Greenhouse Gases Mitigation CO_2 Capture and Utilization

Topic No: 9

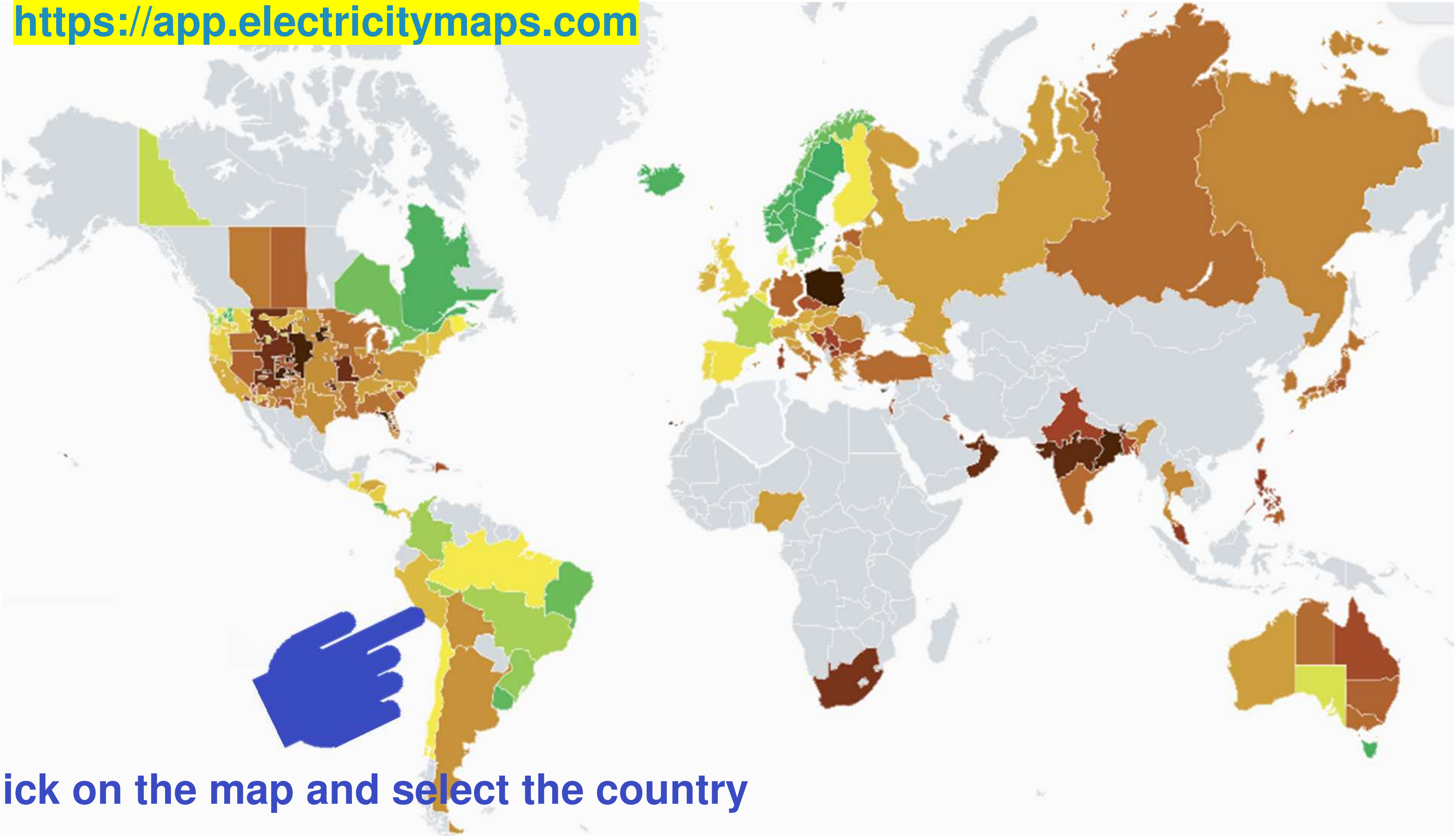
©Marek.Staf@vscht.cz

Table of contents

Reference(s): -

Renewable sources: power fluctuations

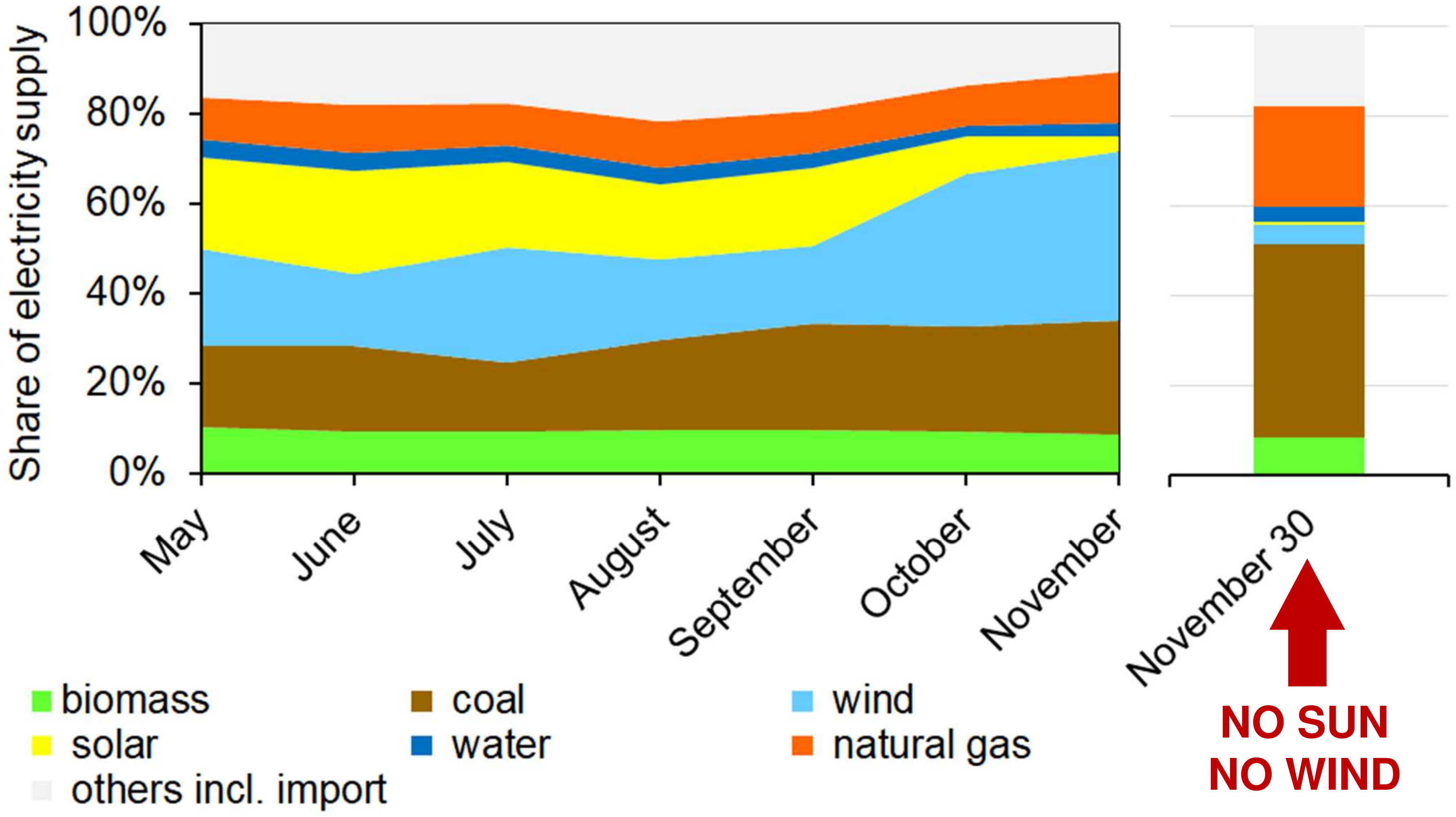
- The main fluctuations occur during the day, week and in the seasons
- Statistical data on electricity production available on the portal:
  - ► **https://app.electricitymaps.com**



Click on the map and select the country

Renewable sources: power fluctuations

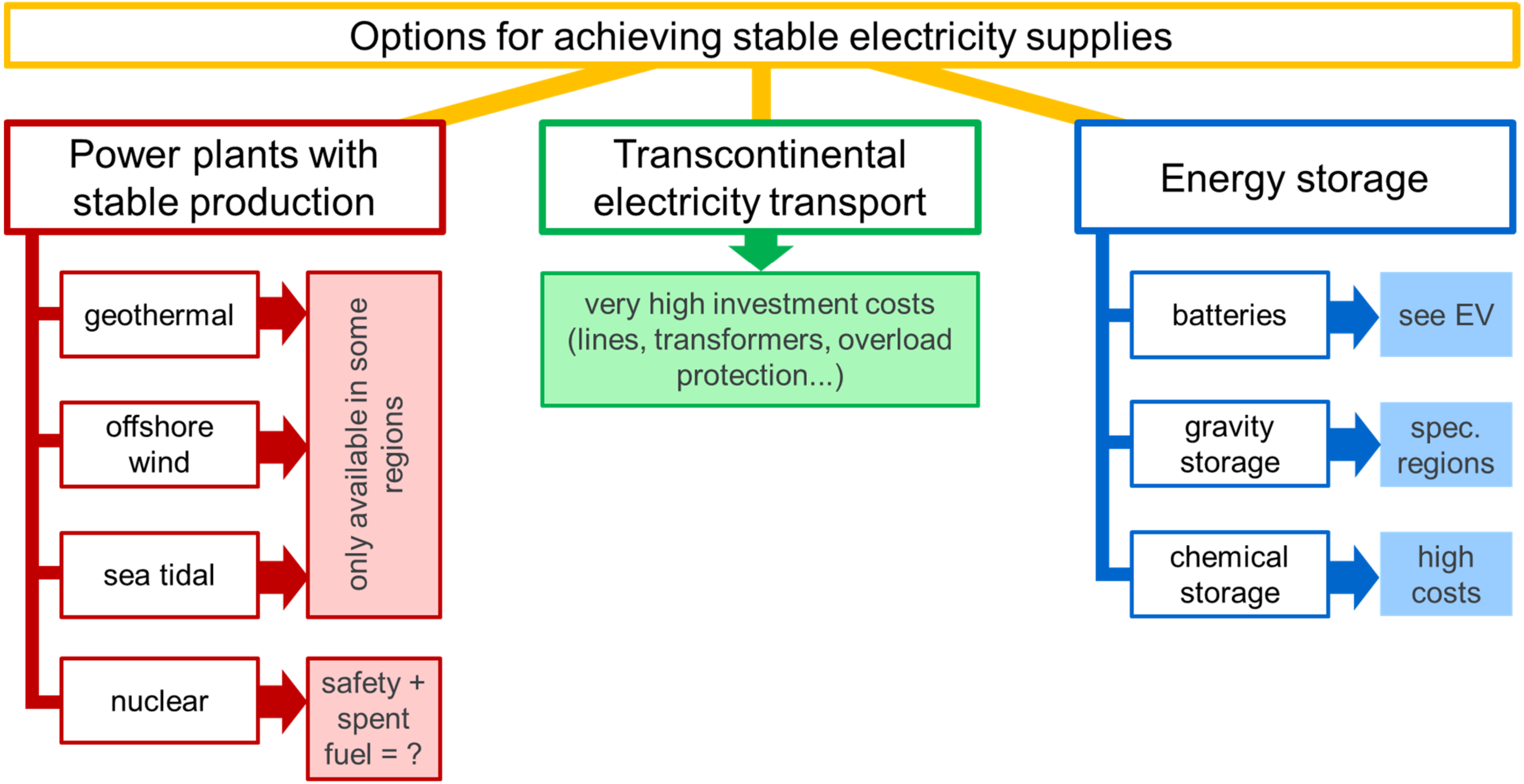
- Example: Germany = EU leader in the installation of renewable sources
  - ► https://app.electricitymaps.com   the situation in 2023



NO SUN
NO WIND

Renewable sources: power fluctuations

- A balance between production and consumption must be achieved
  - There are three basic ways to achieve it:



Options for achieving stable electricity supplies

Power plants with stable production

- geothermal
- offshore wind
- sea tidal
- only available in some regions
- nuclear → safety + spent fuel = ?

Transcontinental electricity transport

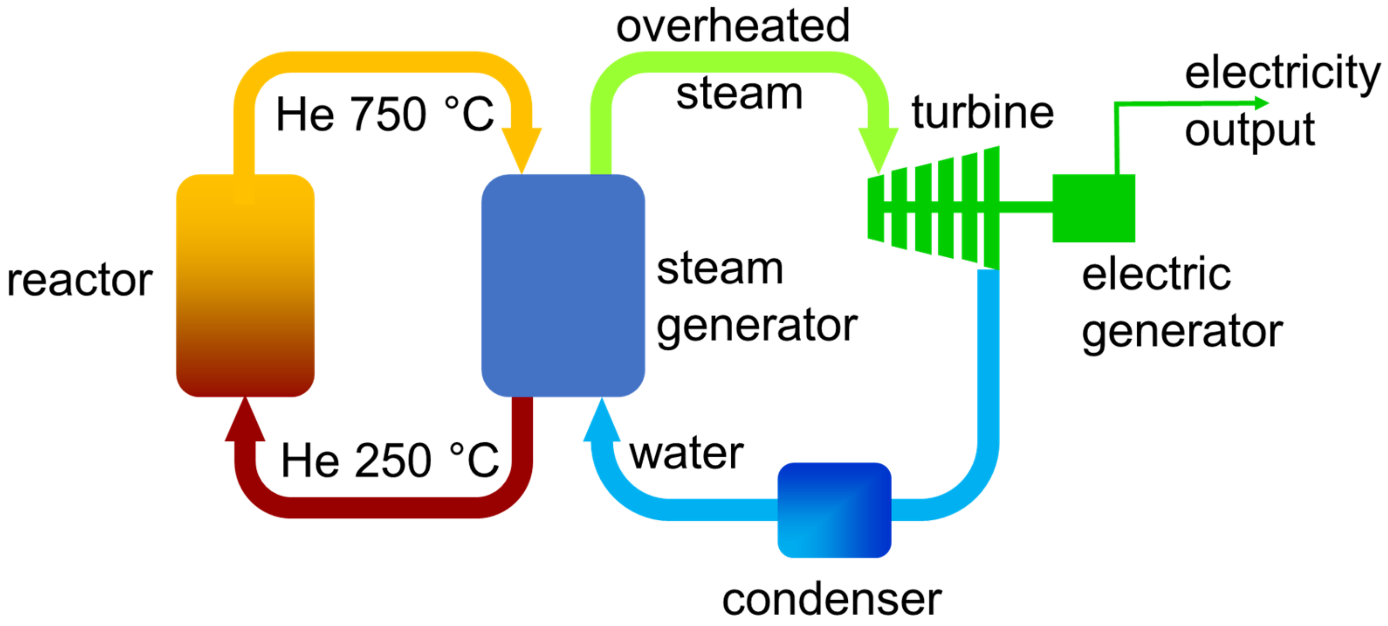
- very high investment costs (lines, transformers, overload protection...)

Energy storage

- batteries → see EV
- gravity storage → spec. regions
- chemical storage → high costs

Is there safer nuclear power?

- Yes, by using Gas-cooled Fast Reactors or High Temperature Reactors
  - so called Generation IV reactors
  - cooled by He or supercritical CO_2 (instead of current pressure water reactors)
  - 2023: first Gen IV reactor enters commercial operation in China
  - 2 modular reactors 2×250 MWt driving a single 210 MWe electric generator
  - closed cycle of fuel: transformation of ^{238}U into fissionable ^{239}Pu
  - 50 time higher use of fuel + lower toxicity of spent fuel



Is there safer nuclear power?

- Generation IV He-cooled High Temperature Reactor
  - ► single-loop systems (higher efficiency) still in R&D

1 – reactor

2 – reactor core

3 – control rods

4 – generator

5 – electrical power

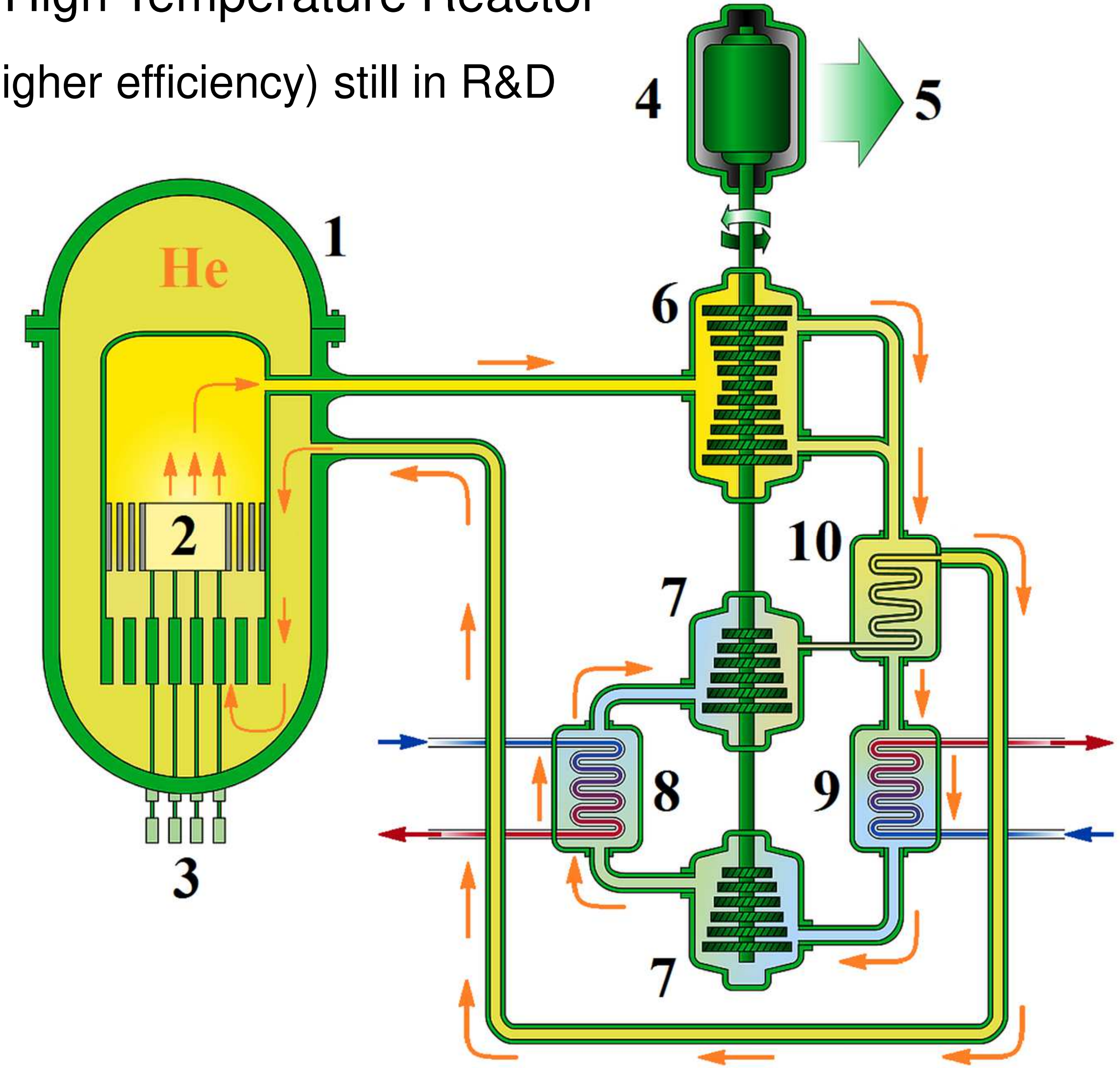
6 – turbine

7 – compressor

8 – intercooler

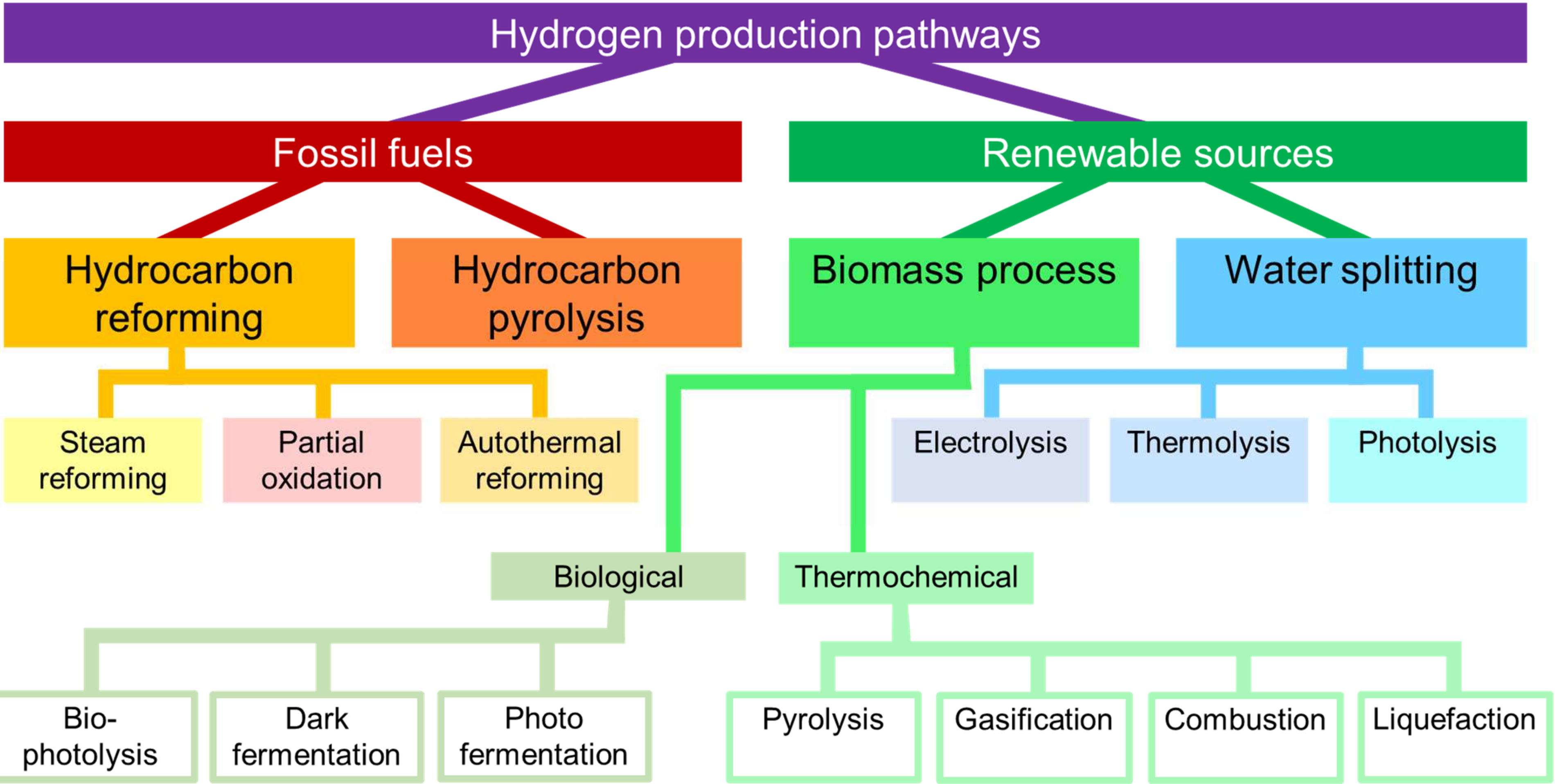
9 – pre cooler

10 - recuperator



Storing energy in hydrogen

- Production of hydrogen from excess energy from renewable sources
  - Still in R&D; there are many technical solutions:



- Hydrogen production pathways
  - Fossil fuels
    - Hydrocarbon reforming
      - Steam reforming
      - Partial oxidation
      - Autothermal reforming
    - Hydrocarbon pyrolysis
  - Renewable sources
    - Biomass process
      - Biological
        - Bio-photolysis
        - Dark fermentation
        - Photo fermentation
      - Thermochemical
        - Pyrolysis
        - Gasification
        - Combustion
        - Liquefaction
    - Water splitting
      - Electrolysis
      - Thermolysis
      - Photolysis

Electrolysis of water

- Three main types of electrolyzers
  - Proton exchange membrane (PEM)

    water introduced at the anode where it is split into H^+

    H^+ travels through membrane to the cathode to form H_2 and O_2

    Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

    Cathode: $4H^+ + 4e^- \rightarrow 2H_2$
  - Alkaline electrolyzers

    water introduced at the cathode where it is split into H_2 and OH^-

    H_2 separated from water in an external separation unit

    OH^- ions travel through the electrolyte to the anode to form O_2

    Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

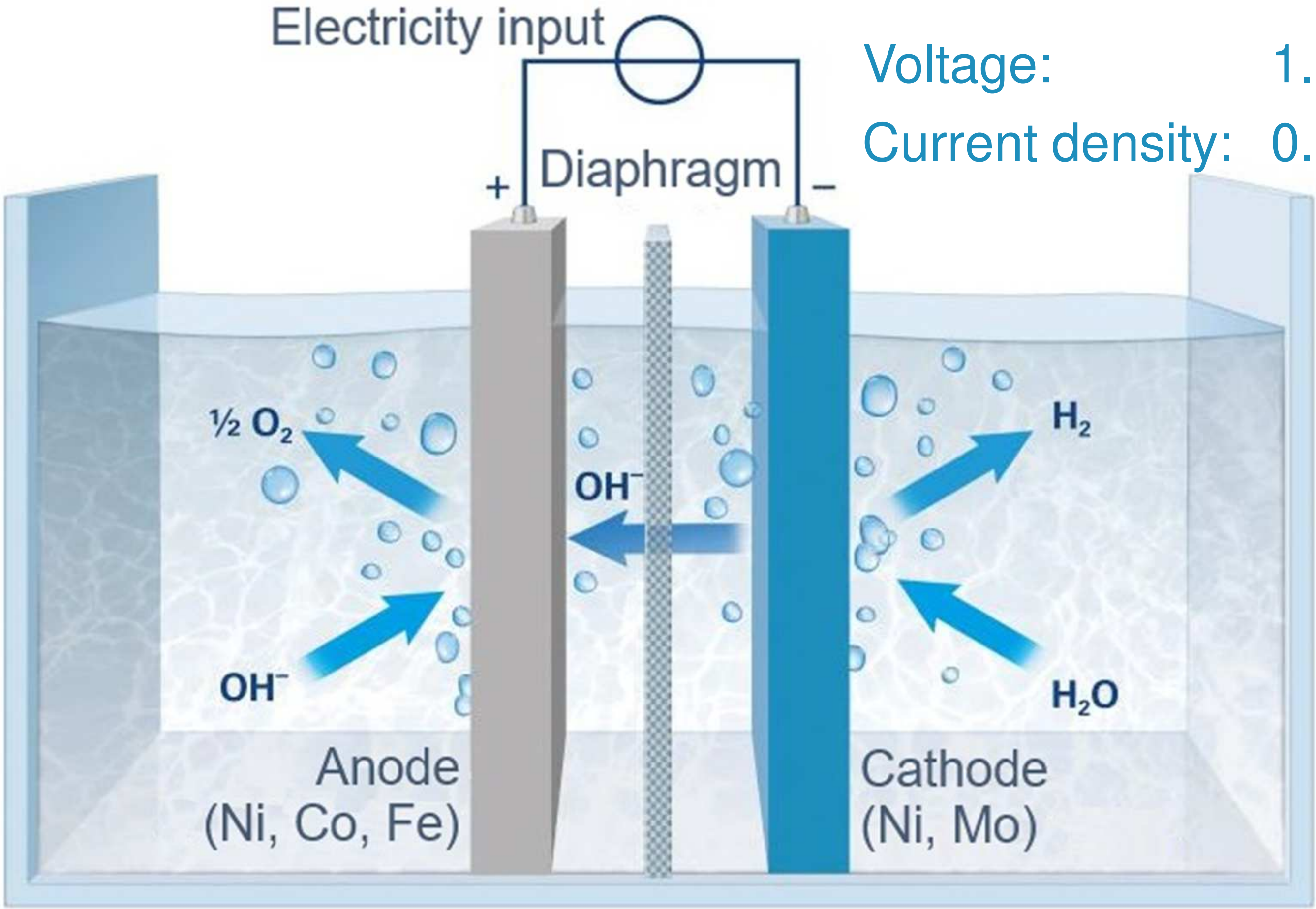
    Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
  - Solid oxide electrolysis cells (SOEC) - the same principle as alkaline but part of electricity replaced with thermal

Reference(s): -

©Marek.Staf@vscht.cz

Electrolysis of water

- Alkaline electrolyzers
  - ► water split into H_2 and OH^- at the cathode
  - ► OH^- ions travel through the electrolyte to the anode to form O_2



Voltage: 1.8 – 2.4 V

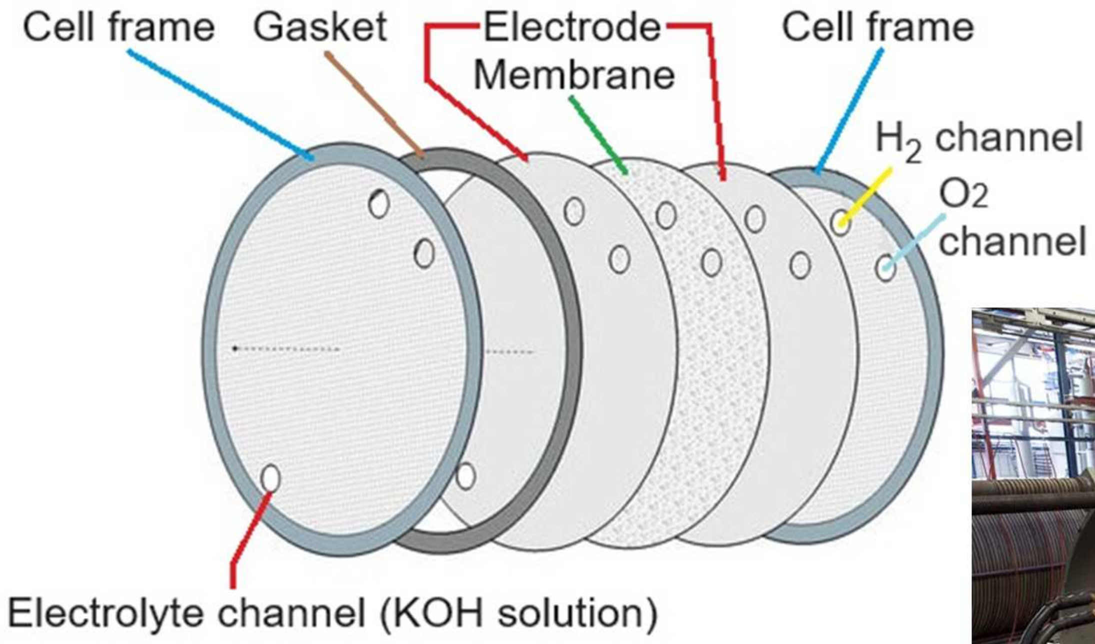
Current density: 0.2 to 0.4 A cm^{-2}

Reference(s): 4

©Marek.Staf@vscht.cz

Electrolysis of water

- Increase in performance, e.g. by increasing the area of the electrodes
  - ► Example: electrodes and diaphragms arranged in a module



Electrolysis of water - parameters

- Operation temperatures

► Proton exchange membrane (PEM)	70 – 90 °C
► Alkaline electrolyzers	< 100 °C
► Solid oxide electrolysis cells (SOEC)	700 – 800°C

- Commercially available alkaline electrolyzers

► Energy consumption	53.4 kWh/kg H_2

  - ► Efficiency up to 73%
  - ► Despite the technical development, the production price is still high.
  - ► Hydrogen production costs depend on different electricity sources.

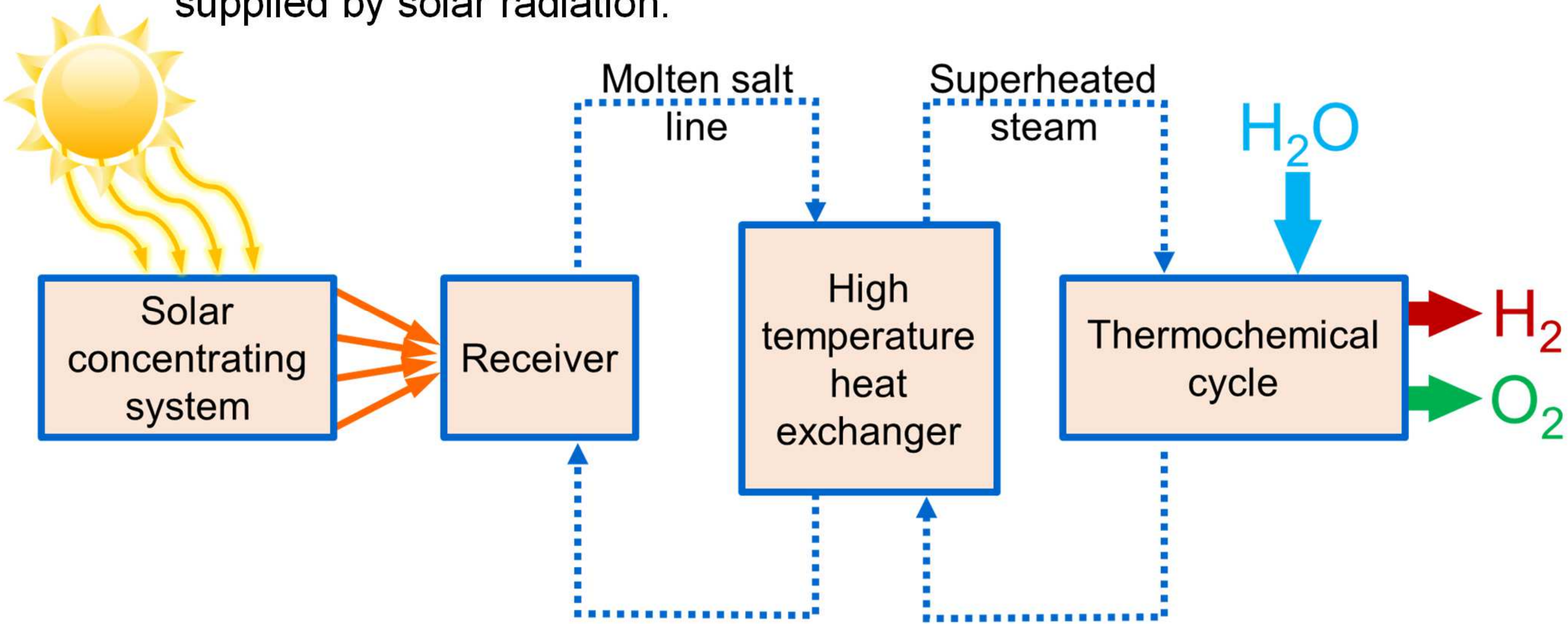
e.g. (2017)	Nuclear	4.15 $/kg
	Solar thermal	7.00 $/kg
	Solar photovoltaic	10.49 $/kg
	Wind	5.10 – 6.46 $/kg

  - ► Energy Earthshots Initiative goal:

Desired H_2 cost	1.00 $/kg

Thermochemical water splitting (Thermolysis)

- Multiple principles (simple thermal and more advanced thermochemical)
  - Simple thermal decomposition requires T > 2,500 °C ⇒ not feasible
  - Thermochemical water-splitting cycles lower the temperature and improve the overall efficiency:
- General principle of thermochemical water-splitting
  - A suitable inorganic salt reacts with steam to produce hydrogen. Heat is supplied by solar radiation.

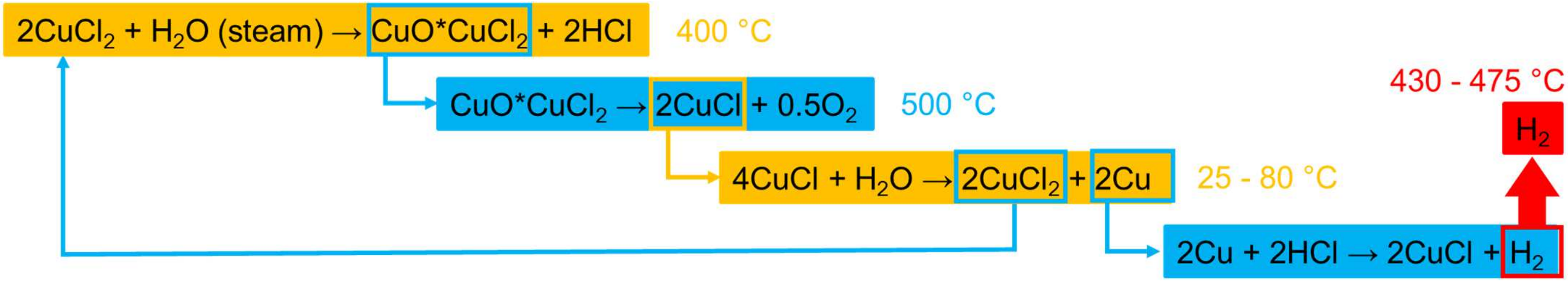


Reference(s): 3

©Marek.Staf@vscht.cz

Thermochemical water splitting (Thermolysis)

- Multiple principles (simple thermal and more advanced thermochemical)
  - Simple thermal decomposition requires T > 2,500 °C ⇒ not feasible
  - Thermochemical water-splitting cycles lower the temperature and improve the overall efficiency:
- Examples of the most promising Thermochemical cycles
  - Cu-Cl cycle



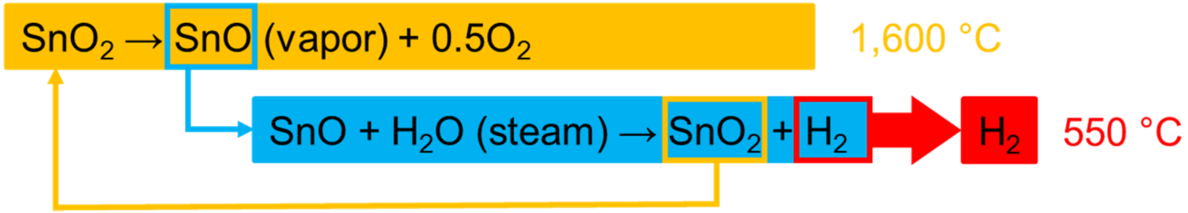
$2CuCl_2 + H_2O \text{ (steam)} \rightarrow CuO{*}CuCl_2 + 2HCl$ 400 °C

$CuO{*}CuCl_2 \rightarrow 2CuCl + 0.5O_2$ 500 °C

$4CuCl + H_2O \rightarrow 2CuCl_2 + 2Cu$ 25 - 80 °C

$2Cu + 2HCl \rightarrow 2CuCl + H_2$ 430 - 475 °C

  - SnO_2/SnO cycle



$SnO_2 \rightarrow SnO \text{ (vapor)} + 0.5O_2$ 1,600 °C

$SnO + H_2O \text{ (steam)} \rightarrow SnO_2 + H_2$ 550 °C

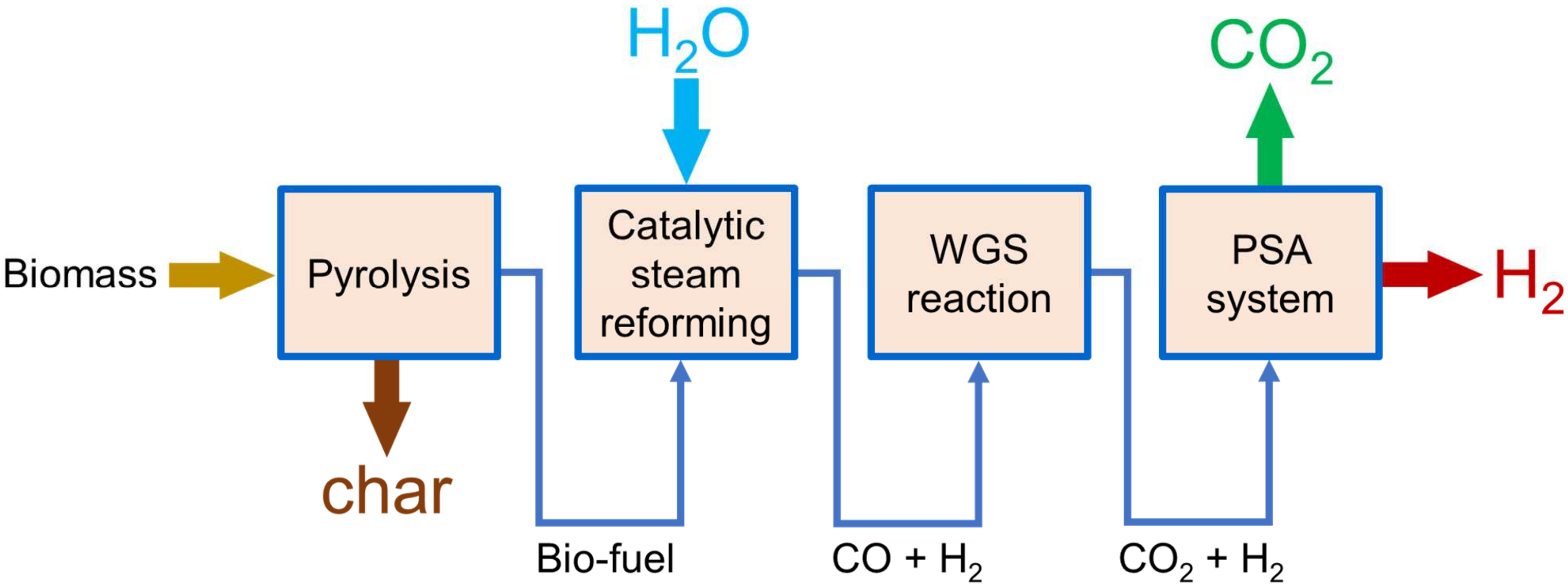
  - Mg-Cl cycle (550 °C)

Reference(s): 3

©Marek.Staf@vscht.cz

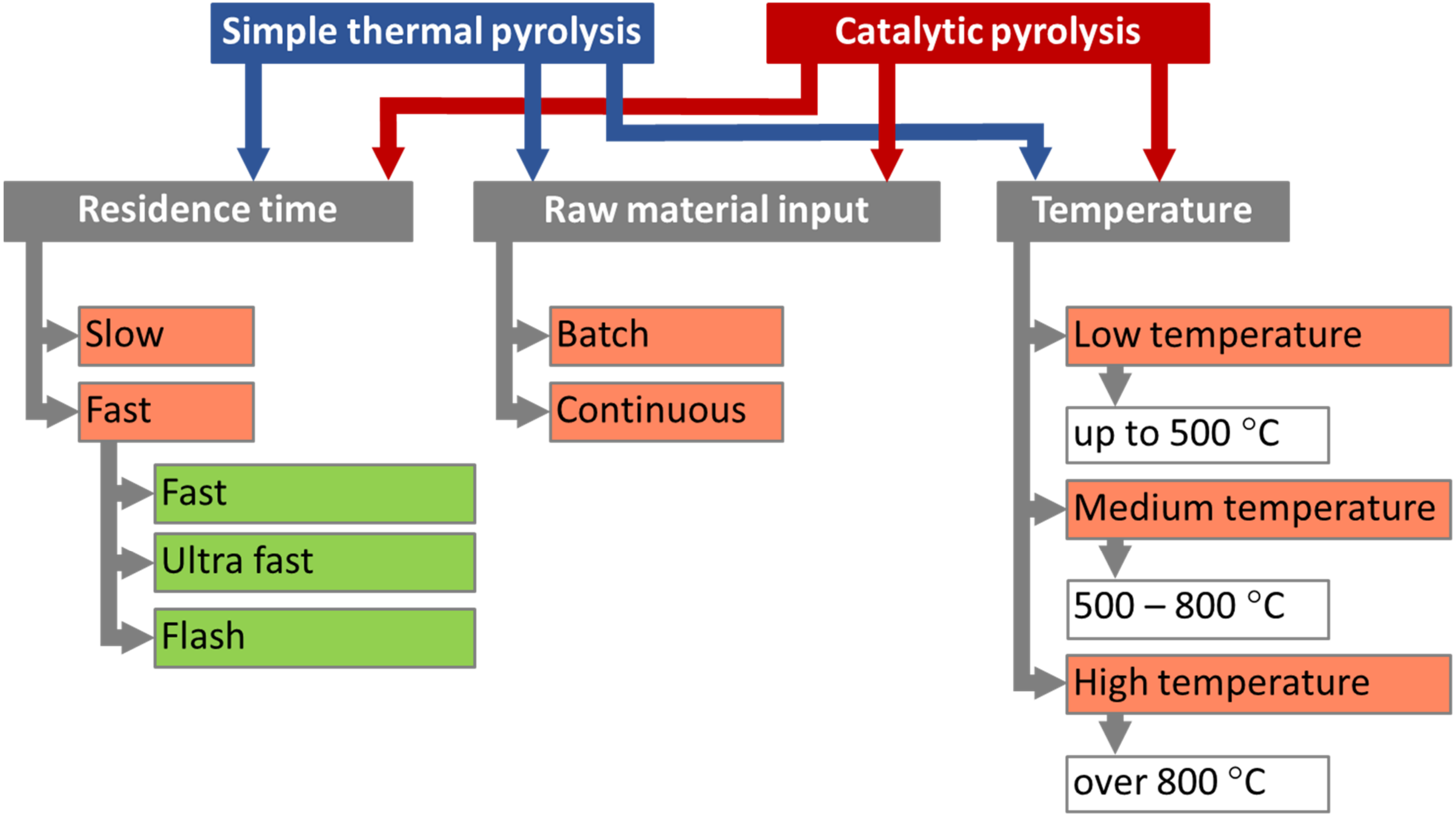
Biomass pyrolysis + bio-fuel processing

- Multi-stage thermochemical process of thermal decomposition of biomass
  - pyrolysis produces solid residue (char), gas (CO, CO_2, H_2, C_xH_y) and condensate (tar)
  - bio-fuel (gas + tar) is reformed by steam to CO + H_2
  - CO undergoes water-gas shift reaction to CO_2
  - CO_2 is separated by adsorption



Distribution of the main pyrolysis techniques

- All of the approaches are less or more suitable for biomass conversion



Simple thermal pyrolysis

Catalytic pyrolysis

Residence time

- Slow
- Fast
  - Fast
  - Ultra fast
  - Flash

Raw material input

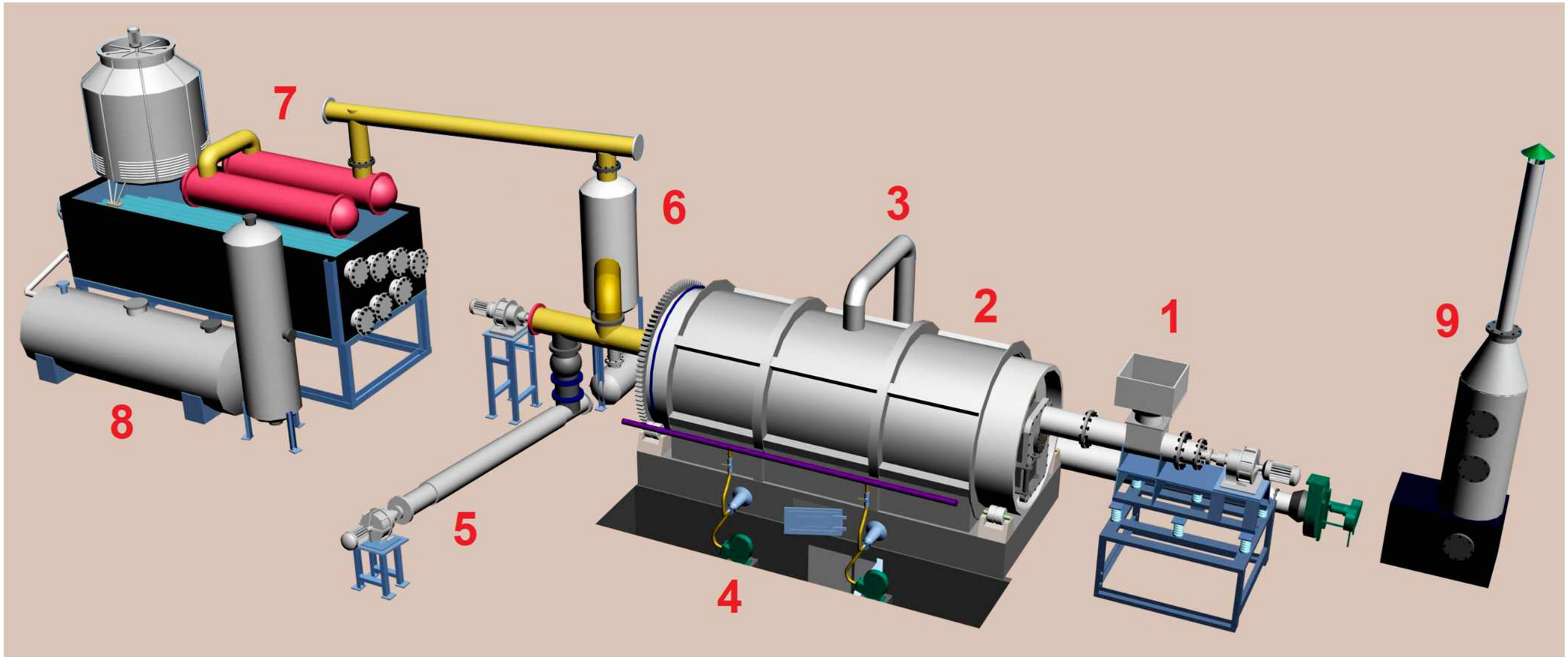
- Batch
- Continuous

Temperature

- Low temperature
  - up to 500 °C
- Medium temperature
  - 500 – 800 °C
- High temperature
  - over 800 °C

Continuous low and medium temperature pyr.

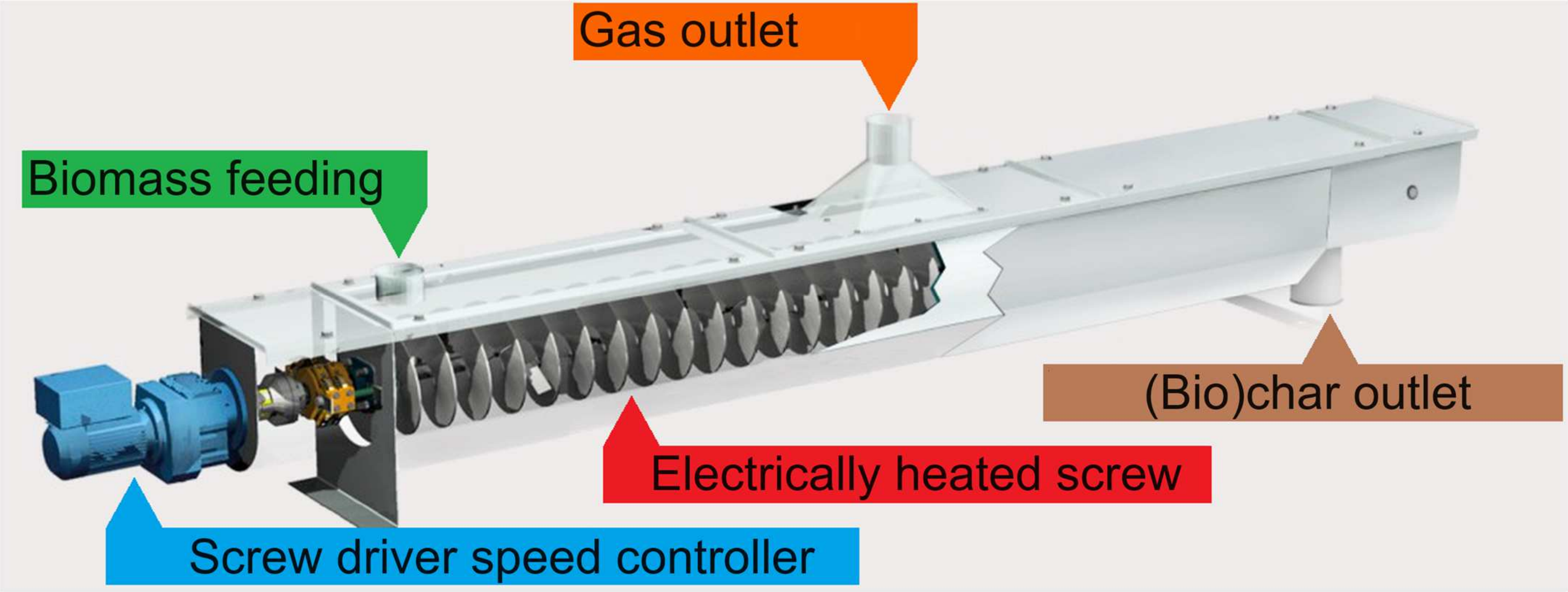
- Rotary cylindrical pyrolyzer with external heating by gas burners
  - cylindrical pyrolyzers exclusively for non-fusible materials



1 – biomass feeder, 2 – reactor, 3 – flue gas outlet, 4 – pyrolysis gas burners, 5 – char screw conveyor, 6 – high temperature tar separator, 7 – condenser, 8 – condensates tank, 9 – flue gas cleaning

Continuous low and medium temperature pyr.

- A screw pyrolyzer, where a heated screw is the heat source
  - heating rate and dwell time given by screw rotation speed



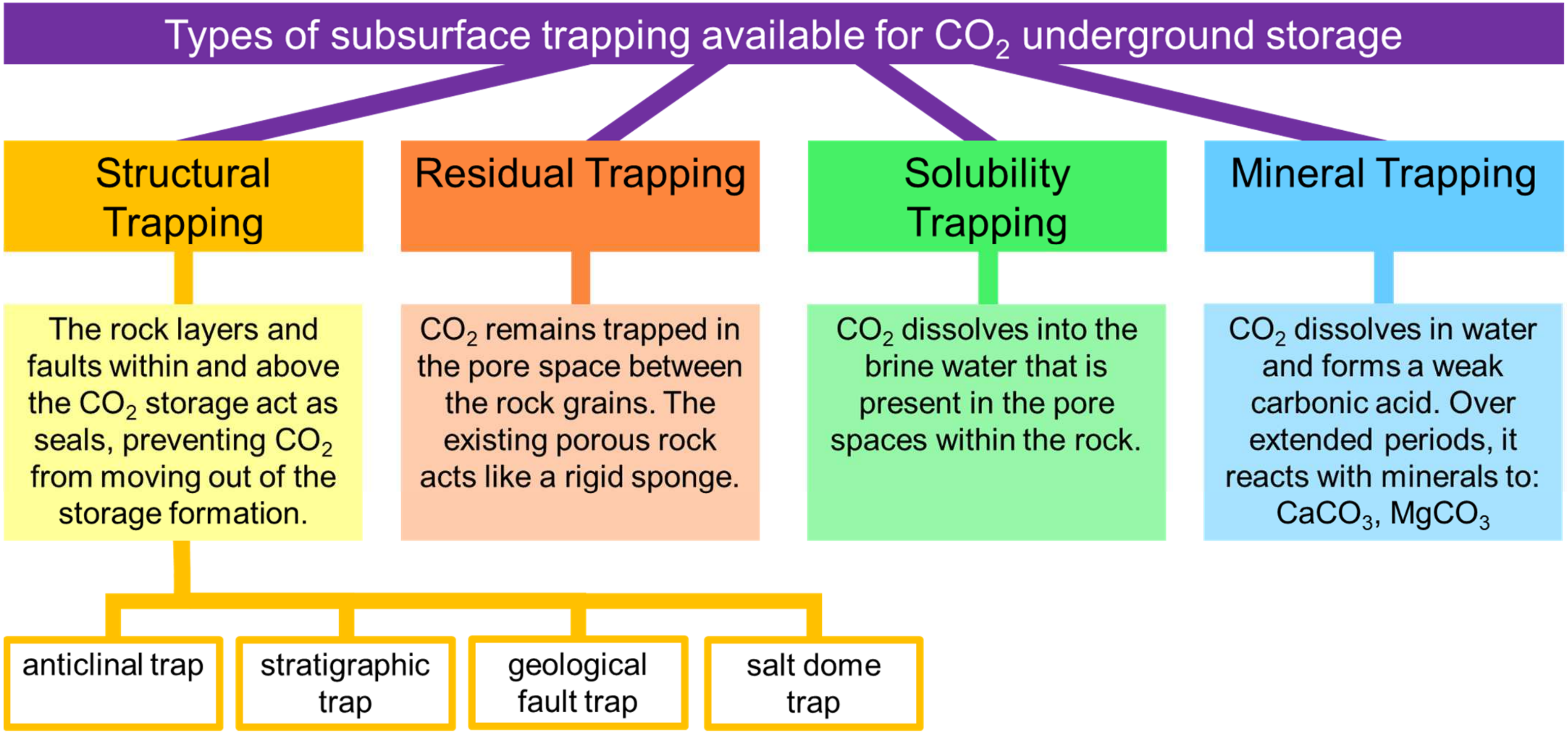
Batch low and medium temperature pyr.

- A retort-type ("kettle") pyrolyzer with a fixed bed
  - The rate of heating and the composition of the products are influenced, among other things, by the size and geometry of the reactor.
  - Almost universal design

1 – reactor with a heating jacket
2 – agitator drive
3 – condenser
4 – condensate tank
5 – level gauge
6 – char screw conveyor

Subsurface CO_2 storage

- Each of the trapping mechanisms plays a role in how the CO_2 remains trapped in the subsurface



Types of subsurface trapping available for CO_2 underground storage

- **Structural Trapping**
  - The rock layers and faults within and above the CO_2 storage act as seals, preventing CO_2 from moving out of the storage formation.
    - anticlinal trap
    - stratigraphic trap
    - geological fault trap
    - salt dome trap
- **Residual Trapping**
  - CO_2 remains trapped in the pore space between the rock grains. The existing porous rock acts like a rigid sponge.
- **Solubility Trapping**
  - CO_2 dissolves into the brine water that is present in the pore spaces within the rock.
- **Mineral Trapping**
  - CO_2 dissolves in water and forms a weak carbonic acid. Over extended periods, it reacts with minerals to: $CaCO_3$, $MgCO_3$

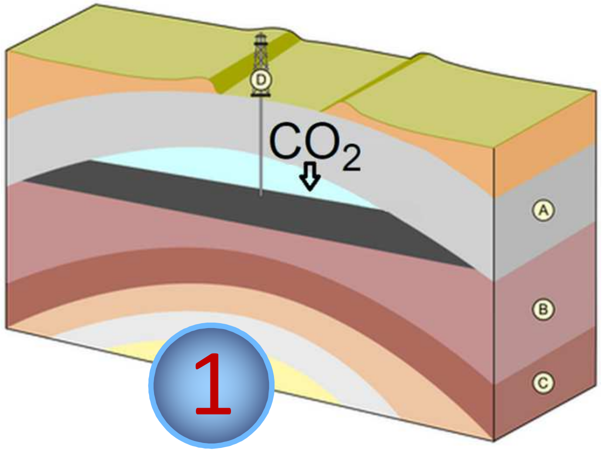
Subsurface CO_2 storage

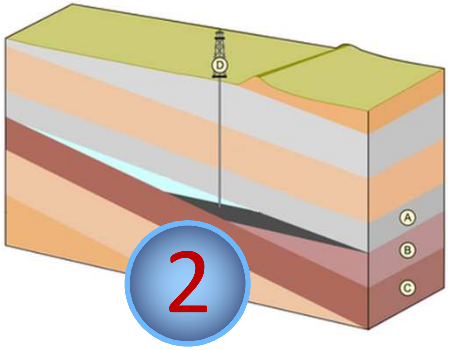
Types of subsurface trapping available for CO_2 underground storage

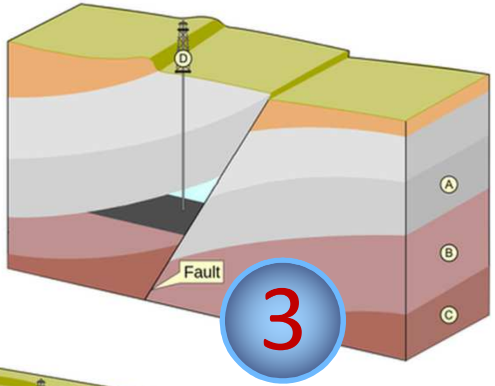
Structural Trapping

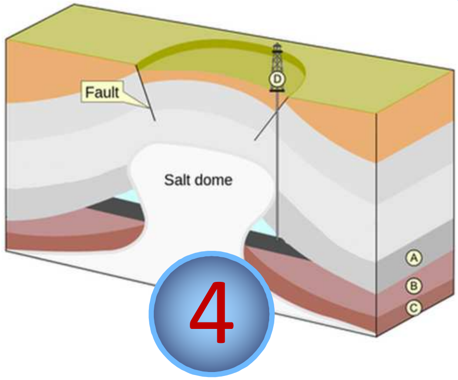
The rock layers and faults within and above the CO_2 storage act as seals, preventing CO_2 from moving out of the storage formation.

- anticlinal trap ①
- stratigraphic trap ②
- geological fault trap ③
- salt dome trap ④

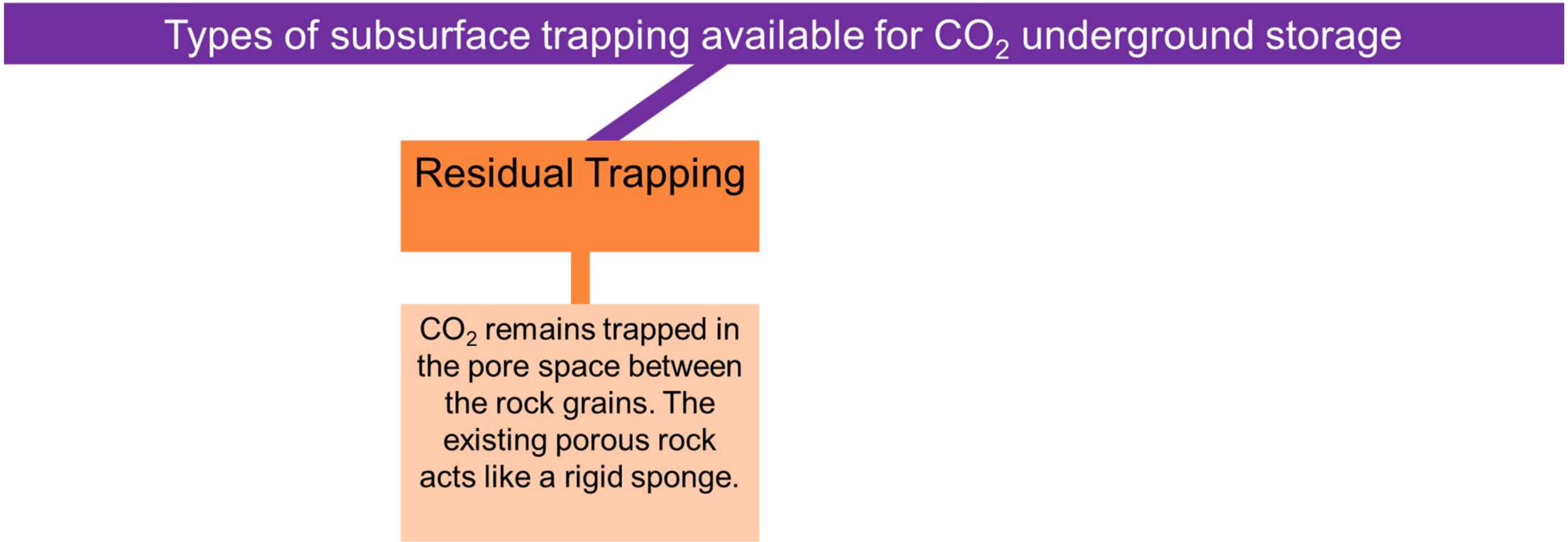








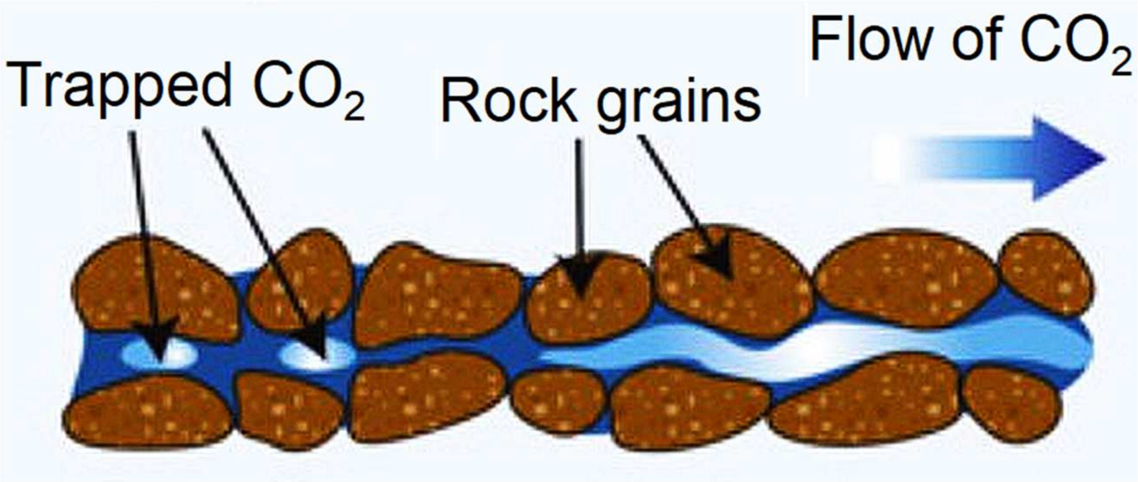
Subsurface CO_2 storage



Types of subsurface trapping available for CO_2 underground storage

Residual Trapping

CO_2 remains trapped in the pore space between the rock grains. The existing porous rock acts like a rigid sponge.

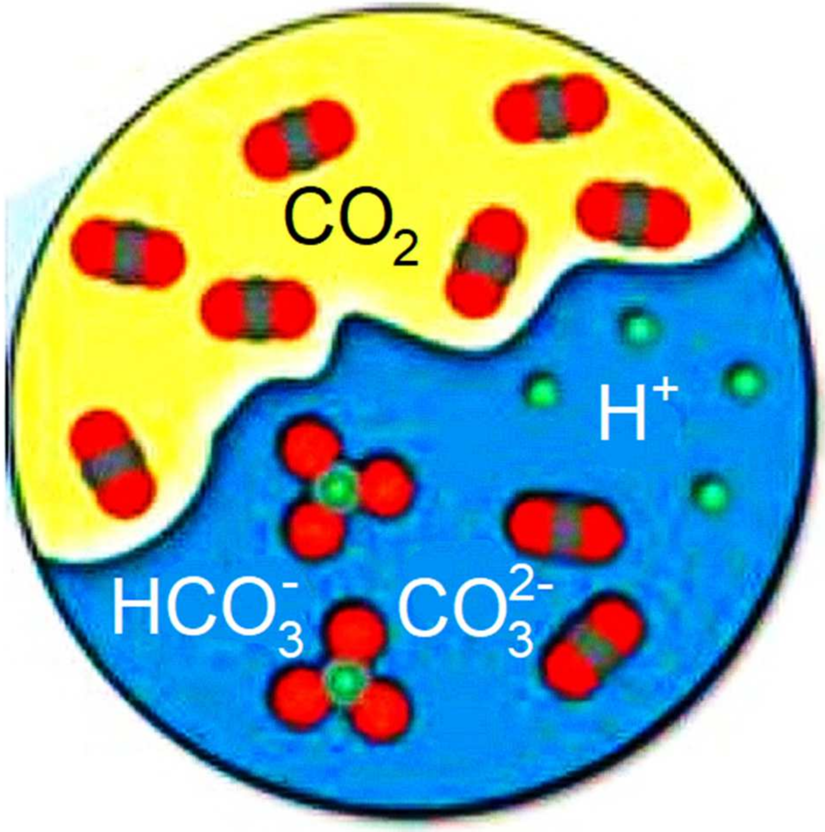


Reference(s): 9

©Marek.Staf@vscht.cz

Subsurface CO_2 storage

Types of subsurface trapping available for CO_2 underground storage

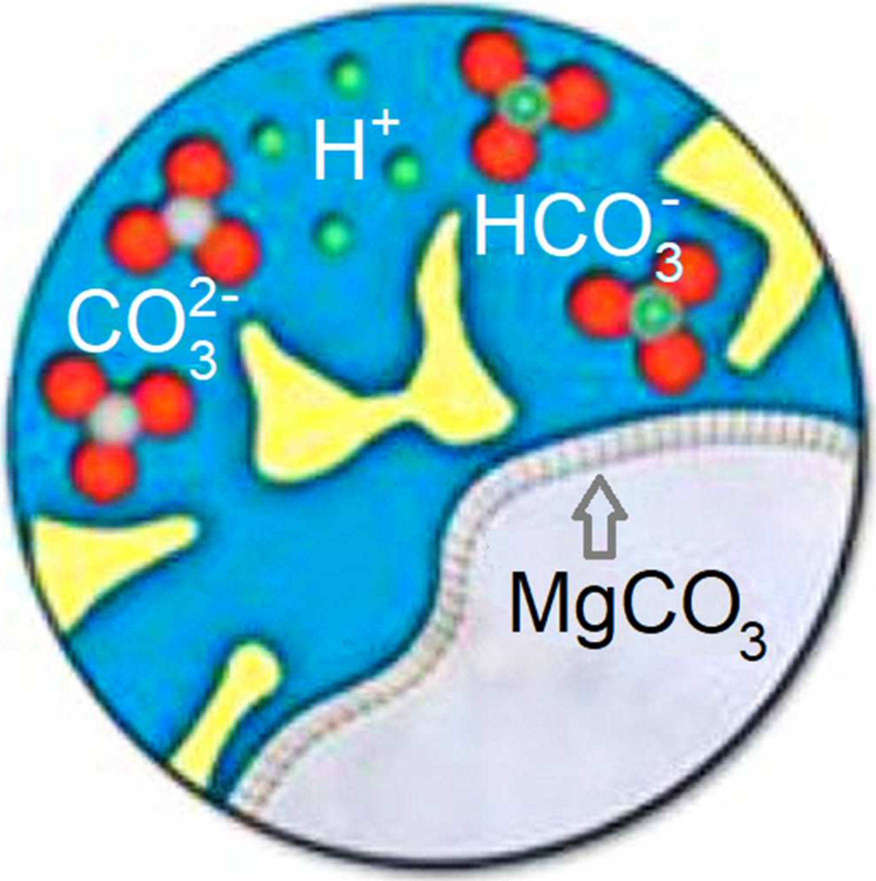


Solubility Trapping

CO_2 dissolves into the brine water that is present in the pore spaces within the rock.

Subsurface CO_2 storage

Types of subsurface trapping available for CO_2 underground storage



Mineral Trapping

CO_2 dissolves in water and forms a weak carbonic acid. Over extended periods, it reacts with minerals to: $CaCO_3$, $MgCO_3$

References (figures)

1. https://app.electricitymaps.com
2. Magwood, W., D., Paillere, H. Looking ahead at reactor development. Progress in Nuclear Energy 2018, 102, 58-67
3. P. 606 Nikolaidis, A. Poullikkas / Renewable and Sustainable Energy Reviews 67 (2017) 597–611
4. https://hydrogen.messergroup.com/facts
5. https://www.mdpi.com/1996-1073/10/7/860
6. https://i0.wp.com/www.h2-international.com/wp-content/uploads/2017/06/Nel-Akzo-Nobel.jpg?ssl=1
7. Bartels JR, Pate MB, Olson NK. An economic survey of hydrogen production from conventional and alternative energy sources. Int J Hydrog Energy 2010;35(16):8371–84.
8. xxx
9. https://netl.doe.gov/carbon-management/carbon-storage/faqs/carbon-storage-faqs