 + 2HI$

610 K
1500 K $\quad H_2SO_4 \leftrightarrow \tfrac{1}{2}O_2 + H_2O + SO_2$

500 K $\quad 2HI \leftrightarrow I_2 + H_2$

$H_2SO_{4,l}$

$O_2 + H_2O + SO_2$

N_2

$SO_3 + H_2O + N_2$

Renewable Energy

- Outline:

  – Conversion pathways solar-to-fuel

  – Hybrid pathways

  – Solar thermochemistry

  – Photochemistry

Photoelectrochemistry

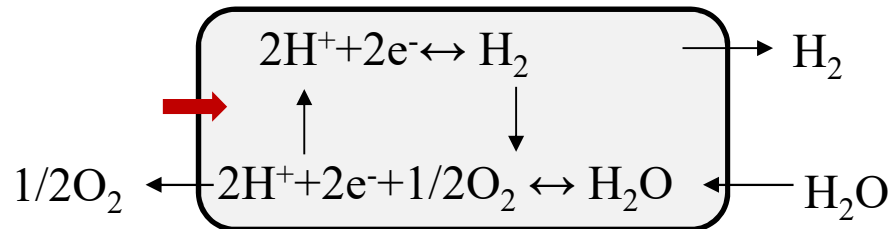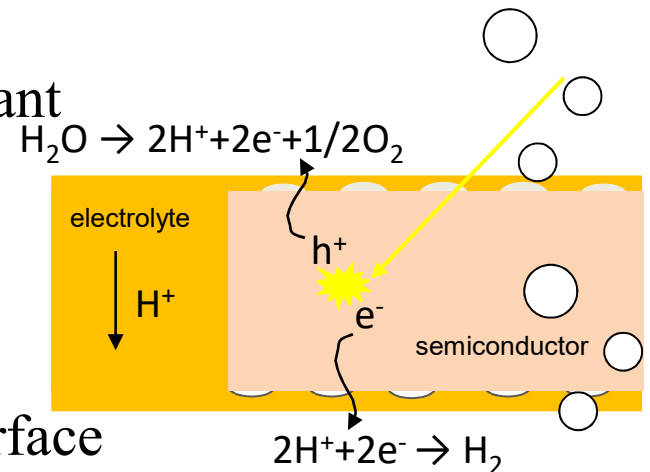- Photoelectrochemical processes
  - Solar energy is used as photon energy for the internal production of charge, which is separated at the solid-liquid junction
  - Multi-step water-splitting reactions (E_0=1.23 V):
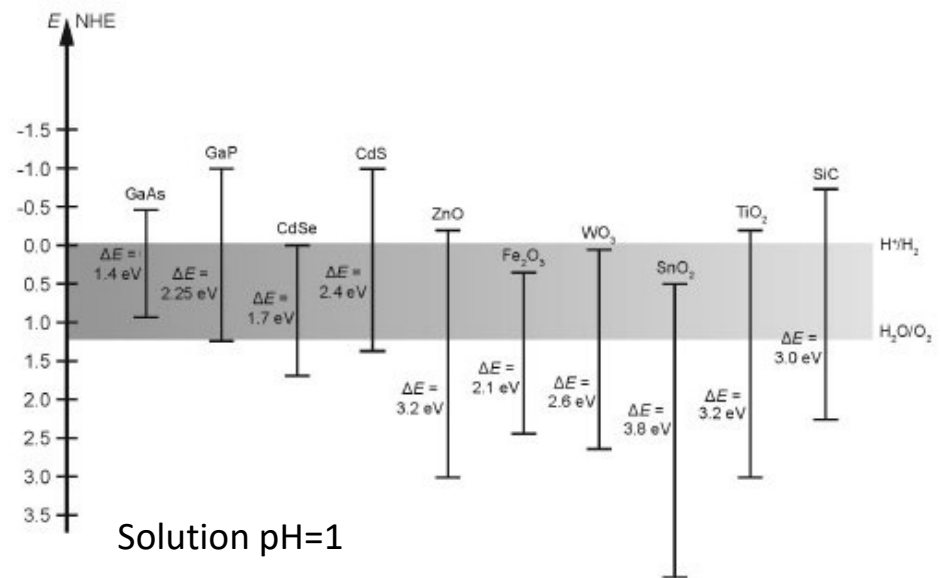

  - Works at room temperature
  - Spectral distribution of solar radiation important
  - Processes:
    - Solar absorption
    - Electron-hole generation
    - Use electron and holes at liquid-solid interface
    - Ionic transport

Photoelectrochemistry

- Stringent material requirements:
  - band gap size
  - suitable band edge position
  - high chemical stability in the dark and under illumination, as well as under highly acidic or base conditions
  - efficient charge transport in the semiconductor
  - selective and efficient electrochemical reactions
 - earth-abundance and low costs

Photoelectrochemistry

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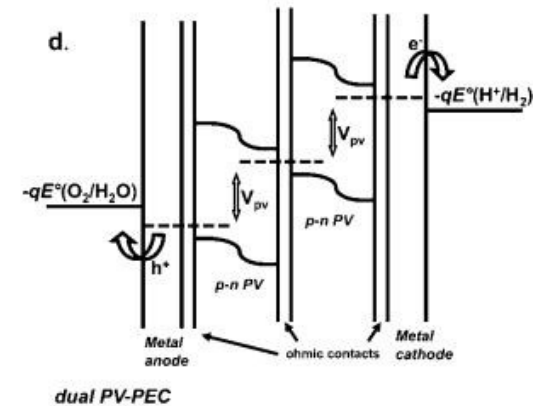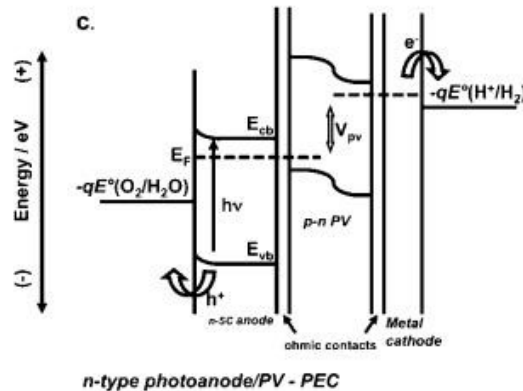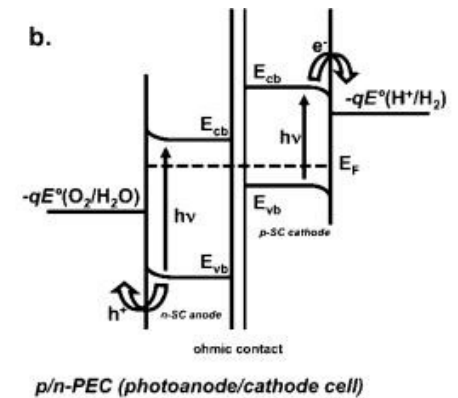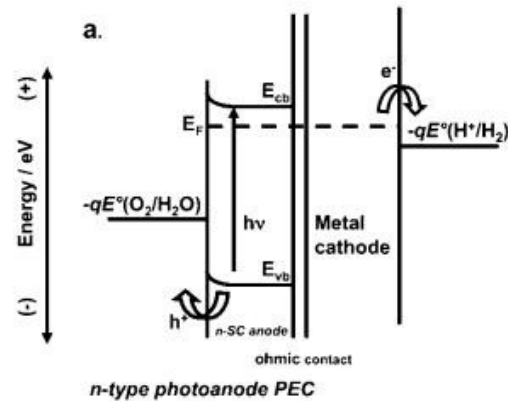 - earth-abundance and low costs

Solution pH=1
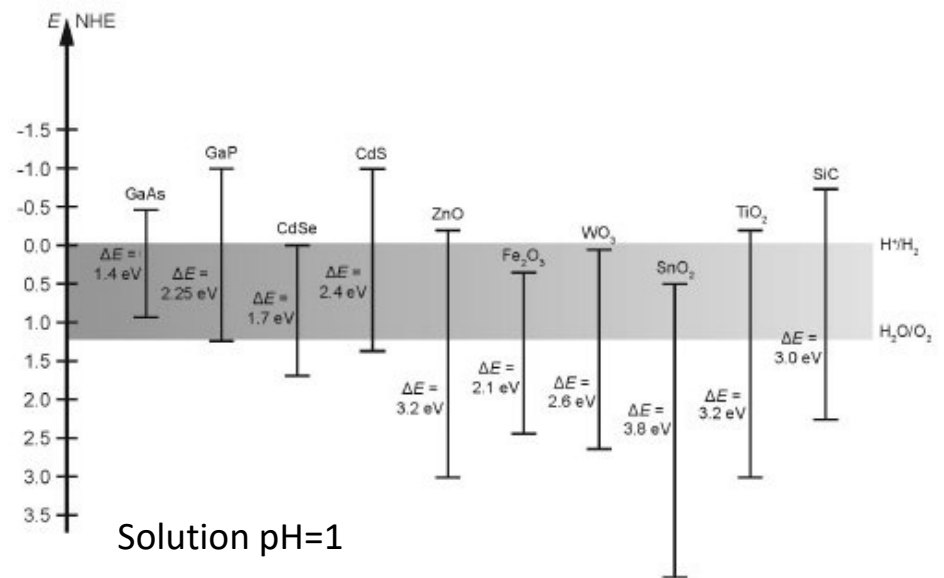
Photoelectrochemistry

- Band gap and band position of photoelectrode material must match reaction potentials:

Walter et al., 2006
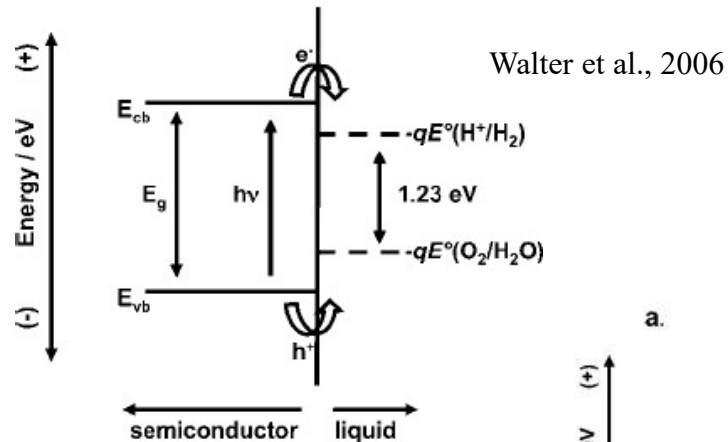
- Various possible architectures:

EPFL

Photoelectrochemistry

- Calculations:
  - Photoactive material(s) will show diode-like current-potential behavior:

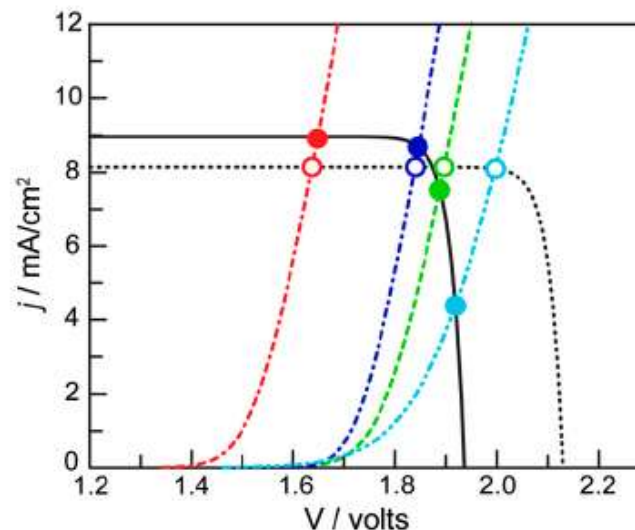$$i = i_L - i_0 \left(\exp\left(\frac{qV}{kT} \right) - 1 \right)$$

  - Electrochemical system shows losses:
    - Reaction overpotentials
    - Ohmic losses

$$E = E_0 + \eta_a + \eta_c + iR_{sol} + E_{mem} + E_{conc} > E_0$$

    - Concentration losses
  - Electrochemical load curve will show electrolyzer like load curve
  - Intersection between both is operating point

Surendranath et al., 2012

Photoelectrochemistry

- Calculations:
  - Electrochemical system shows losses:
    - Reaction overpotentials
      - E.g. via Tafel equations:

Tafel slope

$$\eta_a = a_1 \log\left(\frac{i}{i_{0a}}\right) \qquad \eta_c = a_2 \log\left(\frac{i}{i_{0c}}\right)$$

Exchange current density

      - Or Buttler-Volmer:

$$i_R = i_{0a/c}\left[\exp\left(\frac{\alpha_a F\left(\Phi_s - \Phi_1 - E_0\right)}{RT}\right) - \exp\left(\frac{\alpha_c F\left(\Phi_s - \Phi_1 - E_0\right)}{RT}\right)\right]$$
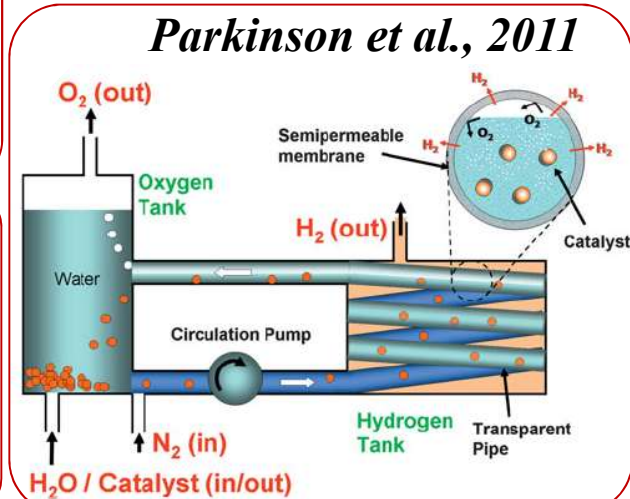
    - Ohmic losses account for resistances in electrolyte, membrane, and solid conductor:

Characteristic ion and electron path length

$$\Delta V_{ohm} = i \rho_{sol} l$$

resistivity

Photoelectrochemistry

- Proposed devices

Spurgeon et al., 2011

Carver et al., 2012

Grätzel et al., 2007

Turner, 2008

Miller et al., 2007

Parkinson et al., 2011

Linkous et al., 1996

Photoelectrochemistry

- Proposed devices

Photoelectrochemistry
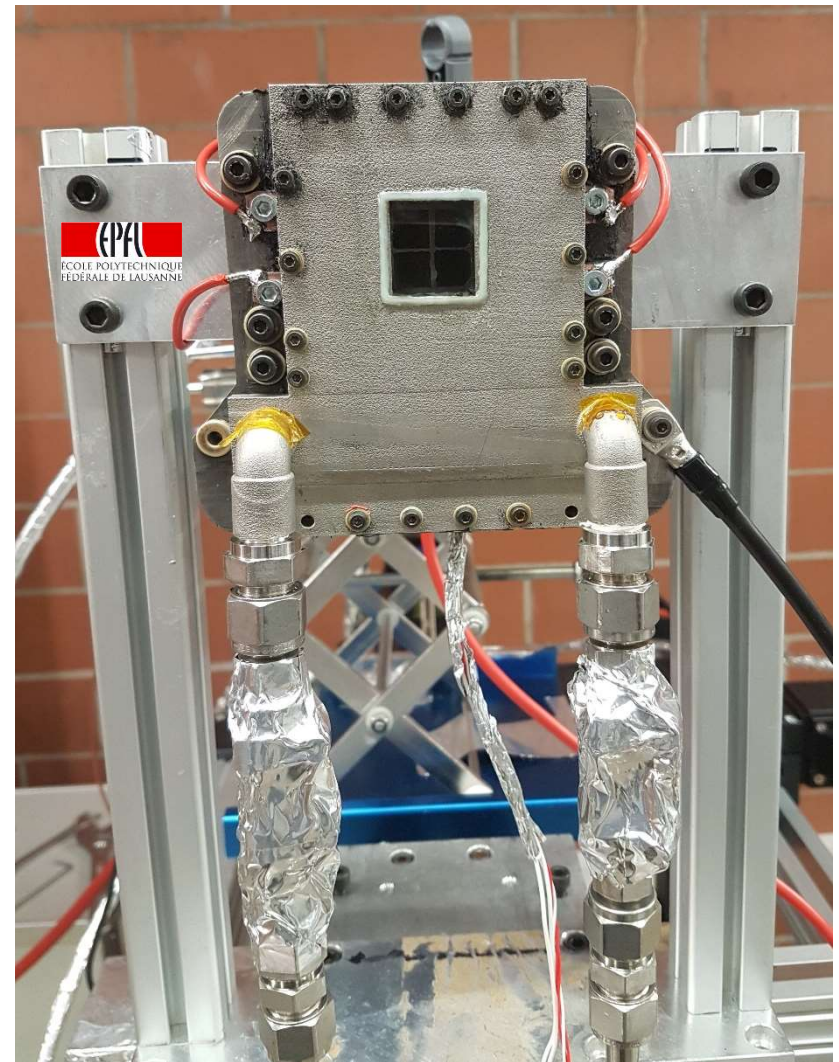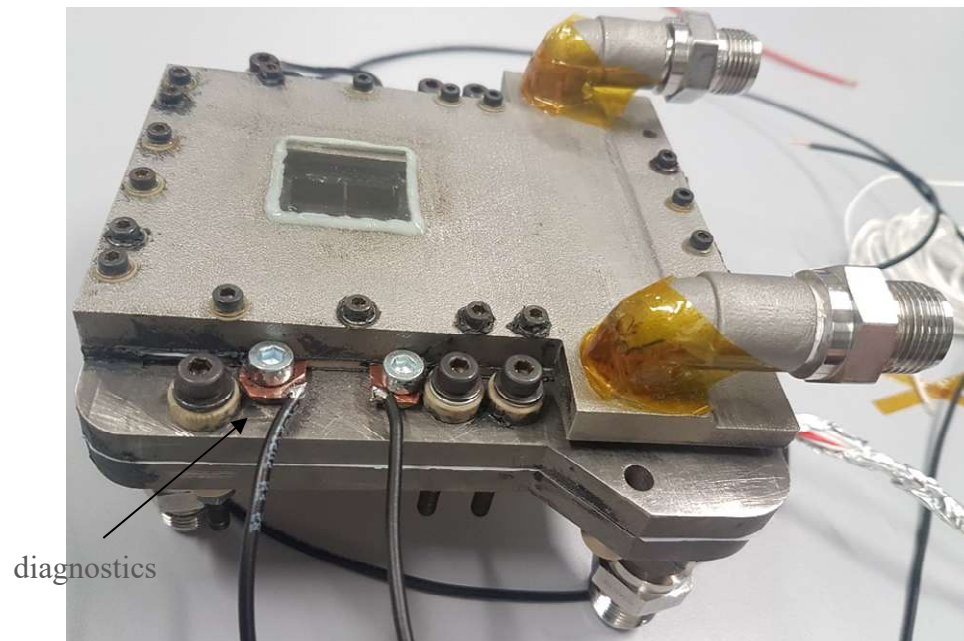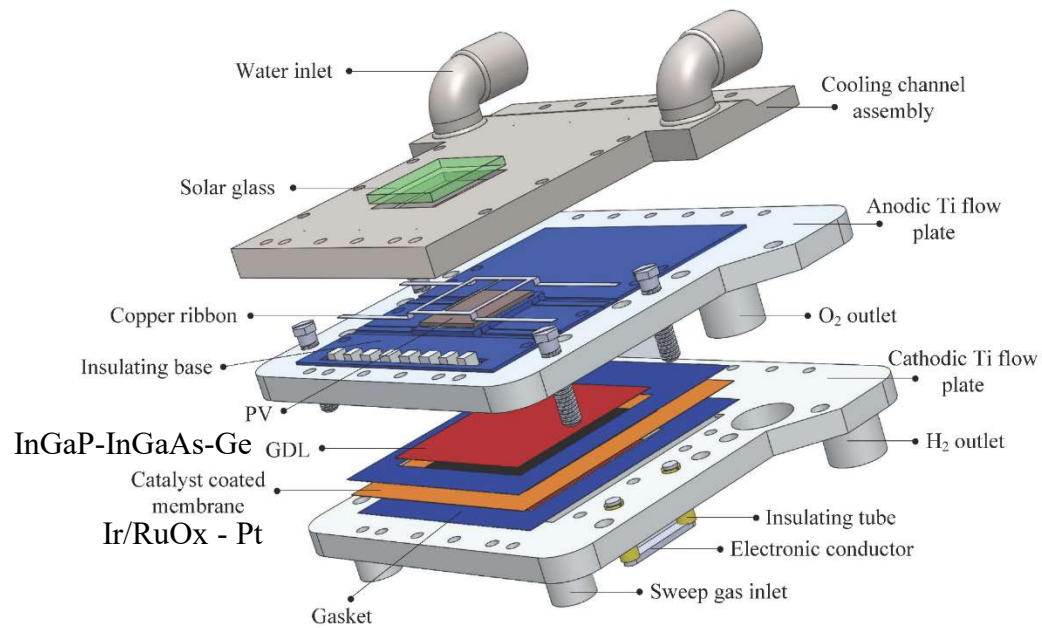
Water inlet
Solar glass
Copper ribbon
Insulating base
PV
InGaP-InGaAs-Ge — GDL
Catalyst coated membrane
Ir/RuOx - Pt
Gasket

Cooling channel assembly
Anodic Ti flow plate
O$_2$ outlet
Cathodic Ti flow plate
H$_2$ outlet
Insulating tube
Electronic conductor
Sweep gas inlet

diagnostics

http:\\specdc.epfl.ch

Photoelectrochemistry

- Proposed devices

http:\\specdo.epfl.ch

Pinaud et al., EES, 2013.
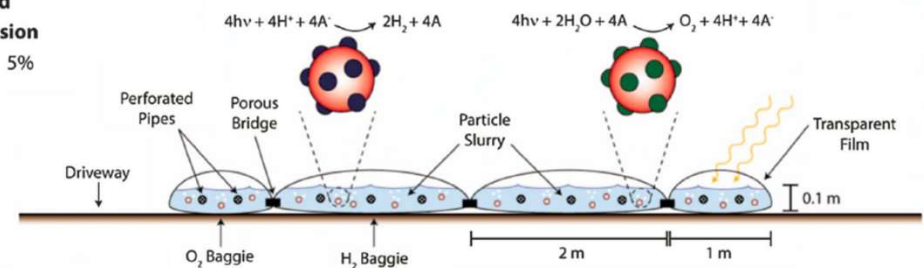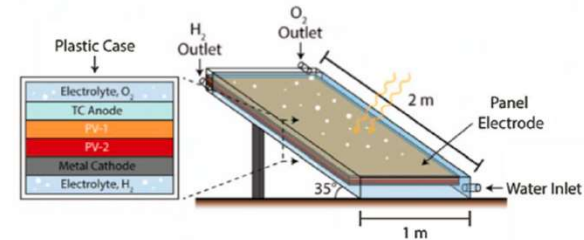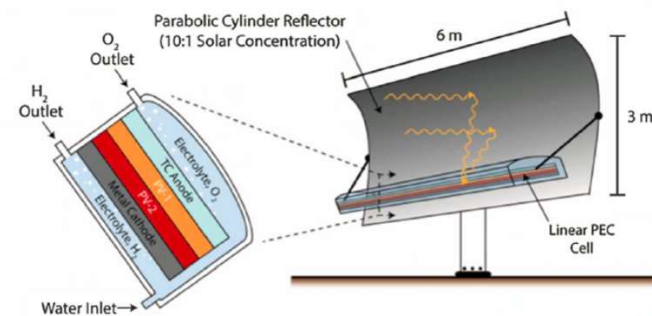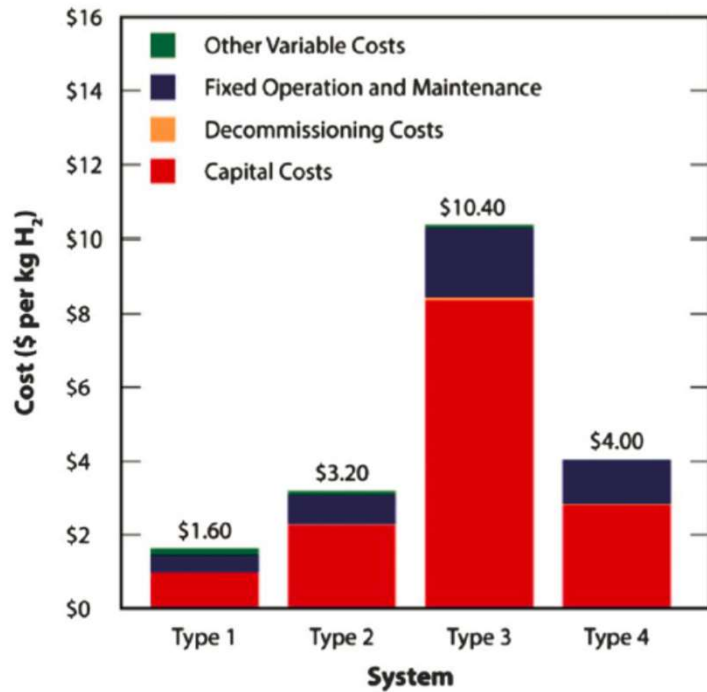
Renewable Energy

- Outline:

  - Conversion pathways solar-to-fuel

  - Hybrid pathways

  - Solar thermochemistry

  - Photochemistry

Sustainability issue

- Solar to fuels:
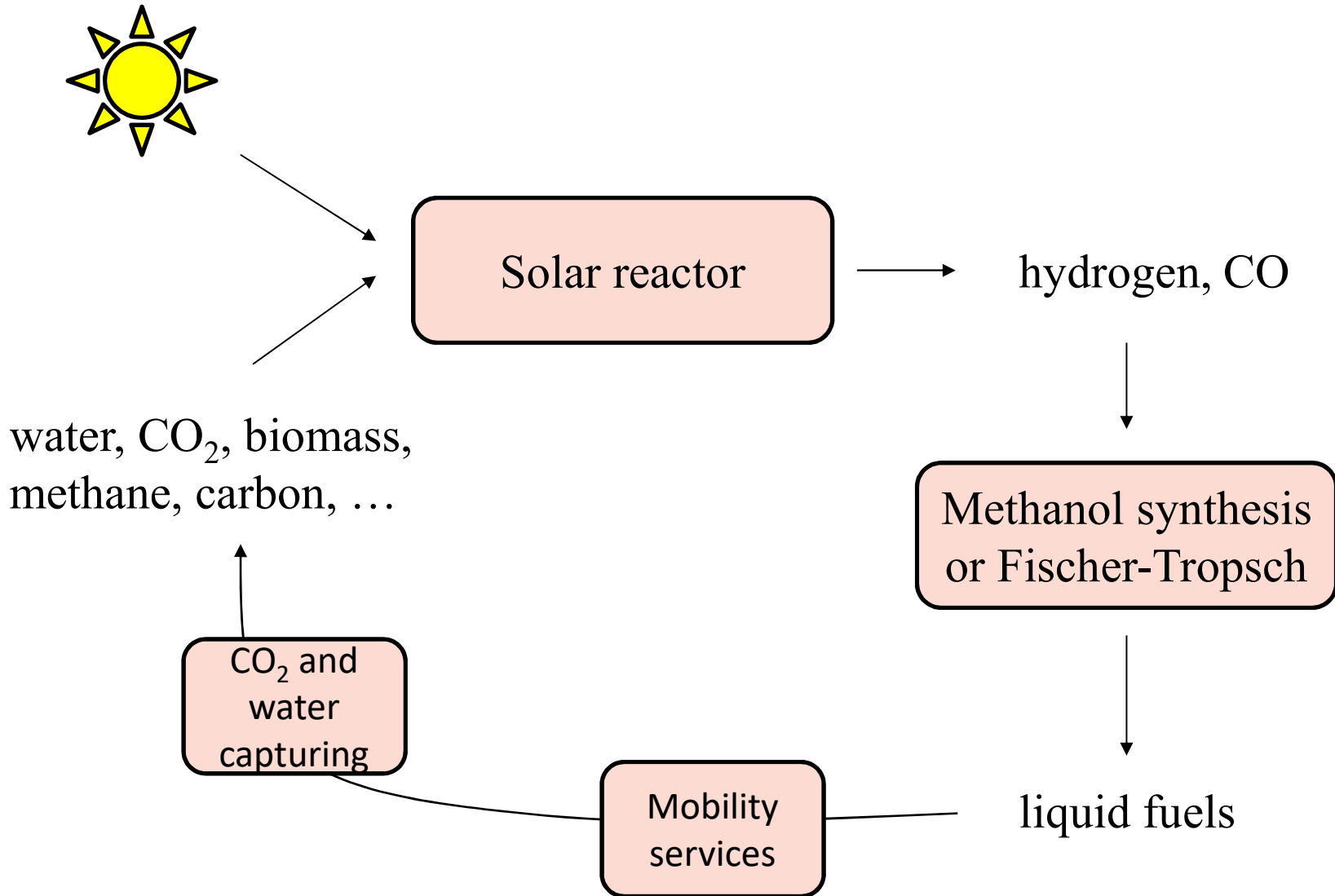
Solar materials

- Solar to materials:
  - In principle any other chemical reaction could be driven by solar thermochemistry or photoelectrochemistry if enthalpy of reaction matches solar irradiation, or equilibrium potential and band edge position matches solar irradiation and material combinations

  - E.g.:
    - Carbothermic reduction of alumina under near vacuum conditions
    - Ammonia production
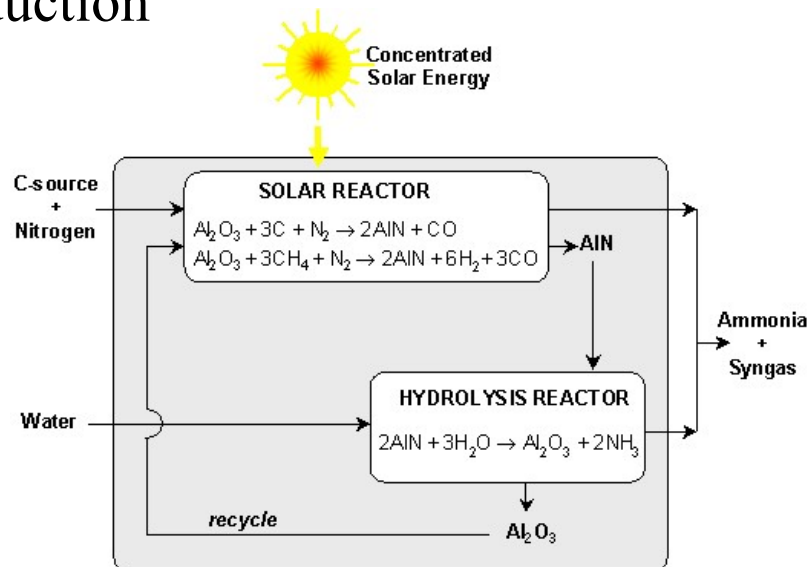
Solar materials

- Thermochemical:
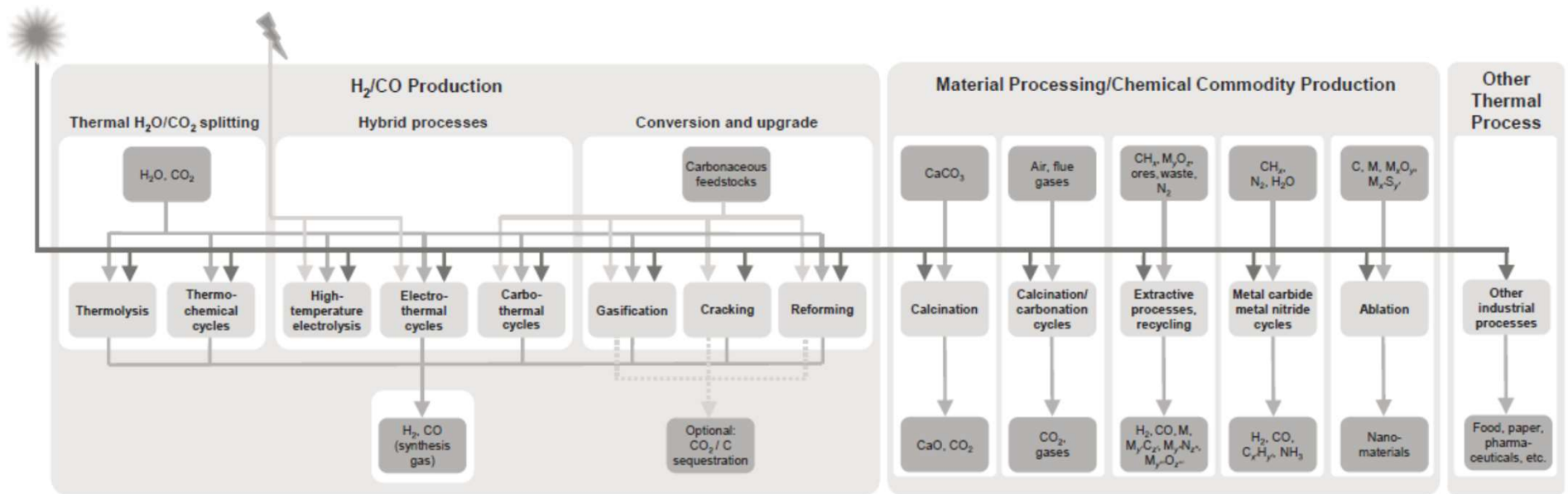
Bader et al., 2016

Solar materials

- (Photo)electrochemical:

Absolute Maximum Value per Energy Input vs Minimum Voltage Required

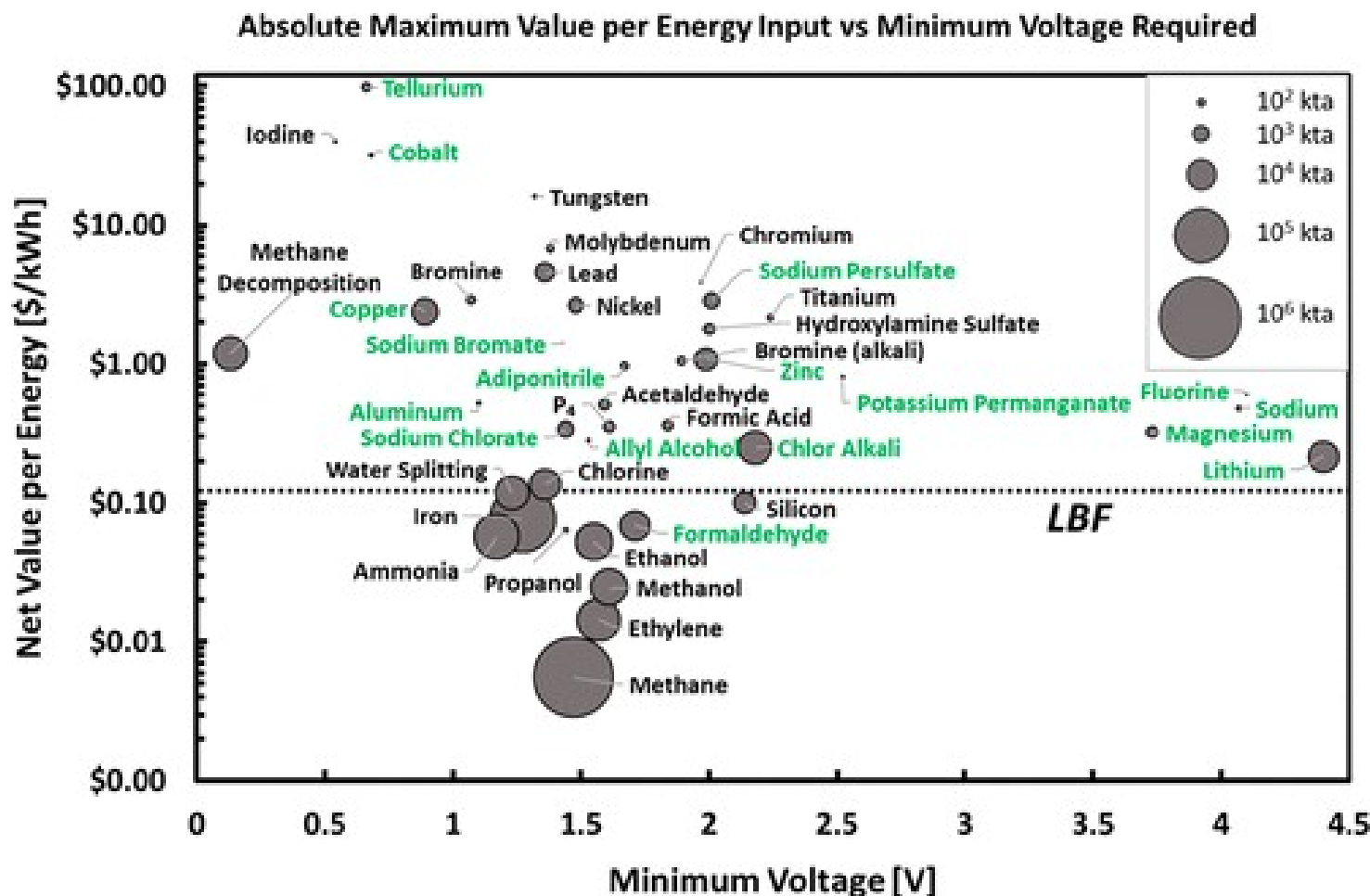Maximum net value per energy input (log scale) plotted versus minimum voltage required for all electrochemical processes or electrochemical equivalents of thermochemical processes. For each point, the width of the circle corresponds to the relative market size. Processes highlighted in green are conducted electrochemically in industry, to any appreciable extent. The lower bound of feasibility (LBF) is plotted as the horizontal dashed line

Palmer et al., Technoeconomics of Commodity Chemical Production Using Sunlight, ACS Sustainable Chemistry & Engineering, 2018

Learning outcomes of todays lecture

- Solar fuels:
  - How can solar energy be converted into fuels?
  - What is a hybrid pathway?
  - Why using fossil fuels together with solar energy?
  - What is solar thermochemistry and how can it be used for solar fuel processing?
  - Why is solar water-splitting via multi-step water splitting cycles preferred compared to direct thermolysis?
  - What is photoelectrochemistry and how can it be used for solar fuel processing?
  - What other chemical commodities or materials can be processed using solar energy?

Solar energy conversion systems

- Literature
  - Review articles:
    - Meier et al., Solar thermochemical production of fuels, Advances in Science and Technology, vol. 74, pp. 303-312, 2010.
    - Lipinski et al., Review of heat transfer research for solar thermochemical applications, Journal of Thermal Science and Engineering Applications, 5: 021005, 2013.
    - Walter et al., Solar water splitting cells, Chemical Reviews, vol. 110, pp. 6446–6473, 2010.