Sustainable technologies for hydrogen

Master in Energy Engineering

Prof. Paolo Canu

Course introduction

Why a dedicated hydrogen course?

- Big expectations from H2:
  - a clean(?) fuel
    where combustion cannot be replaced yet (Hard-to-Abate)
  - a clean energy carrier
    store renewable EE, and feed Fuel Cells
- Small and large initiatives are planned
  are they sustainable?
- moving from R&D to Execution requires skills
  "Hydrogen Systems Engineers" capable of managing large-scale infrastructure.
- H2 is not *just another (gas) fuel*
  high massive energy density: (120 MJ/kg vs. Li-ion <1 MJ/kg) but very low massive density (at low pressure, 1.24 m^3/kg @ 10 bar). Large flammability limits. High flame speed

Are the expectations viable and realistic?

Course structure

3 equal sections
each of 16h=8 lessons

1. Hydrogen Production Technologies (Prof. Canu)

   Steam Methane Reforming (SMR), Auto Thermal Reforming (ATR); POX; Water Electrolysis (Alkaline, PEM, and Solid Oxide Electrolysis); Biomass Gasification; CH4 cracking; NH3 cracking; Metal oxides reduction; Biomass and Biogas Reforming; Photocatalytic and Photoelectrochemical Hydrogen Production; Current Challenges in Hydrogen Production

2. Hydrogen Storage and Transportation (Prof. Azzolin)

   Advanced Hydrogen Storage Technologies;Hydrogen Transportation Infrastructure and Logistics; Safety and Regulatory Considerations; Current Challenges and case studies on hydrogen refueling station.

3. Hydrogen Use (Prof. Stoppato)

   Current Challenges in Hydrogen Utilization; Fuel Cell Applications (Transportation, Stationary Power, Portable Power); Hydrogen Combustion: current technology, challenges, and Environmental and Process Impacts; Use of Hydrogen in Gas Turbines and in Internal Combustion Engines; Hydrogen as a Sustainable Feedstock in Industrial Processes.

Course rules (syllabus)

Assessment of learning

- The course is designed for an <u>active</u> learning, based on full, pro-active participation in the course activities.
- The evaluation is based on <u>3 in-course tests</u>, at the end of each section, based on multiple-choice and open questions, restricted to the subjects taught in the corresponding section.
- Each test is expected to be of <u>45min</u>, followed by an open discussion of the outcome.

Students failing to participate in the course activities will be examined in a <u>single session</u> of 1.5 h, with the same set of questions, from any course section.

Course calendar (1st part)

Seminars from industry

1. 24/2 Paolo Canu, UniPD
   Chemical & Electrochemical routes to H2
2. 26/2 Adam Samir Kadhim, Topsoe, Product Line Manager for NH_3, H_2, CH_3OH, and syngas
   ATR and eReforming technologies in Topsoe
3. 3/3 Rossi Umberto, Air Liquide Germany,
   Methane steam reforming technology
4. 5/3 Galvanin Silvia, Hyter – Pietro Fiorentini,
   Anion exchange membrane water electrolyser technology
5. 10/3 Sune Dalgaard Ebbesen, Topsoe, Partnership & Project Lead | Power to X
   Topsoe SOEC solutions
6. 12/3 Ferrari Fabio, Nextchem,
   Catalytic Partial Oxidation at Short Contact Time
7. 17/3 Luigi Migliorini , Enphos,
   Case studies of different electrolyser installations, comparing expected and field data of technical and economic performances
8. 24/3 learning assessment

H2 production

1) Very rare in nature
2) Must be obtained (produced) from other molecules:
   - H_2O
   - HCs (including biomass; best from CH_4)
   - NH_3
3) Issues:
   - energy cost
   - efficiency
   - byproducts (COx, Nox,..)

Need for an energy system approach

H2 production - colors

Classification of technologies by colors

mixes production technologies, raw materials, source of energy

Types of hydrogen colours	Definition by technologies used	Advantages	Drawbacks
	It is naturally occurring hydrogen molecules formed through fracking and found in underground deposits. Hydrogen is a byproduct of the industrial process.	Naturally occurring hydrogen	–
	Hydrogen is produced by water electrolysis using renewable energy sources such as solar, wind, and hydro.	1. Increase recycling 2. Promote bioenergy 3. Does not emit GHGs 4. Produce from clean electricity 5. Emits no carbon dioxide 6. Expected to have a lower price as it becomes more common.	1. High production costs 2. Energy losses 3. Lack of dedicated infrastructure 4. Need to ensure sustainability 5. Lack of value recognition
	Hydrogen is produced by SMR from fossil fuels (other than coal).	The most common form of hydrogen production.	1. Emits carbon dioxide 2. Emits other GHG 3. Continued use of some fossil fuels.

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H2 production - colors

Classification of technologies by colors

Hydrogen from natural gas is produced through the SMR process to capture and bury GHGs	1. Could capture and remove GHGs using carbon capture and storage (CCS) technology 2. Also known as low-carbon hydrogen.	1. Produce carbon dioxide as a byproduct
Steam methanation of renewable natural gas with CCS.	1. Could capture and store carbon.	1. The process emits a large amount of carbon dioxide.
Hydrogen is derived from the pyrolysis of methane (thermal splitting).	1. Produce hydrogen and solid carbon. 2. In the future, it may be valued as low-emission hydrogen, depending on several factors.	1. Generate a small number of GHGs
Hydrogen is produced by coal gasification.	1. Produce liquefied hydrogen for low-emission usage.	1. This process emits large amounts of carbon dioxide, carbon monoxide, and other GHGs. (Opposite of green hydrogen)

H2 production - colors

Classification of technologies by colors

	Hydrogen is produced using nuclear power plants. This chemo-thermal electrolysis process uses nuclear power and heat to split water.	1. Low carbon emissions	1. Use very high temperatures from a nuclear reactor. 2. Generate a small number of GHGs
	Hydrogen is produced using nuclear energy to power water electrolysis.	1. The steam generated from the nuclear reactors could be used for other hydrogen productions for more efficient electrolysis	1. Use very high temperatures from nuclear reactors. 2. Generate a small amount of GHGs.
	Hydrogen is produced from the energy grid via water electrolysis.	1. Hydrogen is produced through electrolysis using solar power.	1. Carbon emissions vary greatly depending on the sources used to power the grid.
	Thermal energy generated by nuclear power is used to power high-temperature catalytic water splitting. More minor, modular nuclear power plants are being implemented to augment wind, solar, and battery technology in the power sector.	1. No carbon dioxide emissions	1. Uses very high temperatures. 2. Generate a small amount of GHGs.
	Produced from waste plastics through gasification or pyrolysis with CCS.	1. Low raw material costs 2. Requires less energy.	1. At an early stage, more research is needed.

H2 production - colors

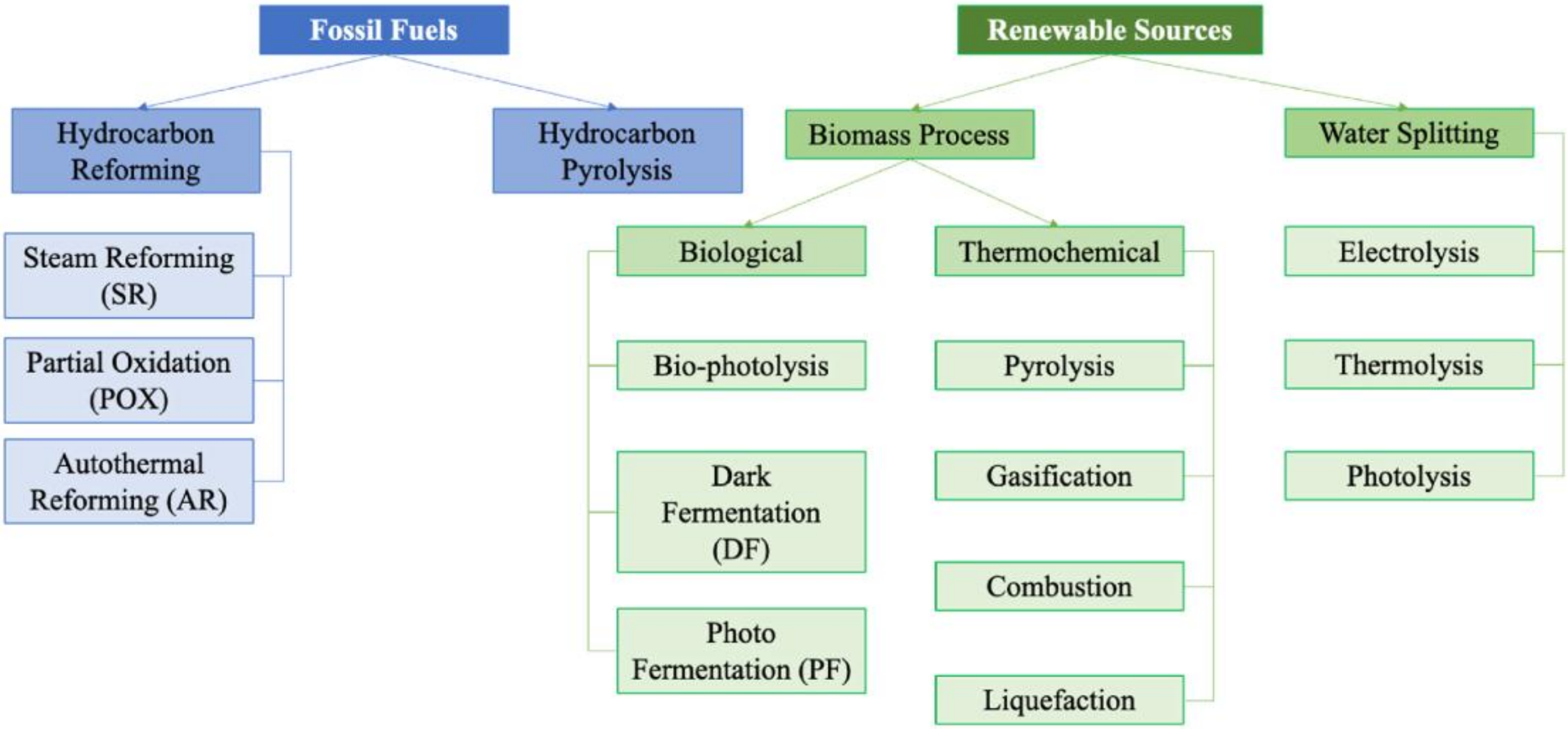
	Terminology	Process / Technology	Feedstock / Energy Source	Products	Carbon Footprint
Production via electricity or biomass	**Green H_2**	Biomass Pyrolysis	Biomass	$CO + H_2 + C + C_mH_n + CO_2$ + Others	Low < 3 kg CO_2eq / kg H_2
		Biomass Gasification		H_2 + CO + CO_2 + CH_4 + Others (mainly tar and char)	
		Water Electrolysis	Water + RES (wind, solar, hydro, geothermal and tidal)	$H_2 + O_2$	Minimal < 2 kg CO_2eq / kg H_2
	Pink H_2	Water Electrolysis	Water + Nuclear	$H_2 + O_2$	Minimal < 2 kg CO_2eq / kg H_2
	Yellow H_2		Water + Electrical Network	$H_2 + O_2$	Low Depending on the source for producing electricity
Production via fossil fuels	**Blue H_2**	Steam reforming + CCS	Natural gas	$H_2 + CO_2$ (% captured and stored)	Low < 3 kg CO_2eq / kg H_2
		Gasification + CCS	Coal	$H_2 + CO_2$ (% captured and stored)	
	Turquoise H_2	Pyrolysis	Natural gas	H_2 + C	Low < 3 kg CO_2eq / kg H_2 + Carbon Black
	Grey H_2	Natural gas reforming	Natural gas	$H_2 + CO_{2(released)}$	High ~11 kg CO_2eq / kg H_2
	Brown H_2	Gasification	Brown coal (lignite)	$H_2 + CO_{2(released)}$	Very High > 20 kg CO_2eq / kg H_2
	Black H_2		Black coal	$H_2 + CO_{2(released)}$	

A different summary, with carbon footprint

Renewable and Sustainable Energy Reviews 225 (2026) 116119

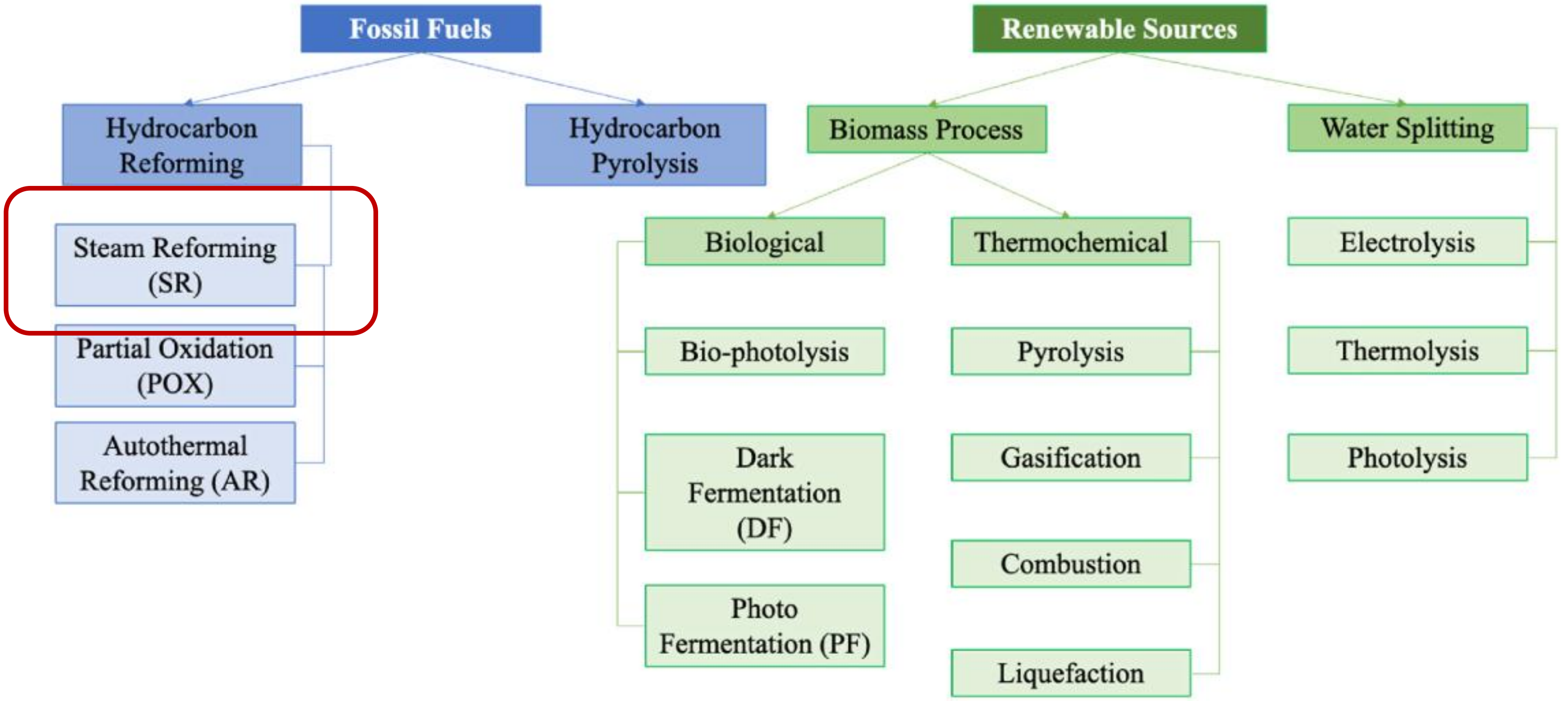
H2 production - technologies

Emphasys on 'green' classification



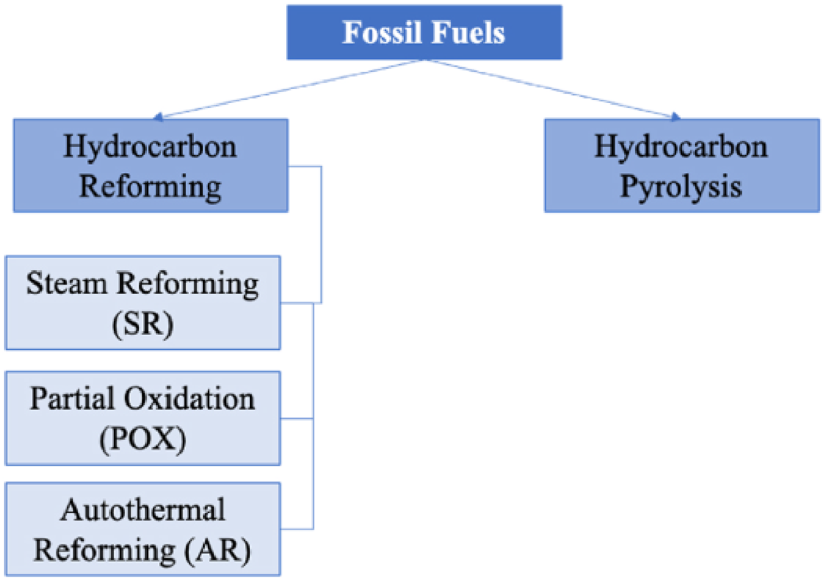
H2 production - technologies

Emphasys on ‘green’ classification



At the present, SR is the dominant, effective process

H2 production - technologies



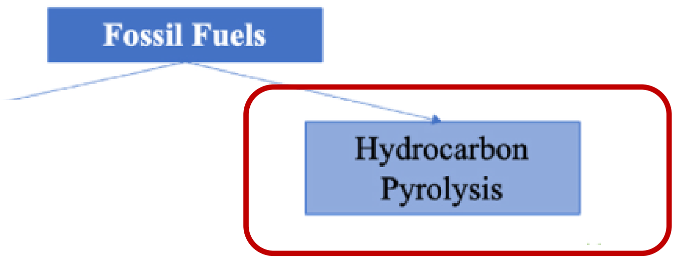
All share similar chemistry:

- isolating H (as H2)
  from C (left as C, CO, CO2)

- Chemically:
  reduction of H^{+1} to H^{0}
  Oxidation of C^{-n} to C^{+m}

- The (use of) products
  make the difference

H2 production – from HCs

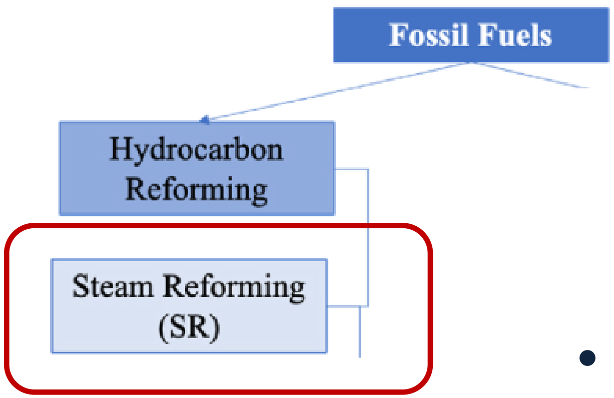


$$C_nH_m \rightarrow nC + \frac{m}{2}H_2$$

- Thermal decomposition
  Catalysts could be used
- No co-reactants (O_2, H_2O,..)
- C is produced as solid (graphite)

- The lower *n/m*, the less C is produced (→ CH_4)

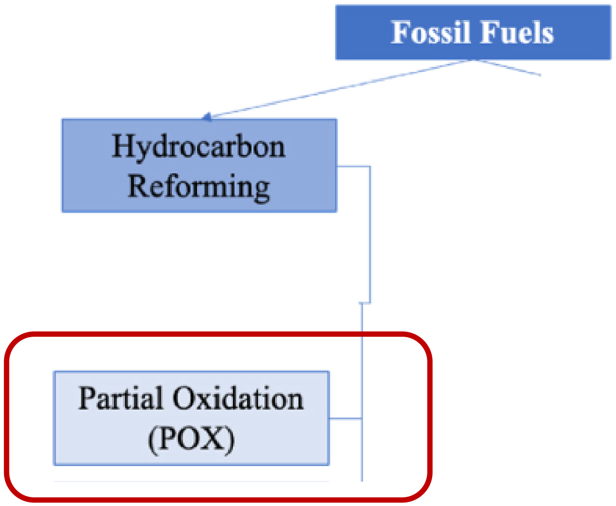
H2 production – from HCs



$$C_nH_m + nH_2O \rightarrow nCO + (n + \frac{m}{2})H_2$$

- Always catalytic
  still T >800°C
- Requires H_2O
  in excess, at high T, pressurized -> energy!
- The lower *n/m*, the less CO_2 is produced (→ CH_4)
- Very endothermic!
- Actually the most economical route to H_2

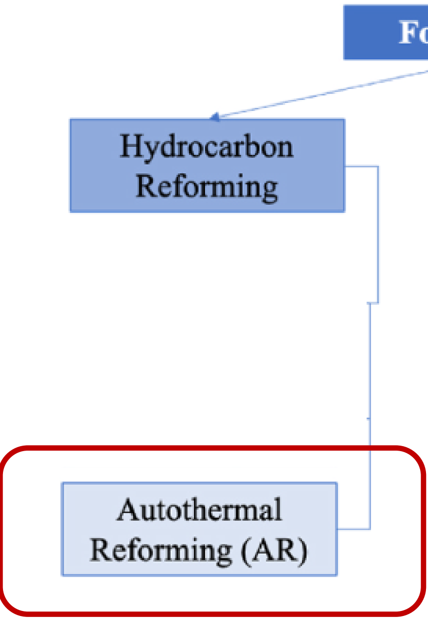
H2 production – from HCs



$$C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2$$

- Better catalytic
- Requires *some* O_2 (better if pure)
- The lower *n/m*, the less CO is produced (→ C
- CO/H2 ratio is higher than SR
- Now exothermic
- Commercial

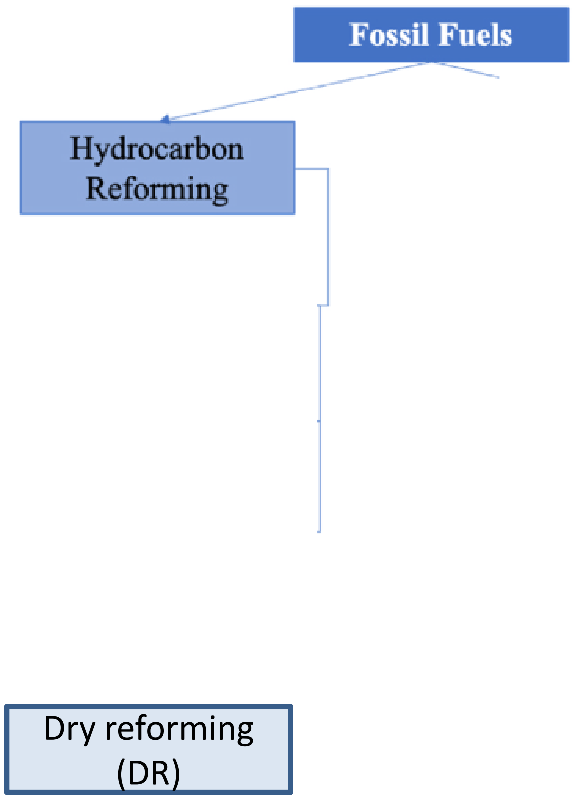
H2 production – from HCs



$$C_nH_m + \frac{n}{2}H_2O + \frac{n}{4}O_2 \rightarrow nCO + (\frac{n}{2} + \frac{m}{2})H_2$$

- Combines SR and POX (endo+exo)
- Always catalytic
- Commercial

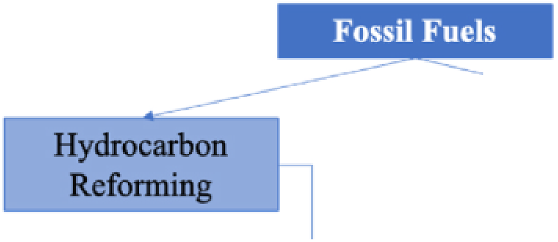
H2 production – from HCs



$$C_nH_m + nCO_2 \rightarrow 2nCO + \frac{m}{2}H_2$$

- (re-)use of CO_2
  turns into CO, to produce CO_2 again by combustion
- Always catalytic
- Coking
- (not in the list of the review)

H2 production – from HCs

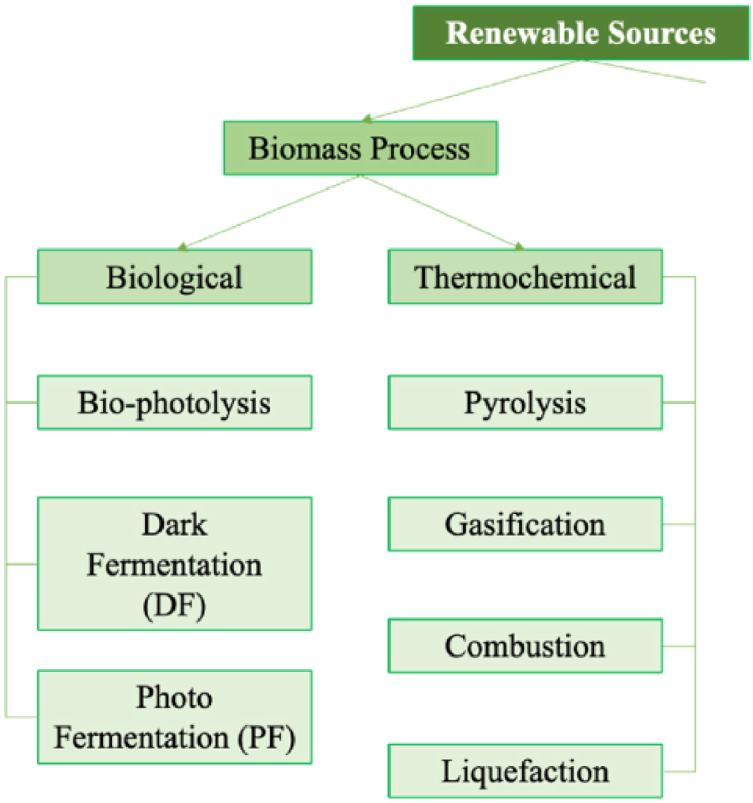


- All reforming reactions produce CO by definition of reforming
- →Water-gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

  - Extracts futher H_2 from steam
  - Always catalytic
  - Occurs at lower T

H2 production - technologies



‘Green’ routes

The bio-based have very low productivity

H2 production - technologies

Biomass thermochemical processes for H_2 production [7,39,50,53,54,57,58,67–69].

Thermochemical processes	TRL	H_2 yield (gH_2/kg feedstock)	Advantages	Disadvantages	Challenges
Biomass Pyrolysis	3-4 (lab scale)	25–65	- Existing industrial design - No oxygen needed	- Formation of char and tar - Catalyst regeneration - Post treatment of exit gases - Variation in H_2 composition due to complexity and variability of biomass - Low H_2 yields - High cost of reactor	- TRL improvement for gaseous H_2 production technology (currently lab-scale) - Effective gas post-treatment for improvement of H_2 quality and yield
Biomass Gasification	5–6	40–190	- Existing industrial design - High biomass conversion efficiency - High H_2 yields among biomass conversion technologies - No expensive oxygen source required in steam gasification	- High operating temperature - Formation of char and tar, causing catalyst deactivation - Catalyst regeneration - Variation in H_2 due to complexity and variability of biomass - Pre treatment optimization - Post treatment of exit gases (fluctuation and variation in gas composition) - Expensive reactor	- Effective tar removal and gas purification for improvement of H_2 quality and yield in gas production - Catalysts optimization
Steam Reforming	–	40–130	- Existing industrial design - No oxygen needed - High conversion efficiency - High H_2 yields among biomass conversion technologies - Well known and established technology, extensively used (i.e. SMR)	- High temperature - Catalysts regeneration - Energy input	- Cost-effectiveness of the SR process to produce green H_2 (use of intermediate products to feed the SR process, while they are readily available for application and direct consumption) - Competitiveness with other technologies that use intermediate products

H2 production - technologies

Gasification

What is this?

- Strictly, turn a solid (or liq) into a gas
  but also combustion does this
- With air?
  If is not a combustion (=total oxid) it is a **partial oxidation**
- With steam?
  The is a **reforming**

H2 production - technologies

Thermochemical processes	TRL	H_2 yield (gH_2/ kg feedstock)
Biomass Pyrolysis	3-4 (lab scale)	25–65
Biomass Gasification	5–6	40–190
Steam Reforming	–	40–130

Critical analysis:

Are these yields (0.025 to 0.19 $kg_{H2}/kg_{feedstock}$) actually possible?

→ Check elemental analysis

H2 production - technologies

Representative proximate analysis, ultimate analysis, and heating value of solid fuels (dry, ash-free)

Fuel type	Wood	Peat	Lignite	Bituminous coal	Refuse-derived fuel
Proximate analysis, wt %					
Volatile matter	81	65	55	40	85
Fixed carbon	19	35	45	60	15
Ultimate analysis, wt %					
Hydrogen	6	6	5	5	7
Carbon	50	55	68	78	52
Sulfur	0.1	0.4	1	2	0.3
Nitrogen	0.1	0.6	1	2	0.7
Oxygen	44	38	25	13	40
HHV					
(Btu/lb_m)	8700	9500	10,700	14,000	9700
(MJ/kg)	20.2	22.1	24.9	32.5	22.5

H in the feedstock is < $7\%_{wt,\ daf}$ = **$0.07\ kg_{H2}/kg_{feedstock,daf}$**

Assuming 50% moisture

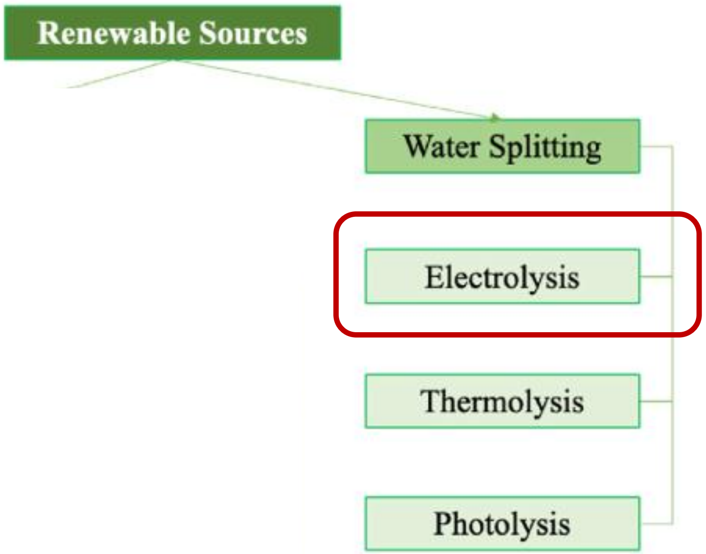
$1\ kg_{feedstock,as\ received} = 0.5\ kg_{daf} + 0.5\ kg_{H2O}$

in terms of H: $0.07\ kg_{H2}/kg_{feedstock,daf} \cdot 0.5\ kg_{daf} + 2/18\ kg_{H2}/kg_{H2O} \cdot 0.5\ kg_{H2O}$

= **$0.09\ kg_{H2}/kg_{feedstock,\ as\ received}$** << max reported in the tables

Additional H comes from (gasification) steam?

H2 production - technologies

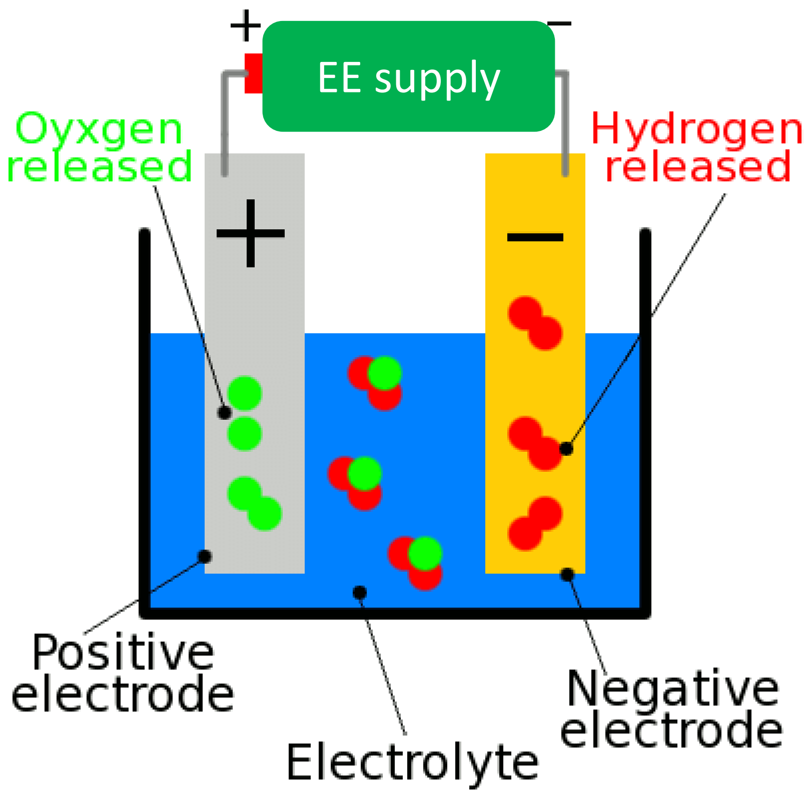


Electrochemistry
is the real alternative to SR

It involves electro-catalysis
(chemistry, materials, transport processes)

H2 production - technologies

Electro-lysis: how does it work



anode

(oxidation)

catode

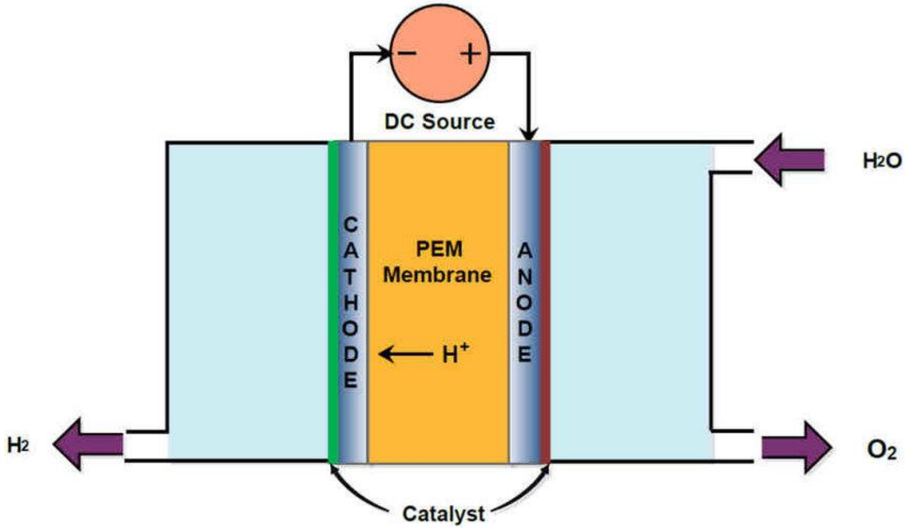
(reduction = use of e^-)

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

H2 production - technologies

Electro-lysis: how does it work



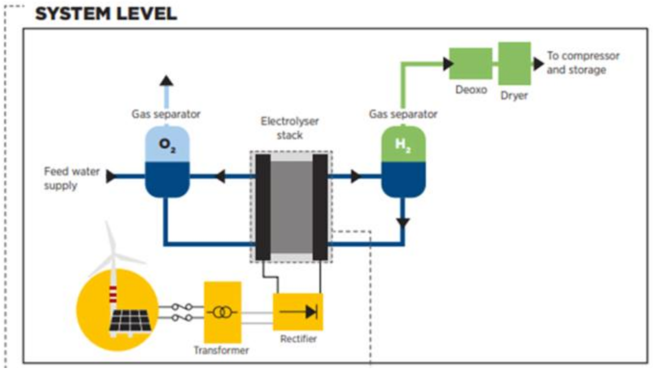
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

A **membrane** allows a selective transport of ions

H^+ or OH^- and separation of H_2/O_2

H2 production - technologies

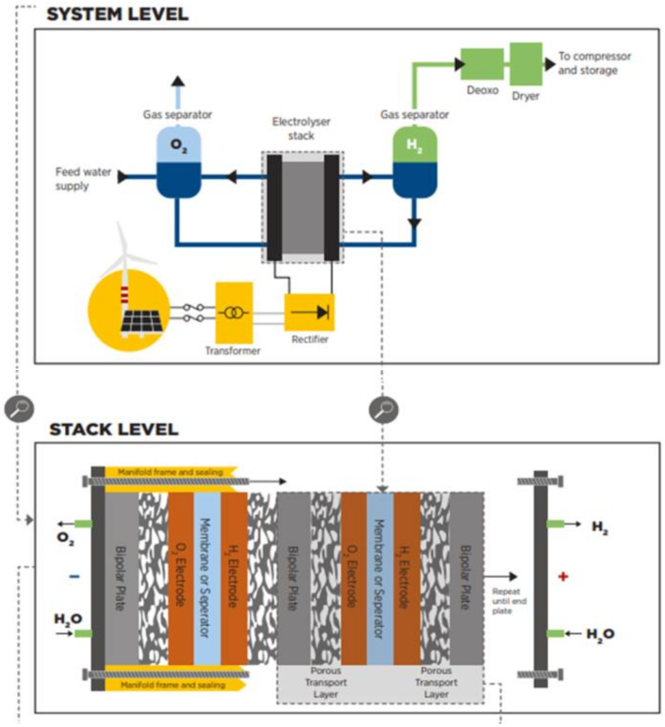


Multiple Scales

Includes:

- equipment for cooling
- processing the H2
  (e.g. for purity and compression),
- converting the electricity input
  (e.g. transformer and rectifier)
- treating the water supply
  (e.g. deionization)
- treating gas output
  (e.g. oxygen)

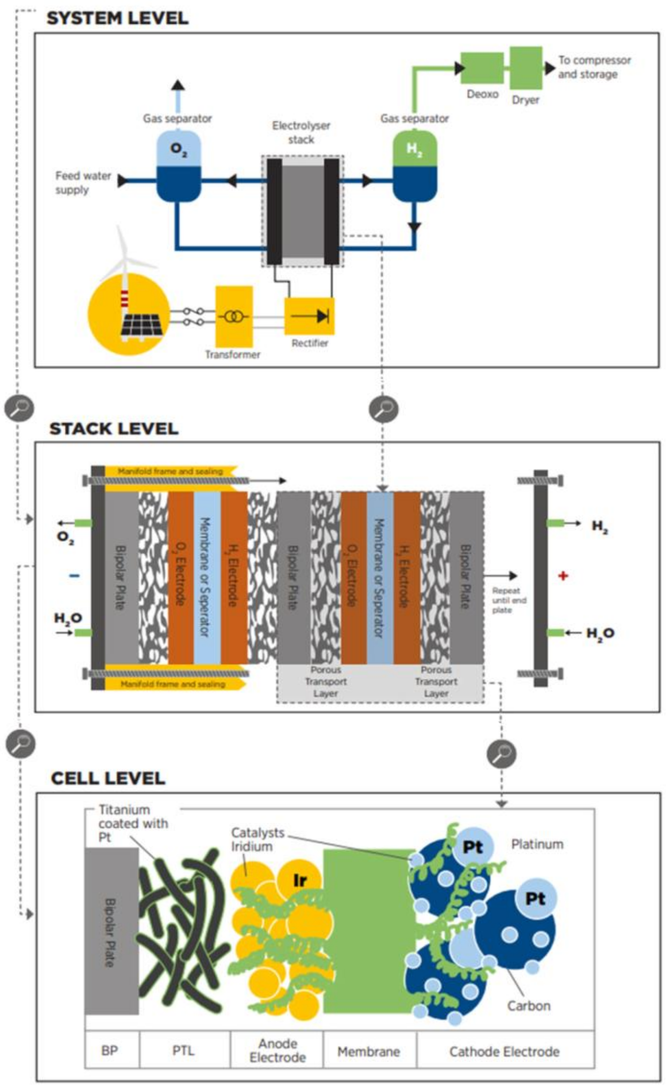
H2 production - technologies



Muliple Scales

- multiple cells connected
- spacers (insulating material between two opposite electrodes),
- Seals
- frames (mechanical support)
- end plates (to avoid leaks and collect fluids)

H2 production - technologies



Muliple Scales

The core!

- diaphragm or membrane between both electrodes to keep H_2 and O_2 separated (crossover)
- Most of the reserch is at laboratory scale overlooking large scale technical issues

H2 production - technologies

Different implementations:

1. Alkaline Water Electrolysis (AWE)
2. Proton Exchange Membrane (PEM)
3. Anion Exchange Membrane (AEM)
4. Solid Oxide Electrolysis (SOE).

H2 production - technologies

1. Alkaline Water Electrolysis (AWE)
   – most mature H2 production technology
   – KOH (or NaOH) at 20–40 % electrolyte
   – cobalt, nickel or simply stainless electrodes
   – 70 to 90 ◦C, <30 bar
   – about 0.2–0.4 A/cm2 (faily **low - low H2 production rate**)
   – cell voltage between 1.8 and 2.4 V, efficiencies between 62 and 82 %

H2 production - technologies

2. Proton Exchange Membrane (PEM)
   - Commercial
   - most effective water electrolysis process for H2 generation
   - critical: proton conductive membrane
   - electrodes pressed against the membrane, forming a sandwich, (membrane electrode assembly, MEA).
   - MEA immersed in ultrapure water (highly sensitive to water impurities and can suffer from calcination)
   - requires expensive materials
     - Nafion-based membranes
     - expensive noble metals
     - titanium stack components

H2 production - technologies

3. Anion Exchange Membrane (AEM)
   - one of the latest water electrolysis technologies
   - integrates the benefits of both conventional PEM and AWE (less harsh environment than AWE and efficiency of a PEM)
   - promising solution for large-scale H_2 production
   - performance is still lower than conventional electrolysis
   - inability to maintain high-pressure H2 (porous diaphragm)

H2 production - technologies

4. Solid Oxide Electrolysis (SOE)
   - also known as steam electrolysis
     (T>700°C to achieve conductivity)
   - ceramics materials (yttria-stabilized zirconia, YSZ, electrolytes)
   - electricity usage is significantly lower than other processes
   - regarded as the most efficient electrolysis technologies for H_2
   - thermochemical challenges (undert T cycles)
     → accelerated degradation and shorter lifetimes
   - Critical scaling