Production and use of green hydrogen in the industrial sector

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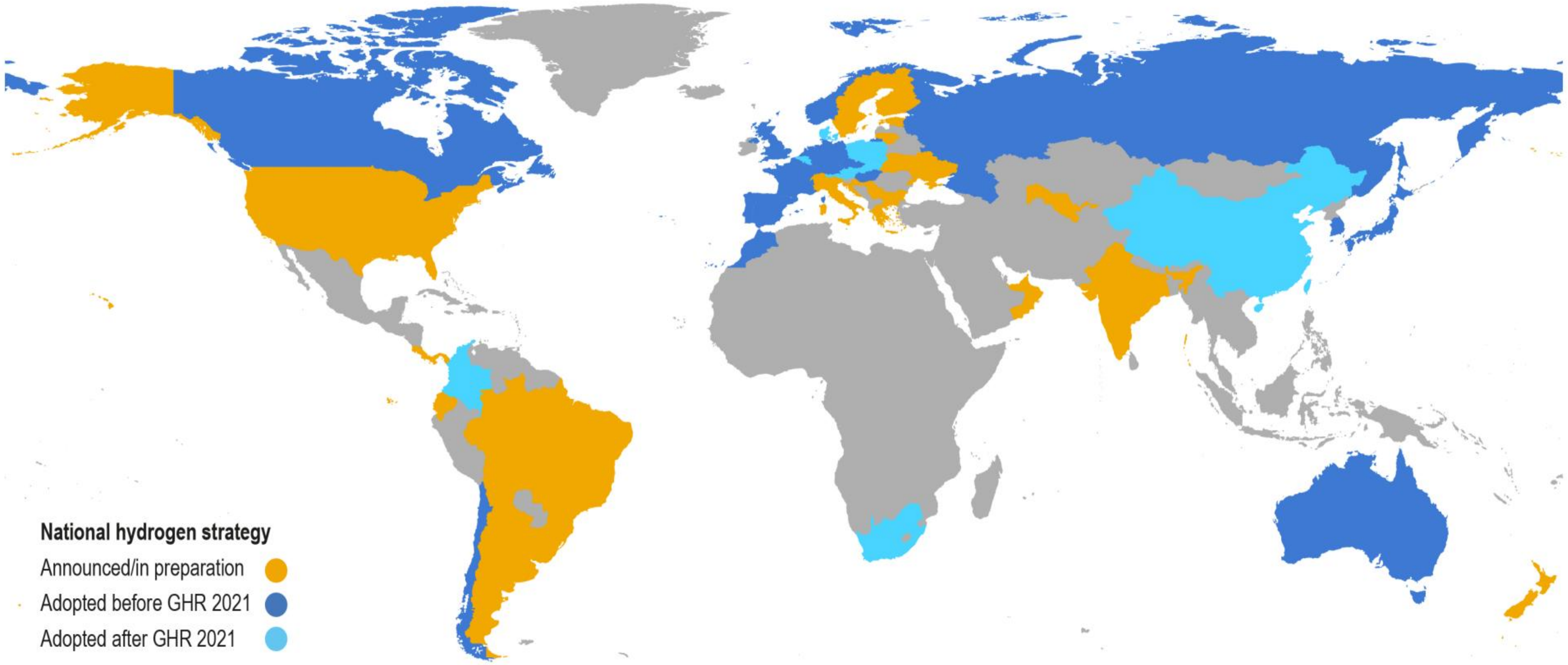
Introduction



TODAY	2050
94 Mt	530 Mt
99.96% H_2 – grey	62% H_2 – green 38% H_2 – blu
Refineries and Petrochemical industry	19% Power 35% Industry 39% Transports

Data from IEA: Global Hydrogen Review 2022

Past energy transitions

Biomass-coal-oil-gas-renewables

- Scarcity of source (locally or globally) leading to higher prices=>new source cheaper
- Technological improvement and innovation=>more efficient and cheaper production
- Ultimate goal was to improve well-being (increase productivity and income)
- Now we add climate issues

New energy transition

Biomass-coal-oil-gas-renewables/hydrogen(?)

- energy transition not linked to the availability of a new energy source or favored by the invention of a new technology but promoted by a change in the market structure as a result of the need to reduce carbon dioxide emissions
- Transition accompanied by an increase in the cost of energy and products

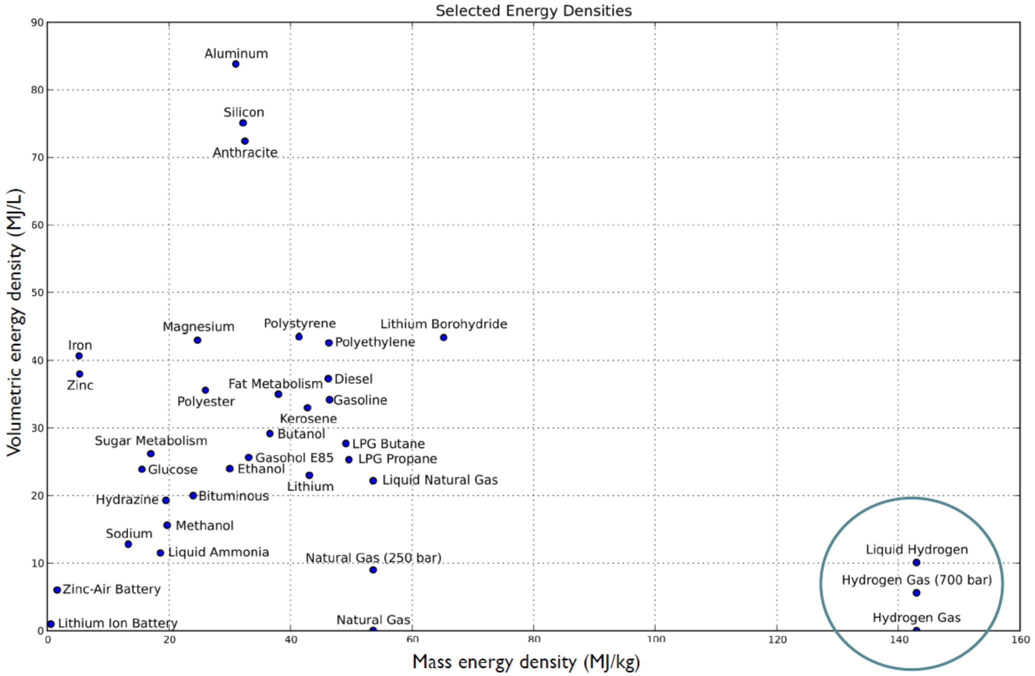
Hydrogen

- It can be produced from excess renewable energy, stored, and used to supplement the variability of RES
- Its combustion does not emit carbon dioxide
- It can be stored and transported in several ways
- Improve energy security thanks to the diversification of sources
- It can be used to produce ammonia and other synthetic fuels

Introduction

Why hydrogen?

- Most abundant element in the universe
- High energy content:
  - 140 MJ/kg for H2
  - 44 MJ/kg for petrol
- Almost no emissions (only water)
- Acts as an energy carrier, not a primary source



- On a mass basis, the energy contained in a unit of hydrogen is at least **2.5 times greater** than that contained in the same unit of another fuel

Property	Gasoline	Methane	Hydrogen
Density (kg/m^3)	4.40	0.65	0.084
Diffusion coefficient in air (cm^2/s)	0.05	0.16	0.610
Ignition limits in air (%vol)	1.0-7.6	5.3-15.0	4.0-75
Ignition energy in air (mJ)	0.24	0.29	0.02
Ignition temperature (°C)	501-744	813	858
Flame temperature in air (°C)	2470	2148	2318
Explosion limits in air (%vol)	1.1-3.3	6.3-14	18-59

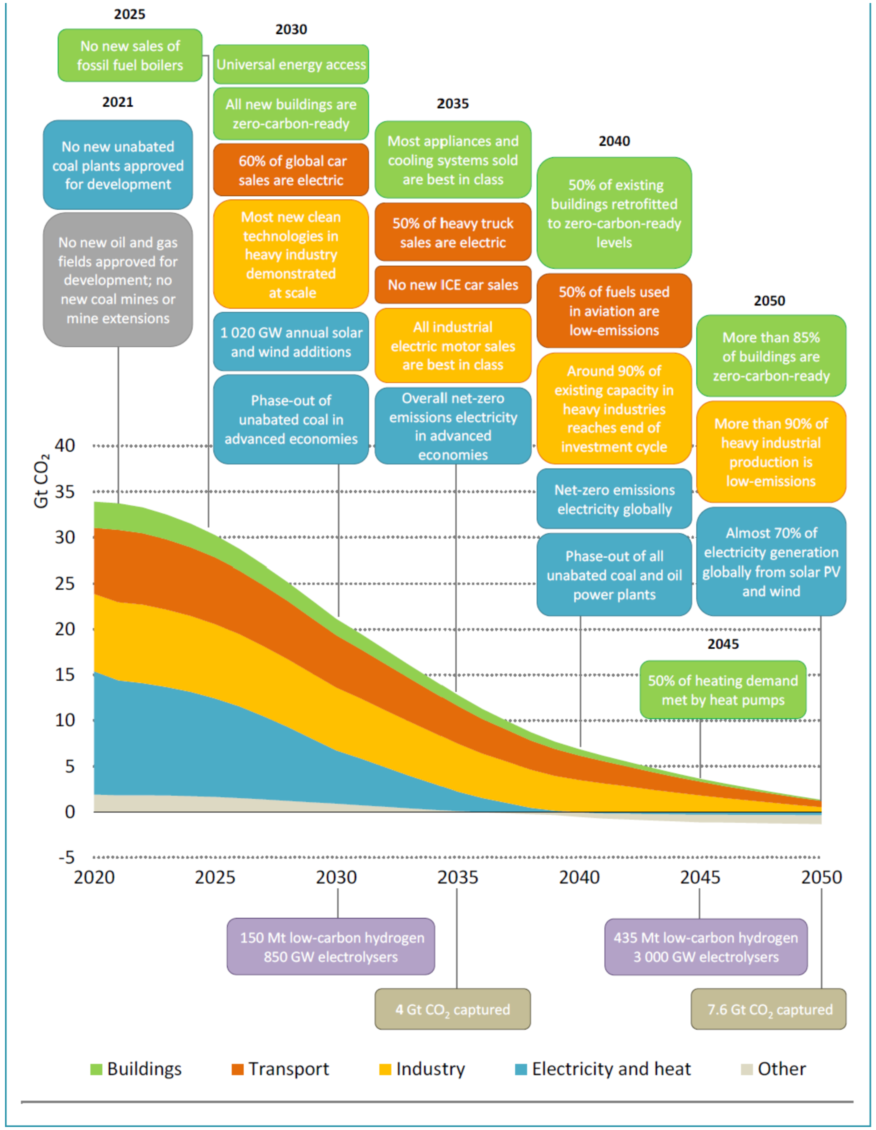
Volume Basis:

Fuel	LHV (MJ/m^3)	Gaseous phase condiditions	Physical state
Hydrogen	10.7 1.852 4.5 8.491	15°C, 1 atm 15°C, 200 atm 15°C, 690 atm -	Gas Gas Gas Liquid
Methane	32.56 6.86 20.92	15°C, 1 atm 15°C, 200 atm -	Gas Gas Liquid
Gasoline	31.15	-	Liquid
Diesel	31.436	-	Liquid
Methanol	15.8	-	Liquid
Biodiesel	30.8	-	Liquid
Biogas	18	15°C, 1 atm	Gas

Mass Basis:

Fuel	HHV (MJ/kg)	LHV (MJ/kg)	Physical state (25°C, 1 atm)
Hydrogen	141.86	119.93	Gas
Methane	55.3	50.02	Gas
Propane	50.36	45.6	Gas
Gasoline	47.5	44.5	Liquid
Diesel	44.8	42.5	Liquid
Methanol	19.96	18.05	Liquid
Coke	36	31	Solid
Wood	16	13	Solid
Biodiesel	37	35	Liquid
Biogas	27	25	Gas

Introduction

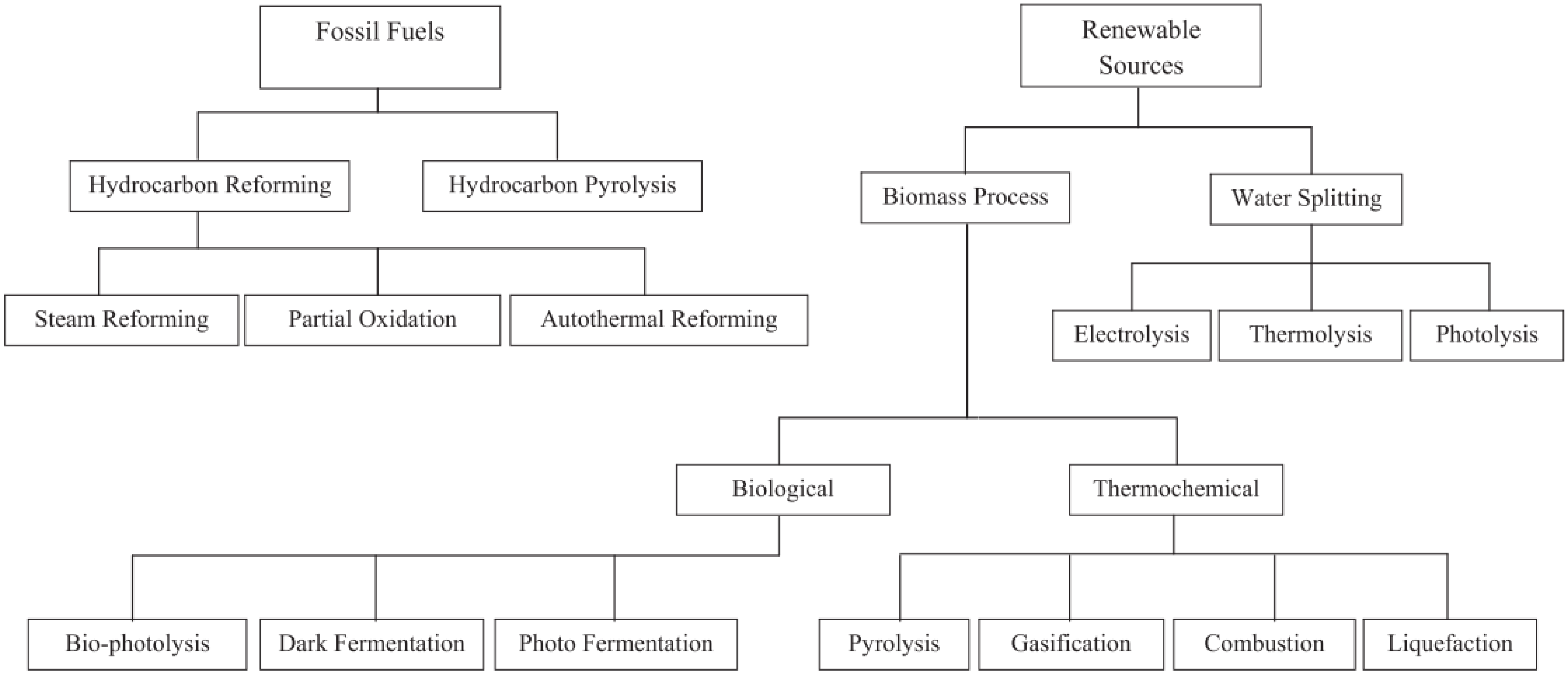


Introduction

- It seems to be necessary for a green transition

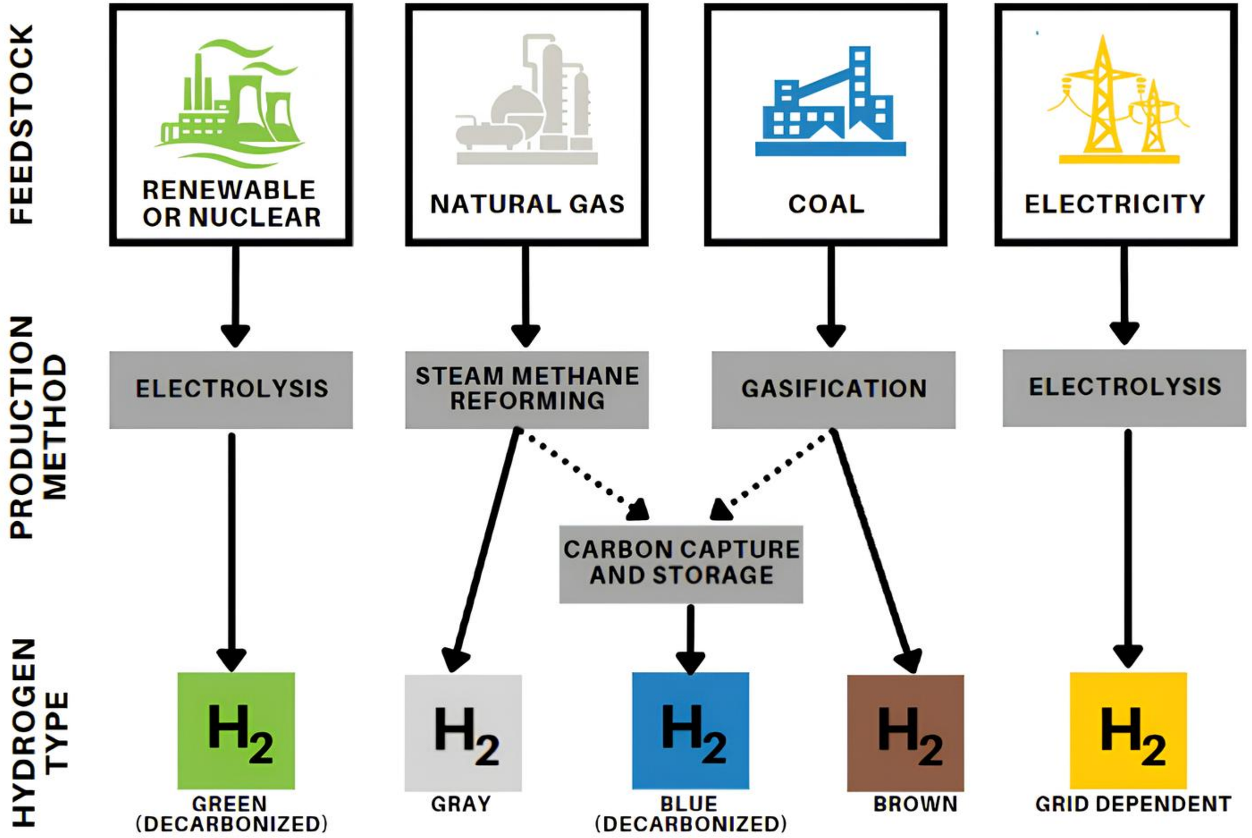
- The present state of the art is not green

Production



From: P. Nikolaidis and A. Poullikkas, “A comparative overview of hydrogen production processes,” *Renew. Sustain. Energy Rev., 2017*

Production

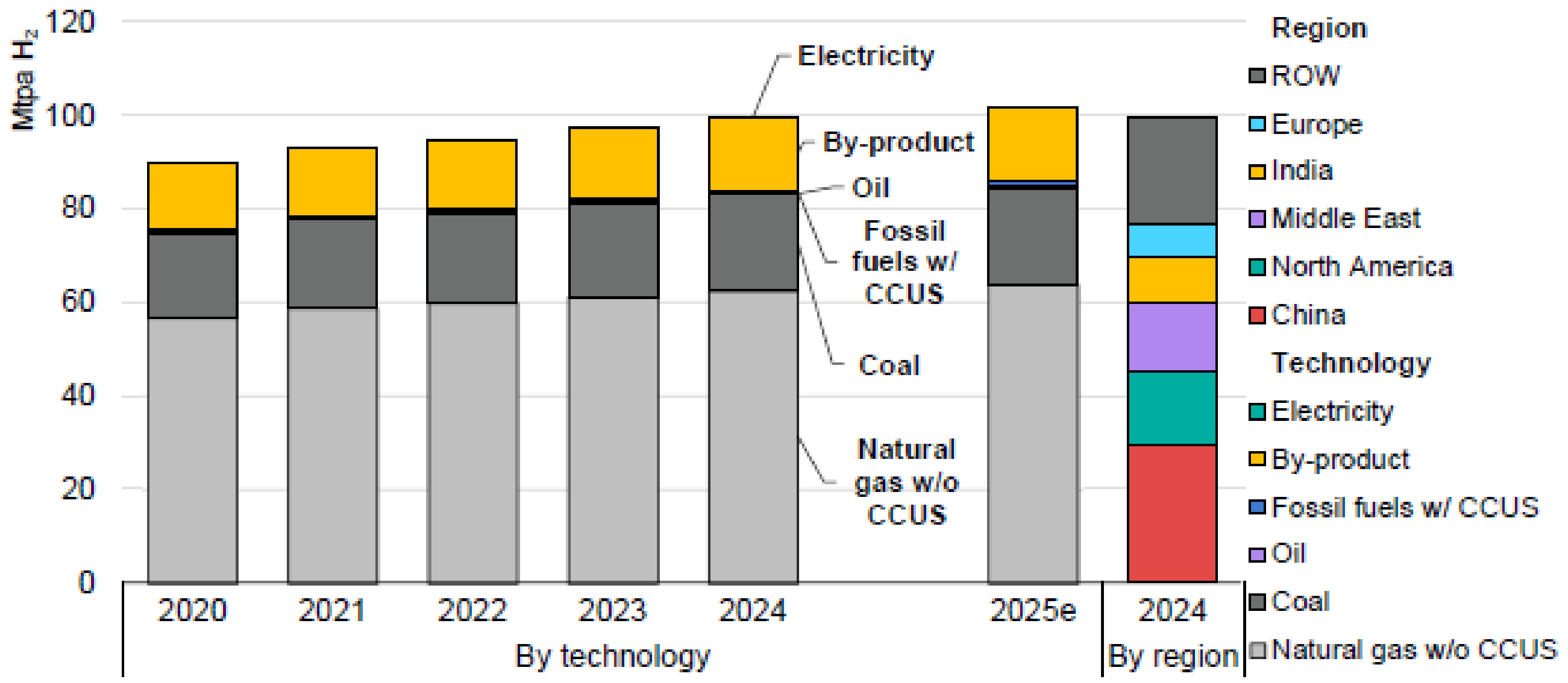


Hydrogen is usually classified based on his production method:

- **Green hydrogen:** electrolysis powered by renewables
- **Grey hydrogen:** fossil-based, no CO_2 capture
- **Blue hydrogen:** steam methane reforming + carbon capture
- **Brown/Black hydrogen:** from coal or lignite
- Pink Hydrogen: electrolysis powered by nuclear energy
- **Yellow hydrogen** electrolysis powered by grid energy
- **Biohydrogen:** produced from biomass or organic waste (dark fermentation)

Production

Figure 3.1 Hydrogen production by technology and by region, 2020-2025e



Notes: CCUS = carbon capture, utilisation and storage; ROW = rest of world; 2025e= estimate for 2025, based on trends observed until July 2025. By-product hydrogen includes production in catalytic naphtha crackers and steam crackers which is subsequently used in refining.

Production

Sector	2020	2030	2050
Total production hydrogen-based fuels (Mt)	**87**	**212**	**528**
Low-carbon hydrogen production	9	150	520
share of fossil-based with CCUS	*95%*	*46%*	*38%*
share of electrolysis-based	*5%*	*54%*	*62%*
Merchant production	15	127	414
Onsite production	73	85	114
Total consumption hydrogen-based fuels (Mt)	**87**	**212**	**528**
Electricity	0	52	102
of which hydrogen	0	43	88
of which ammonia	0	8	13
Refineries	36	25	8
Buildings and agriculture	0	17	23
Transport	0	25	207
of which hydrogen	0	11	106
of which ammonia	0	5	56
of which synthetic fuels	0	8	44
Industry	51	93	187

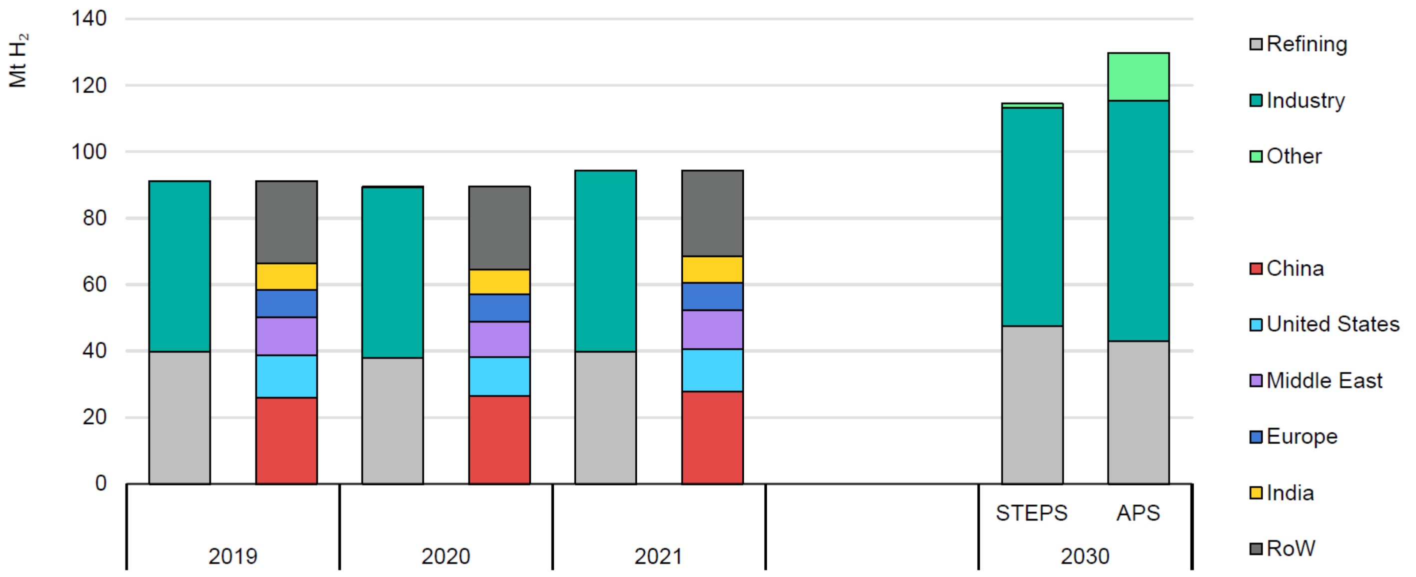
Note: Hydrogen-based fuels are reported in million tonnes of hydrogen required to produce them.

IEA, Net Zero by 2050 A Roadmap for the Global Energy Sector

Use

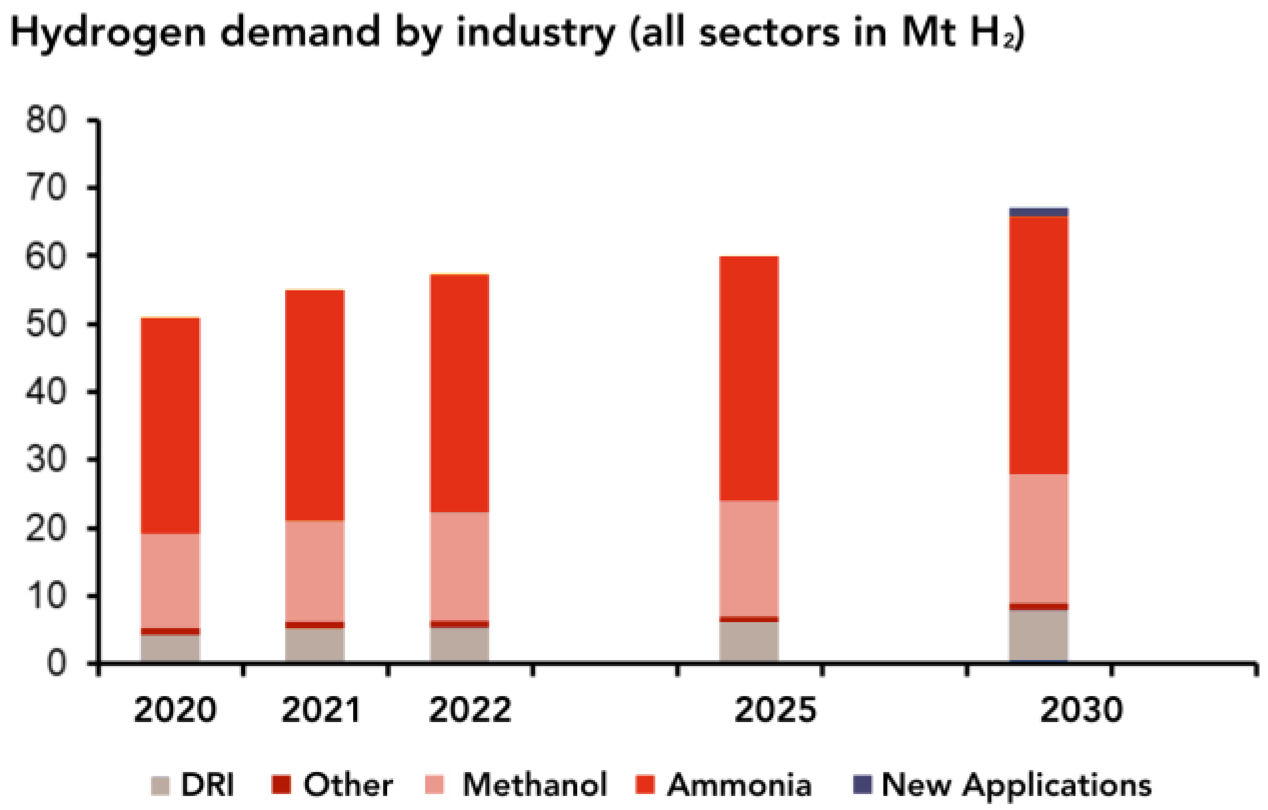
Global hydrogen demand increased 5% in 2021, reflecting recovery of economic activity in traditional applications from the pandemic-related curtailments

Hydrogen demand by sector and by region in the Stated Policies and Announced Pledges scenarios, 2019-2030



Notes: Mt H_2 = million tonnes of hydrogen; STEPS = Stated Policies Scenario; APS = Announced Pledges Scenario. *Other* includes transport, buildings, power generation sectors and production of hydrogen-derived fuels and hydrogen blending.

Use


Hydrogen demand by industry (all sectors in Mt H2)
80
70
60
50
40
30
20
10
0
2020
2021
2022
2025
2030
DRI
Other
Methanol
Ammonia
New Applications

Use

- Present
- Potential

Present

- Pure H2
  - Refineries (38 Mton)
  - Ammonia (31 Mton)➔ fertilizers
  - Other (4 Mton)

- Blended with other gases
  - Direct Reduced Iron (4 Mton)
  - Methanol (12 Mton)
  - Other (1 Mton)

- We need to create the demand
  - as feedstock
  - as energy vector

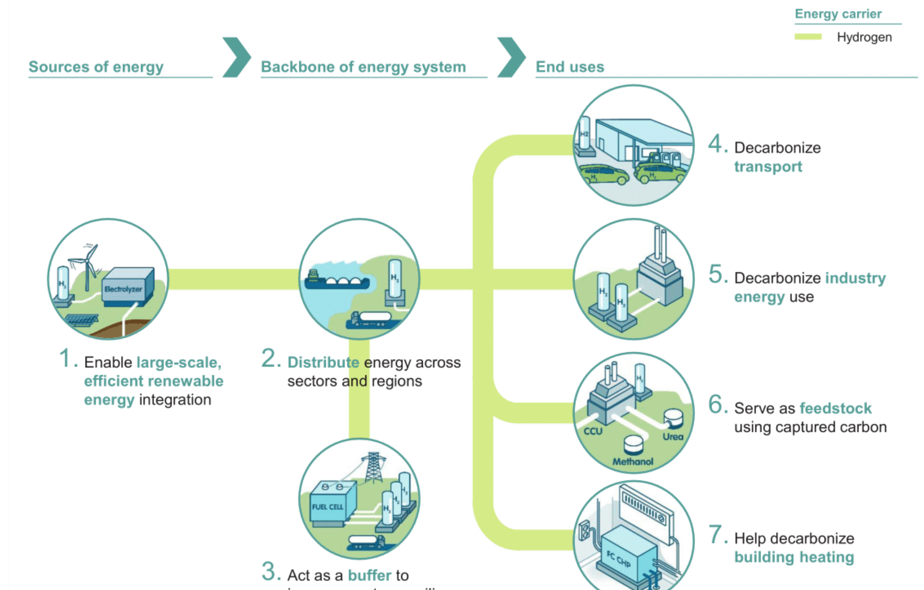
  - Hard-to-Abate Industries

Use in industry

Hydrogen represents a key enabler of sustainable industry and energy:

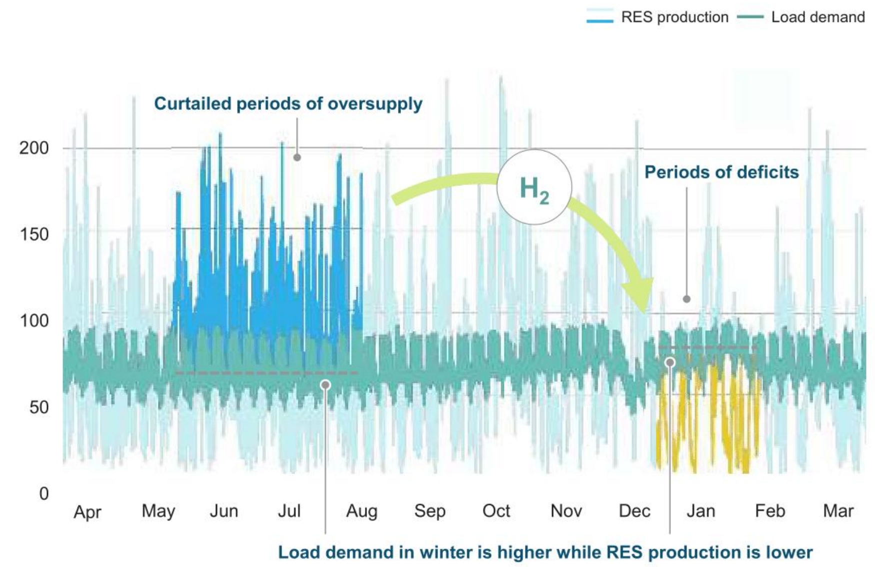
- **Hard-to-decarbonize sectors:** steel, chemicals, cement
- **Transport and mobility:** heavy-duty vehicles, ships, aircraft
- **Power generation:** via fuel cells (PEM, SOFC) or combustion
- **Energy storage:** seasonal storage of renewable electricity
- **Circular economy:** H_2 from organic waste adds value to residues

Figure 2: Hydrogen has seven roles in decarbonizing major sectors of the economy



Source: Hydrogen Council

Figure 3: Excess power can be used to produce hydrogen for seasonal energy storage
Simulation for Germany 2050, in GW

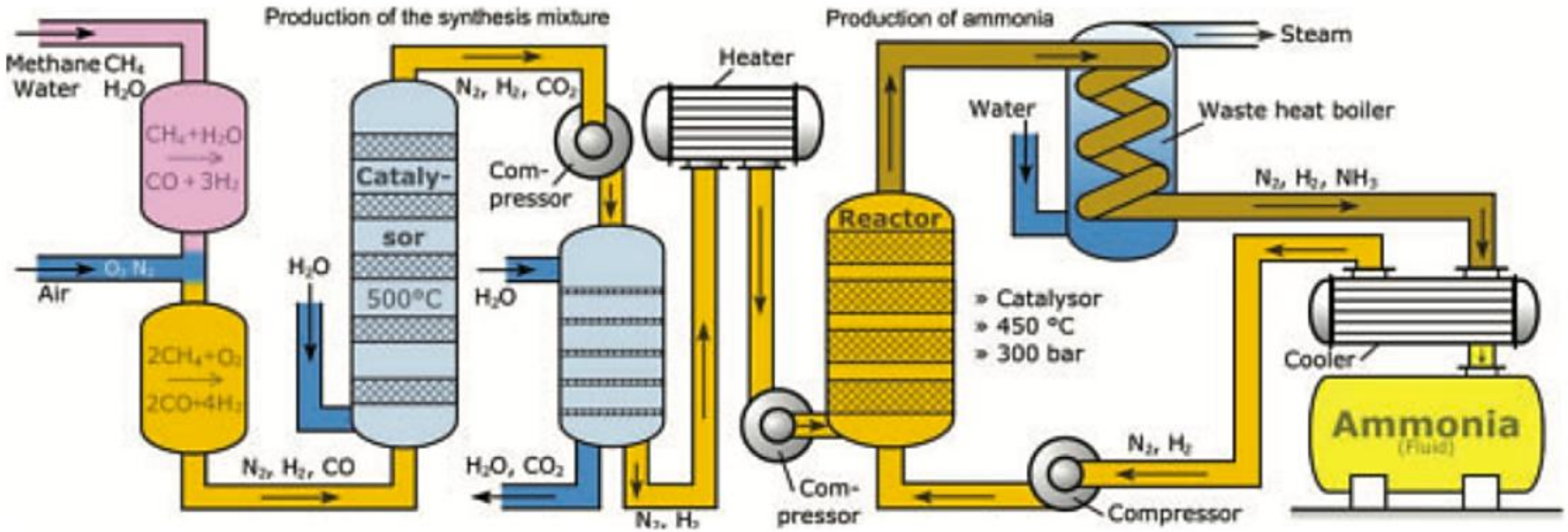


Source: EC 2050 scenario, McKinsey analysis

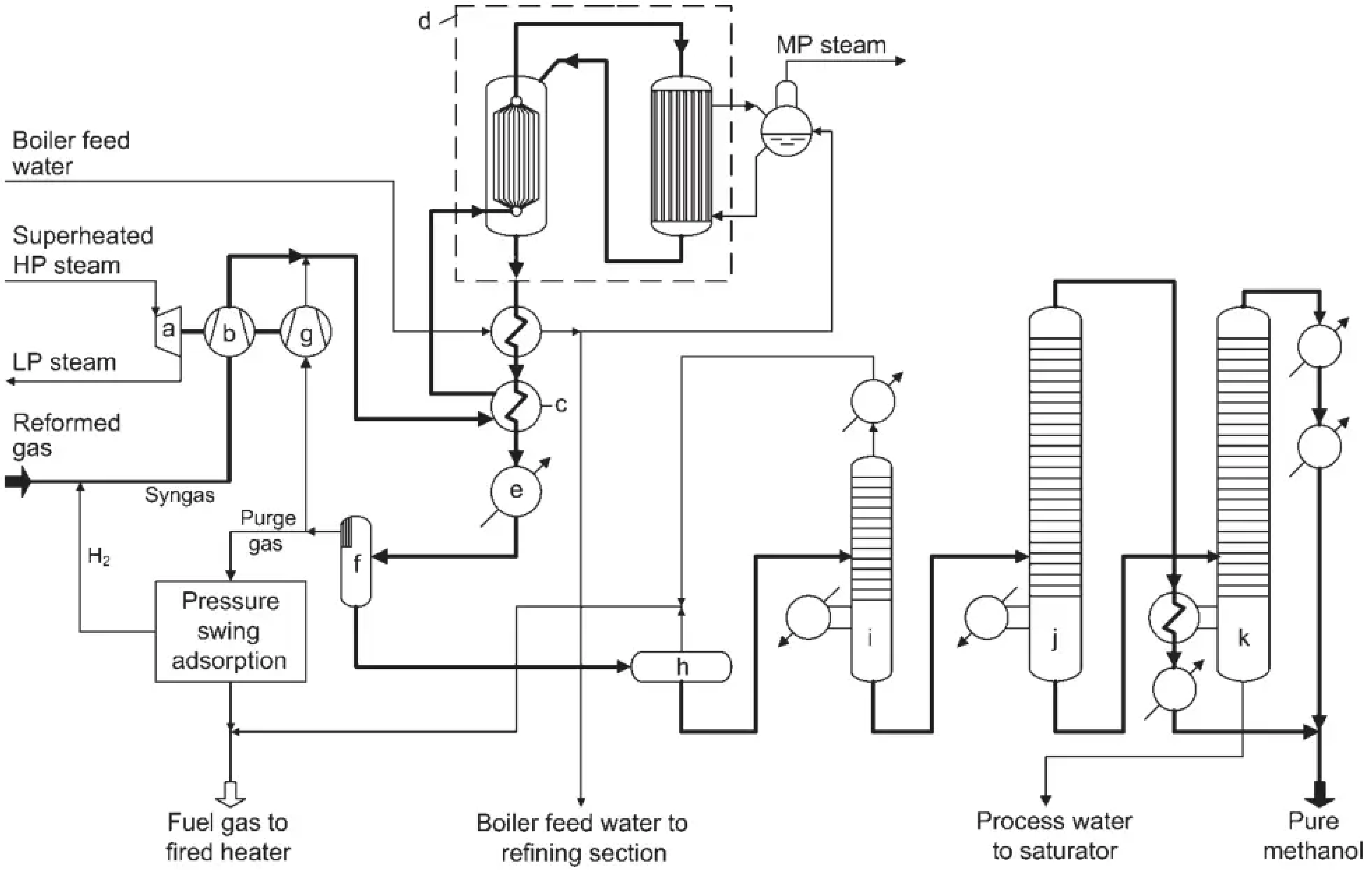
Potential

- Refineries (hydrocracking)
- Ammonia
- Methanol
- Iron Metallurgy (integral cycle, direct reduced iron, hydrogen electrical arc furnaces, hydrogen preheating and heat treatment furnaces)
- HCl, H_2O_2, hydrogenate agents
- Concrete, glass , ceramics (hydrogen cement firing kilns, oxi-combustion for glass production, roller kilns, …)
- Use of electricity from fuel cells or gas turbines fed by hydrogen
- Transport (bound fleets)

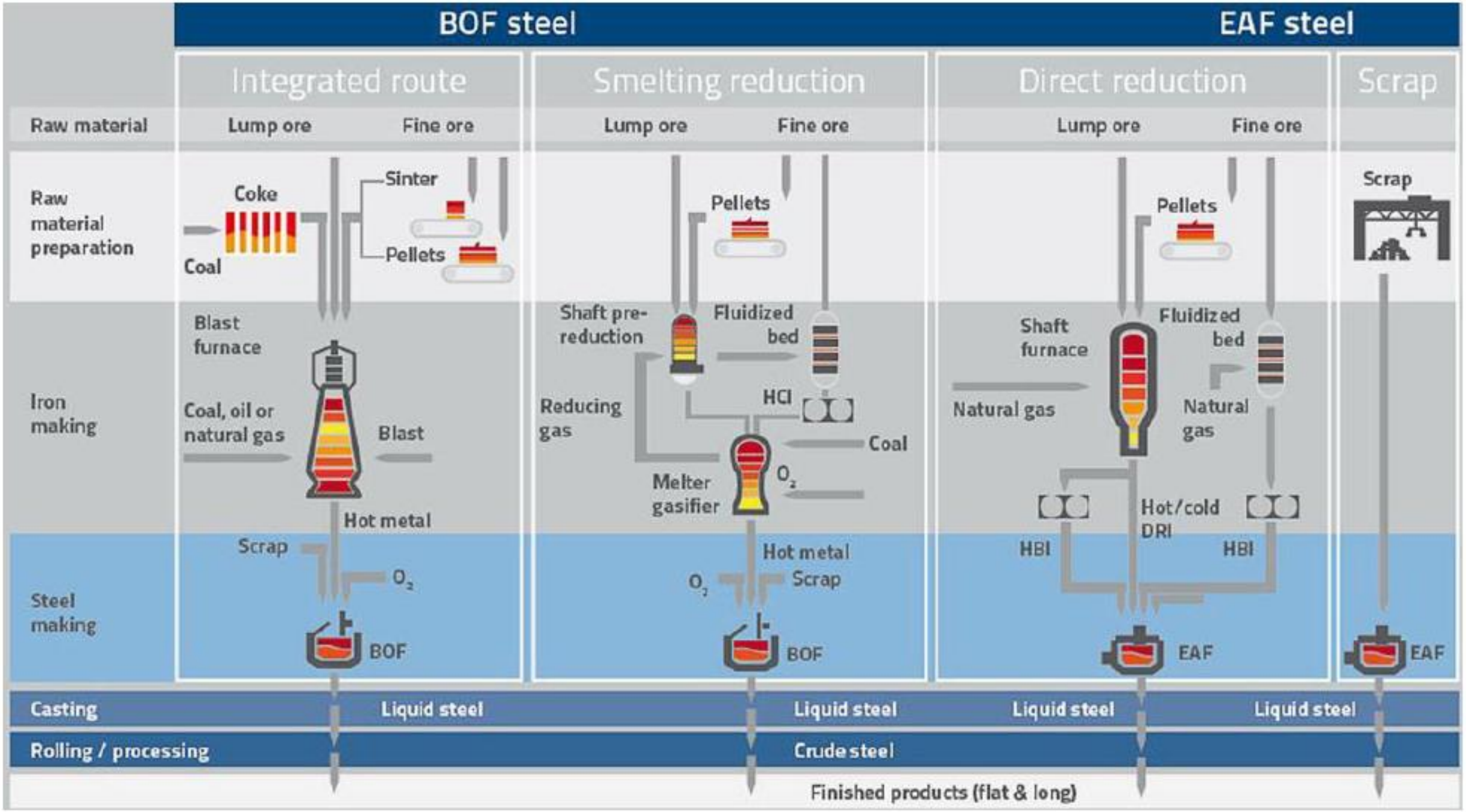
Use for NH_3 production



Use for CH_3OH production



Use for direct Iron reduction



Use for direct Iron reduction

The chemical reactions involved in the direct reduction of iron are the following:

With H_2

$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O4 + H_2O$

$Fe_3O_4 + H_2 \rightarrow 3\ FeO + H_2O$

$FeO + H_2 \rightarrow Fe + H_2O$

With CO

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO$

$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

With solid carbon in reaction

$CO_2 + C \rightarrow 2CO$

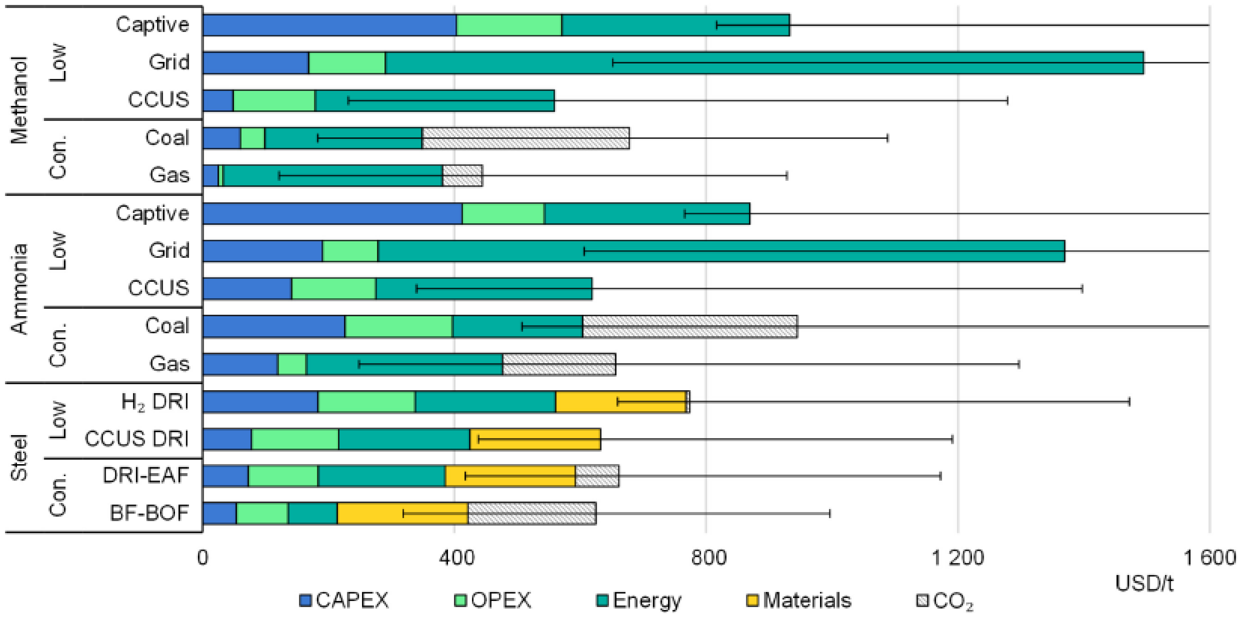
Simplified Reduction

(1)	Fe_2O_3	+	3CO	-----→	2Fe	+	$3CO_2$	(ΔH_R = - 24kJ/mol)
(2)	Fe_2O_3	+	$3H_2$	-----→	2Fe	+	$3H_2O$	(ΔH_R = 99kJ/mol)

Use in refineries

- For **Hydrotreating** (desulfurization): Hydrogen reacts with the sulfur contained in petroleum fractions, converting it into hydrogen sulfide (H_2S), which can be easily separated, in order to produce low-sulfur fuels that comply with environmental regulations.
- For **Hydrocracking**: A process that uses hydrogen at high temperatures and pressures to break down long, heavy molecules (residues) into shorter, more valuable products (gasoline, kerosene, diesel).

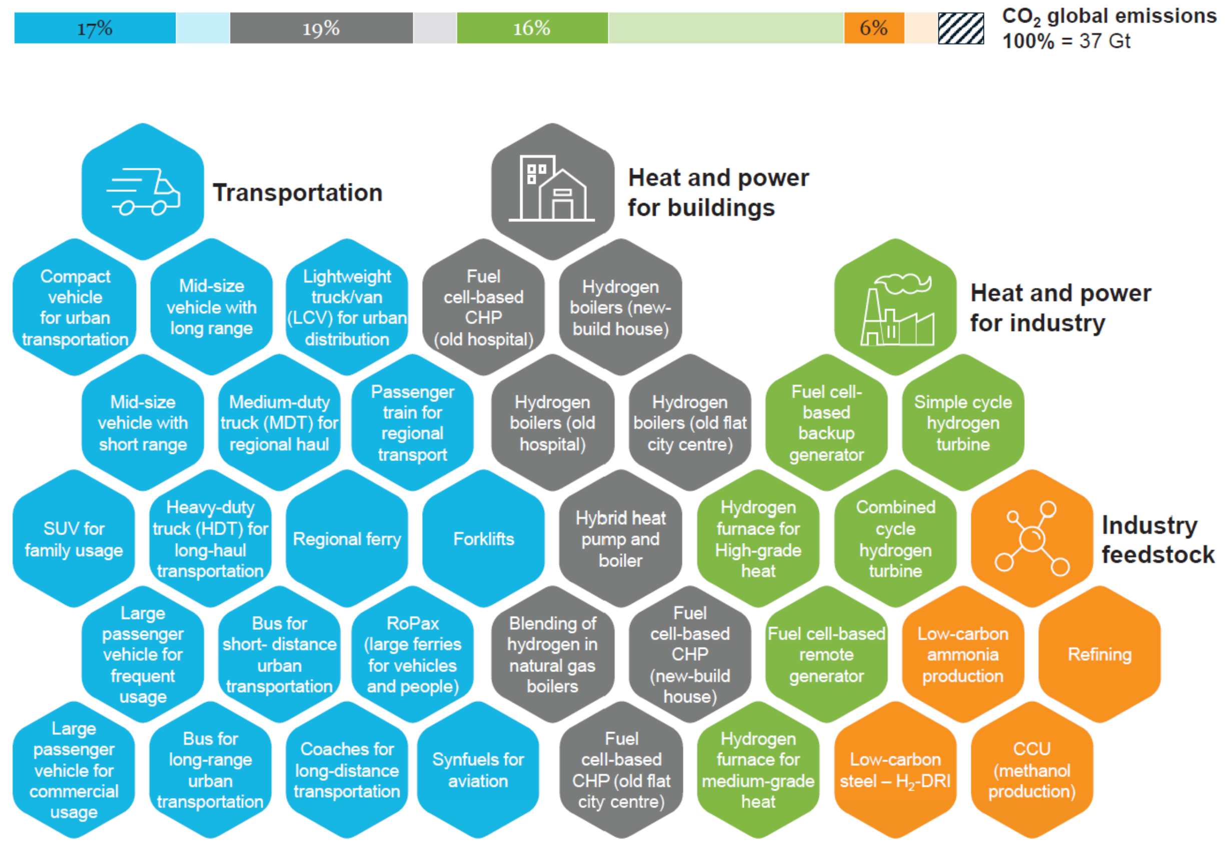
Figure 2.9 Levelised cost of production of selected materials by technology, 2024



Notes: Con. = Conventional; Low = Low-emissions; CCUS = carbon capture, utilisation and storage; DRI = direct reduced iron; EAF = electric arc furnace; BF = blast furnace; BOF = basic oxygen furnace; H_2 = hydrogen. Grid and Captive refer to electrolysis-based routes using either grid electricity or captive renewable production. CCUS refers to carbon capture and storage applied to natural gas. H_2 DRI uses captive power. The cost of the CO_2 input for methanol production and the cost of CO_2 transport and storage for CCUS are included in the OPEX category. CO_2 represents the cost increase if a USD 100/t CO_2 tax were in place. Error bars represent regional variation together with cost uncertainty for near-zero emissions technologies for material production. Energy costs are based on regional end-user prices for industry, including taxes and charges, and include fuel use for energy and for feedstock. The base case values and the ranges are as follows: USD 10/Mbtu for natural gas (USD 2.5-23/Mbtu); USD 100/t for coal (USD 17-200/t); USD 100/MWh for grid electricity (USD 30-300/MWh); USD 30/MWh for captive electricity (USD 20-50/MWh); USD 900/kW for electrolyser CAPEX in China and USD 2 300/kW elsewhere. Costs shown here do not include explicit financial support but may include financial support embedded in individual cost components (e.g. fossil fuel subsidies). See technical annex for further detail on technoeconomic assumptions.

Use in industry

Exhibit 4 | Overview of hydrogen applications



In addition, hydrogen can also be used in, e.g.

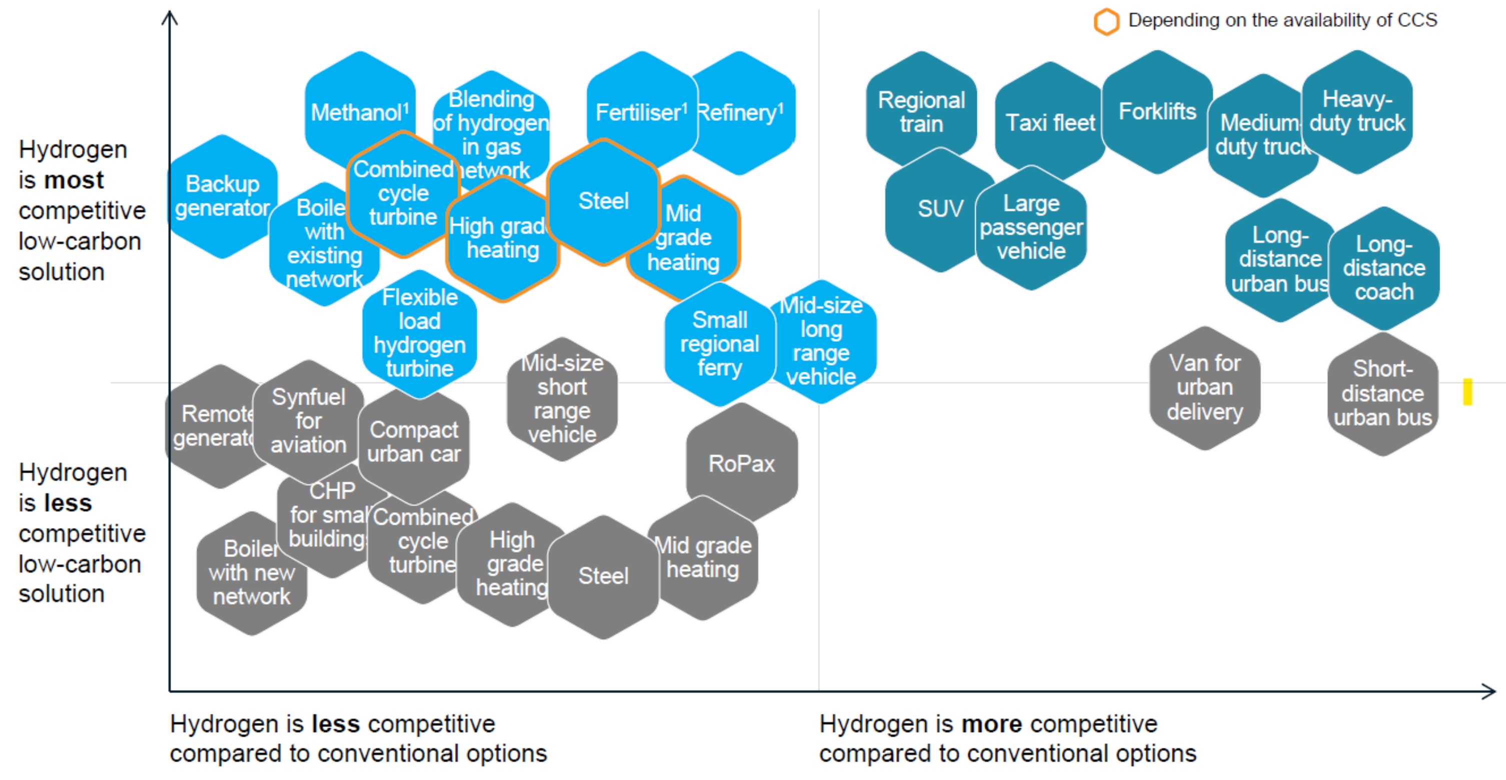
Mobility: Container ships, tankers, tractors, container ships, motorbikes, tractors, off-road applications, fuel cell airplanes.

Other: Auxiliary power units, large scale CHP for industry, mining equipment, metals processing (non-DRI steel), etc..

From A path to hydrogen cost competitiveness, Hydrogen Council, 2020

Use in industry

Exhibit 5 | Competitiveness of hydrogen applications versus low-carbon and conventional alternatives



1. Hydrogen is the only alternative and low-carbon/renewable hydrogen competing with grey (optimal renewable or low-carbon shown)

From A path to hydrogen cost competitiveness, Hydrogen Council, 2020

Use in industry

- Production, **storage, transport,** and use
- Hydrogen valley

Use in industry

- Production, **storage, transport,** and use

- Hydrogen valley
- Sector coupling
- **Circularity/ electrification** -use of **renewable** or low emissions fuels
- Hydrogen as a link between gas-electricity-heat networks
- Flexibility:
  - Regulate the demand profile
  - Store energy (hydrogen electricity, heat, gas) for the whole energy system

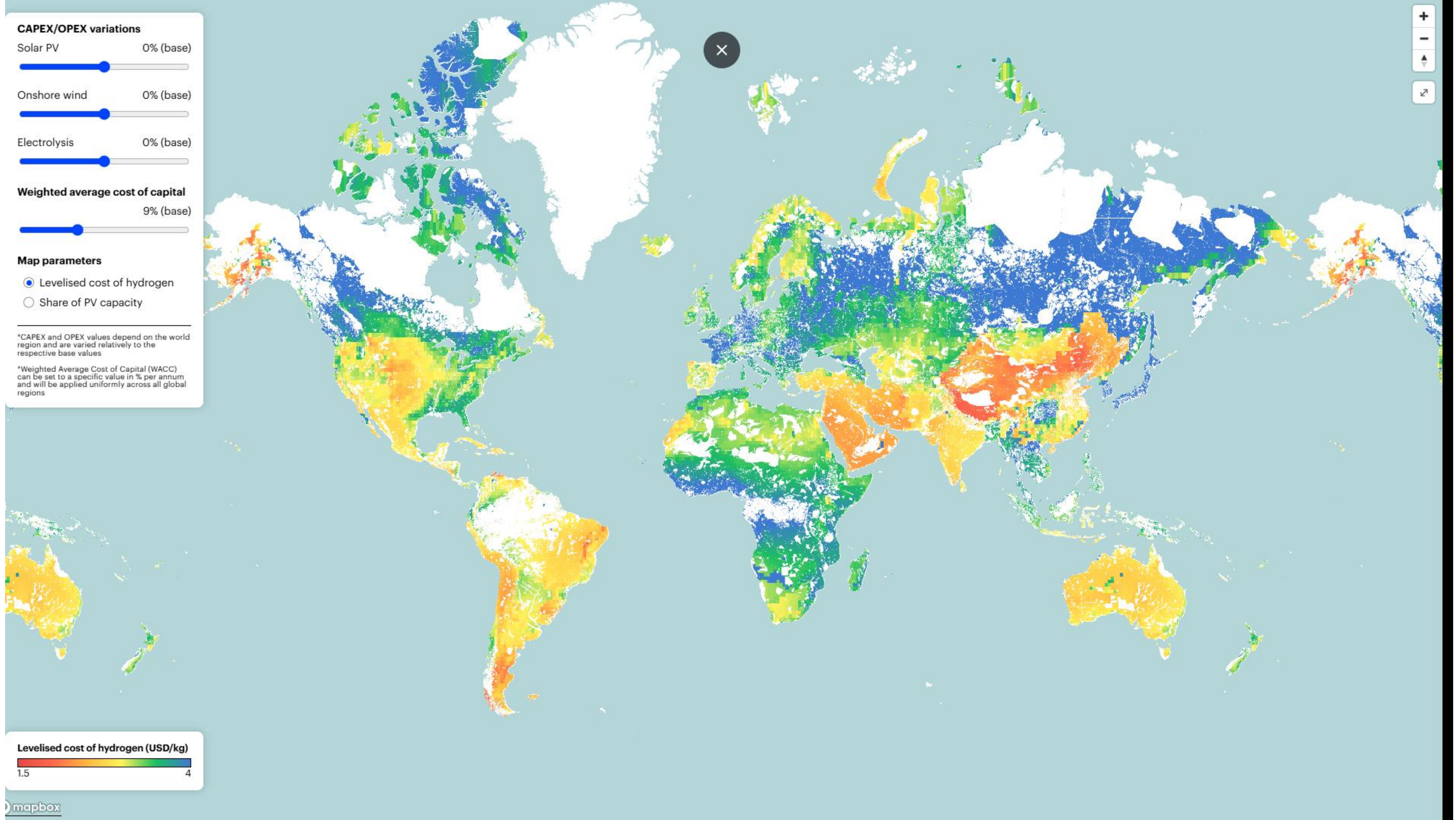
Use in industry

Category		Acronym	Definition
Power-to-Hydrogen	H_2	PtH	Hydrogen production (and storage when requested) from low-carbon electricity either from the grid or off-grid.
Hydrogen-to-Power		HtP	Supply of electricity to the grid from hydrogen with a fuel cell or a gas turbine
Hydrogen-to-Gas		HtG-H2	Hydrogen injection in natural gas grid
		HtG-M	synthetic methane injection in natural gas grid, synthetic methane is obtained from Hydrogen from PtH through methanation processes
Hydrogen-to-Fuel		HtF-H2	Hydrogen in a vehicle to be injected in a fuel cell
		HtF-S	Hydrogen for liquid synfuel applications: liquid biofuels, synthetic liquid fuels, methanol
		HtF-G	Hydrogen for mobility through gas fuels (Hythane®, biogas, synthetic methane)
Hydrogen-to-Industry		HtI	Hydrogen from PtH and for industrial applications (e.g. Refinery)
Hydrogen-to-Heat		HtQ	Hydrogen-to-heat via H2-fired boilers; Hydrogen-to-heat and power via CHPs (fuel cells, turbine etc.)
Hydrogen-to-Chemicals		HtCh	Other pathways to industrial chemical intermediates from hydrogen which we may want to include explicitly: 1. H2 to methanol to C2, C3 olefins 2. H2 to syngas to C2, C3 olefins 3. Methanol/syngas to >C1 hydrocarbons and >C1 alcohols 4. H2 to ammonia and formic acid (which could also be used as alternative renewable energy storage)

https://doi.org/10.1016/j.ijhydene.2019.08.260

Issues to solve

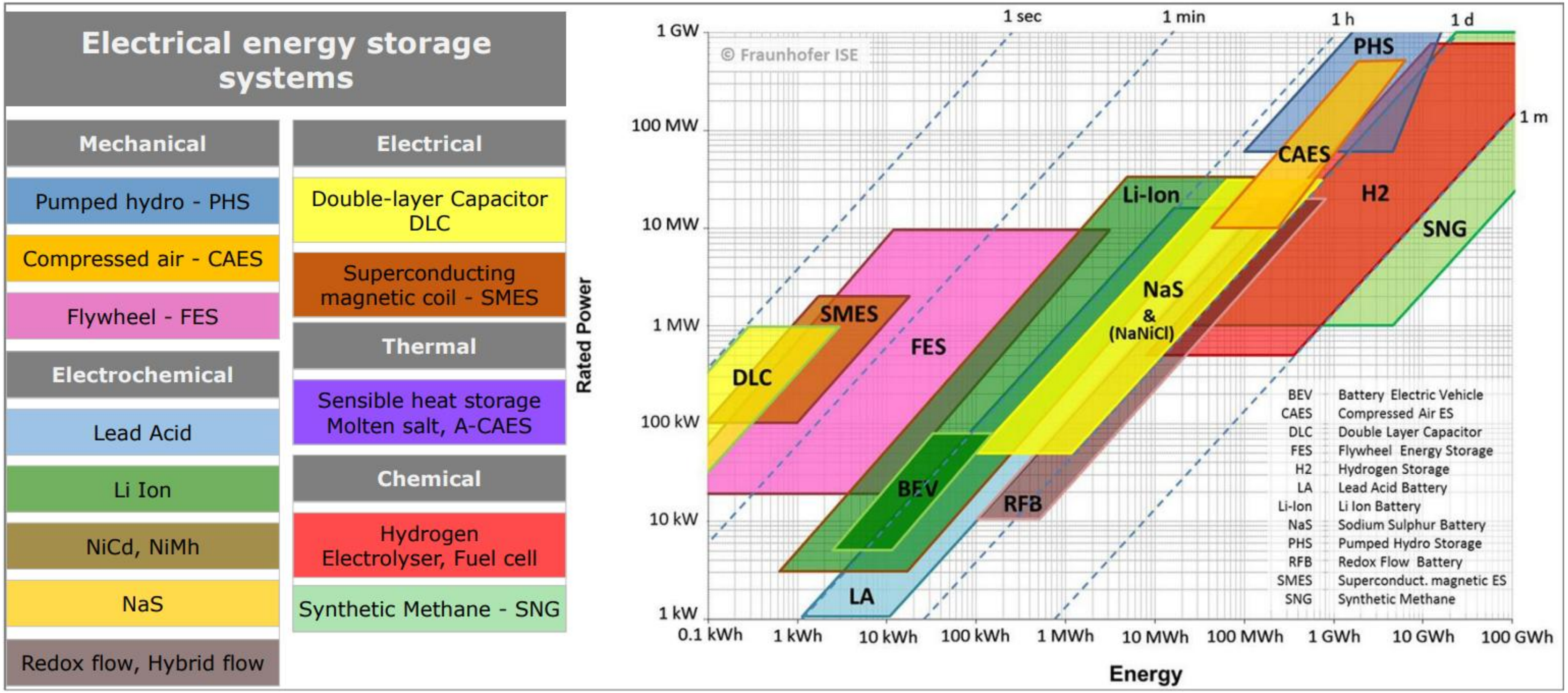
- **Costs**
- **Technologies**


CAPEX/OPEX variations
Solar PV
0% (base)
Onshore wind
0% (base)
Electrolysis
0% (base)
Weighted average cost of capital
9% (base)
Map parameters
Levelised cost of hydrogen
Share of PV capacity
*CAPEX and OPEX values depend on the world region and are varied relatively to the respective base values
*Weighted Average Cost of Capital (WACC) can be set to a specific value in % per annum and will be applied uniformly across all global regions
Levelised cost of hydrogen (USD/kg)
1.5
4
mapbox

Competitors

- Electrification

COMPETITORS- STORAGE



Classification of electrical energy storage systems according to energy form (a);
Comparison of rated power, energy content and discharge time of different EES technologies (b),
own representation based on International Electrotechnical Commission (IEC), 2011.

Conclusion

- Hydrogen is a possible solution, not the solution
- Still a lot of uncertainty
- Importance of national and global strategies

HYDROGEN GAS APPLICATION(FUEL CELL)

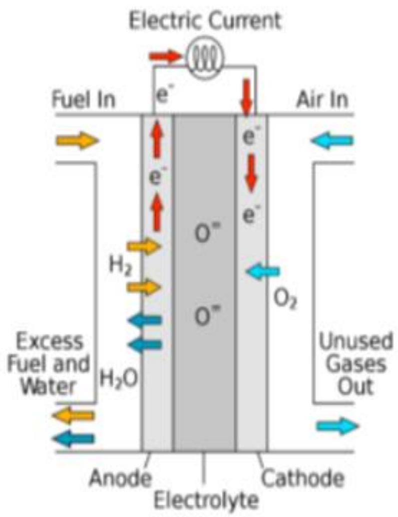
- Electrochemical reaction between hydrogen and oxygen
- Environmentally clean
- Widely used in **transportation**
- Deployed in **stationary power systems**

Two common types:

- **SOFC(50-80% pure hydrogen)**
- **PEMFC(99.5% pure hydrogen)**

SOFC

- Solid Oxide Fuel Cell
- **YSZ (Yttria-Stabilized Zirconia)-** Solid electrolyte in SOFC that conducts O^{2-} ions at high temperatures (~1000 °C)
- Fuel-flexible but required high temp(1000 °C)

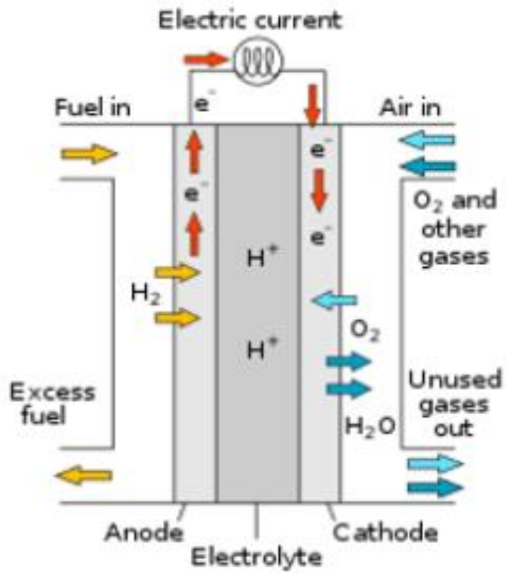


CELL PLATES	REACTIONS
Cathode	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
Anode	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

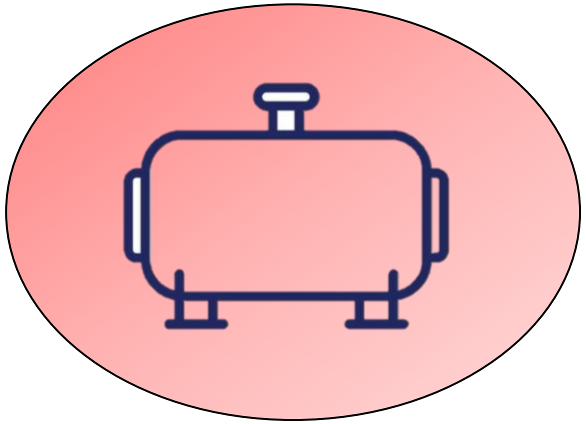
PEMFC

- Proton Exchange Membrane Fuel Cell
- Low temperatures (<100°C)
- Polymer electrolyte membrane, typically Nafion.
- High-purity hydrogen (≈99.99%)

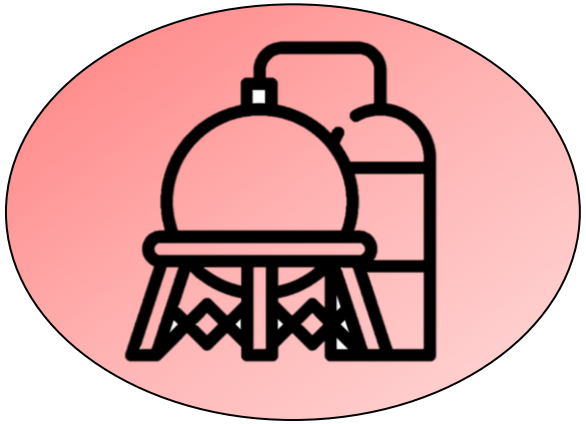
CELL PLATES	REACTIONS
Cathode	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Anode	$H_2 \rightarrow 2H^+ + 2e^-$



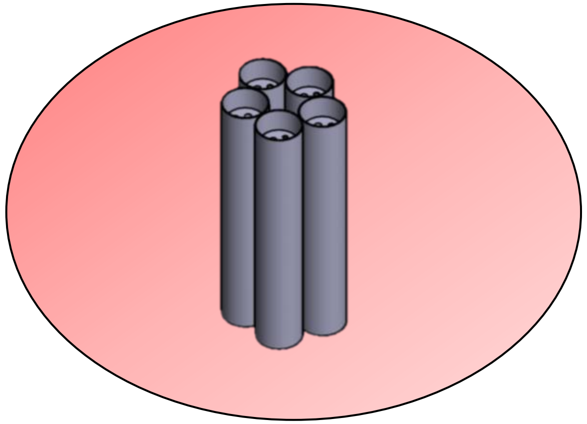
Storage



Compressed Hydorgen



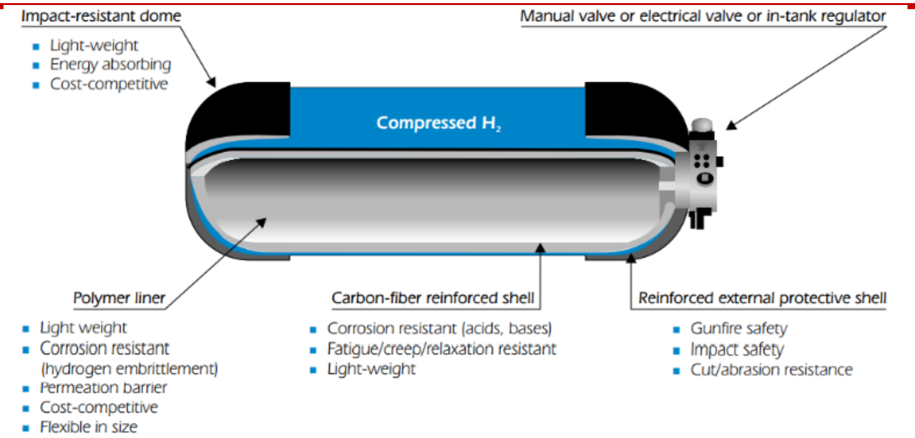
Liquified Hydrogen



Metal Hydrides

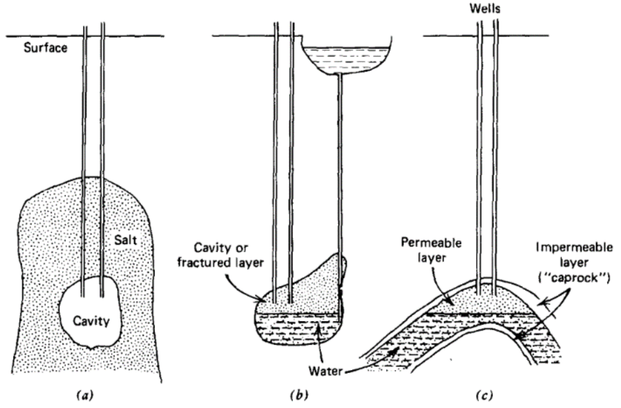
Storage

Compression is the simplest method to increase the volumetric energy density of hydrogen.
•At atmospheric pressure: **0.0899 kg/m³**
•At 700 bar: **~42 kg/m³**
•Even at high pressure, hydrogen energy density is only about **15% of gasoline**



Storage in tanks:
•Typically made of **composite materials**
•With **external reinforcement** and **internal polymer liner**

Alternative storage methods:
•**Geological storage**, such as:
- Salt caverns
- Rock cavities
- Underground aquifers

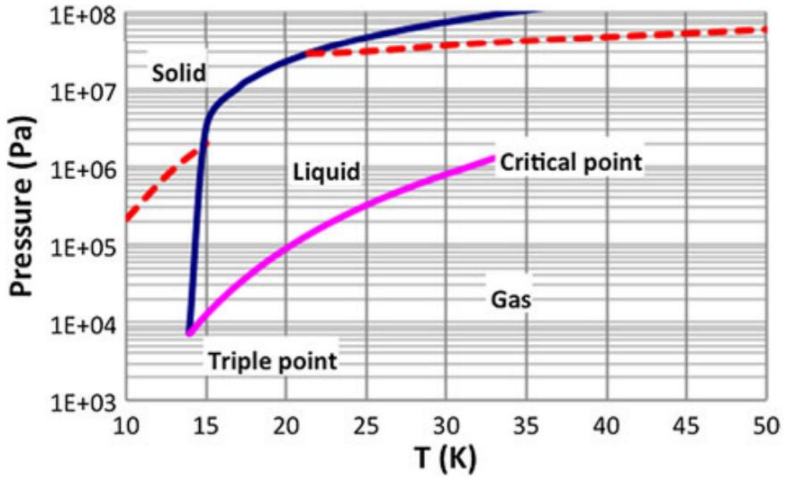


Storage

Hydrogen Liquefaction

•To liquefy hydrogen, it is necessary to cool it below its critical point, which is **20 K at atmospheric pressure**

•Under these conditions, hydrogen reaches a density of **70.8 kg/m³**



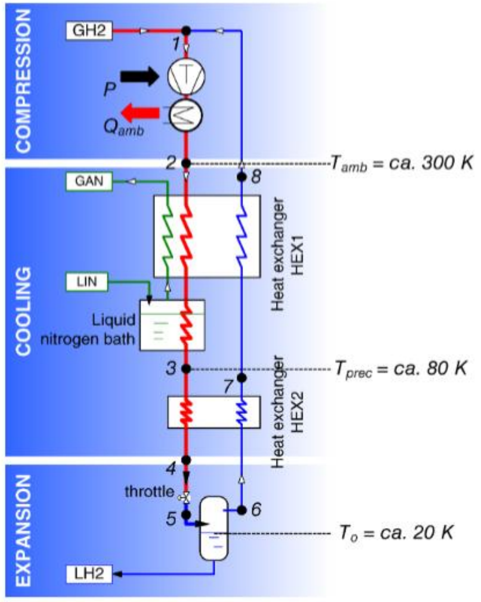
Liquefaction Process

The liquefaction process includes:

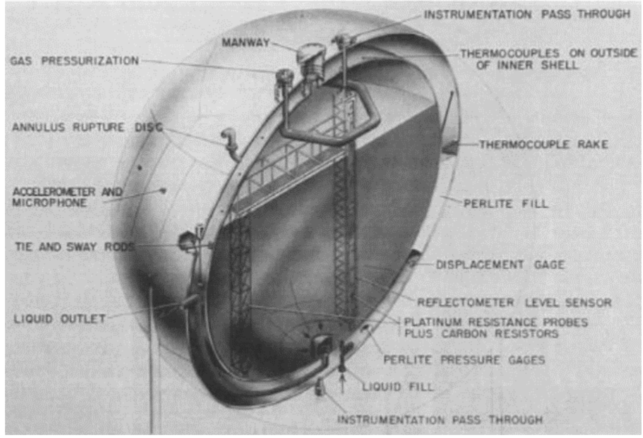
•**Compression** to pressures above the critical point

•**Cooling** and conversion from **ortho- to para-hydrogen**

•**Expansion (throttling)**

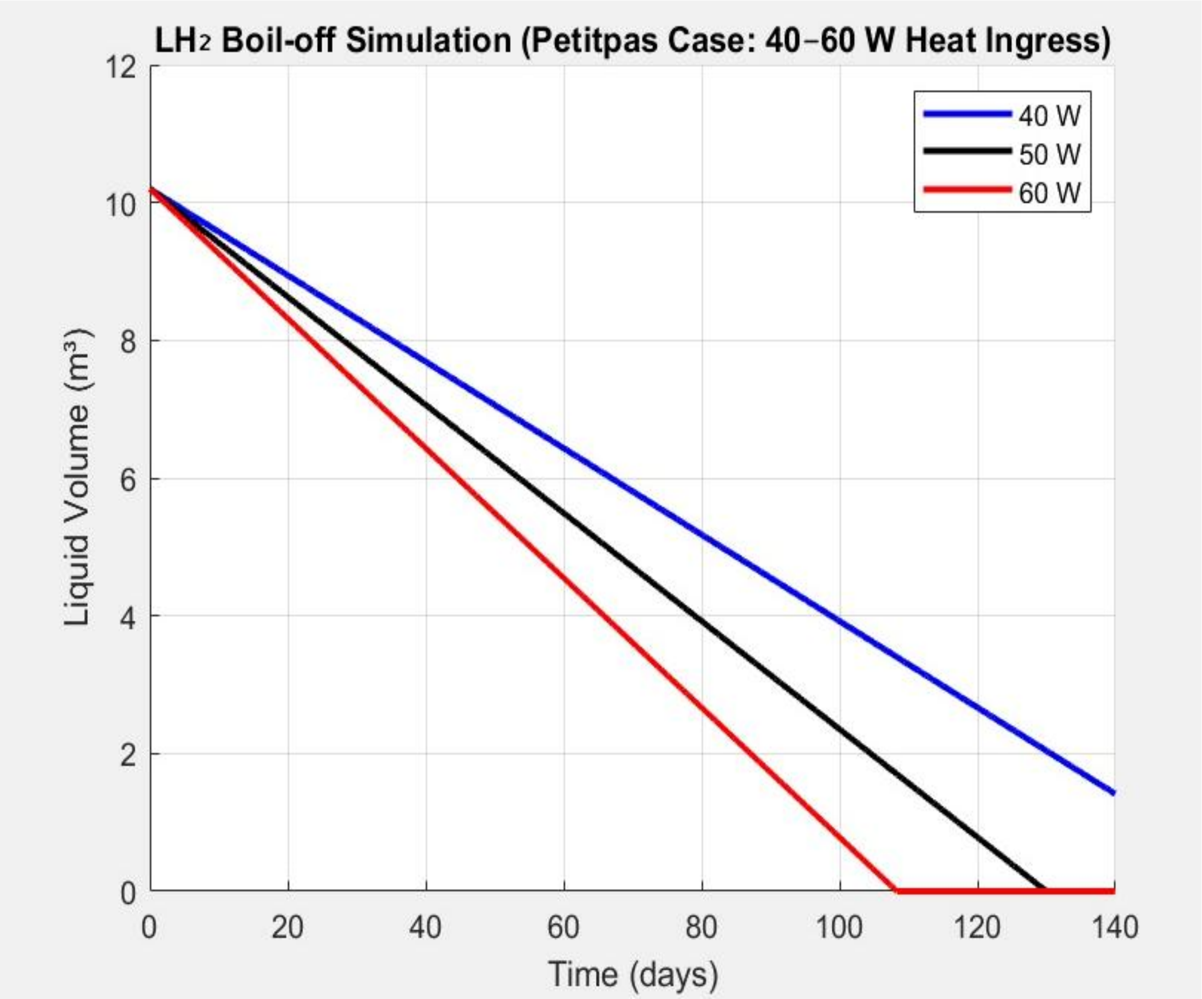


Liquid Hydrogen



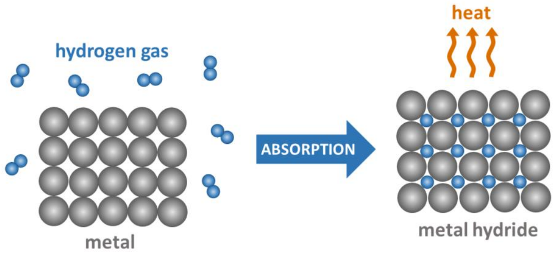
LIQUIFIED HYDROGEN

The liquid hydrogen (LH_2) volume depletion over time in a 12.5 m³ tank with an initial fill volume of 10.2 m³, subjected to constant heat ingress levels of 40 W, 50 W, and 60 W.



Simulated LH_2 depletion at 40–60 W heat ingress (BoilFAST model)

Storage



Storage in solid form

Reactions:

$$M + \frac{1}{2} xH_2 \leftrightarrow MH_x$$

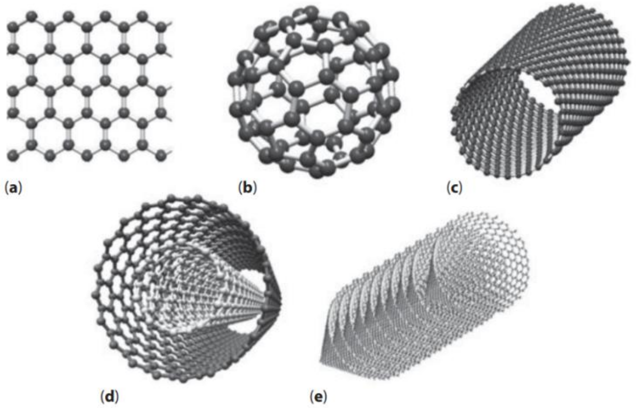
Storage form	Energy density		Density
	kJ kg^{-1}	MJ m^{-3}	kg m^{-3}
Hydrogen, gas (ambient 0.1 MPa)	120 000	10	0.090
Hydrogen, gas at 20 MPa	120 000	1 900	15.9
Hydrogen, gas at 30 MPa	120 000	2 700	22.5
Hydrogen, liquid	120 000	8 700	71.9
Hydrogen in metal hydrides	2 000–9 000	5 000–15 000	
Hydrogen in metal hydride, typical	2 100	11 450	5 480

Hydrogen Storage in Solids

•Hydrogen can be stored in solid materials through:

- •**Chemisorption**, forming ionic or covalent bonds with the material
- •**Physisorption**, attaching to the surface via hydrogen bonding or Van der Waals forces

Some carbon-based materials exhibit interesting properties for hydrogen storage. These include activated carbons, graphite, and nanostructured materials (nanofibers, SWCNTs, MWCNTs).

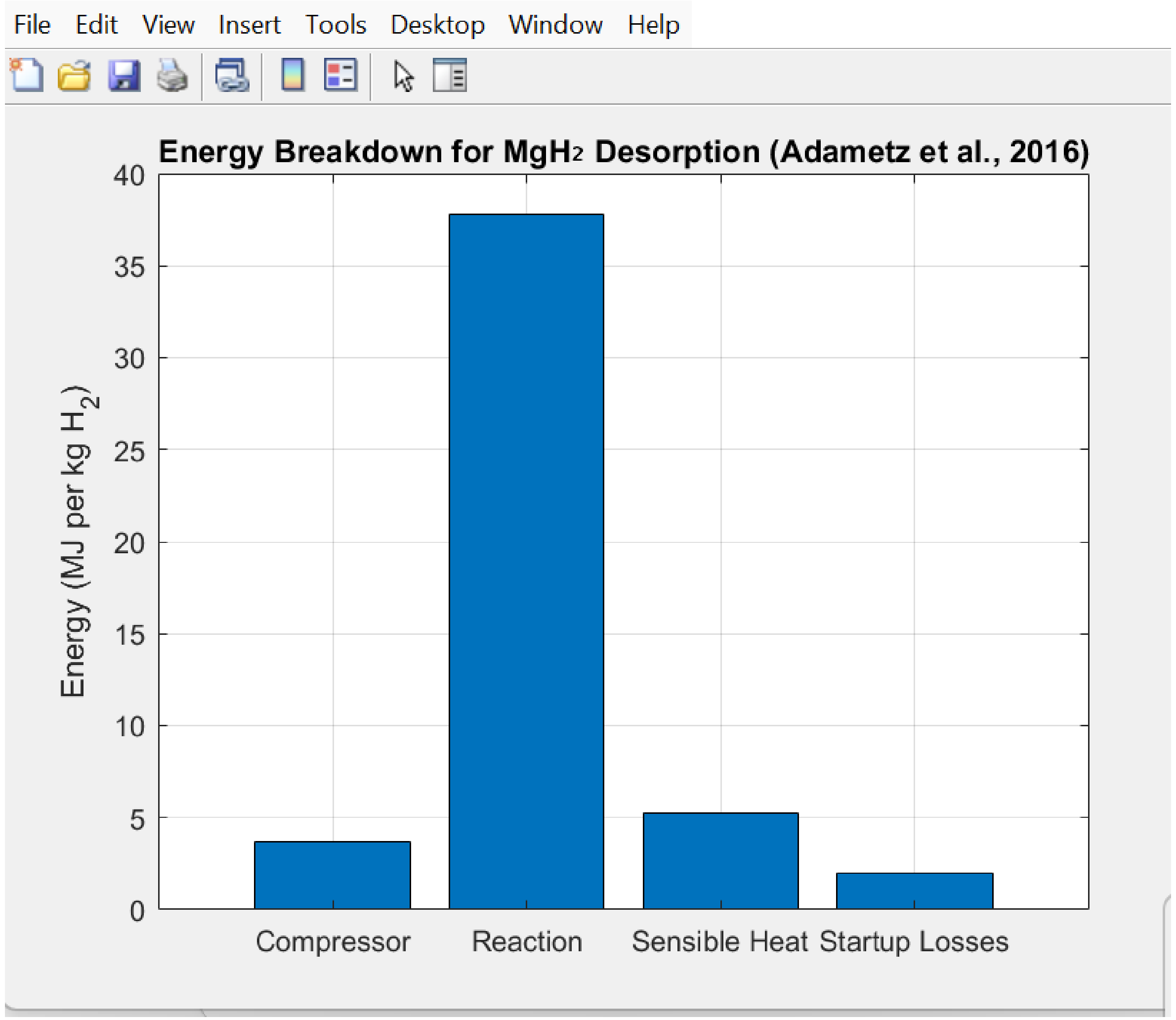


Storage method	Materials	Storage capacity; ρ_m (wt%)	P_{eq}, T
Adsorption	Activated carbon	5.5	80 bar, 298 K
	Graphite	4.48	100 bar, 298 K
	SWCNT	4.5	4 bar, 298 K
	MWCNT	6.3	148 bar, 298 K
	CNF	6.5	120 bar, 300 K

DATA VALIDATION: METAL HYDRIDE

System-level modelling conducted by Adametz et al. (2016), which assessed the **energetic performance of MgH_2 storage systems**

Parameter	Symbol	Value
Reaction enthalpy	ΔH	76,150 J/mol H_2
Specific heat of MgH_2	cp	35.334 J/mol·K
Hydrogen mass fraction (wt%)	—	8.3% or 0.083
Desorption temperature	T_{des}	598.15 K (325 °C)
Ambient temperature	T_{amb}	298.15 K (25 °C)
Compressor work	W_{comp}	3.7 MJ/kg H_2
Startup/system heat loss	$Q_{startup}$	2 MJ/kg H_2
Heat transfer efficiency	$\eta_{thermal}$	0.85



WEIGHT PARAMETERS

Pipeline

- Volumetric Capacity
- System Efficiency
- Cost per kg Stored
- Stability / Losses
- Operating Pressure

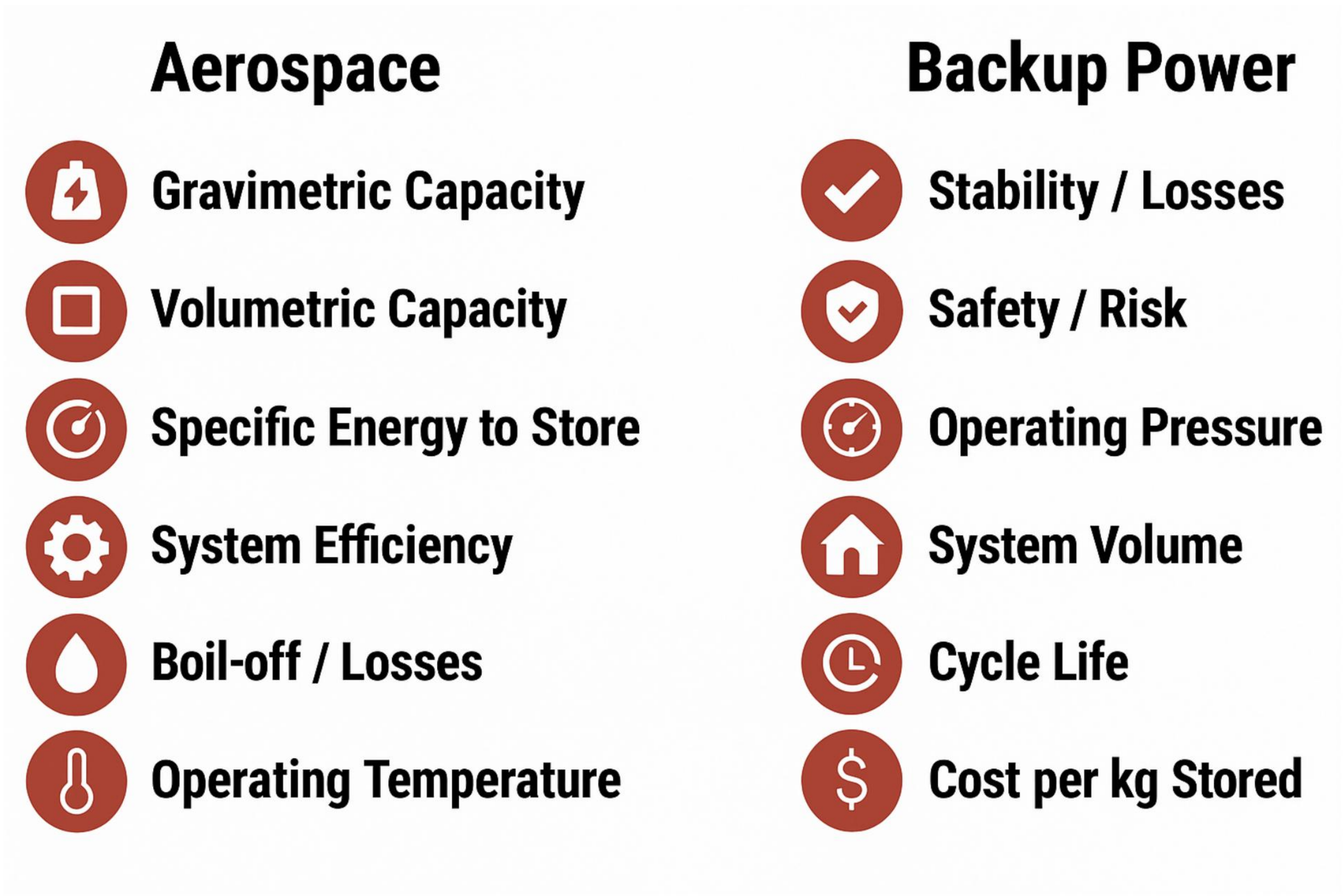
Heavy-Duty FCEVs

- Gravimetric Capacity
- Volumetric Capacity
- Refueling Time
- Hydrogen Flowrate
- System Efficiency

700-bar Fuel CEVs

- Gravimetric Capacity
- Volumetric Capacity
- Refueling Time
- System Efficiency
- Operating Pressure
- Safety / Risk

WEIGHT PARAMETERS



700 BAR FUEL CELL ELECTRIC VEHICLES

Parameter	Weight
Gravimetric Capacity	0.25
Volumetric Capacity	0.20
Refueling Time	0.15
System Efficiency	0.10
Safety	0.10
Cost per kg Stored	0.10
System Complexity / Maturity	0.10
Total	1.00

Parameter	CGH_2–700	CGH_2–350	LH_2	MH
Gravimetric Capacity (wt%)	4.79	3.89	30	0.8
Volumetric Capacity (kg/m^3)	25.37	11.75	70.85	83
Refueling Time (min)	2.42	3.98	6	78
System Efficiency (%)	86	87.24	60	58
Safety	High	Medium	High	Medium
Cost per kg Stored (€/kg)	6.8	3.5	7	8
System Complexity / Maturity	0.7	1.0	0.3	0.6

Method	Final Score
CGH_2–700	0.743
CGH_2–350	0.704
LH_2	0.628
MH	0.350

PIPELINE APPLICATION

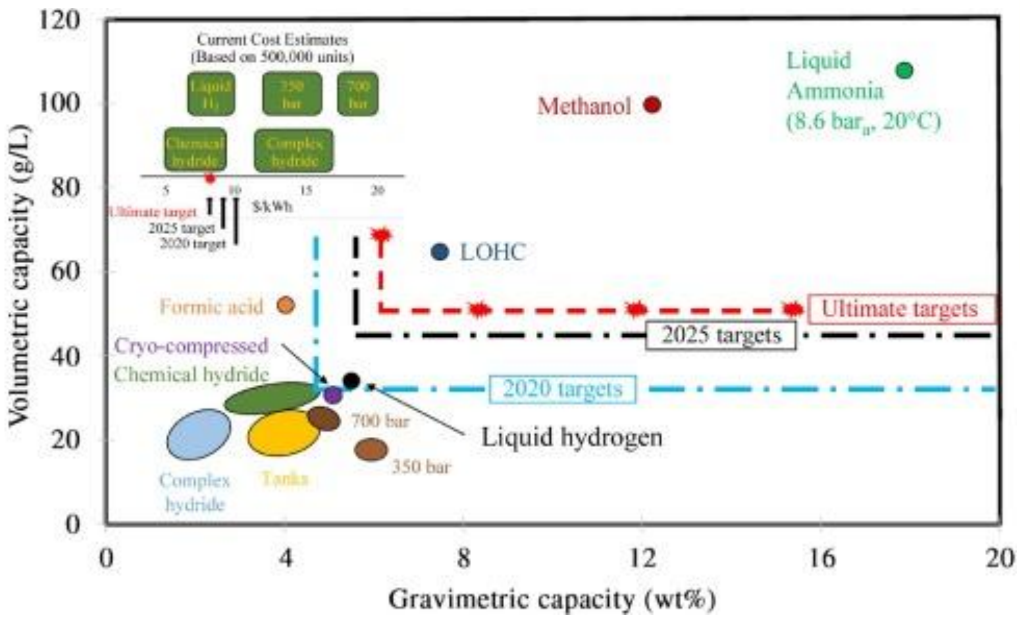
Parameter	CGH_2–100	CGH_2–350	LH_2	MH
Volumetric Capacity (kg/m³)	7.8	11.75	70.85	83
Specific Energy to Store (MJ/kg)	2.1	12.96	12	2.5
System Efficiency (%)	89.2	87.24	60	58
Safety	Medium	Medium	High	Medium
Stability / Loss Rate	High	High	High	Medium
Cost per kg Stored (€)	2	3.5	7	8

Pipeline length: 150 km

A 150 km pipeline length was assumed, consistent with Hua et al. (2011), representing a typical regional hydrogen transport scenario.

Method	Final Score
CGH_2–100	0.79
CGH_2–350	0.51
LH_2	0.49

RESULTS



- **Pipeline Applications** → 100 bar CGH_2
- **Heavy-Duty FCEVs** → 350 bar CGH_2
- **700-bar Fuel Cell Electric Vehicles** → 700 bar
- **Aerospace Applications** → LH_2
- **Stationary Backup Power Systems** → MH (MgH_2)

No single best storage method — depends on the application

CGH_2 is the most flexible and mature

LH_2 offers highest density but requires cryogenics

MH is safest for long-term stationary storage

Energetic performance was the only evaluation criterion

Storage method affects system design decisions, like insulation needs or tank materials.

HYDROGEN GAS APPLICATION(FUEL CELL)

- Electrochemical reaction between hydrogen and oxygen
- Environmentally clean
- Widely used in **transportation**
- Deployed in **stationary power systems**

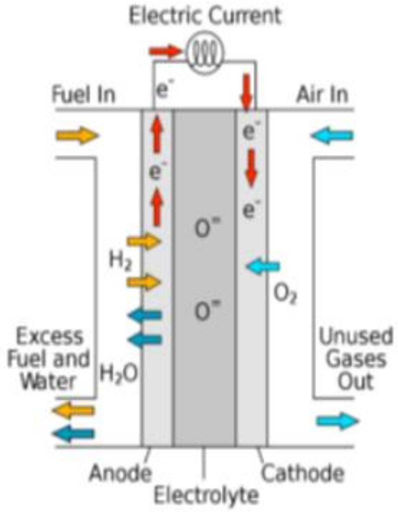
Two common types:

- **SOFC(50-80% pure hydrogen)**
- **PEMFC(99.5% pure hydrogen)**

SOFC

- Solid Oxide Fuel Cell
- **YSZ (Yttria-Stabilized Zirconia)-** Solid electrolyte in SOFC that conducts O^{2-} ions at high temperatures (~1000 °C)
- Fuel-flexible but required high temp(1000 °C)

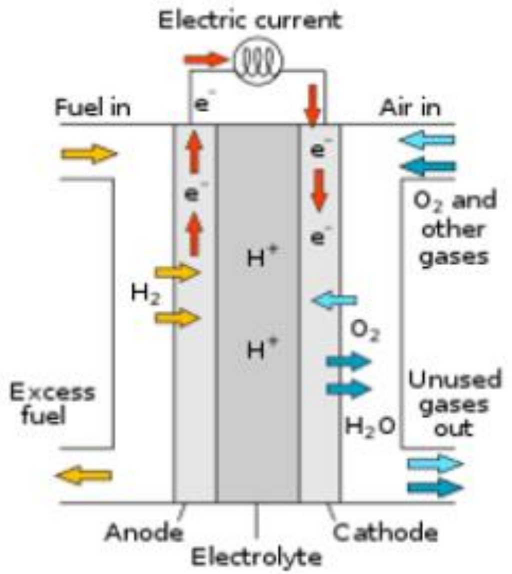
CELL PLATES	REACTIONS
Cathode	$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
Anode	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$



PEMFC

- Proton Exchange Membrane Fuel Cell
- Low temperatures (<100°C)
- Polymer electrolyte membrane, typically Nafion.
- High-purity hydrogen (≈99.99%)

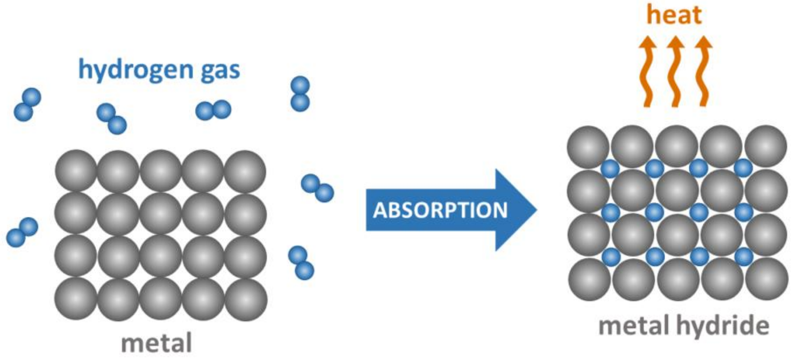
CELL PLATES	REACTIONS
Cathode	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Anode	$H_2 \rightarrow 2H^+ + 2e^-$



GREEN H_2 PRODUCTION, STORAGE AND UTILIZATION

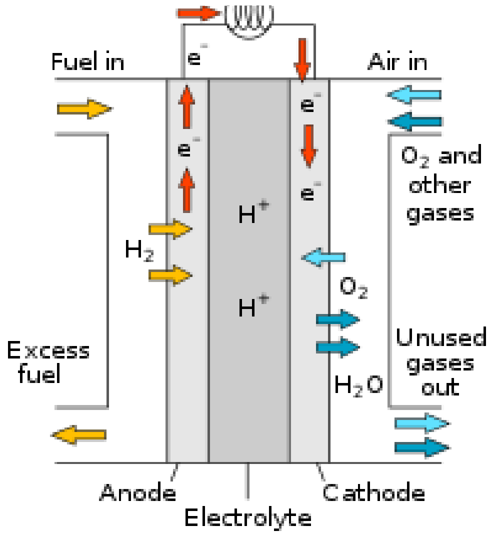
Topics:

- H_2 production from RE → Alternative to batteries:
  1. $H_2O + e.e. \longleftrightarrow H_2 + \frac{1}{2}O_2$ (ΔV=1,229 V)
  2. Dark fermentation of organic waste



- How do we store H_2? → Conventional storage require great amount of energy (d = 0,089 g/l ; T_m = -259,2 °C)
  - Metal Hydrides

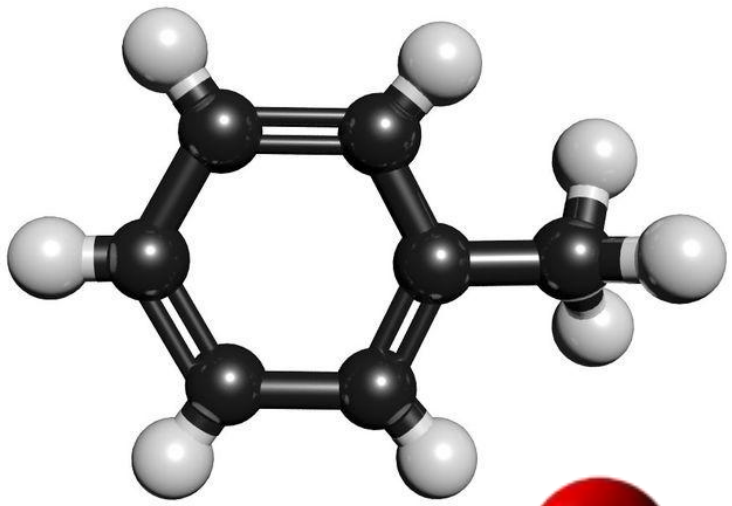
- Energy production → Exploit fuel cells to convert H_2 into electricity:



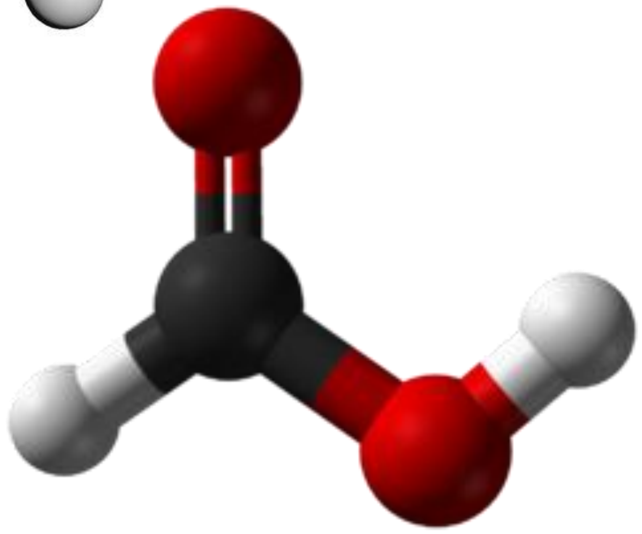
LIQUIDI ORGANICI LOHC

Cicloalcani
- Liquidi a temperatura ambiente
- Alto punto di ebollizione
- Bassa tossicità
- Capacità di idrogeno del 6-8%
- Deidrogenazione ad alte temperature

Eterocicli: introduzione di un eteroatomo nei cicloalca
- Minore temperatura di deidrogenazione



Acido formico
- Formula chimica HCOOH
- Contenuto di idrogeno del 4.4 wt.%
- Sintetizzato a partire da H_2 e da CO_2



PRO: sicurezza e facilità di trasporto
CONTRO: rigenerazione dei vettori, temperature di deidrogenzazione

COMPOSTI AZOTATI

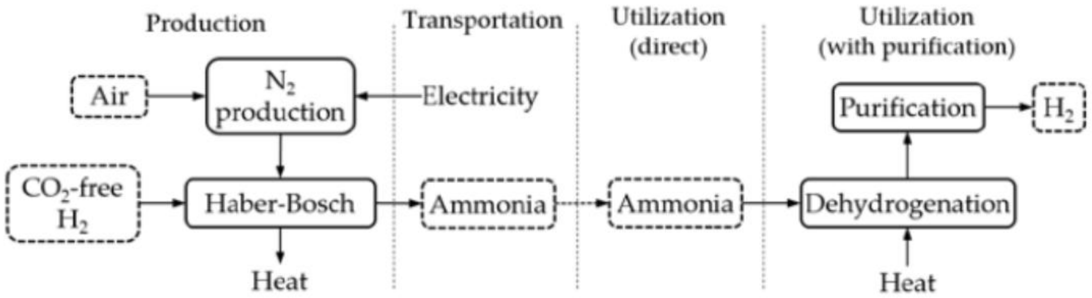
L'**ammoniaca** oggi viene utilizzata soprattutto nella produzione di fertilizzanti. La produzione globale è di 185 Mt (2020).

La densità energetica è il doppio di quella dell'idrogeno liquido. È facile da trasportare, potrebbe essere usata come combustibile (efficienza di produzione, trasporto e utilizzo in fuel cell del 37%).

Per produrre ammoniaca si utilizza il processo **Haber-Bosh**:

$$N_2 + \text{energy } (0{,}67 \times 10^6 \text{ J/mol}) \rightarrow 2N,$$
$$2N + 3H_2 \rightarrow 2NH_3$$

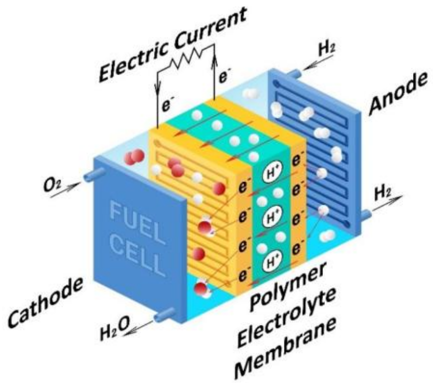
La **decomposizione** dell'ammoniaca in idrogeno è endotermica. Il processo complessivo è il seguente:



Per far fronte al problema della tossicità, per certe applicazioni si può stoccare NH_3 in **ammine metalliche**.

CELLE A COMBUSTIBILE

Una cella a combustibile è un dispositivo in grado di **convertire** l'energia chimica di un combustibile, come **idrogeno**, metanolo o gas naturale, in energia elettrica. Nel caso dell'idrogeno, gli unici prodotti delle reazioni che avvengono al suo interno, oltre all'**elettricità**, sono **acqua** e **calore**.



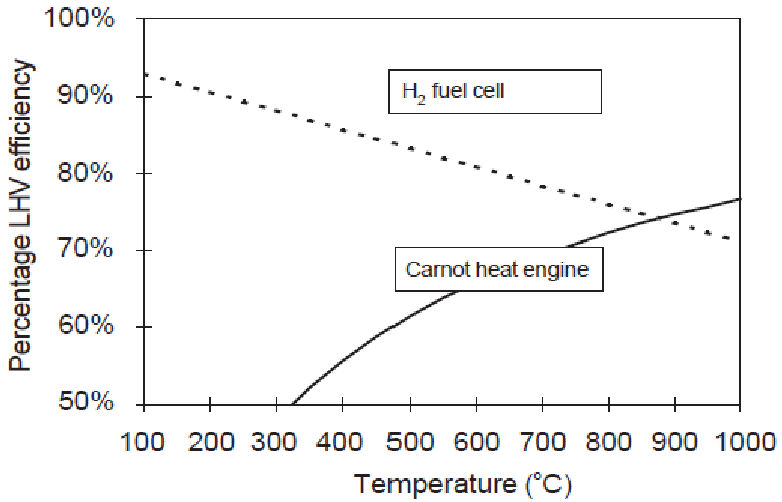
Componenti principali :

- Strato diffusivo
- Strato catalitico
- Elettrolita
- Piatti bipolari
- Guarnizioni
- Piatti terminali
- Collettori di corrente

Anodo – reazione di ossidazione: $2H_2 \longrightarrow 4H^+ + 4e^-$

Catodo – reazione di riduzione: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Rispetto alle tradizionali tecnologie basate sulla combustione sono **più silenziose** e possono trasformare l'energia chimica dei combustibili direttamente in elettricità con **rendimenti maggiori**, eccedenti anche il 60% (rispetto ad un massimo di circa 42% per una turbina a gas o 35-40% per un motore endotermico



SVILUPPO DELLE CELLE A COMBUSTIBILE

6 tipologie di celle a combustibile:

PEMFC – membrana a scambio protonico

AFC – alcaline

DMFC – a metanolo diretto

MCFC – a carbonati fusi
PAFC – ad acido fosforico
SOFC – ad ossidi solidi
} stazionarie

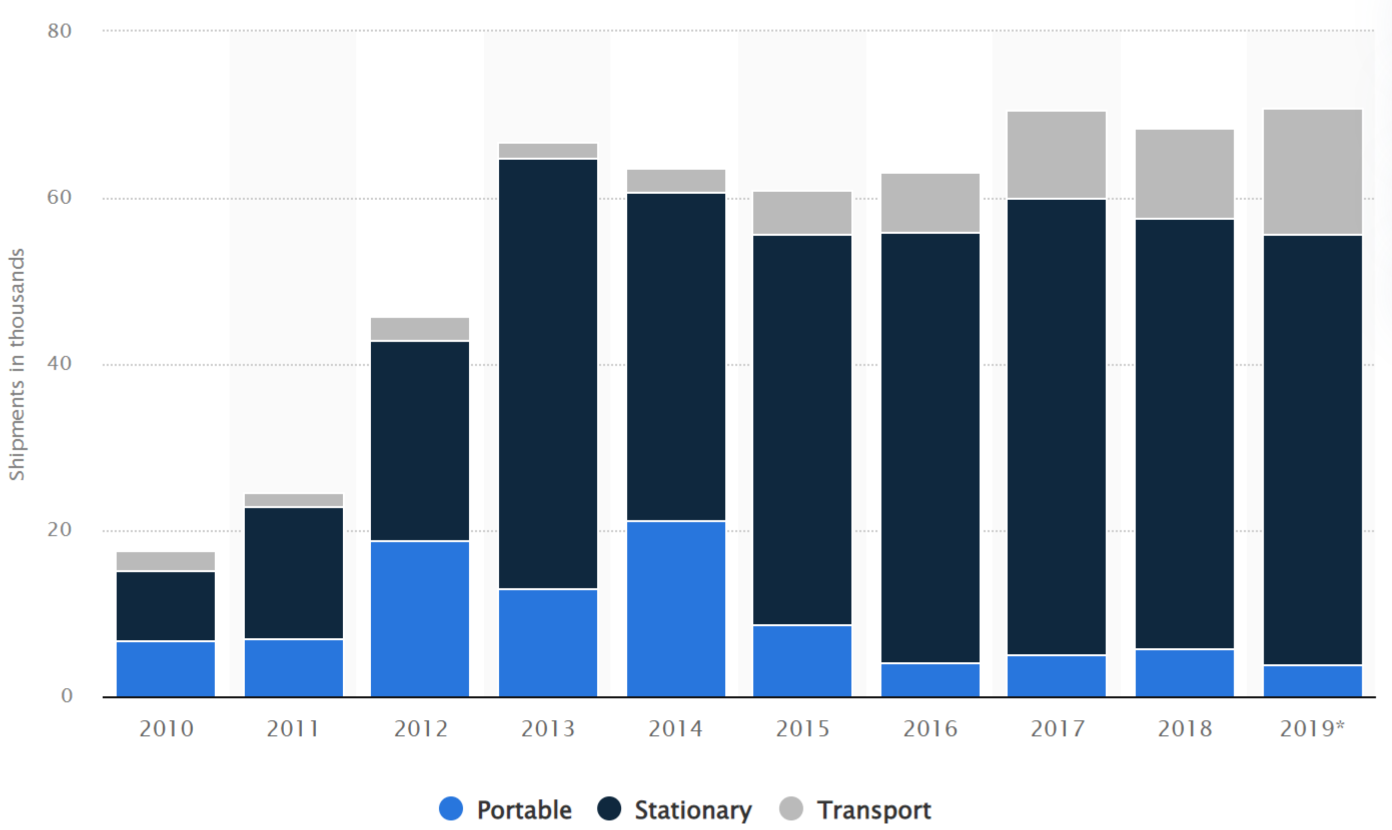
Le celle **stazionarie** sono utilizzate per la **generazione** di **energia** elettrica (e anche calore in alcuni casi). Nel 2018 la capacità totale installata era di 1.6 GW di cui solamente 70 MW alimentata ad idrogeno.

+ 350'000 unità installate nel mondo.
Germania, Giappone, Korea, Stati Uniti i **leader nel settore**

Nell'ultimo decennio le vendite annuali di celle a combustibile sono cresciute notevolmente sia settore energetico che in quello dei trasporti

2010 – 2019 20'000 → 70'000 c.a. unità spedite all'anno

2016 – 2019 **500 → + 1100 MW** capacità delle unità spedite all'anno



TURBINE A GAS

Componenti principali

- Compressore – innalza p dell'aria
- Camera di combustione – fa raggiungere Tmax
- Espansore – converte en. cinetica in meccanica

Applicazioni

- Copertura picchi della domanda
- Impianti cogenerativi

η = 35 – 45 %

- Cicli topping in impianti combinati
- Ripotenziamento impianti a vapore

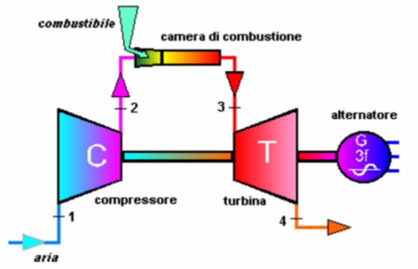
η = > 60 %

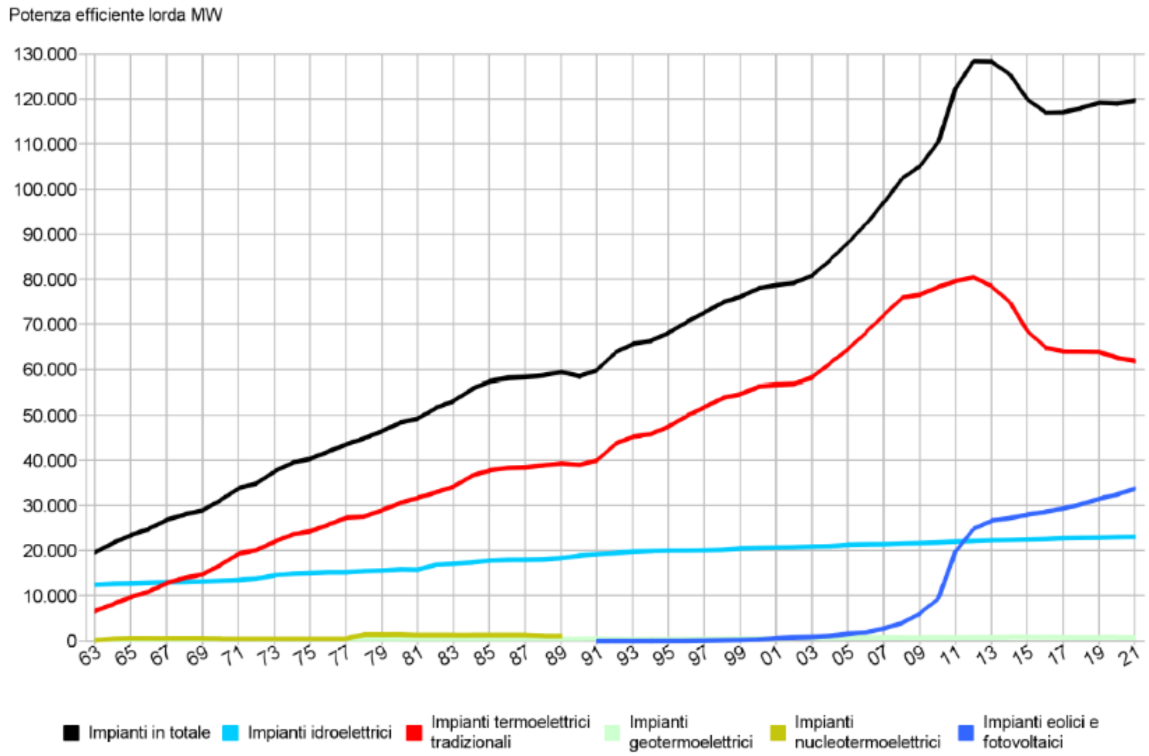
Ciclo aperto di base

1 – 2 Compressione aria

2 – 3 Combustione miscela aria-fuel

3 – 4 Espansione fumi prodotti





Italia è il paese europeo con la maggior capacità installata, **40 GW**.

45 impianti per sola produzione elettrica (30 con P_n < 25 MW)

81 in impianti cogenerativi (75 con P_n < 25 MW)

Per più del 50% dei casi sono alimentati a **gas naturale**, gli altri combustibili impiegati sono: biogas, gpl, gasolio

IDROGENO & TURBINE A GAS

L'obbiettivo è arrivare a gestire **miscele NG/H_2** con contenuto di idrogeno variabile tra 0 – 100 % →

per H_2 < 10 vol% non sono necessarie modifiche all'impianto

per H_2 > 30 vol% modifiche significative

L'idrogeno è molto **più reattivo** del metano (componente principale del gas naturale) e sono significative le differenze tra le grandezze caratteristiche della loro combustione

- Tad di fiamma maggiore → NO_x ↑
- SL di fiamma maggiore → Flashback ↑
- Tempo di ritardo ↓
- maggior reattività → miscele più povere
- Emissioni **CO_2** e CO ↓

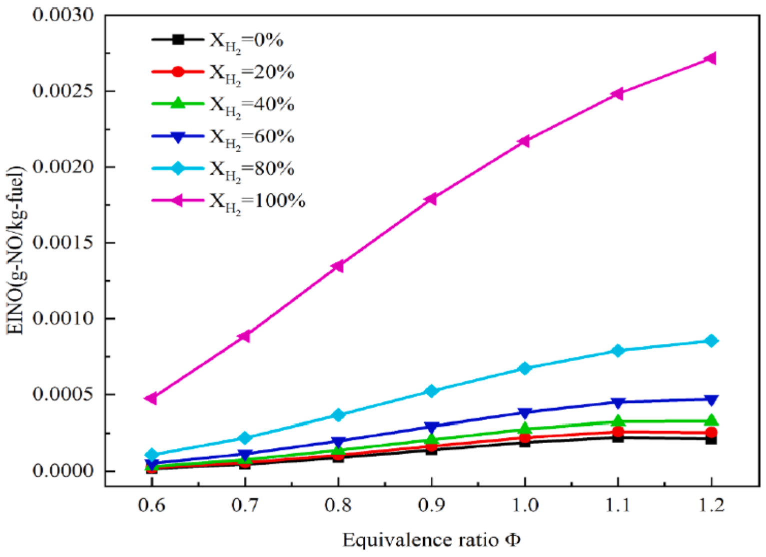
Tre **fattori** che oggi **limitano** l'adozione dell'idrogeno sono:

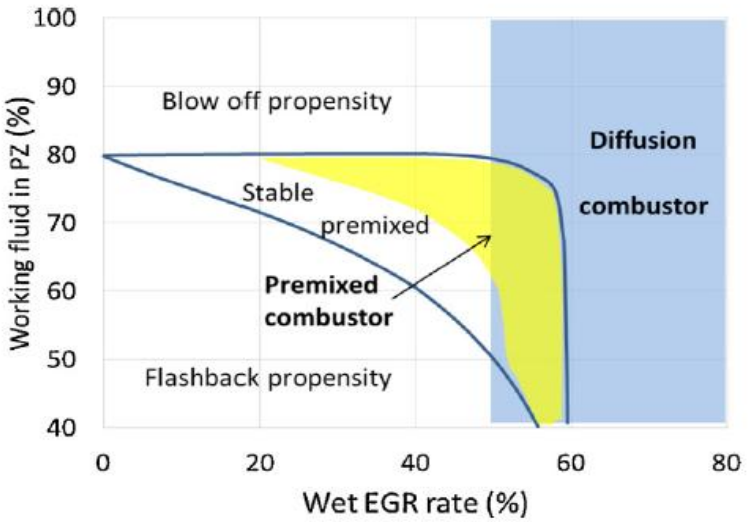
- Emissioni di NO_x →
- Mancanza infrastruttura
- Costo dell'idrogeno

Soluzioni proposte in letteratura:

Benaissa et al. – combustore diffusivo e Φ ↓

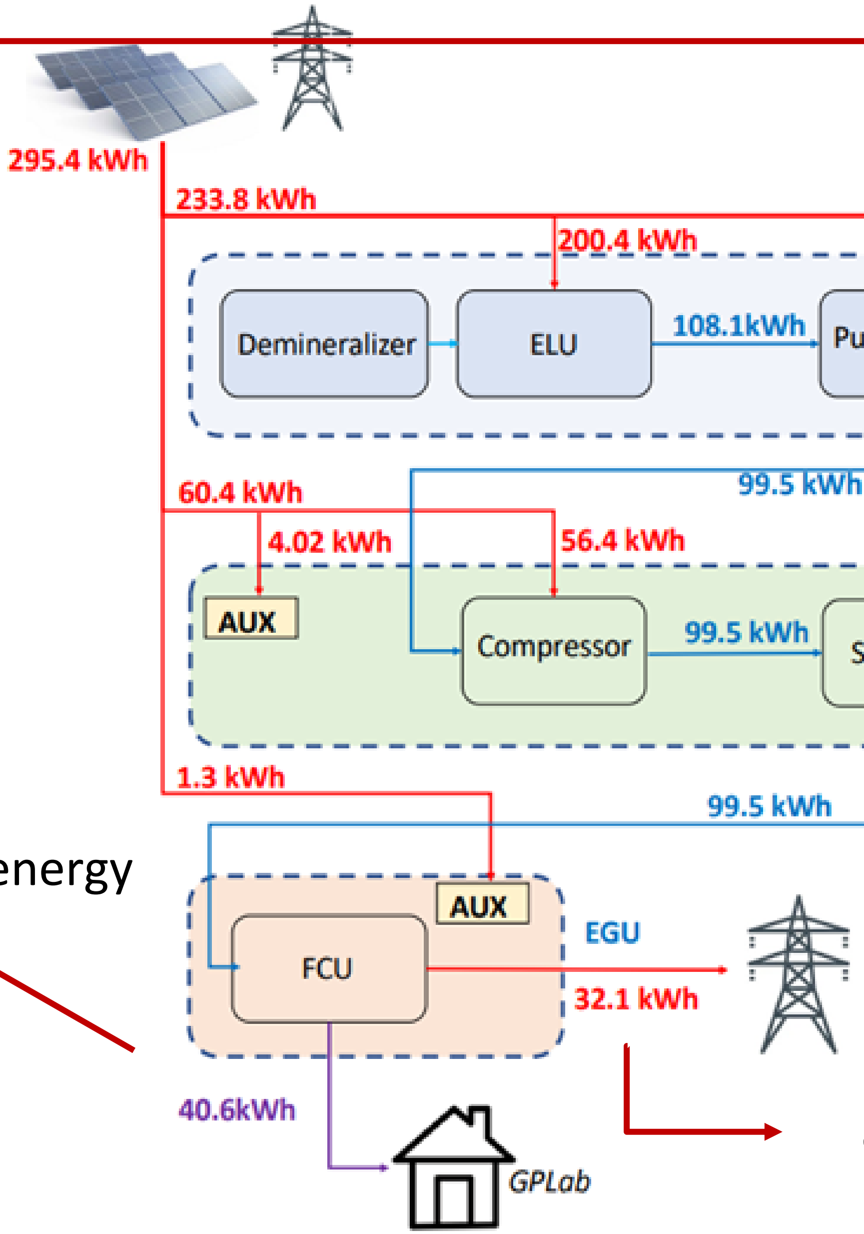
Ditaranto et al. – combustore diffusivo con ERG





Example

Max P



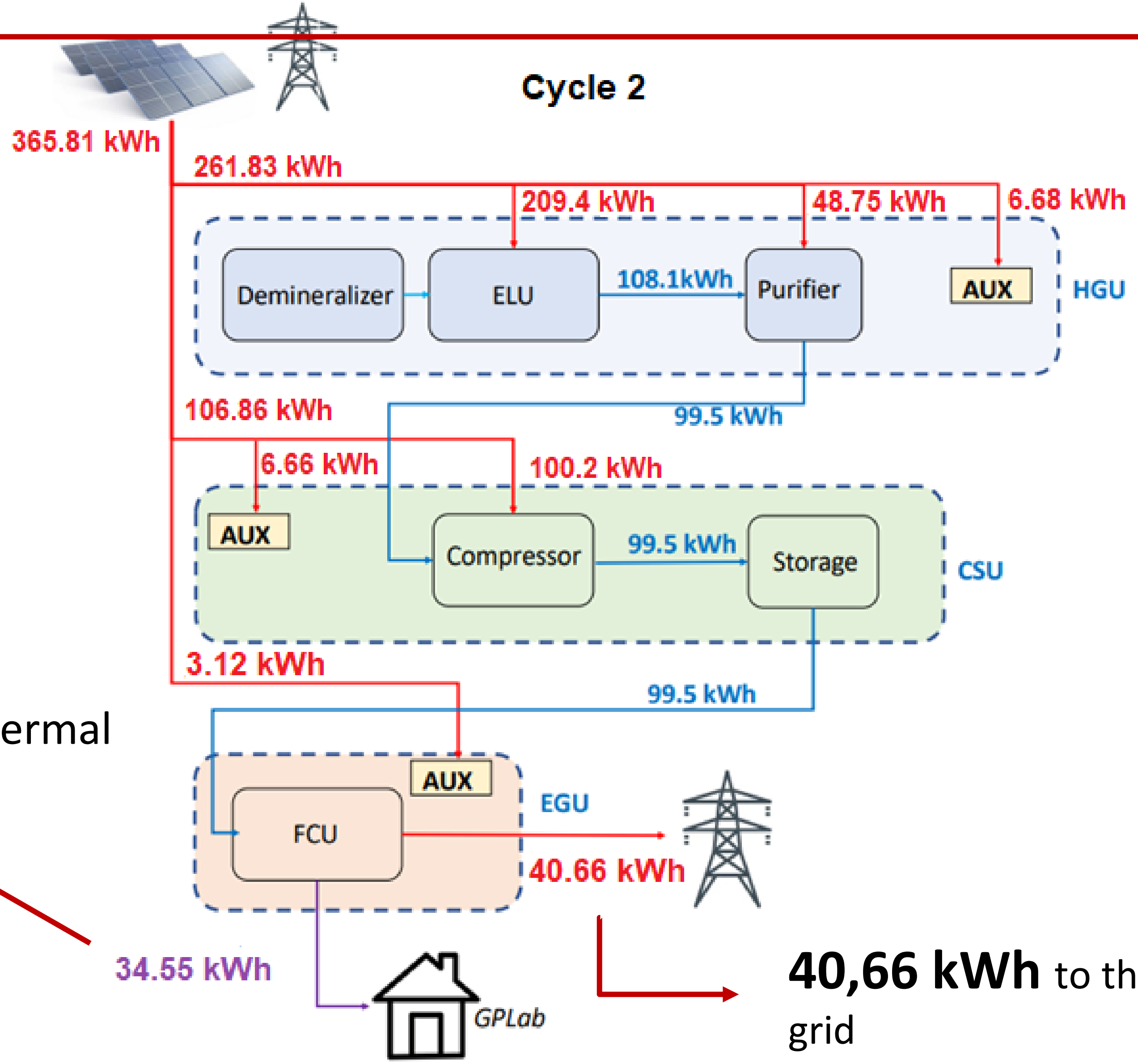
40,6 kWh thermal energy

32,1 kWh to the grid

- Charge/discharge Cycle efficiency **10,5 %** in full electric mode
- **24,3 %** in cogenerative operation

Example

Partial load



34,55 kWh of thermal energy

40,66 kWh to the grid

- Charge/discharge Cycle efficiency **9,5 %** in full electric mode
- **18,3 %** in cogenerative operation

GREEN H_2 PRODUCTION, STORAGE AND UTILIZATION

Topics:

- H_2 production from RE → Alternative to batteries:
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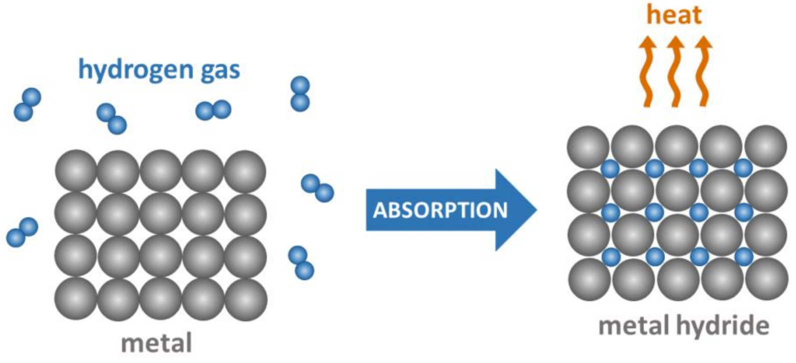
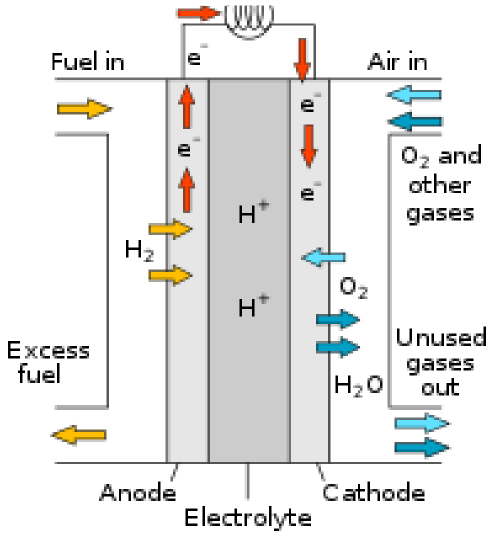
  2. Dark fermentation of organic waste



- How do we store H_2? → Conventional storage require great amount of energy (d = 0,089 g/l ; T_m = -259,2 °C)
  - Metal Hydrides

- Energy production → Exploit fuel cells to convert H_2 into electricity:



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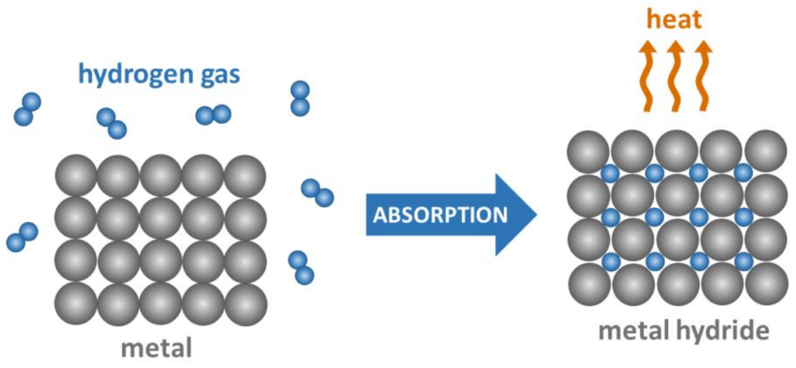

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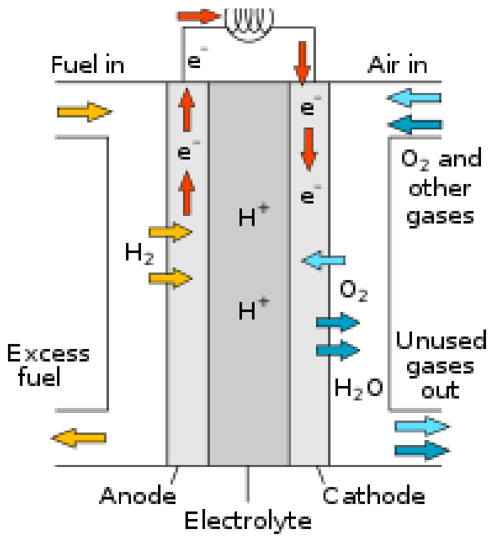
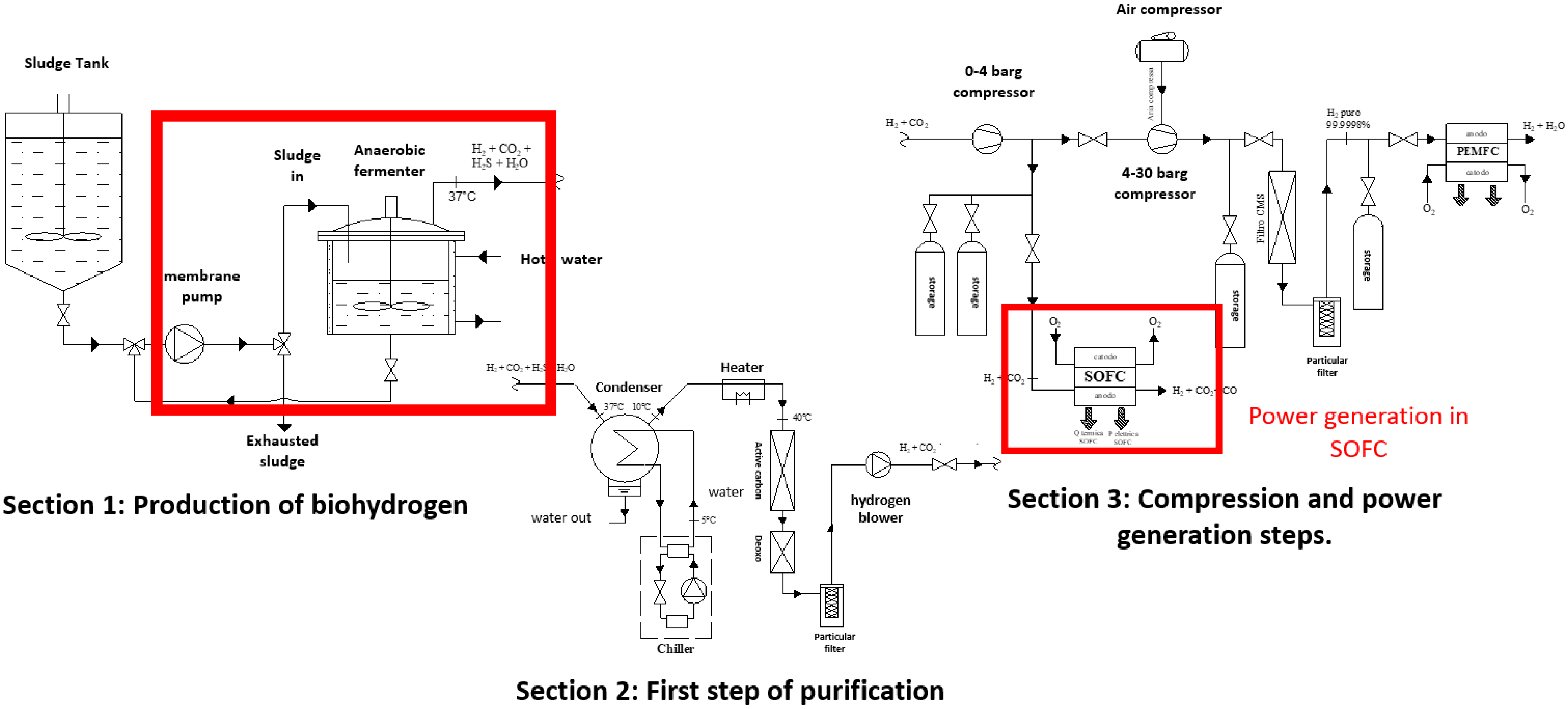
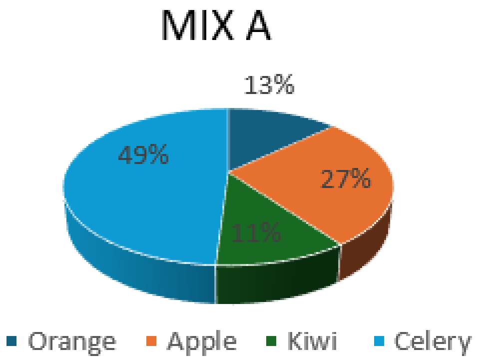
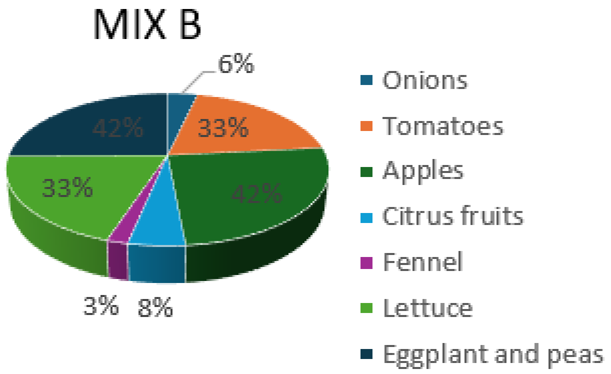


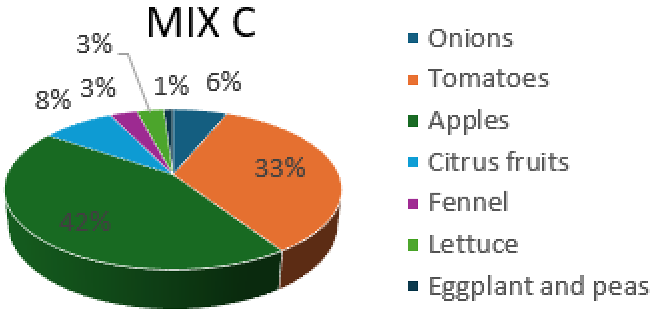
Bioreactor setup

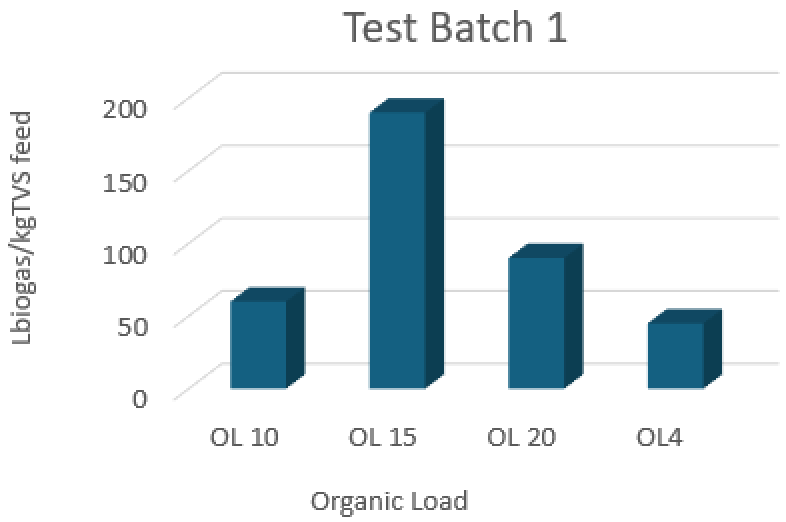


Results of the research: batch tests

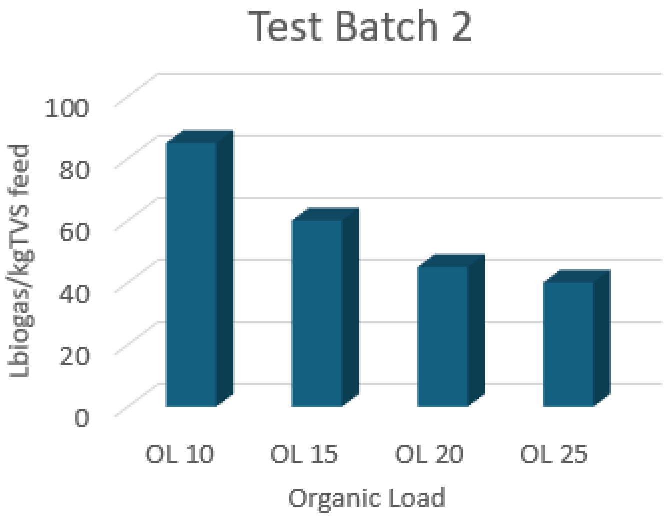








Parameter	MIX C	MIX A+B
TS (gTS/kgTO)	102.4	78.5
TVS (gTS/kgTO)	98.8	72.4
sCOD (gO2/L)	198.0	91.2
pH	3.9	4.5
Ammonia (mg/L)	44.7	36.4



O.L.	%H2	SGP (NL/kgVS)	SHP (NLH2/kg VS)
10	35	71.92	25.11
15	32	65.96	21.75
20	30	39.70	12.31
25	32	32.44	10.65

Results of the research: SOFC for electricity

Solid Oxide Fuel Cell: 2R-cell™ from Fiaxcell, A_{cella} = 4.9 cm^2, ASC, T = 800 °C.

Fonte	Temperatura °C	Potenza specifica di picco mW/cm²	Composizione del gas di alimentazione % vol
(A. Le Gal La Salle)	800	537	20% H_2 - 20% CO - 10% CO_2 – 50 % N_2

$$P_{max,cell} = 537 \cdot 4.9 = 2636\ \text{mW} = \mathbf{2.636\ W}$$

Hypothesis:

- The composition of the gas produced is assumed to be fixed and equal to that shown in the table.
- Feeding the anode with the produced gas and with a flow rate of 0.1 NLM.
- 10 cells in series each fed with the same flow rate

1. OBJECTIVE OF THE THESIS WORK

North Africa can generate huge amounts of renewable energy for domestic and export purposes, and Europe can share industrial legacy that Africa needs. Hence keeping this in mind, I will;

- ✓ Analyze the production of hydrogen using PV power in North Africa (case study: Tamanrasset Algeria) and how it can be traded
- ✓ Analyze the hydrogen energy transport methods in terms of how much energy is needed to transport hydrogen relative to the delivered one (energy of delivered hydrogen).
- ✓ Analyze the economic consequence or advantage of one method over the other.

KEY ADVANTAGES OF SOLAR POTENTIAL OF N. AFRICA

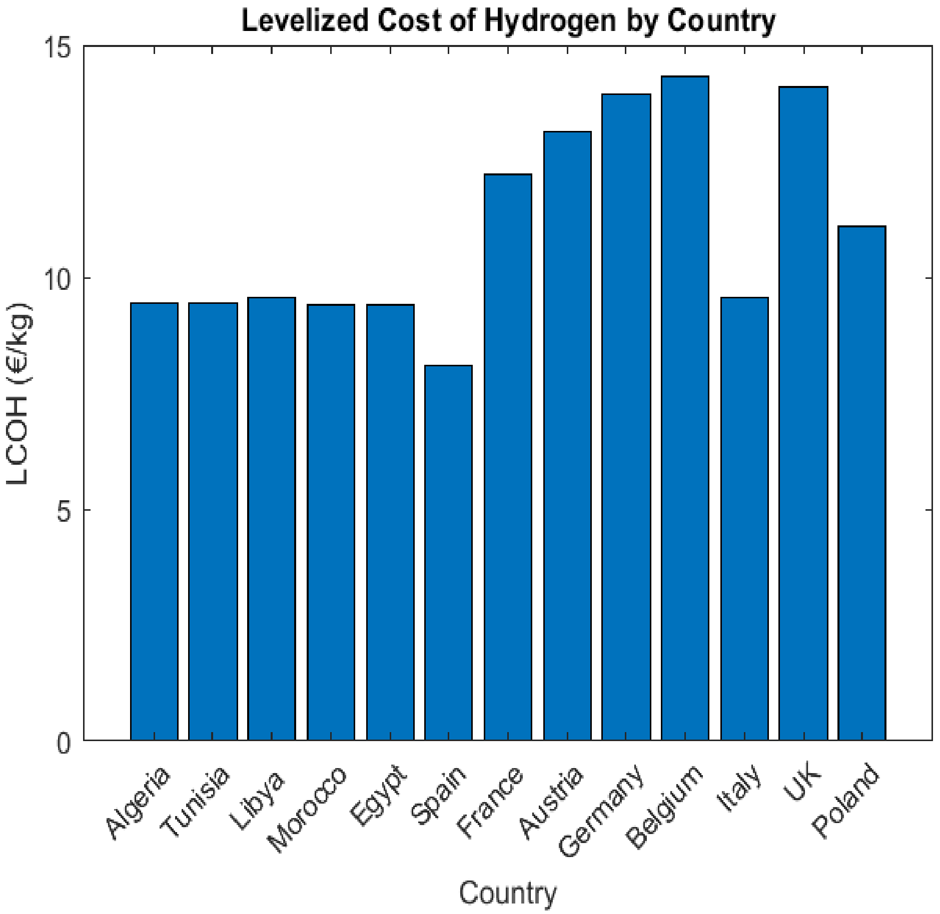


Figure: Levelized cost of hydrogen generation (LCOHG) by country

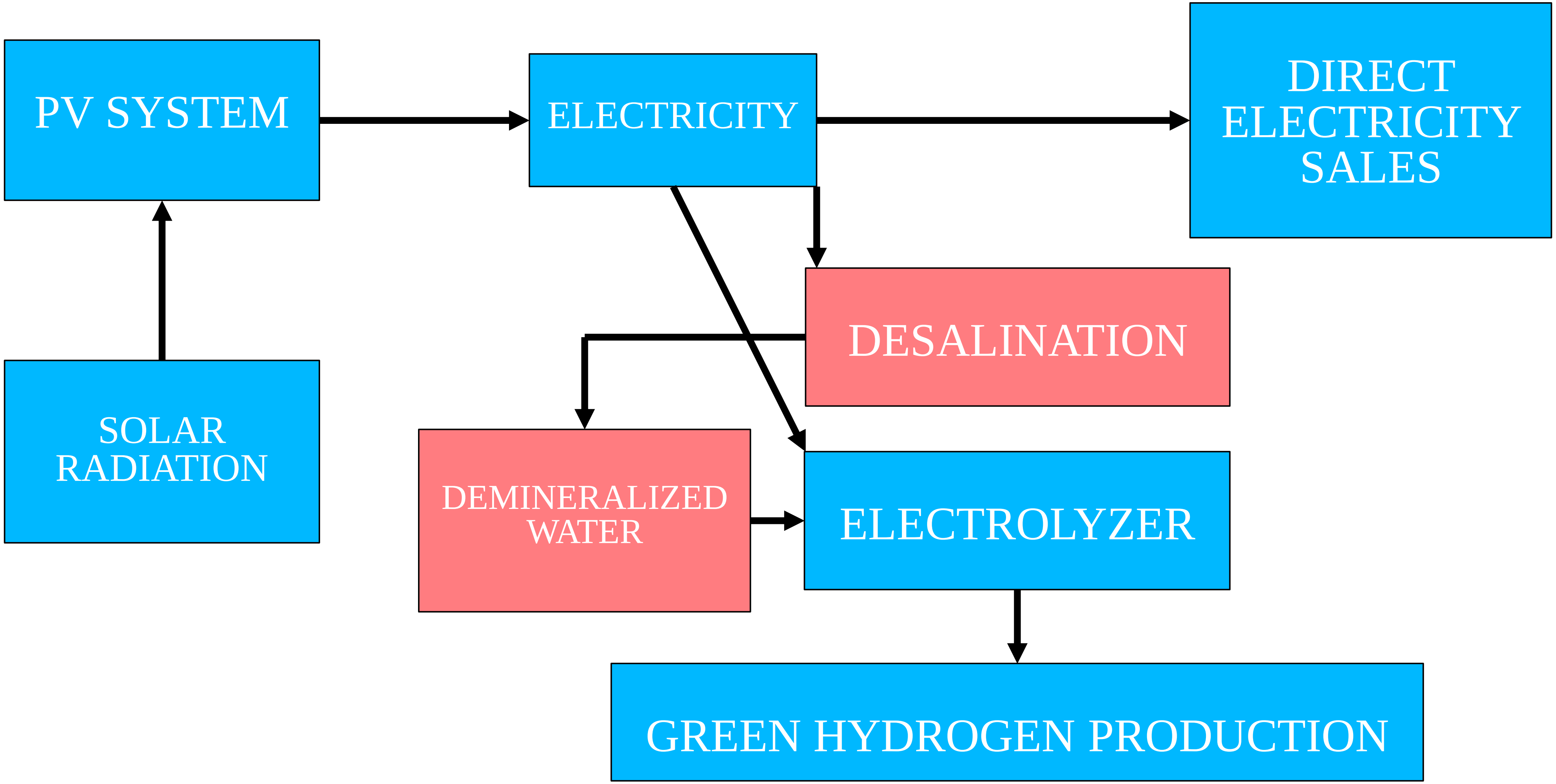
2- LCOHG: Main factors that influence the result

- Solar electricity levelized cost
- Operating hours: number of hours for irradiance values >= 150 W/m^2

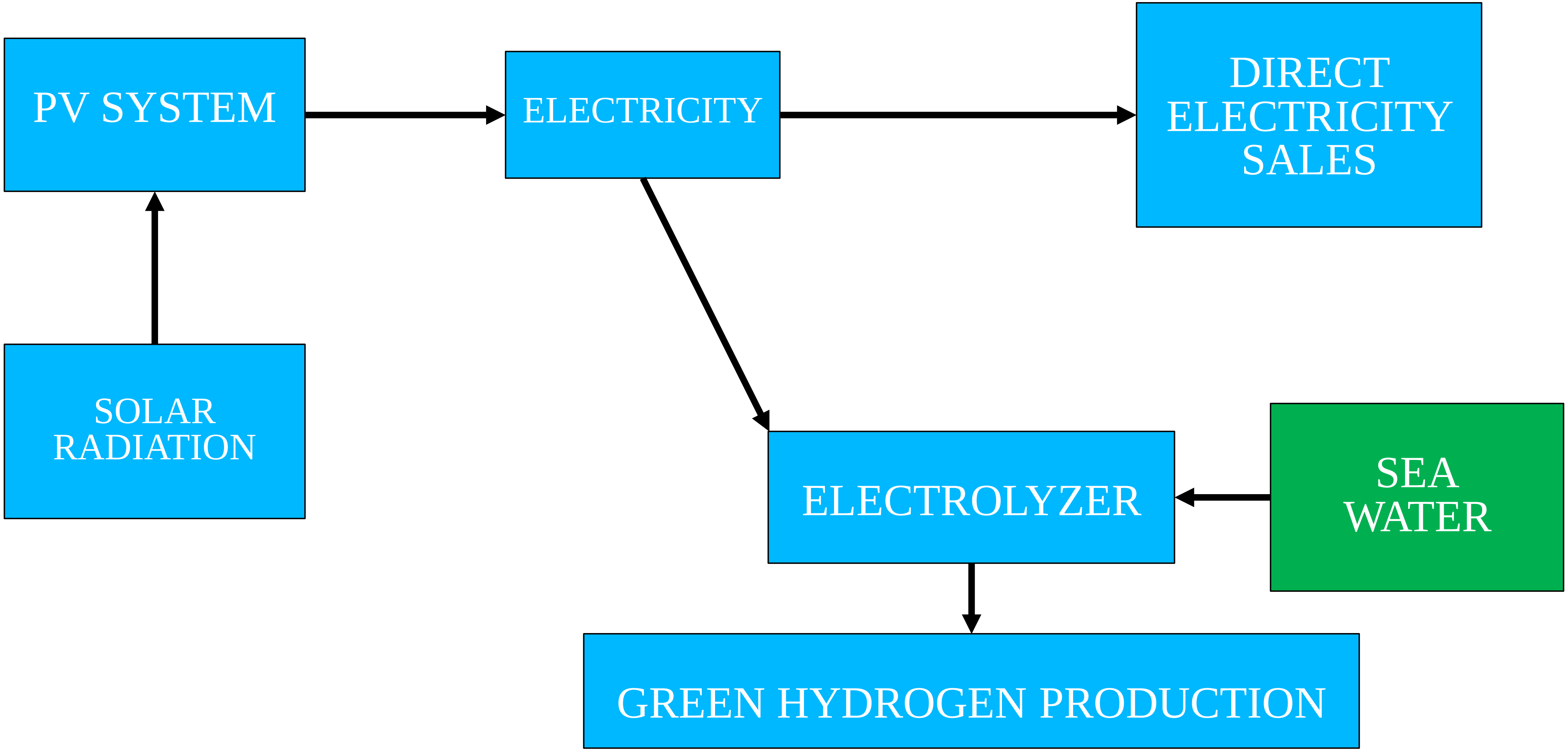
3- Population density in 2024 (people/km^2) according to Worldometer

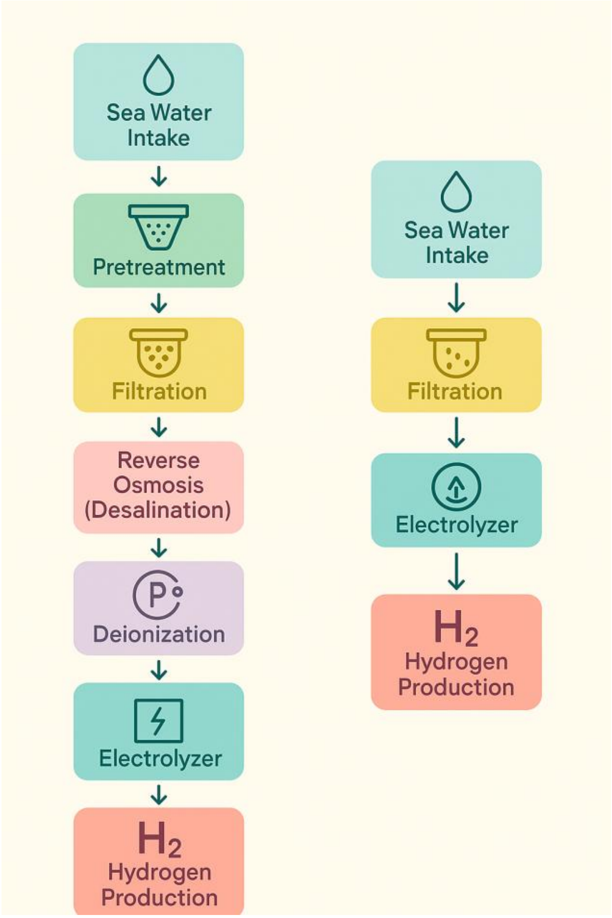
- Algeria, Tunisia, Libya, Morocco => 19, 80, 4, 85, 113 respectively
- Italy, Portugal, Spain, France, Germany => 200, 112, 95, 118, 239

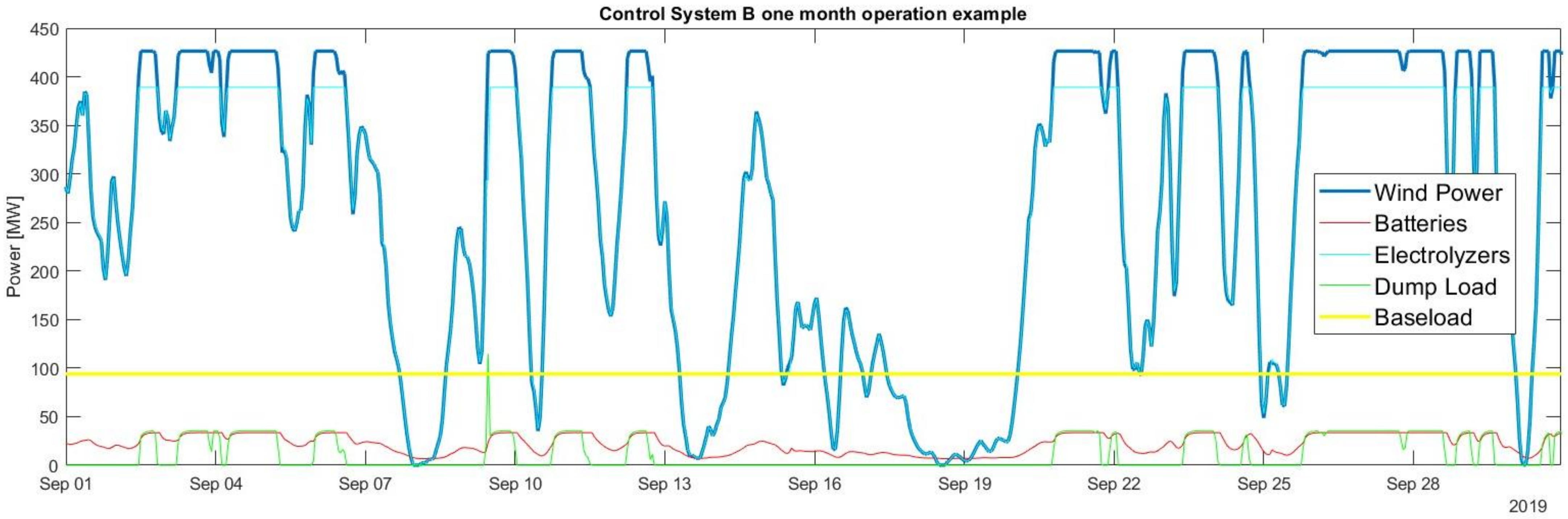
MODEL IMPLEMENTATION – FRESHWATER ELECTROLYSIS



MODEL IMPLEMENTATION – SEAWATER ELECTROLYSIS




Sea Water
Intake
Pretreatment
Filtration
Reverse
Osmosis
(Desalination)
Deionization
Electrolyzer
H_2
Hydrogen
Production
Sea Water
Intake
Filtration
Electrolyzer
H_2
Hydrogen
Production



Control System B one month operation example
Power [MW]
450
400
350
300
250
200
150
100
50
0
Sep 01
Sep 04
Sep 07
Sep 10
Sep 13
Sep 16
Sep 19
Sep 22
Sep 25
Sep 28
2019
Wind Power
Batteries
Electrolyzers
Dump Load
Baseload

Production

Table 2. Midpoint life-cycle environmental indicators of hydrogen production pathways (values for 1 kg of H_2).

Impact Category [2]	Unit	H_2 Production Pathways [1]											
		SMR	CG	BMG	BDL-E-Corn	BDL-E-Wheat	E-PEM	E-PEM-R	E-SOEC	E-SOEC-R	DF-MEC w/out ER	DF-MEC w/ER	DF-MEC w/H_2 Recovery
GWP	kg CO_2-eq	12.13	24.2	2.67	9.193	14.02	29.54	2.21	23.32	5.10	16.29	6.60	14.57
ODP	kg CFC-11-eq	2.99×10^{-6}	3.35×10^{-6}	2.18×10^{-5}	1.70×10^{-4}	1.23×10^{-4}	1.22×10^{-5}	1.40×10^{-6}	9.36×10^{-6}	2.16×10^{-6}	4.16×10^{-5}	3.79×10^{-5}	4.11×10^{-5}
IRP	kBq Co-60-eq	0.501	1.188	0.406	0.835	0.87	19.33	0.52	12.8505	0.3142	7.53	2.11	7.50
EOFP	kg NO_x-eq	0.0085	0.055	0.00375	0.037	0.0424	0.0487	0.0039	0.0349	0.0050	0.0247	0.01055	0.024
PMFP	kg $PM_{2.5}$-eq	0.002	0.039	0.00284	0.007	0.021	0.0337	0.0041	0.0222	0.0025	0.0172	0.008266	0.016989
HOFP	kg NO_x-eq	0.0089	0.055	0.00382	0.037	0.043	0.0492	0.0041	0.0353	0.0052	0.025	0.010696	0.023983
TAP	kg SO_2-eq	0.0087	0.139	0.03706	0.124	0.112	0.1087	0.0118	0.0724	0.0078	0.104	0.074636	0.103
FEP	kg P-eq	0.0007	0.008	0.00081	0.003	0.00568	0.0242	0.0014	0.0162	0.0009	0.0098	0.00312	0.009749
TETP	kg 1,4-DCB-eq	0.0005	0.003	0.0003	0.007	0.142	0.012	0.0048	0.0078	0.0030	0.0041	0.001442	0.003977
FETP	kg 1,4-DCB-eq	0.0208	0.268	0.01875	0.162	0.646	0.7519	0.15	0.4974	0.097	0.268	0.080308	0.27
METP	kg 1,4-DCB-eq	0.0423	0.377	0.02706	0.227	0.483	1.07	0.22	0.7111	0.145	0.384	0.12	0.38
HTPc	kg 1,4-DCB-eq	0.0803	0.64	0.0433	0.128	0.357	1.58	0.43	1.1213	0.356	0.565	0.16	0.55
HTPnc	kg 1,4-DCB-eq	21.36	277.6	19.69	284.129	268.94	764.98	157.25	507.42	102.26	272.6	82.10	269.3
LOP	m^2a crop-eq	0.008272	0.235	0.02062	23.518	20.2	0.22	0.05	0.1525	0.04	0.104	0.043	0.102467
SOP	kg Cu-eq	0.00389	0.004	0.00186	0.028	0.04	0.12	0.16	0.0632	0.09	0.0153	0.006	0.014159
FFP	kg oil-eq	4.45	4.914	0.655	1.524	3.042	7.81	0.62	6.5058	1.72	4.38	1.68	3.78
WCP	m^3 consumed	5.77	13.1	4.94	2.246	3.875	223.39	16.40	146.82	8.82	84.9	23.98	84.50
WSF	m^3	247.5	570.2	212.4	94.61	149.4	9604.3	629.8	6312.3	379.3	3650.2	1030.8	3632.9

[1] SMR: Steam methane reforming; CG: Coal gasification; BMG: Biomass Gasification; BDL: Biomass Reformation; E-PEM: Electrolysis with Proton exchange membrane (PEM): E-PEM-R: Electrolysis with Proton exchange membrane with wind energy; E-SOEC: Electrolysis with Solid oxide electrolysis cells (SOEC); E-SOEC-R: Electrolysis with Solid oxide electrolysis cells with wind energy; DF-MEC: Dark fermentation + microbial electrolysis cell (MEC) without energy recovery, with energy recovery and H_2 recovery. [2] Global warming potential (GWP); Stratospheric ozone depletion (ODP); Ionizing radiation (IRP); Photochemical oxidant formation: human health (HOFP); Photochemical oxidant formation: ecosystem quality (EOFP); Human toxicity potential: cancer (HTP_c); Human toxicity potential: non-cancer (HTP_{nc}); Terrestrial ecotoxicity freshwater ecotoxicity (TETP); Freshwater ecotoxicity (FETP); Marine ecotoxicity (MAETP); Freshwater eutrophication potential (FEP); Fine particulate matter formation (PMFP); Terrestrial acidification (TAP); Land use (LOP); Water consumption potential (WCP); Mineral resource scarcity (SOP); Fossil resource scarcity (FFP); Water Scarcity Footprint (WSF).

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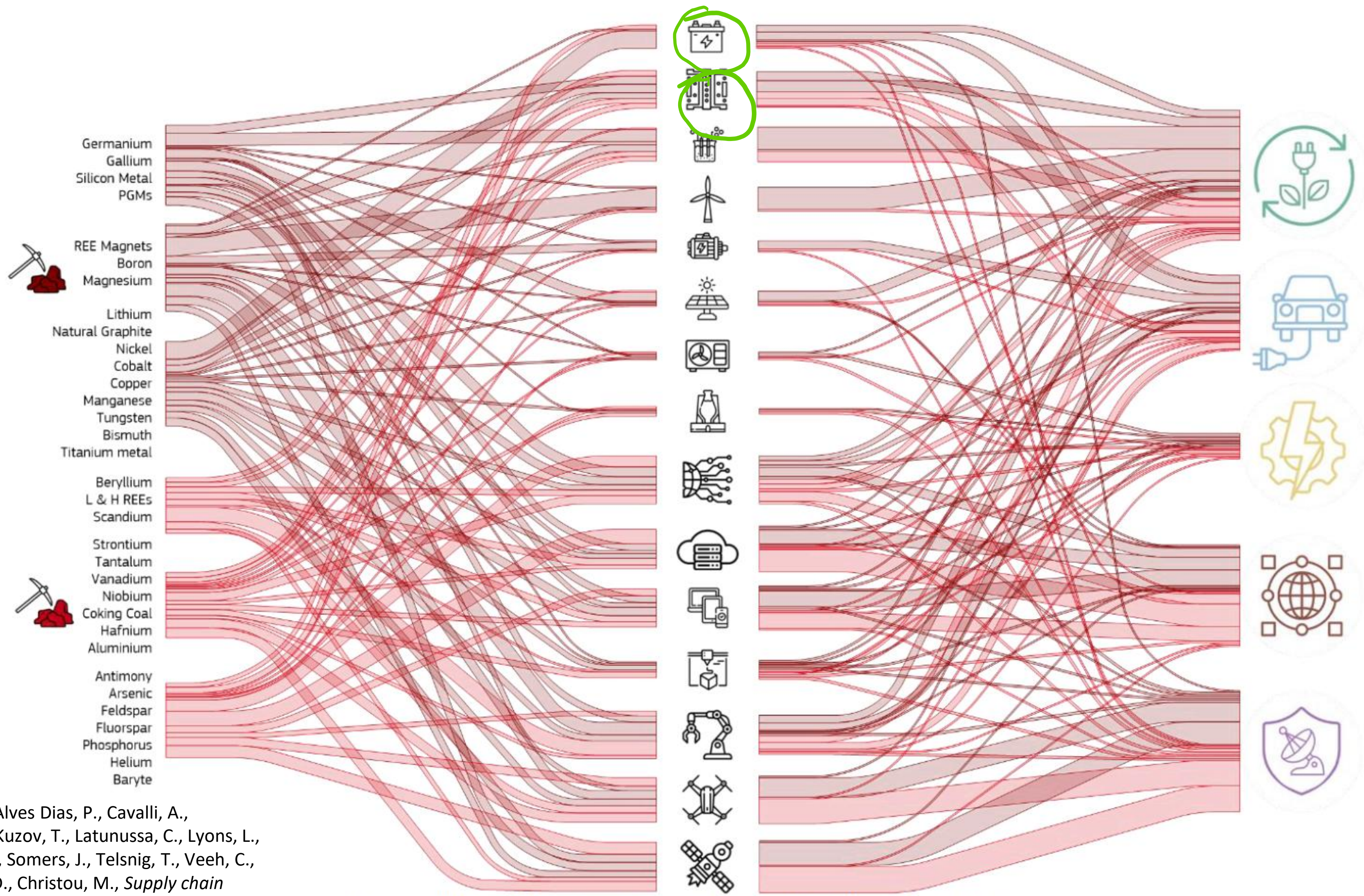
Production

Figure 2. Semi-quantitative representation of flows of raw materials to the fifteen technologies and five sectors

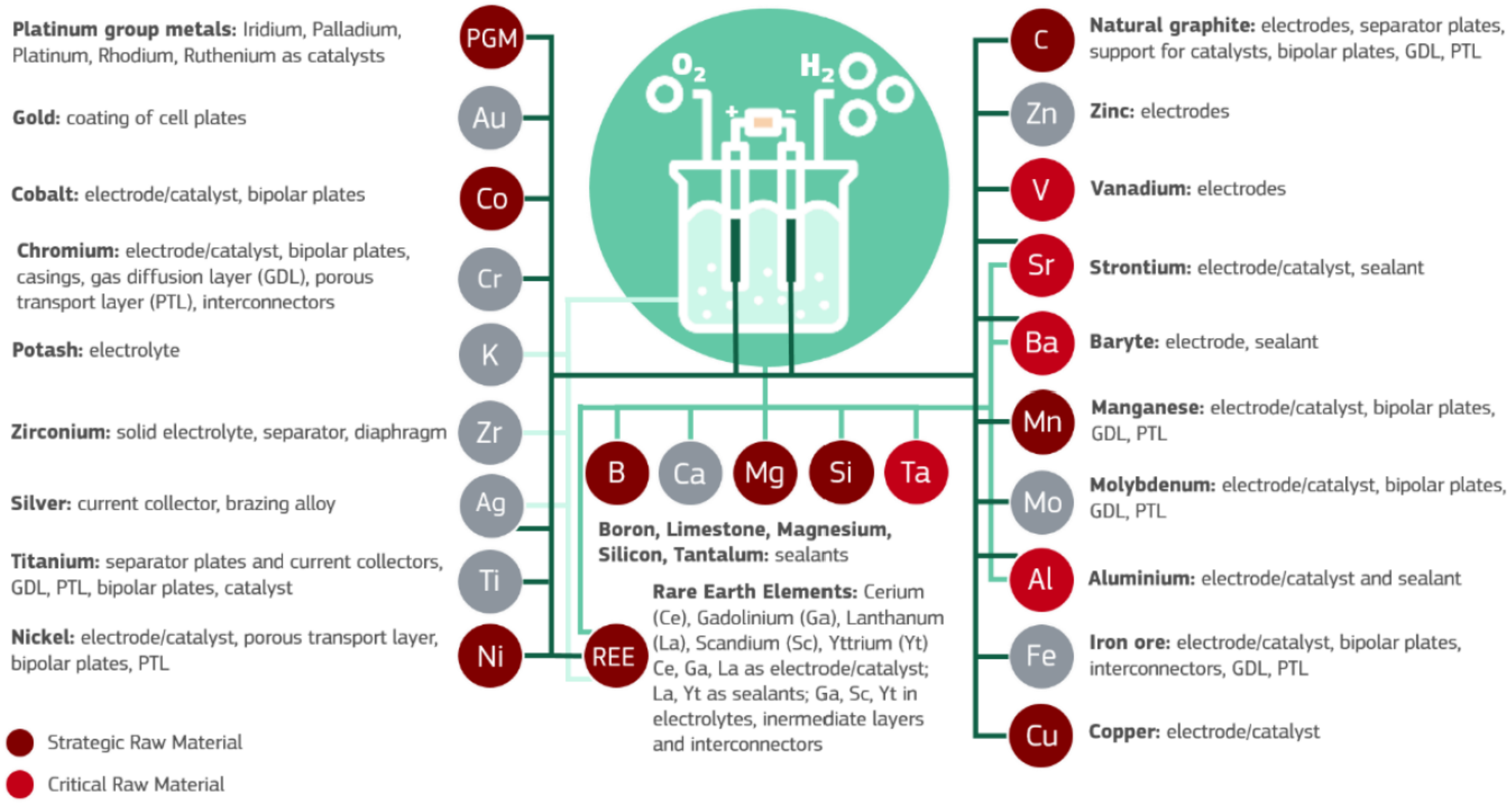


Source: JRC analysis (see Annex 3 for methodological details).

Carrara, S., Bobba, S., Blagoeva, D., Alves Dias, P., Cavalli, A., Georgitzikis, K., Grohol, M., Itul, A., Kuzov, T., Latunussa, C., Lyons, L., Malano, G., Maury, T., Prior Arce, Á., Somers, J., Telsnig, T., Veeh, C., Wittmer, D., Black, C., Pennington, D., Christou, M., *Supply chain analysis and material demand forecast in strategic technologies and sectors in the EU – A foresight study*, Publications Office of the European Union, Luxembourg, 2023, doi:10.2760/386650, JRC132889

Production

Figure 21. Selection of raw materials used in electrolysers and their function



Source: JRC analysis.

Carrara, S., Bobba, S., Blagoeva, D., Alves Dias, P., Cavalli, A., Georgitzikis, K., Grohol, M., Itul, A., Kuzov, T., Latunussa, C., Lyons, L., Malano, G., Maury, T., Prior Arce, Á., Somers, J., Telsnig, T., Veeh, C., Wittmer, D., Black, C., Pennington, D., Christou, M., *Supply chain analysis and material demand forecast in strategic technologies and sectors in the EU – A foresight study*, Publications Office of the European Union, Luxembourg, 2023, doi:10.2760/386650, JRC132889.

Production

Table 7 – Costs of various hydrogen production technologies.

Method		Cost ($/kg H_2)
Fossil fuels to hydrogen	SMR	2.08
	SMR with CCS	2.27
	CG	1.34
	CG with CCS	1.63
	ATR with CCS	1.48
Biomass to Hydrogen	Biomass gasification	1.77–2.77
	Direct biophotolysis	2.13
	Indirect biophotolysis	1.42
	Photo fermentation	2.83
	Dark fermentation	2.57–6.98
Electrolysis	Grid electrolysis	5.73–8.54
	PV electrolysis	5.78–23.27
	Wind electrolysis	5.27–9.37
	Nuclear electrolysis	3.56–7.00
	High-temperature electrolysis (SOEL)	2.89–6.03
Thermolysis & thermochemical cycles	Nuclear thermolysis	2.17–2.63
	Solar thermolysis	7.98–8.40
	S–I cycle	1.99–14.85
	Cu–Cl cycle	1.71–14.20
	Ca–Br cycle	7.06
	Mg–Cl cycle	3.67

Avoid CO_2 emission cost