Renewable Energy

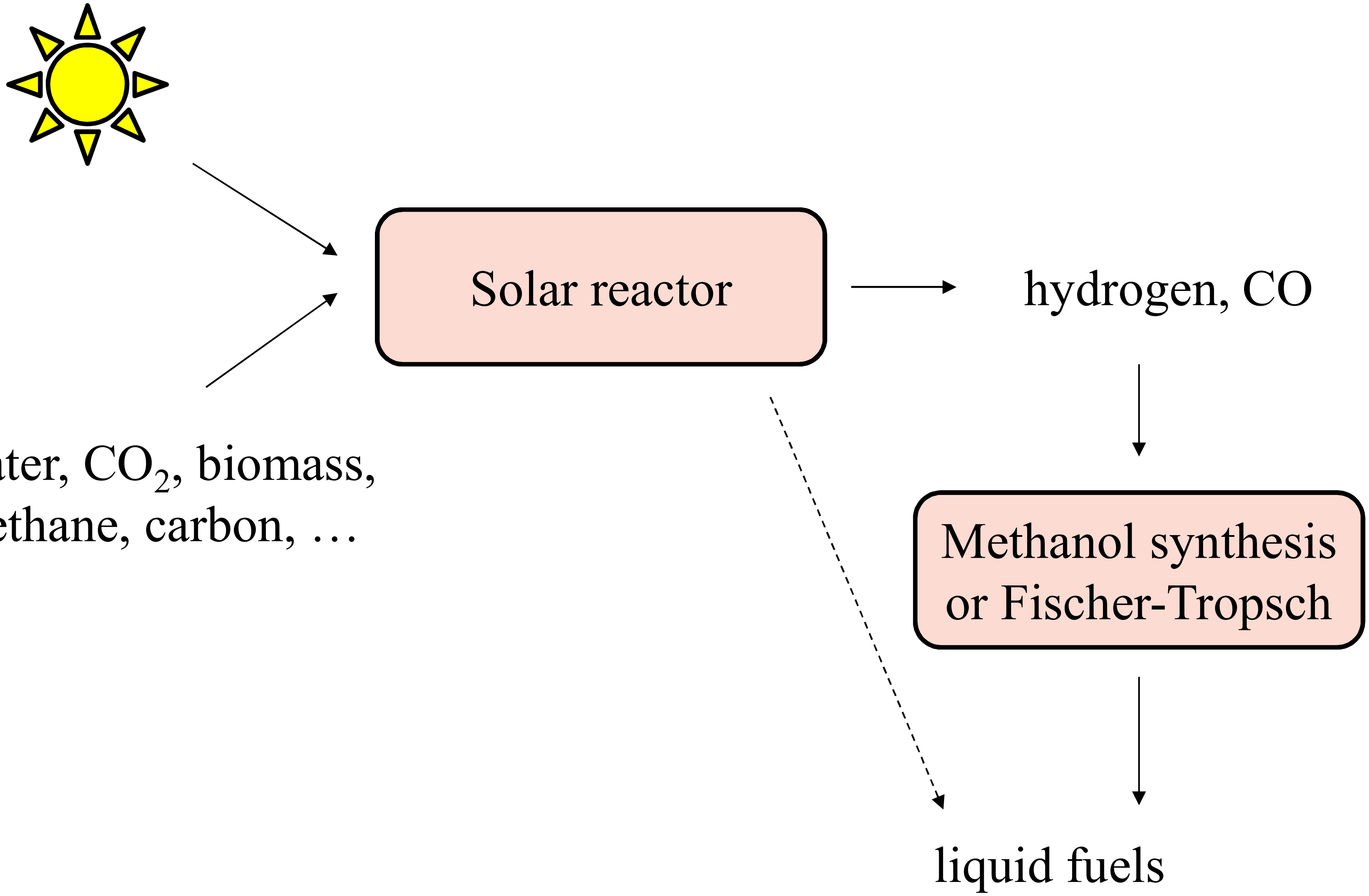
- Outline:
  - Conversion pathways solar-to-fuel
  - Hybrid pathways
  - Solar thermochemistry
  - Photochemistry

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:



Solar reactor

hydrogen, CO

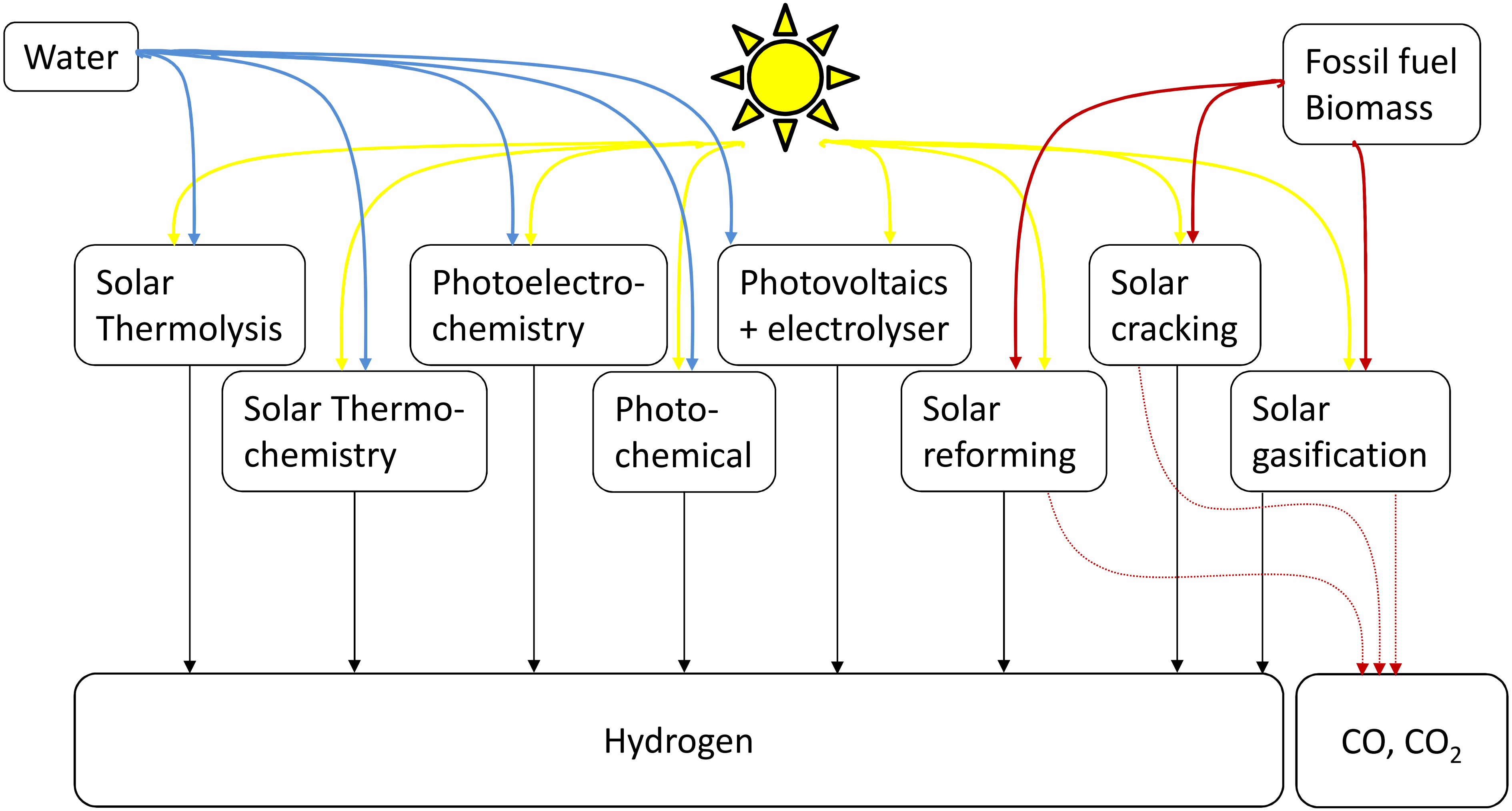
water, CO_2, biomass, methane, carbon, …

Methanol synthesis or Fischer-Tropsch

liquid fuels

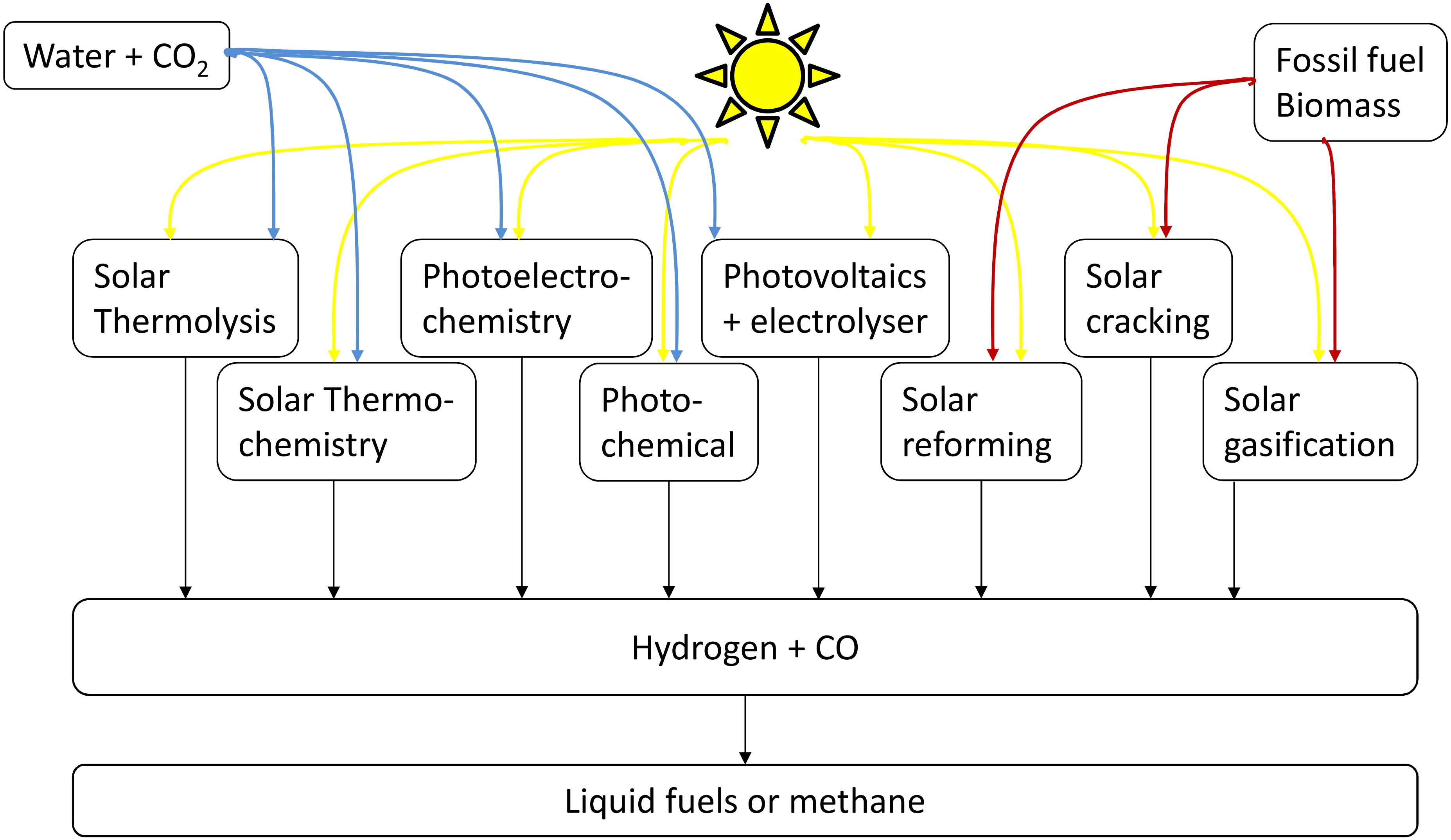
Conversion pathways

- Solar to hydrogen:



Conversion pathways

- Solar to synthesis gas (H_2+CO):



Water + CO_2

Fossil fuel
Biomass

Solar
Thermolysis

Solar Thermo-
chemistry

Photoelectro-
chemistry

Photo-
chemical

Photovoltaics
+ electrolyser

Solar
reforming

Solar
cracking

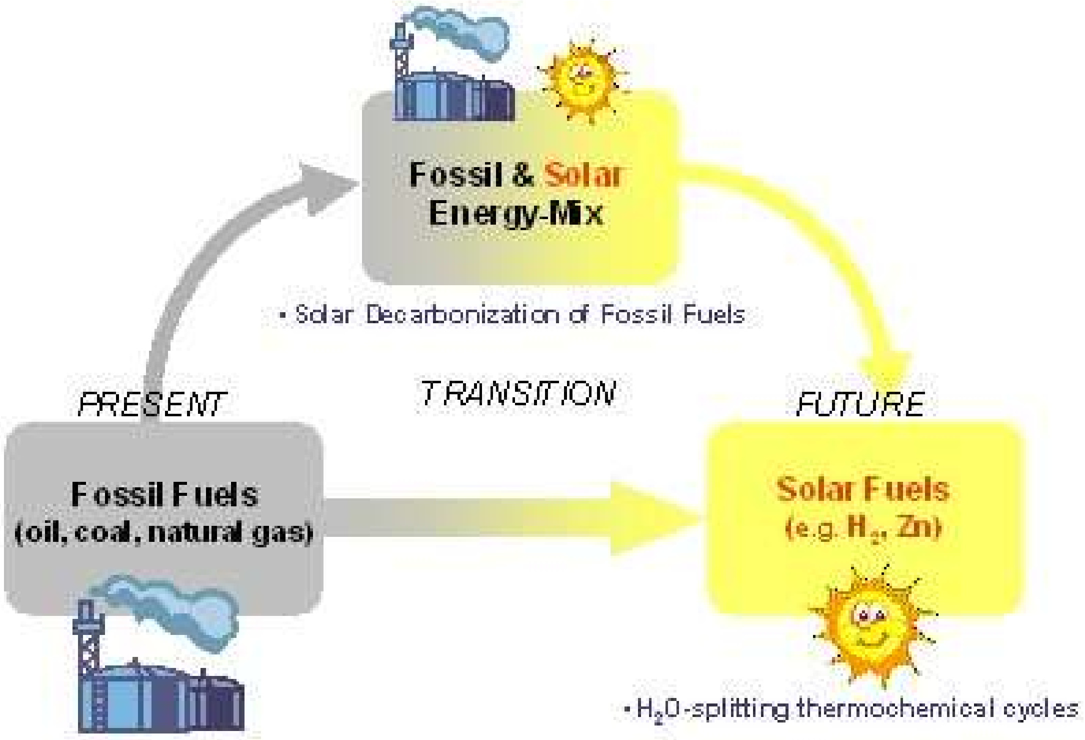
Solar
gasification

Hydrogen + CO

Liquid fuels or methane

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



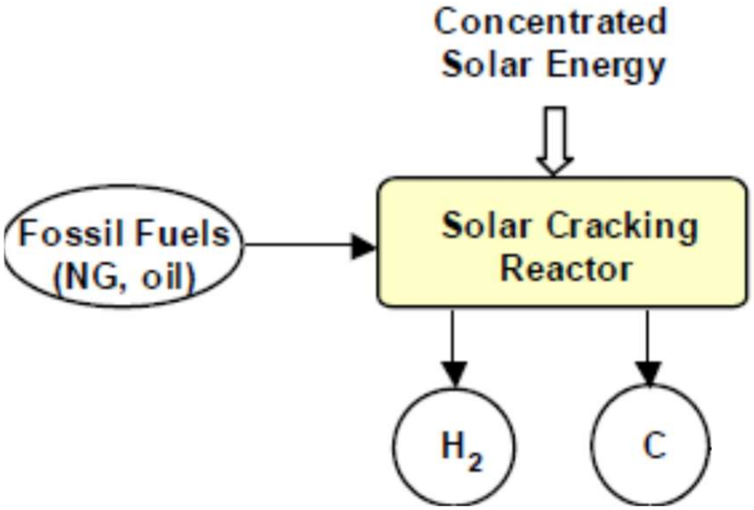
Hybrid solar conversion

- **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

$$CH_4 \rightarrow C + 2H_2 \ (\Delta H = 74.85 \text{ kJ/mol})$$

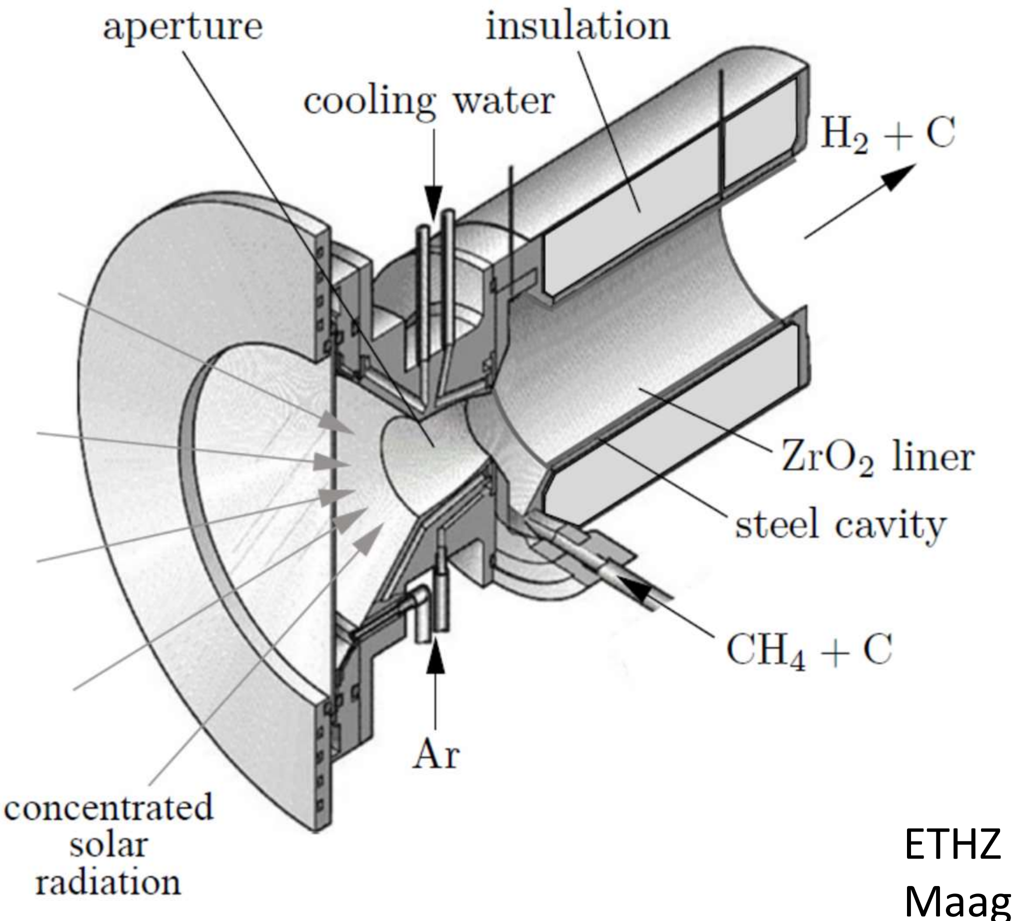
- General:

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



Hybrid solar conversion

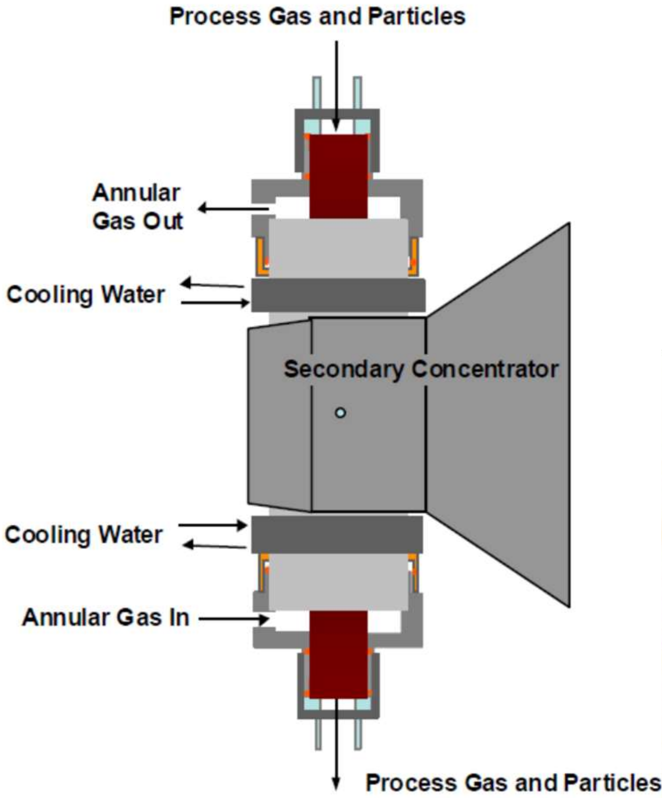
- Solar reactors developed for thermal cracking:



ETHZ and PSI
Maag et al., 2010.

Hybrid solar conversion

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



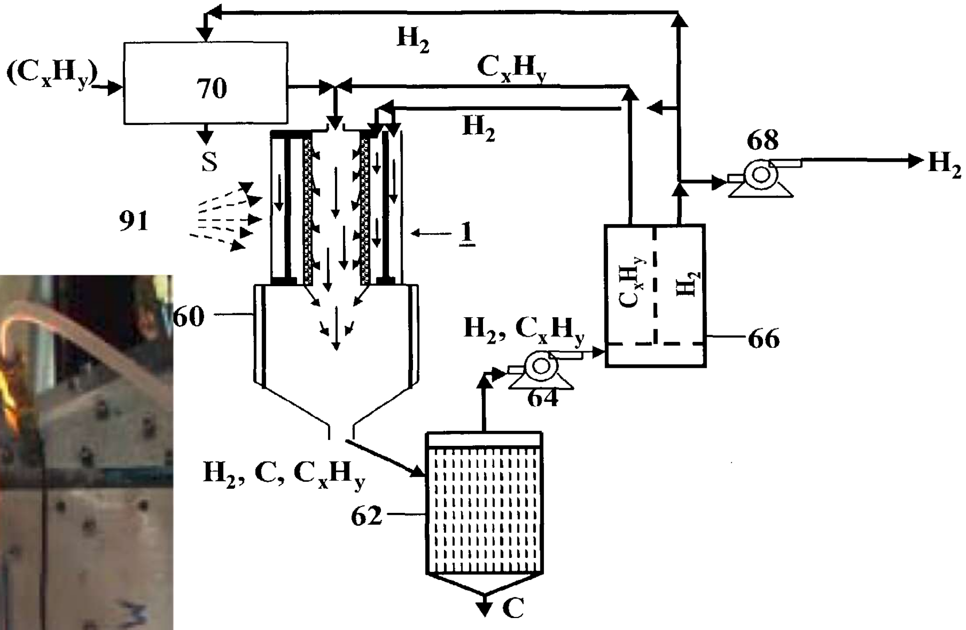


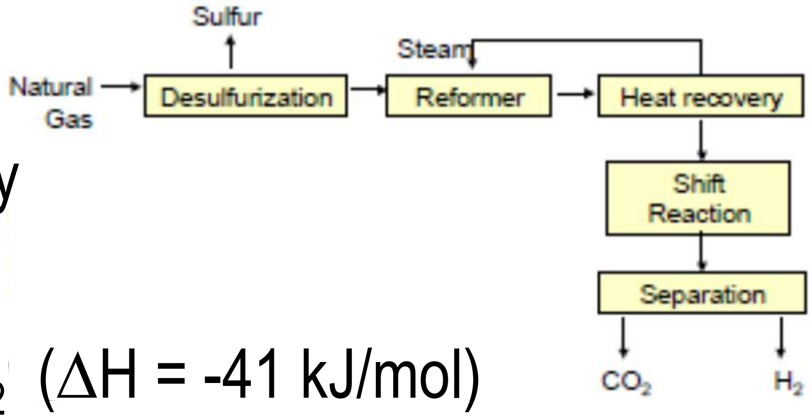
Figure 4

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



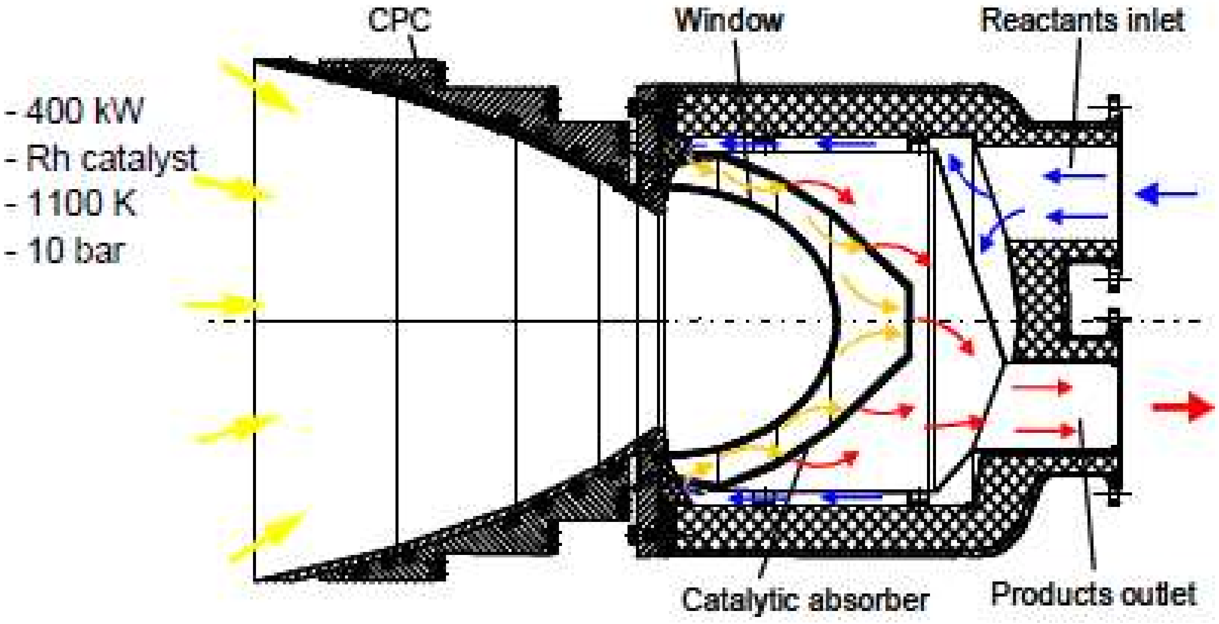
water gas shift: $CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H = -41 \text{ kJ/mol})$

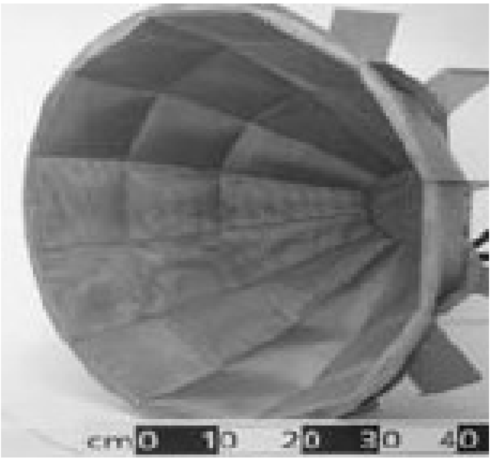
Hybrid solar conversion

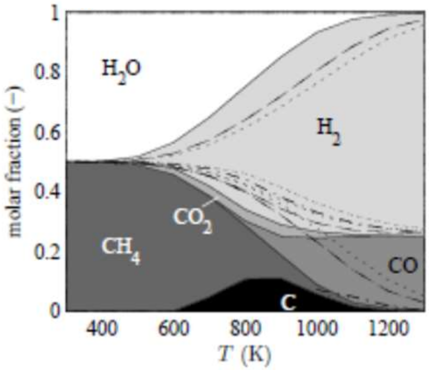
- Solar reactors developed for steam reforming

  Solar gasification of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$), DLR

  SOLREF project







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

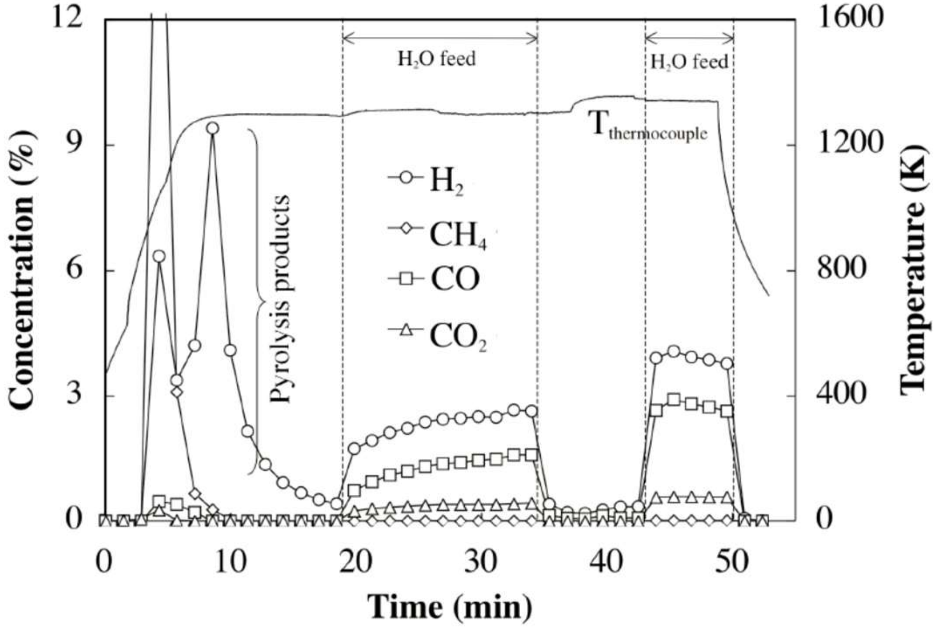
$$C + H_2O \rightarrow CO + H_2$$

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

$$\mathrm{CH}_x\mathrm{O}_y\mathrm{S}_z\mathrm{N}_u + (1-y)\mathrm{H_2O} = \frac{1}{2}(x+2(1-y)-2z)\mathrm{H_2} + \mathrm{CO} + z\mathrm{H_2S} + \frac{1}{2}u\mathrm{N_2}$$

Hybrid solar conversion

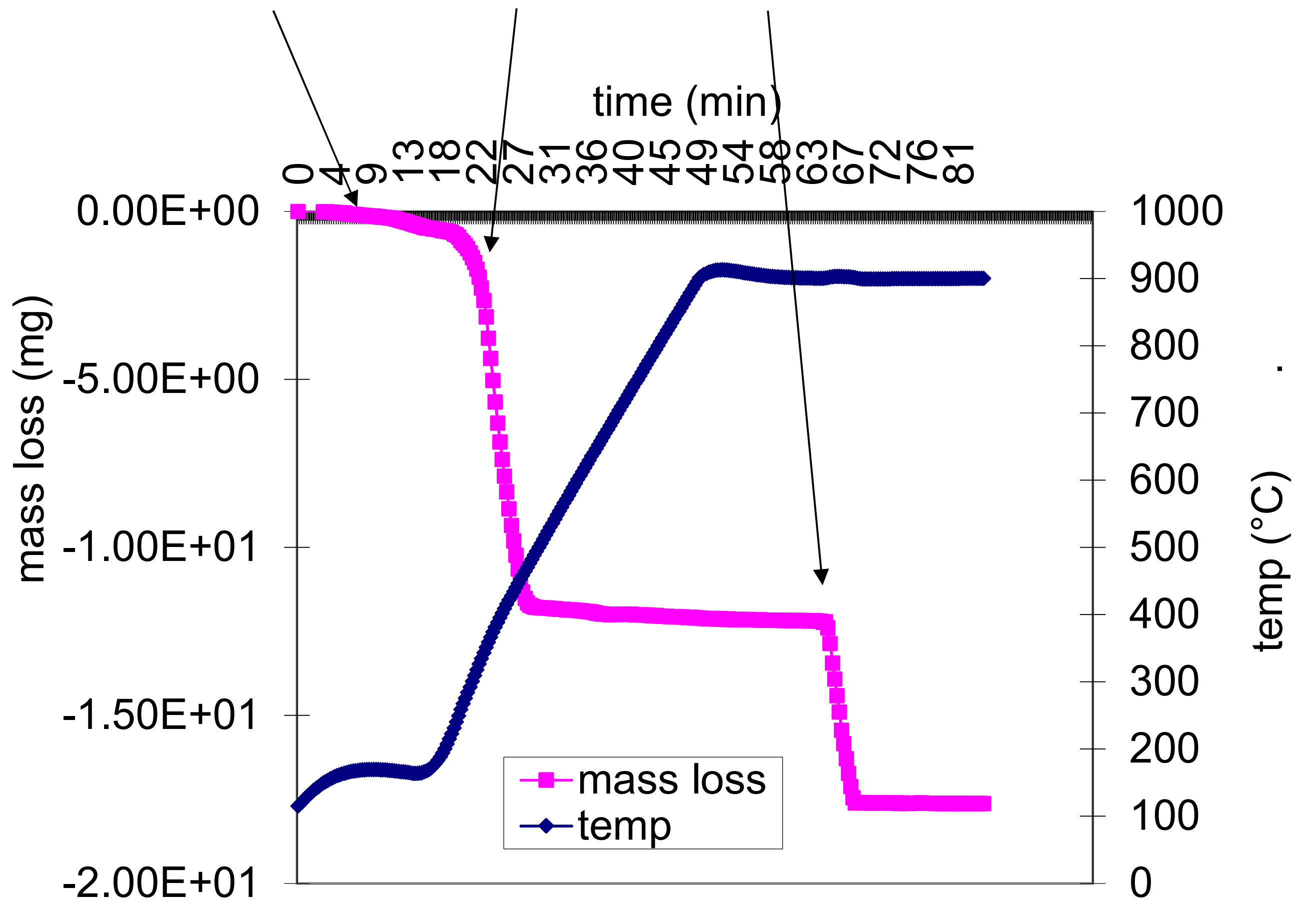
- Consists of (sequential or simultaneous):
  - Dehydration
  - Pyrolysis (thermal decomposition in the absence of O_2, devolatilization)
  - Gasification (heterogeneous gas-soild reaction of pyrolysis residue with reactive gas)
  - Combustion
  - Water-gas-shift



Trommer, Diss ETH, 2006.

Hybrid solar conversion

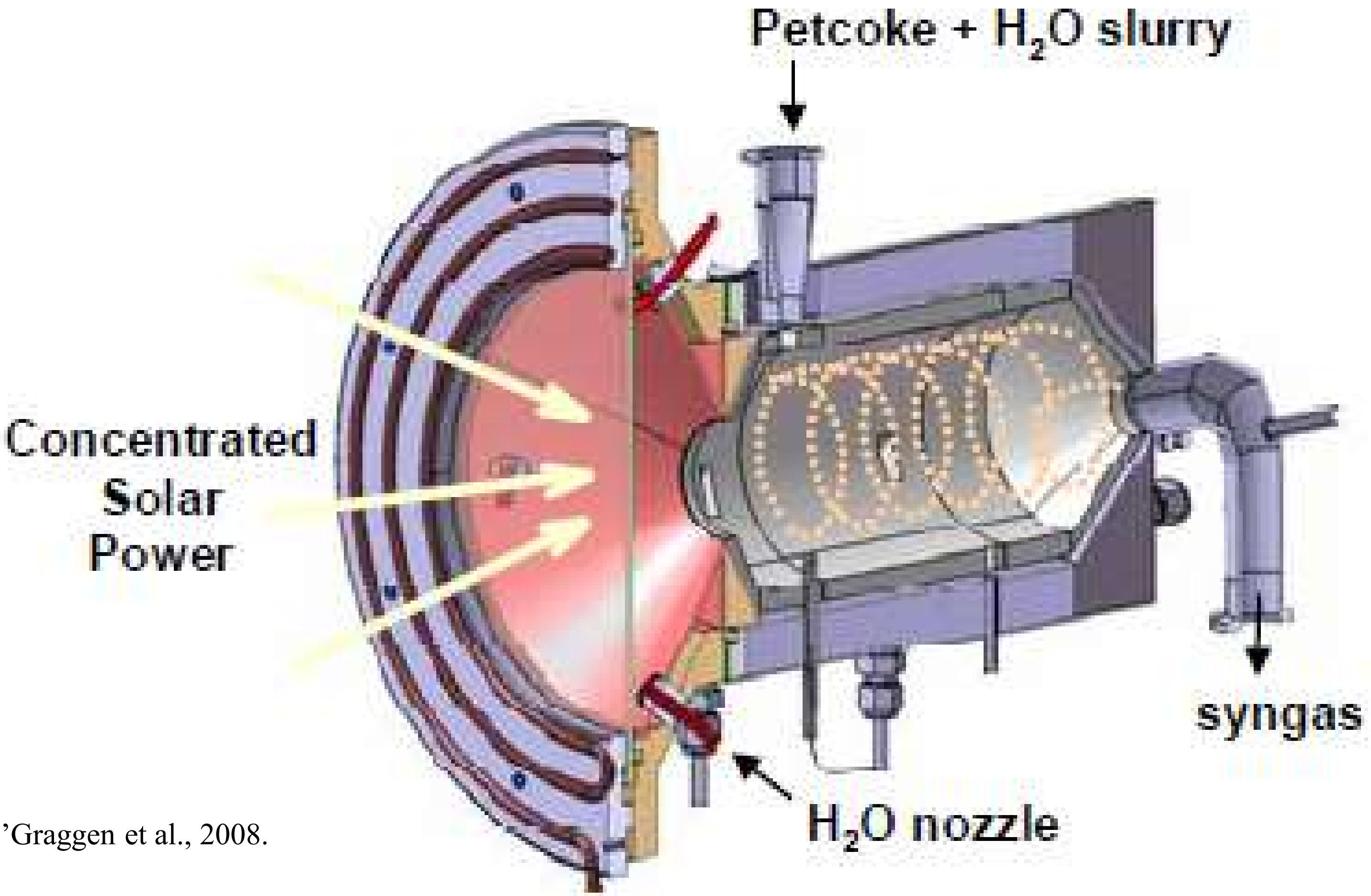
- Gasification (thermographimetric experiment):



Dehydration, Pyrolysis, Gasification

Hybrid solar conversion

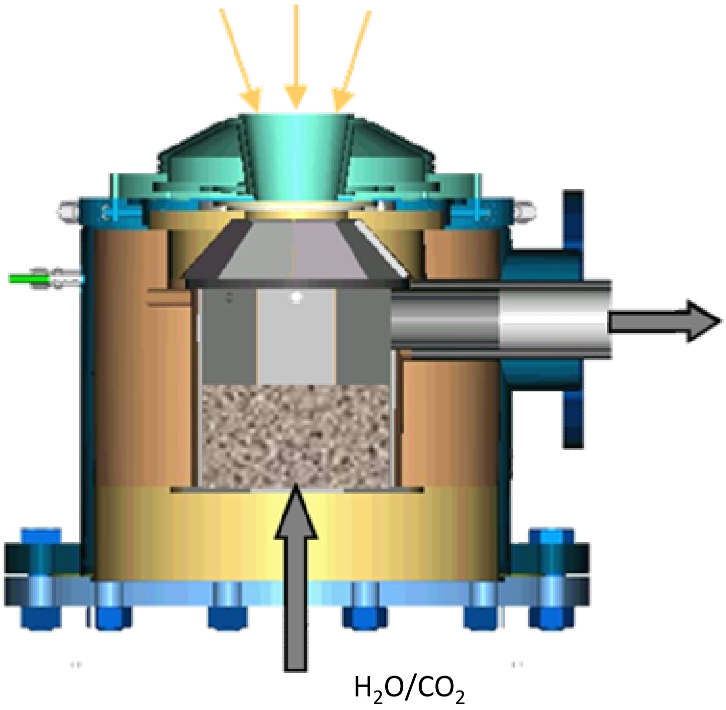
- Solar reactors developed for gasification:
  - Steam gasification of petcoke, ETH

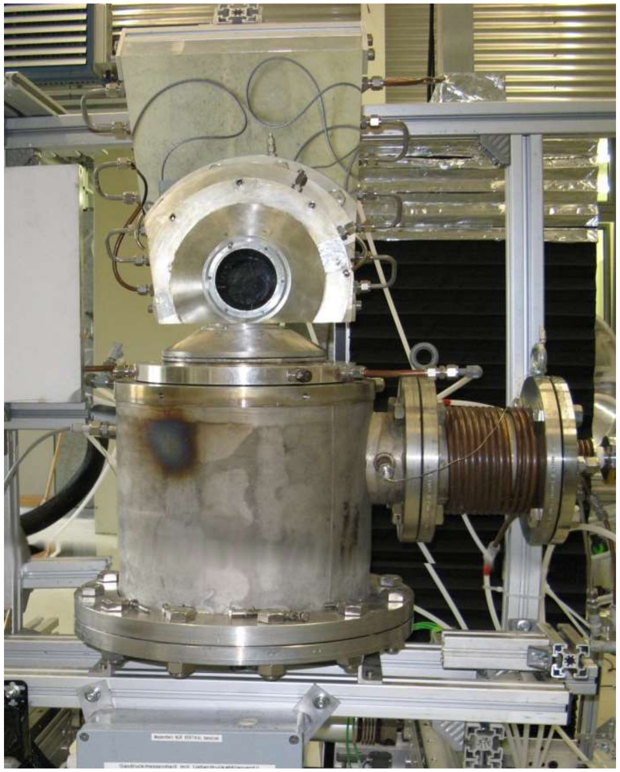


Z’Graggen et al., 2008.

Hybrid solar conversion

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

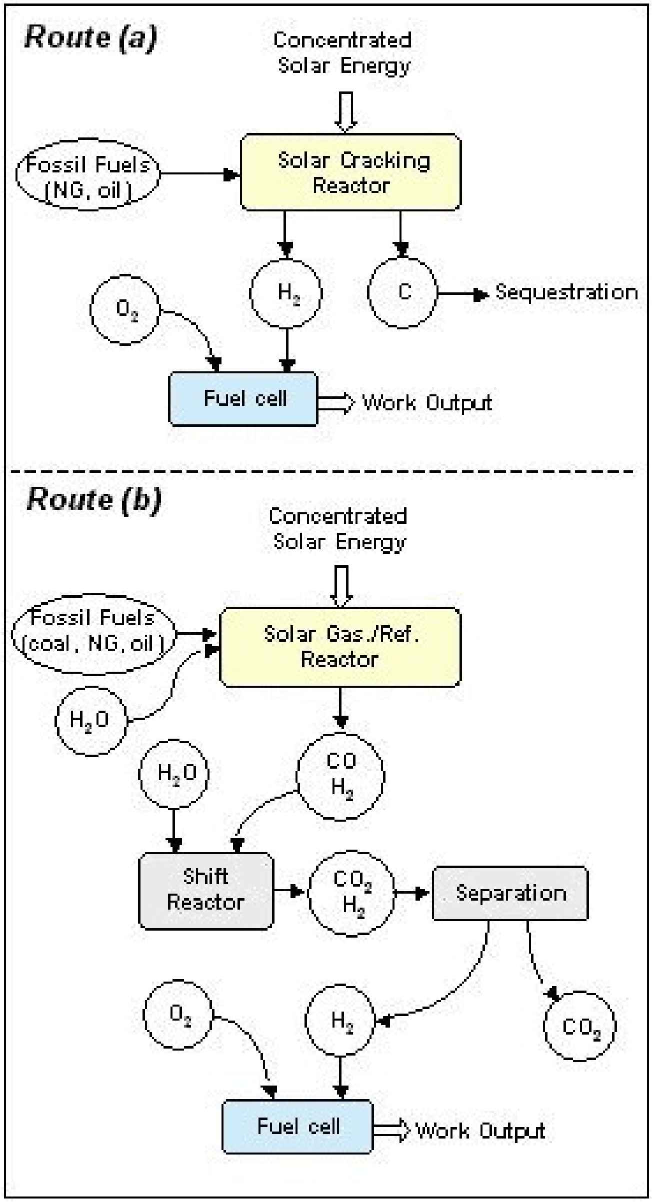




Piatkowski et al., 2010.

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

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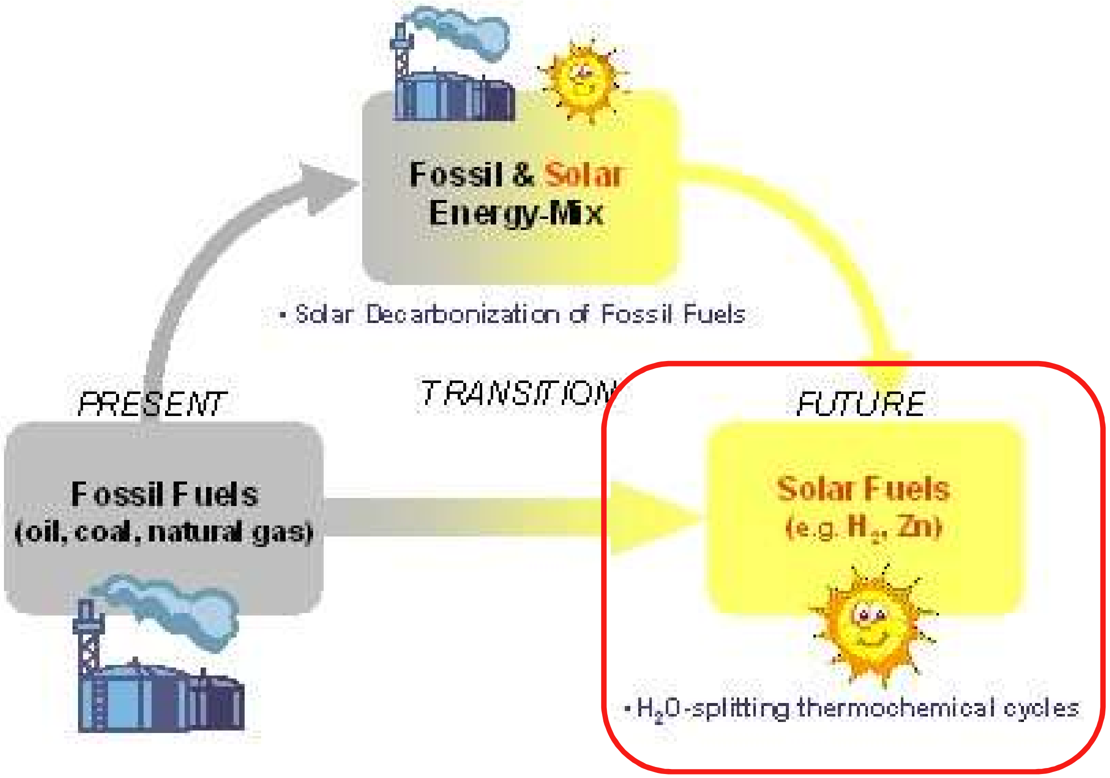
  - Solar thermochemistry
  - Photochemistry

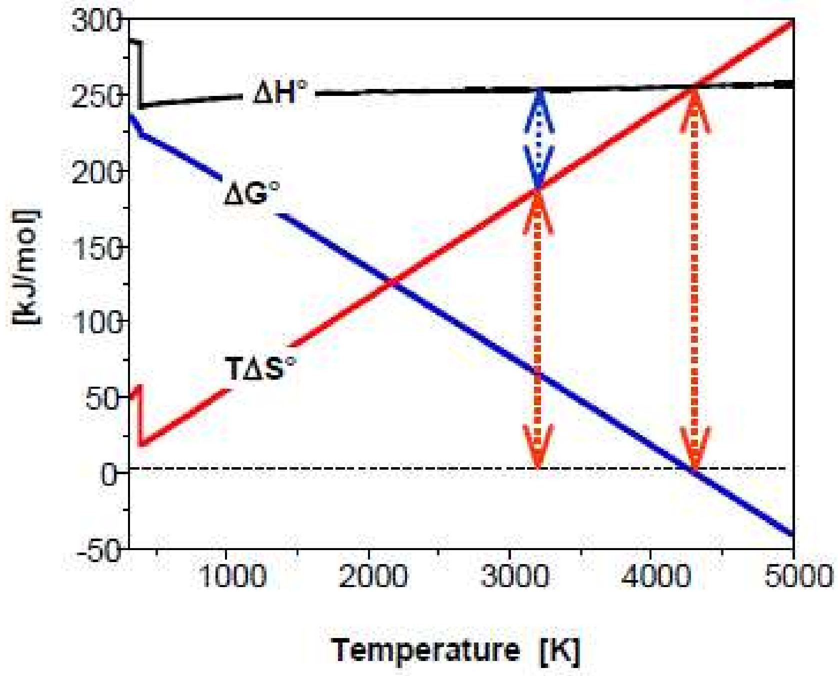
Solar thermolysis and thermochemistry

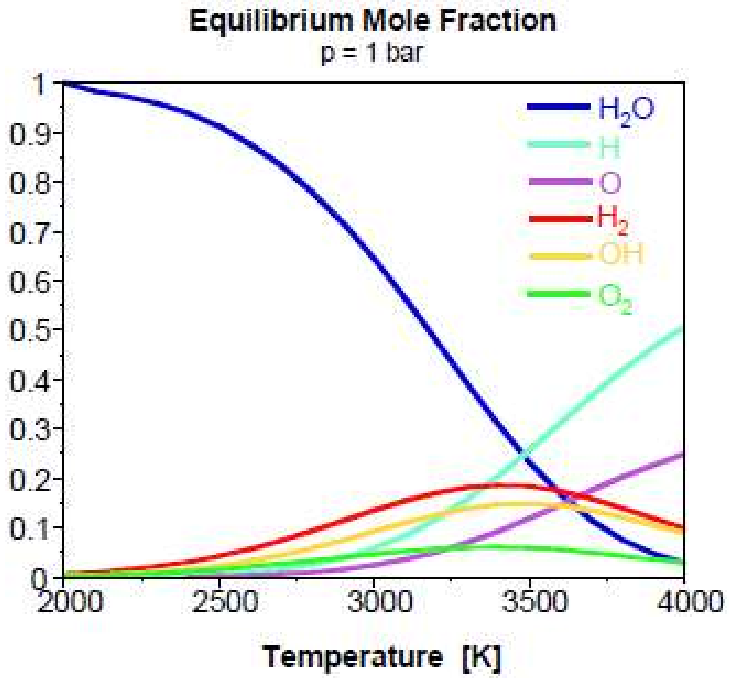
- In the transition to a renewable future, hybrid pathways using fossil fuels exclusively as chemical source for the fuel production and solar energy as the process heat



Solar thermolysis

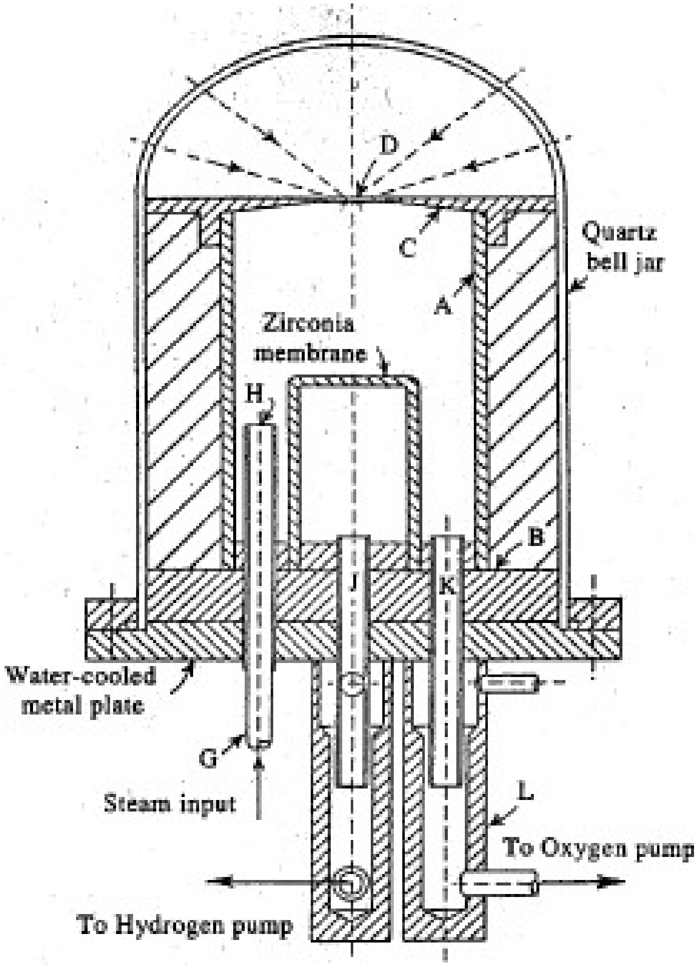
- Solar **thermolysis**
  - Solar energy is used as process heat of chemical reaction
  - Direct thermolysis of water: $H_2O \rightarrow 1/2O_2 + H_2$





Solar thermolysis

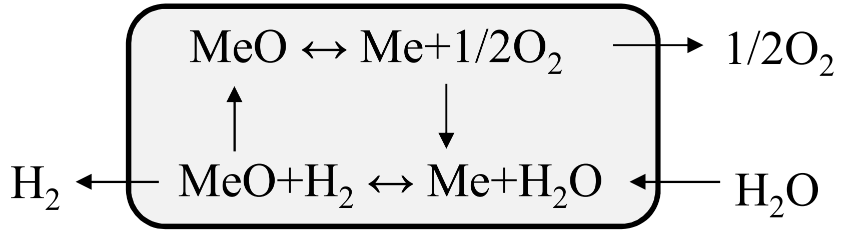
- Reactor concept for solar thermolysis
  - Product separation by:
    - High temperature membranes
    - Rapid quenching of products



Kogan et al., 1998.

Solar thermochemistry

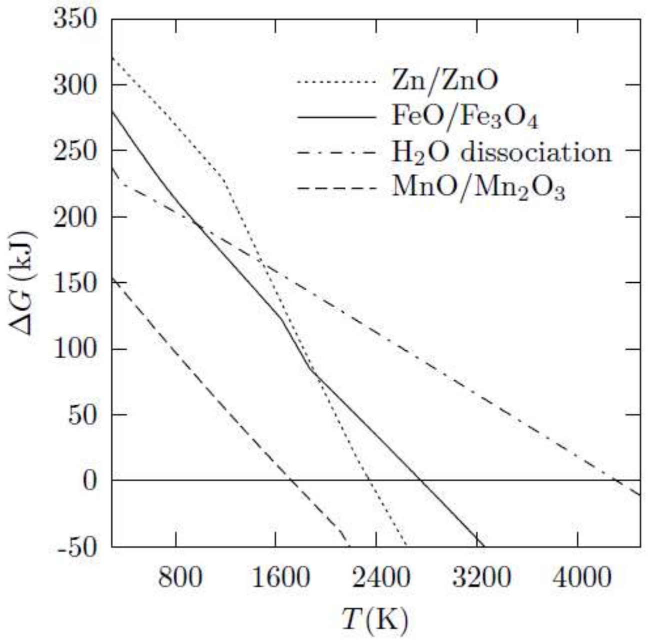
- Solar **thermochemical** cycles
  - Solar energy is used as process heat of chemical reaction
  - Multi-step water-splitting reactions:



$MeO \leftrightarrow Me + 1/2O_2$ → $1/2O_2$

H_2 ← $MeO + H_2 \leftrightarrow Me + H_2O$ ← 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 …



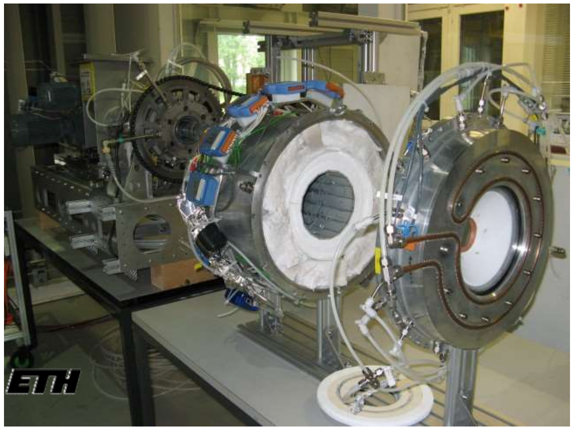
Solar thermochemistry

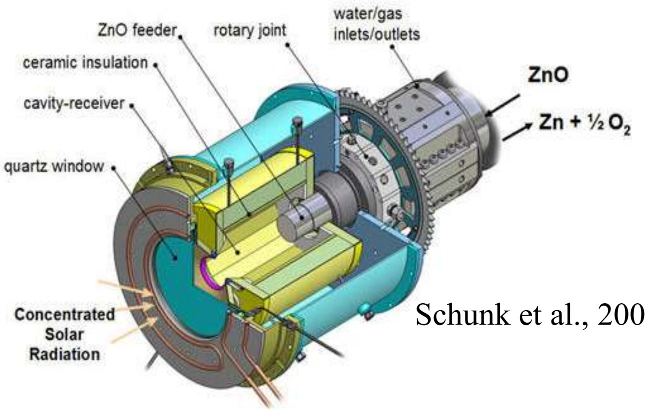
- Possible redox pairs for two-step cycles:

Cycle	Reactions	Cycle	Reactions
Zn/ZnO	$ZnO \rightarrow Zn + O_2$	SoO_2/SiO	$SiO_2 \rightarrow SiO + 1/2\ O_2$
	$Zn + H_2O \rightarrow ZnO+H_2$		$SiO+H_2O \rightarrow SiO_2+H_2$
Fe_3O_4/FeO	$Fe_3O_4 \rightarrow 3\ FeO + ½\ O_2$	W/WO_3	$WO_3 \rightarrow W+3/2\ O_2$
	$3\ FeO + H_2O \rightarrow Fe_3O_4 + H_2$		$W+3H_2O \rightarrow WO_3+3H_2$
In_2O_3/In_2O	$In_2O_3 \rightarrow In_2O+1/2\ O_2$	Hg/HgO	$Hg+H_2O \rightarrow HgO+H_2$
	$In_2O+2H_2O \rightarrow In_2O_3+2H_2$		$HgO \rightarrow Hg+1/2O_2$
SnO_2/Sn	$SnO_2 \rightarrow Sn+O_2$	Cd/CdO	$Cd+H_2O \rightarrow CdO+H_2$
	$Sn+2H_2O \rightarrow SnO2+2H_2$		$CdO \rightarrow Cd+1/2O_2$
$MnO/MnSO_4$	$MnSO_4 \rightarrow MnO+SO_2+1/2O_2$	CO/CO_2	$CO+H_2O \rightarrow CO_2+H_2$
	$MnO+H_2O+SO_2 \rightarrow MnSO_4+H_2$		$CO_2 \rightarrow CO+1/2O_2$
$FeO/FeSo_4$	$FeSO_4 \rightarrow FeO+SO_2+1/2O_2$	Ce_2O_3/CeO_2	$CeO_2 \rightarrow Ce_2O_3$
	$FeO+H_2O+SO_2 \rightarrow FeSO_4+H_2$		$Ce_2O_3+H_2O \rightarrow 2CeO_2+H_2$
$CoO/CoSO_4$	$CoSO_4 \rightarrow CoO+SO_2+1/2O_2$	Mg/MgO	$MgO \rightarrow Mg+1/2O_2$
	$CoO+H_2O+SO_2 \rightarrow CoSO_4+H_2$		$Mg+H_2O \rightarrow MgO+H_2$
$Fe_3O_4/FeCl_2$	$Fe_3O_4+6HCl \rightarrow 3FeCl_2+3H_2O+1/2O_2$	SnO/SnO2	$SnO_2 \rightarrow SnO+1/2O_2$
	$3FeCl_2+4H_2O \rightarrow Fe_3O_4+6HCl+H_2$		$SnO+H_2O \rightarrow SnO_2+H_2$
Mo/Mo_2	$MoO_2 \rightarrow Mo+O_2$		
	$Mo+2H_2O \rightarrow MoO_2+2H_2$		

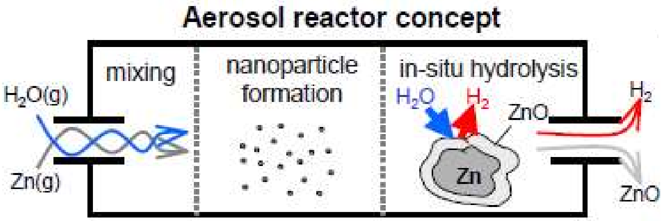
Solar thermochemistry

- 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.



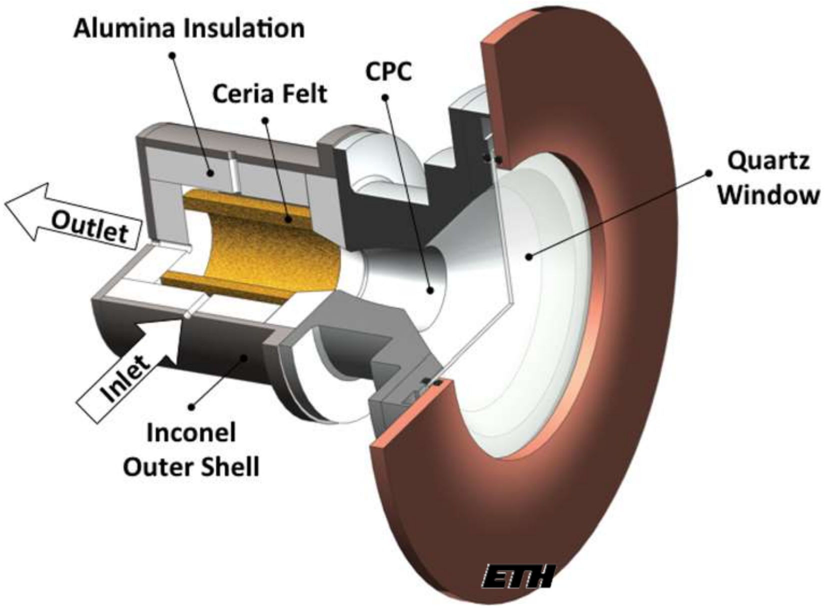
Melchior et al., 2009.

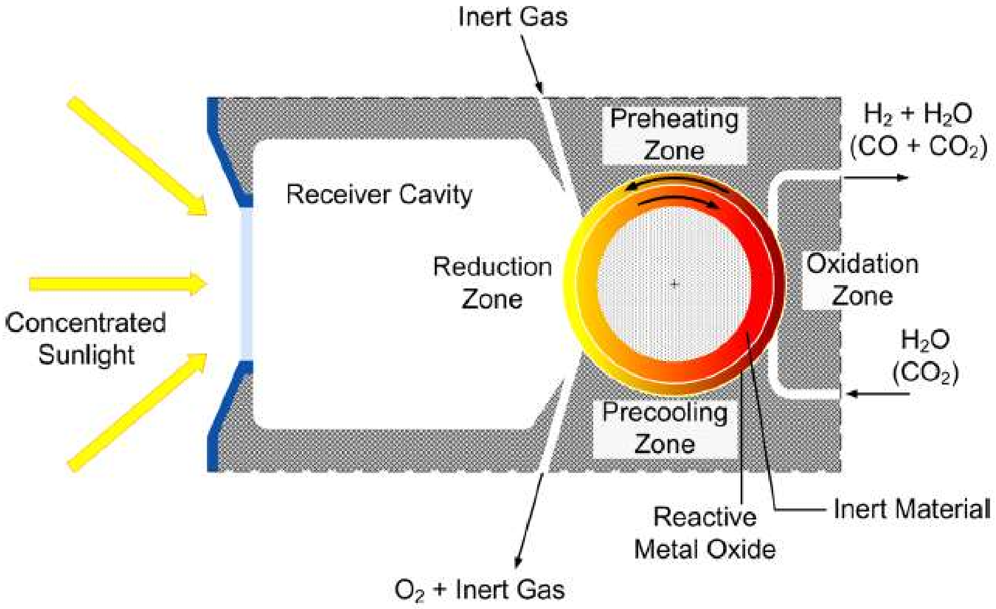
Solar thermochemistry

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

ETH Zürich

University of Minnesota





Temperature in reduction reaction: ~ 1800 K

Temperature in oxidation reaction: ~ 1200 K

Renewable Energy

- Outline:
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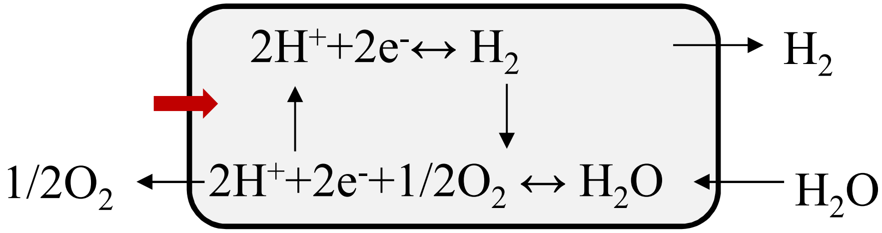
  - Photochemistry

Photoelectrochemistry

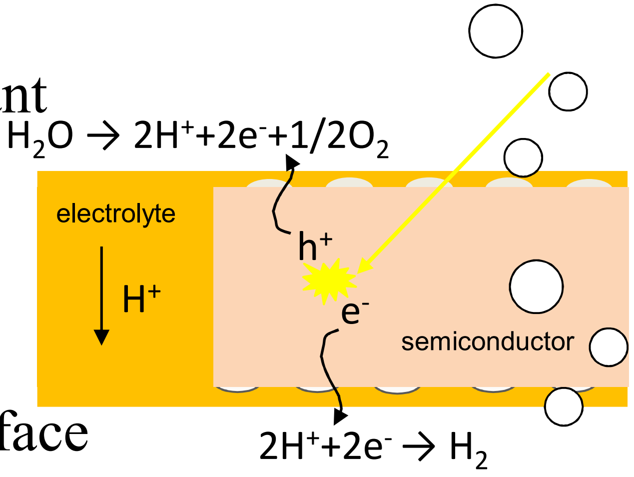
- Photoelectrochemical processes
  - Solar energy is used as photon energy for the internal production of charge, which is separated at the solid-liquid junction
  - Multi-step water-splitting reactions (E_0=1.23 V):



$2H^+ + 2e^- \leftrightarrow H_2$ → H_2

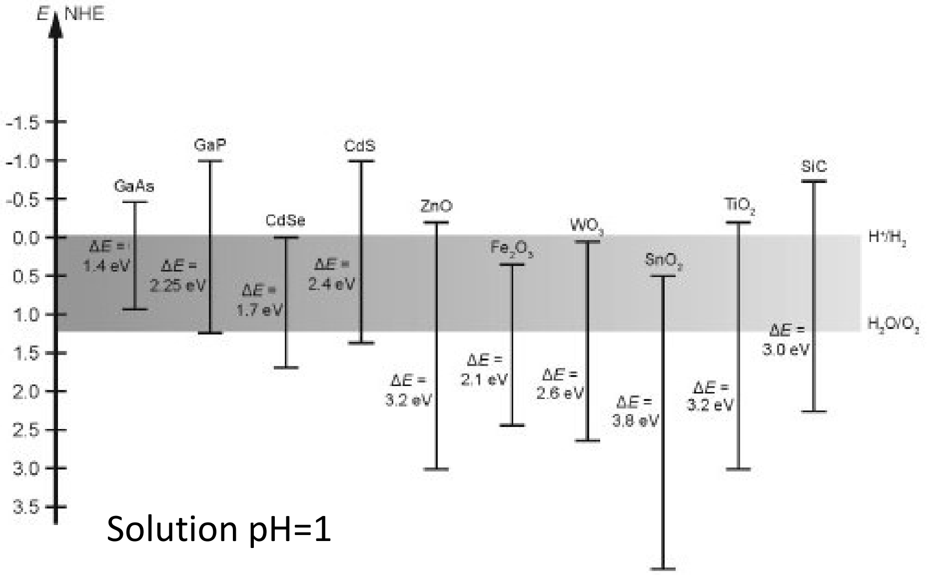
$1/2O_2$ ← $2H^+ + 2e^- + 1/2O_2 \leftrightarrow H_2O$ ← H_2O

  - 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



Solution pH=1

Photoelectrochemistry

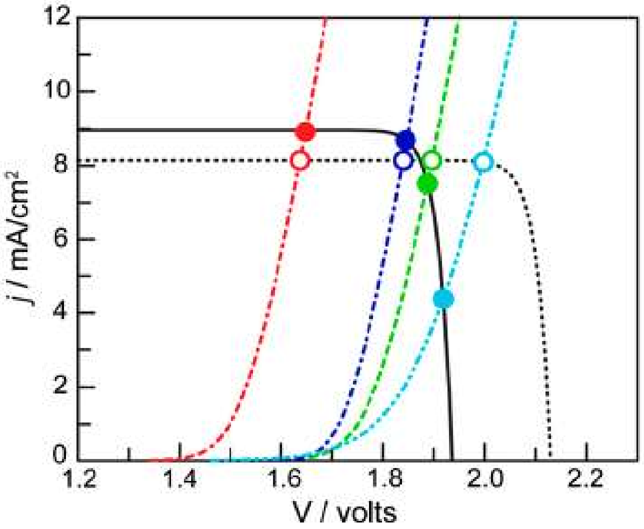
- Calculations:
  - Photoactive material(s) will show diode-like current-potential behavior:

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

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

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

  - 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:

$$i_R = i_{0a/c}\left[\exp\left(\frac{\alpha_a F\left(\Phi_s - \Phi_l - E_0\right)}{RT}\right) - \exp\left(\frac{\alpha_c F\left(\Phi_s - \Phi_l - E_0\right)}{RT}\right)\right]$$

    - Ohmic losses account for resistances in electrolyte, membrane, and solid conductor:

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

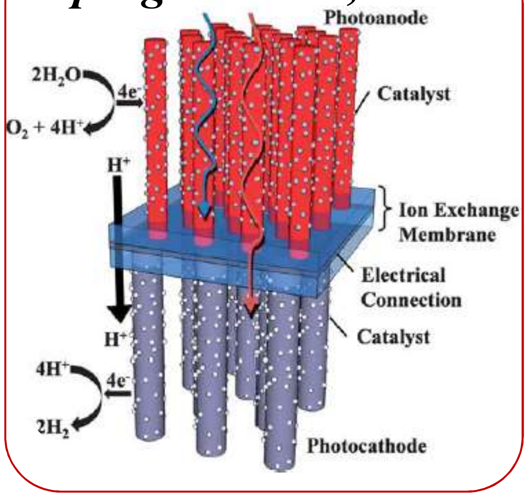
Characteristic ion and electron path length

resistivity

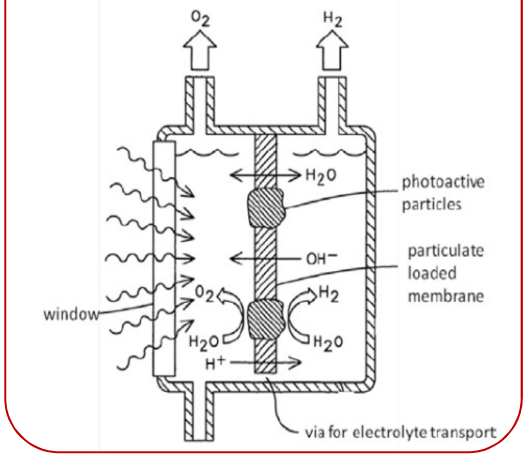
Photoelectrochemistry

- Proposed devices

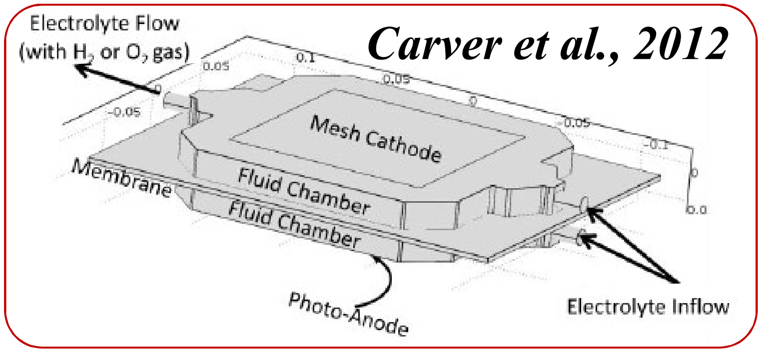
Spurgeon et al., 2011



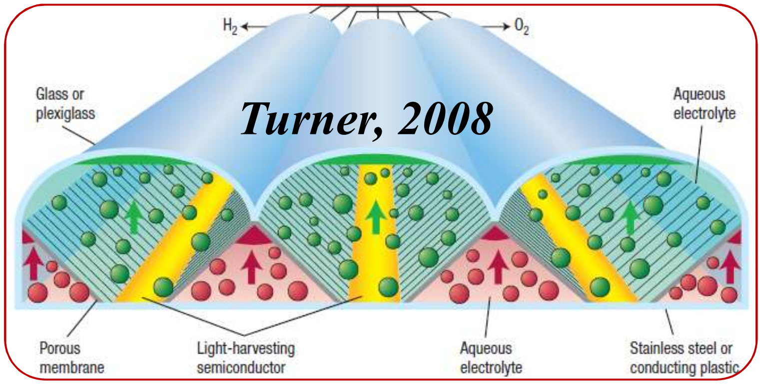
Miller et al., 2007



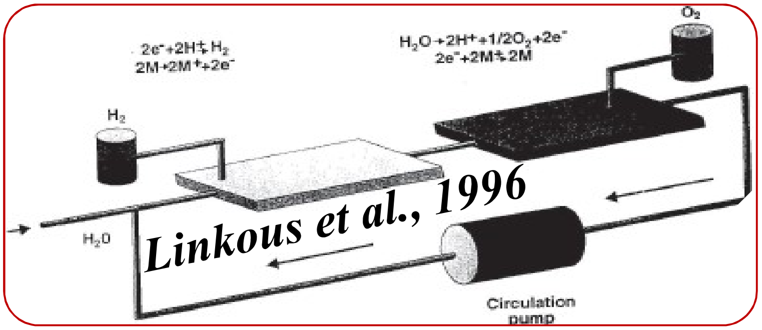
Carver et al., 2012



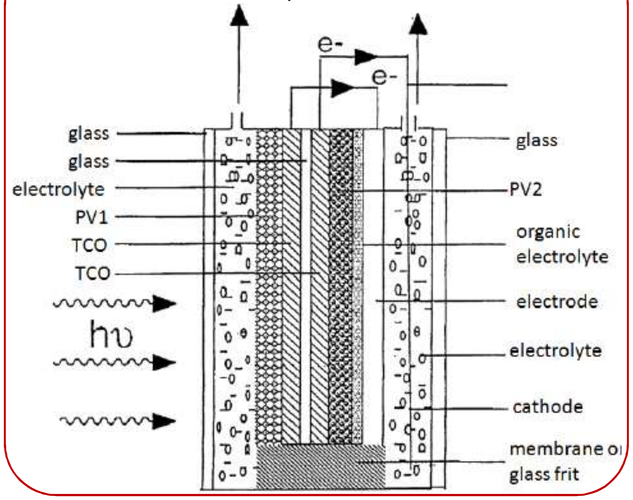
Turner, 2008



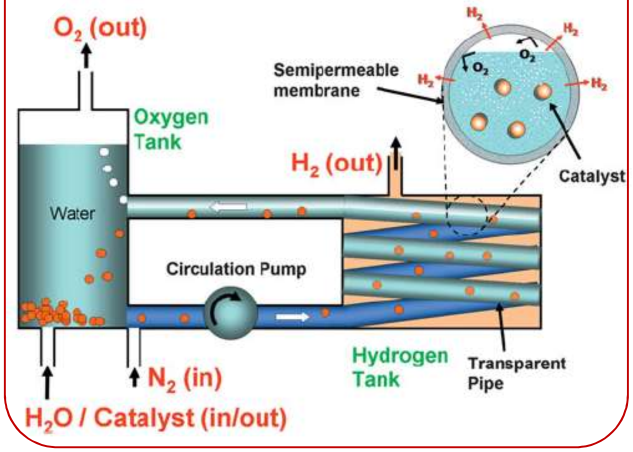
Linkous et al., 1996



Grätzel et al., 2007



Parkinson et al., 2011

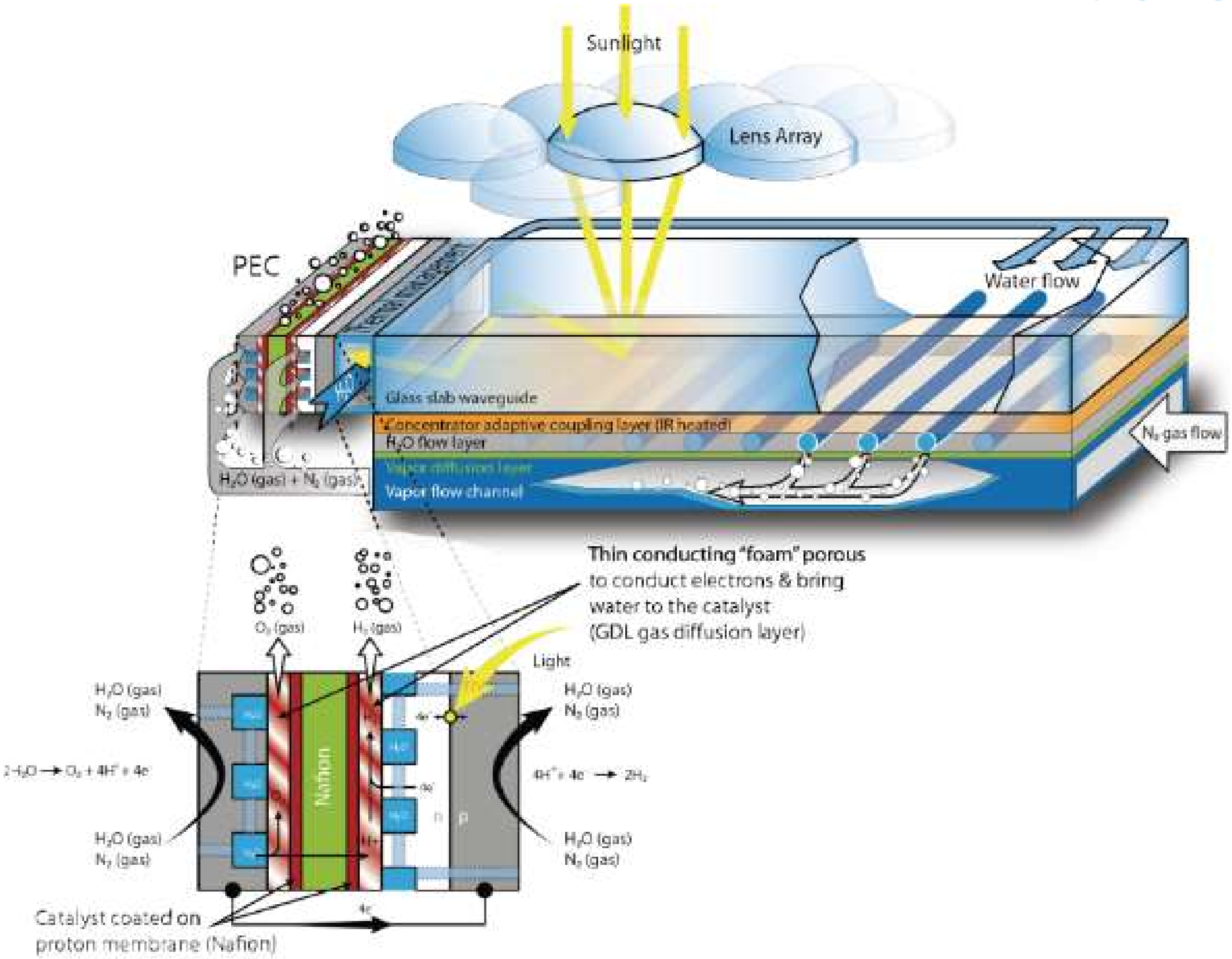


Photoelectrochemistry

- Proposed devices

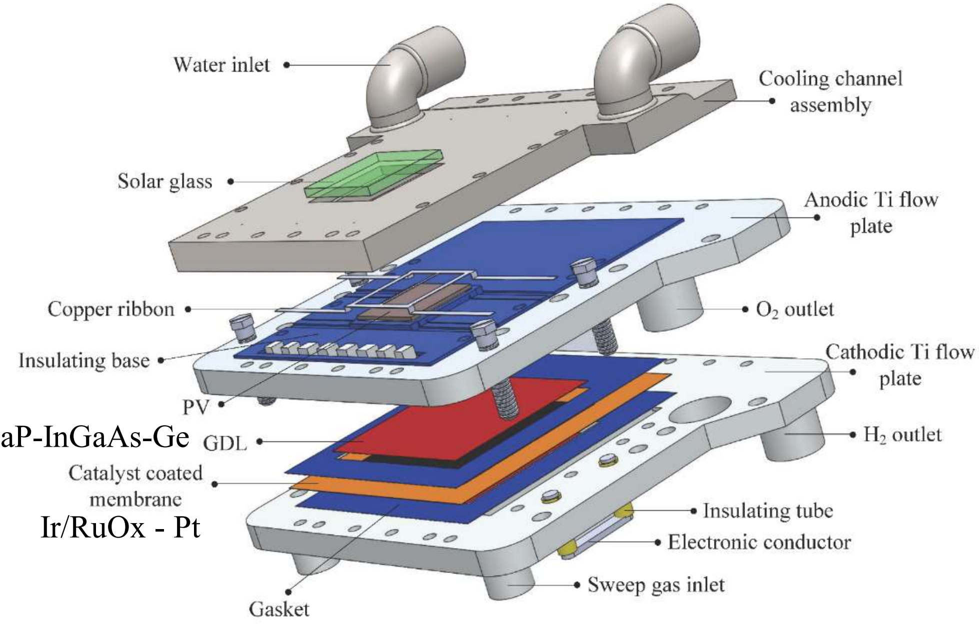
SHINE
Solar Hydrogen Integrated Nano Electrolysis

ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE



Photoelectrochemistry

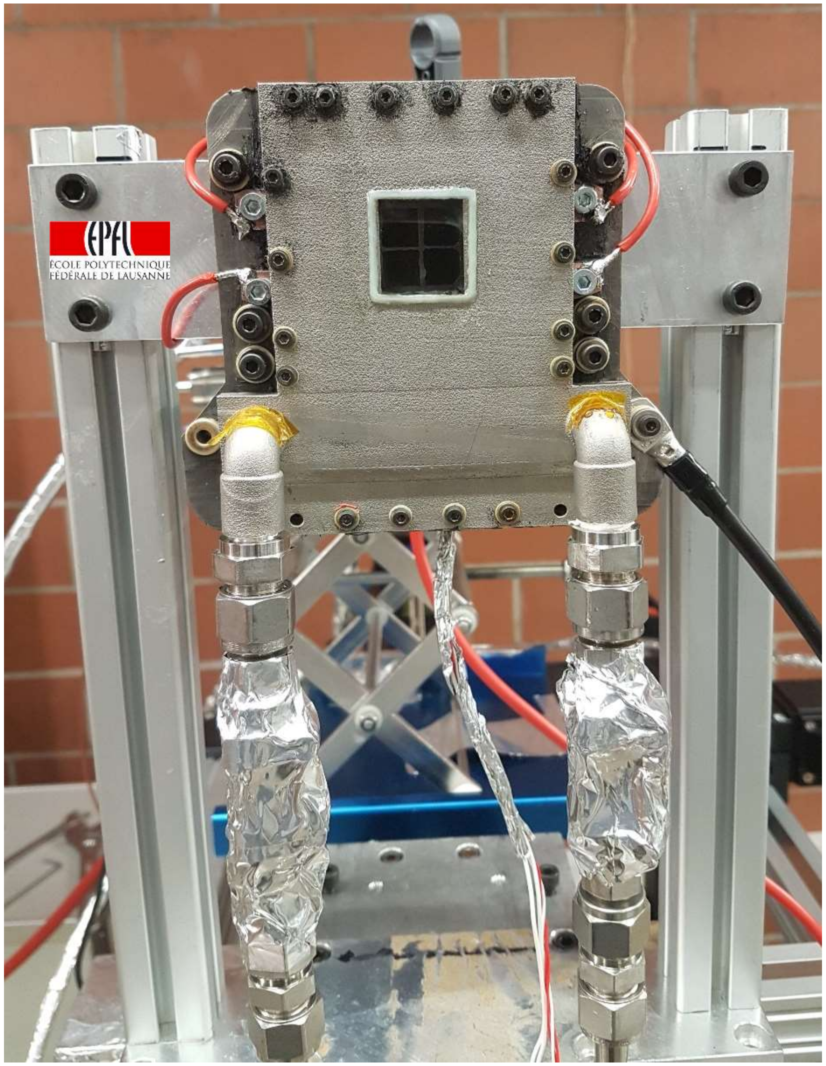
US Patent 62/376923
EP Patent 16020308.9



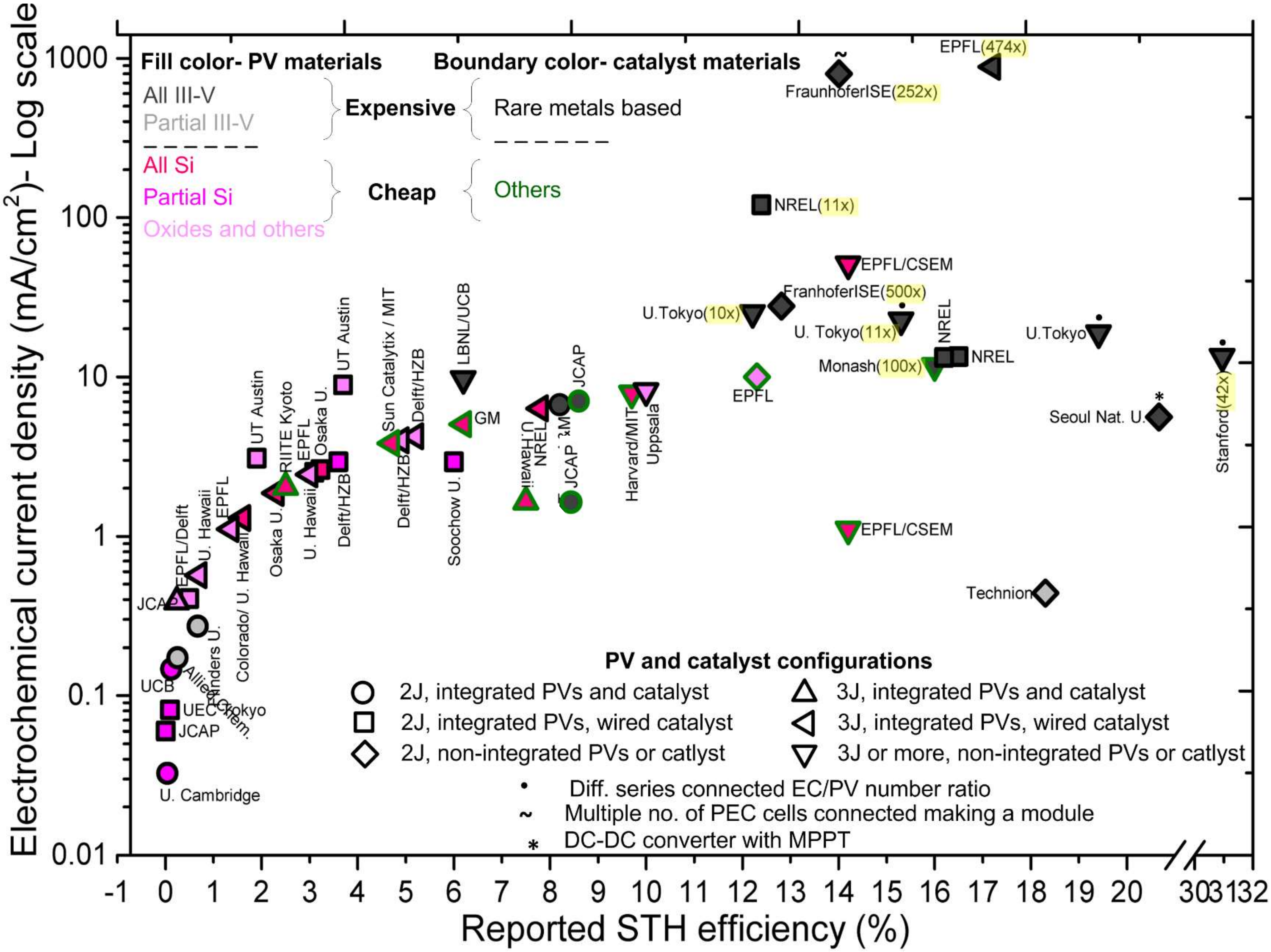
InGaP-InGaAs-Ge

Ir/RuOx - Pt

diagnostics



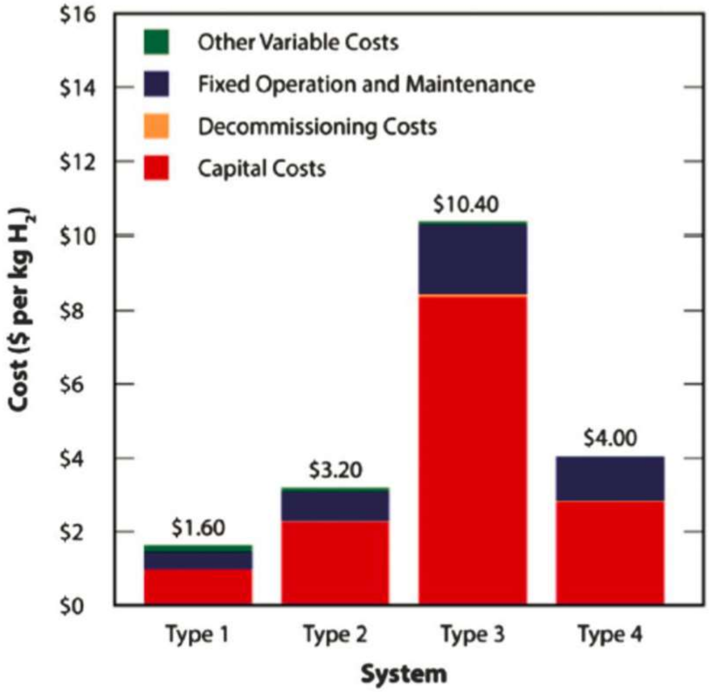
Photoelectrochemistry - Comparison

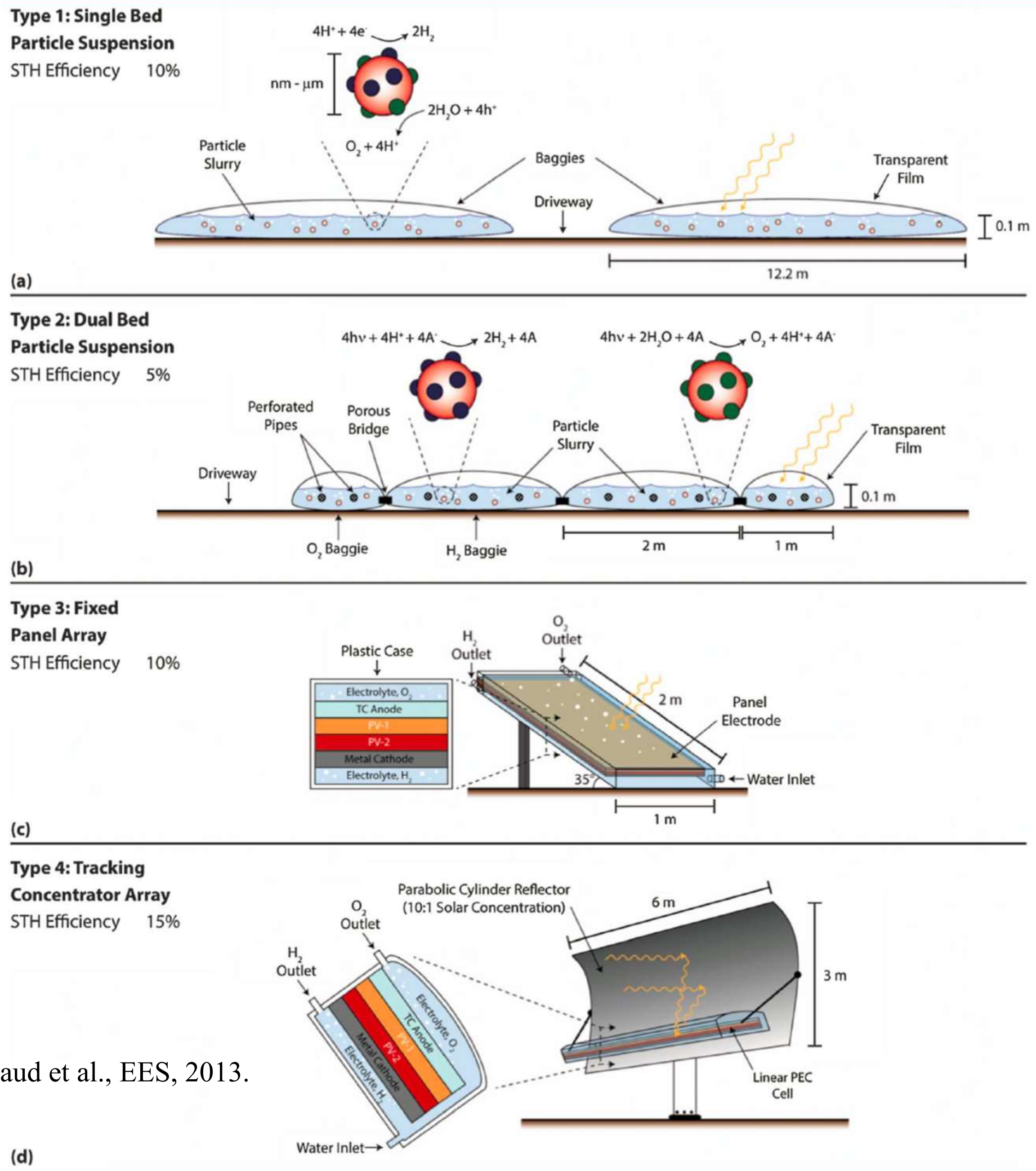


http:\\specdc.epfl.ch

Photoelectrochemistry

- Proposed devices





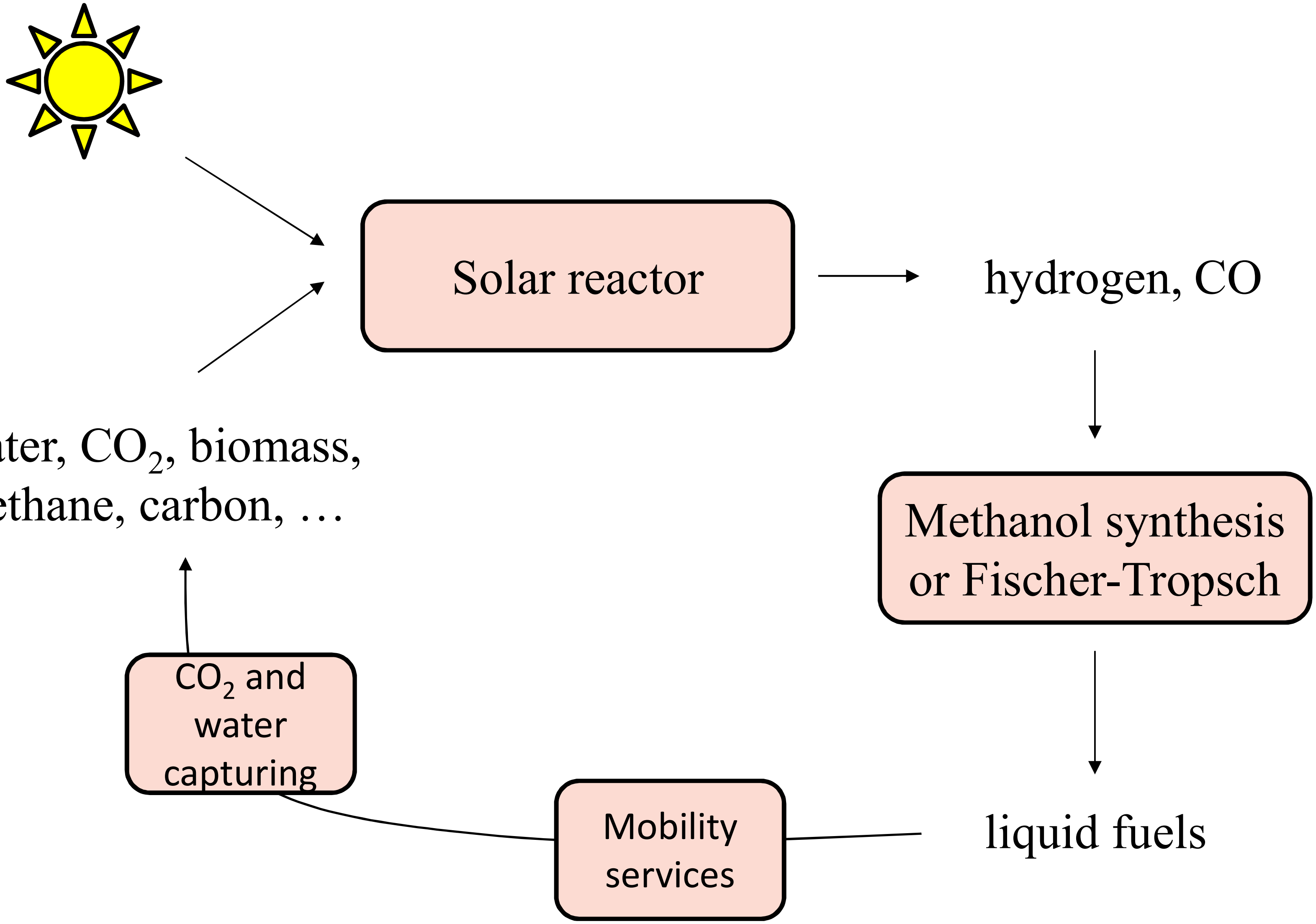
Pinaud et al., EES, 2013.

Renewable Energy

- Outline:
  - Conversion pathways solar-to-fuel
  - Hybrid pathways
  - Solar thermochemistry
  - Photochemistry

Sustainability issue

- Solar to fuels:



Solar reactor

hydrogen, CO

Methanol synthesis or Fischer-Tropsch

liquid fuels

Mobility services

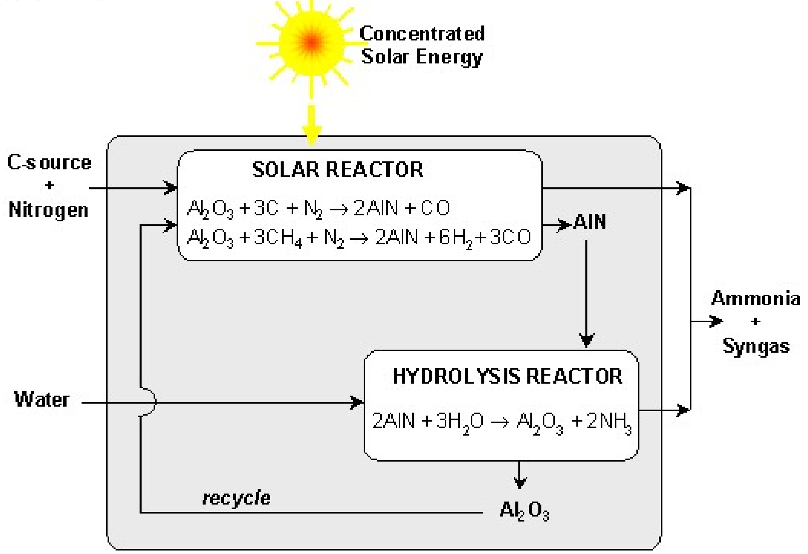
CO_2 and water capturing

water, CO_2, biomass, methane, carbon, …

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



Concentrated Solar Energy

C-source + Nitrogen

SOLAR REACTOR

$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + CO$

$Al_2O_3 + 3CH_4 + N_2 \rightarrow 2AlN + 6H_2 + 3CO$

AlN

Ammonia + Syngas

Water

HYDROLYSIS REACTOR

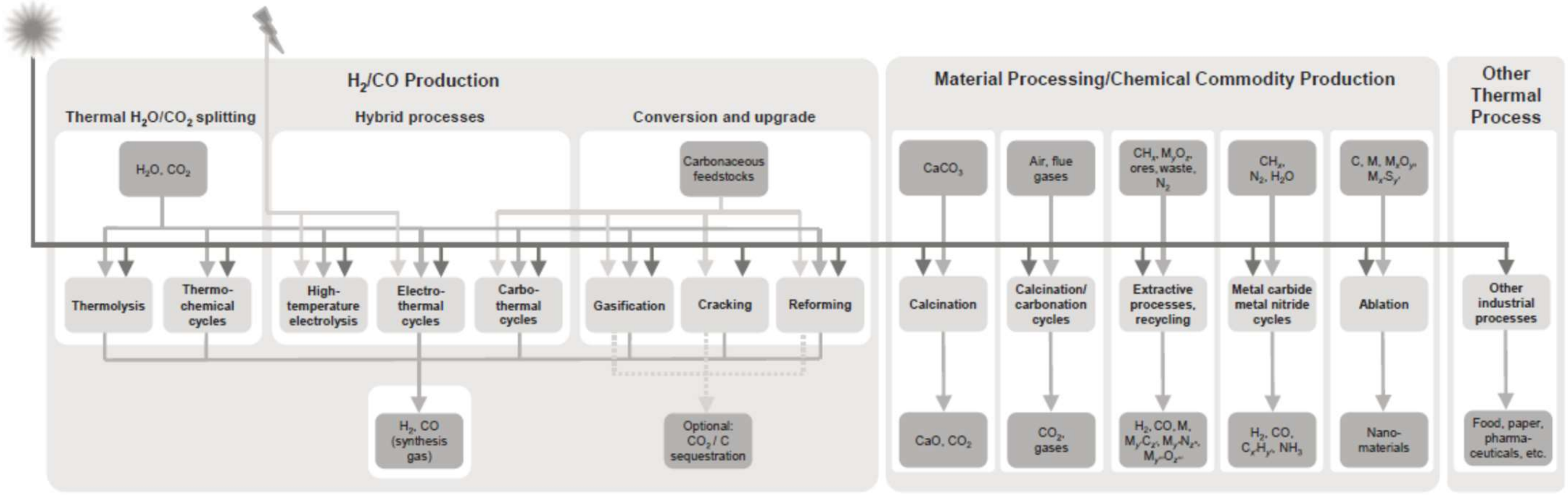
$2AlN + 3H_2O \rightarrow Al_2O_3 + 2NH_3$

recycle

Al_2O_3

Solar materials

- Thermochemical:



H$_2$/CO Production

Thermal H$_2$O/CO$_2$ splitting

H$_2$O, CO$_2$

Thermolysis

Thermo-chemical cycles

Hybrid processes

High-temperature electrolysis

Electro-thermal cycles

Carbo-thermal cycles

H$_2$, CO (synthesis gas)

Conversion and upgrade

Carbonaceous feedstocks

Gasification

Cracking

Reforming

Optional: CO$_2$ / C sequestration

Material Processing/Chemical Commodity Production

CaCO$_3$

Calcination

CaO, CO$_2$

Air, flue gases

Calcination/ carbonation cycles

CO$_2$, gases

CH$_x$, M$_y$O$_z$, ores, waste, N$_2$

Extractive processes, recycling

H$_2$, CO, M, M$_y$C$_z$, M$_y$N$_z$, M$_y$O$_z$

CH$_x$, N$_2$, H$_2$O

Metal carbide metal nitride cycles

H$_2$, CO, C$_x$H$_y$, NH$_3$

C, M, M$_x$O$_y$, M$_x$S$_y$

Ablation

Nano-materials

Other Thermal Process

Other industrial processes

Food, paper, pharma-ceuticals, etc.

Bader et al., 2016

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.