

UNIVERSITY OF PISA



Engineering School of Pisa

PhD course in Energy, Systems, Territory and Constructions Engineering

Green hydrogen and final industrial uses

Presentation at the end of the 1st year of the course – 14/03/2024

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Academic Year 2022/2023



Green hydrogen and final uses

Nowadays, hydrogen is mainly produced from fossil fuels and is principally used in refining, chemical and steel industries [1]. To reduce carbon dioxide emissions, hydrogen can be generated by electrolysis powered with green energy. Green hydrogen has an important potential in the process of scaling up renewable energy sources providing a long-term energy storage solution.

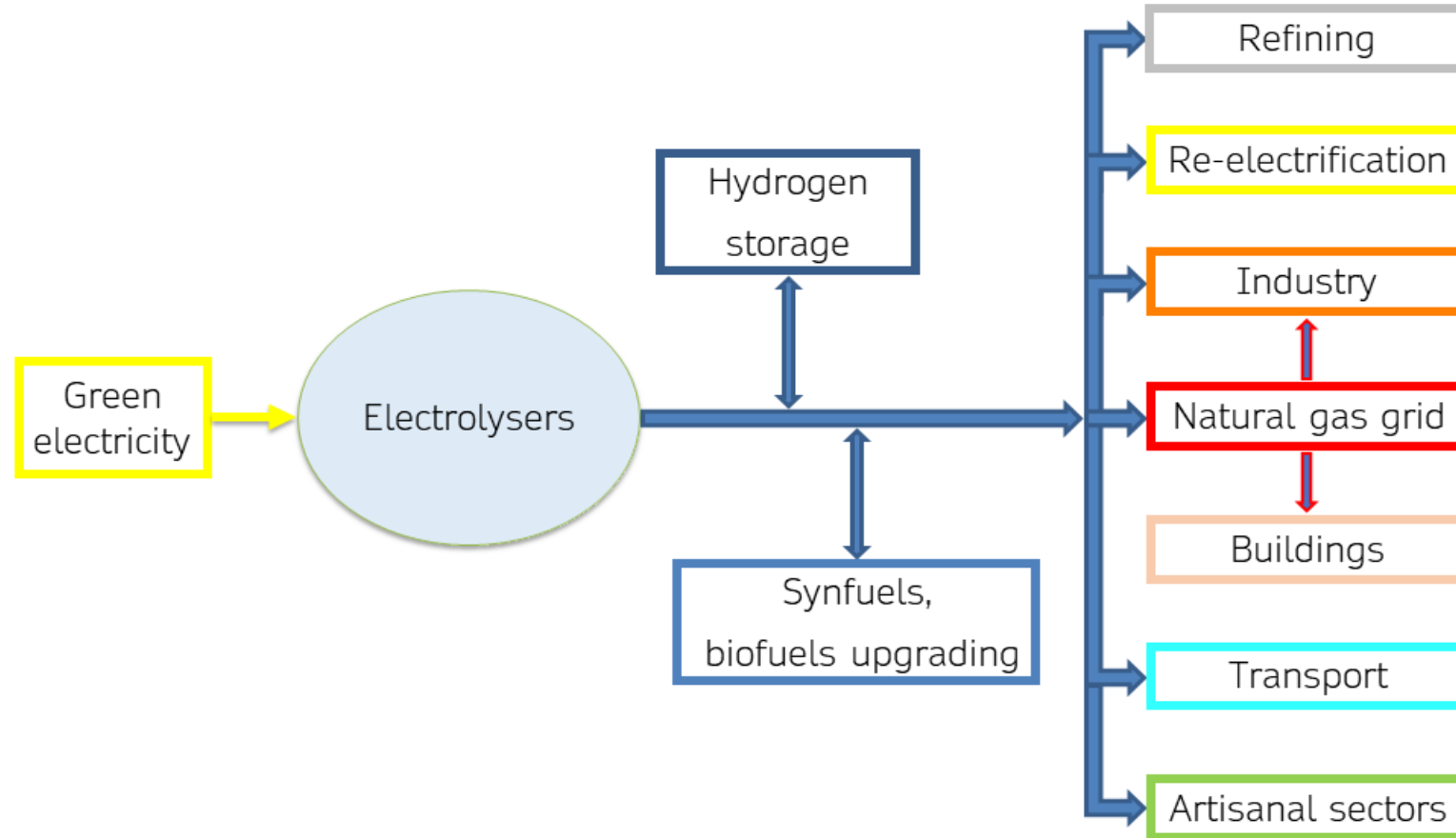


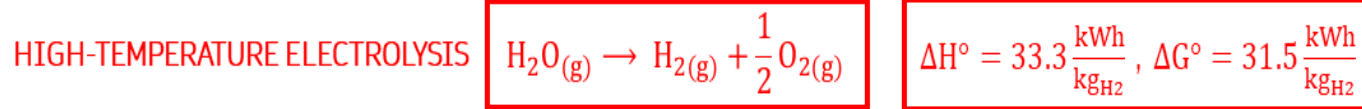
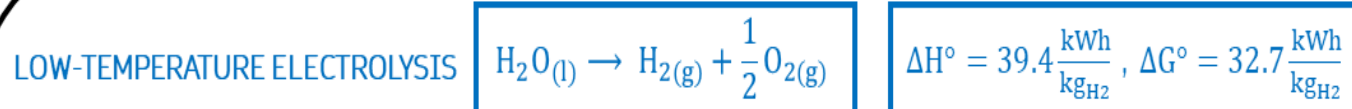
Fig. 1. Electrolytic hydrogen production, with electricity from renewable energy sources, and potential end-uses [2].

[1] International Energy Agency. IEA Report, Global Hydrogen Review. 2023. Available online: <https://www.iea.org/reports/global-hydrogen-review-2023>.

[2] Franco, A., & Giovannini, C. (2023). Recent and Future Advances in Water Electrolysis for Green Hydrogen Generation: Critical Analysis and Perspectives. *Sustainability*, 15(24), 16917. <https://doi.org/10.3390/su152416917>

Water electrolysis for hydrogen production: electrochemical model

The electrochemical model of electrolysis and the main correlations for energy analysis of electrolytic cells (Tab. 1) were identified.



$\Delta H = \Delta G + T \cdot \Delta S$ Total energy demand

Amount of electrical work $\Delta G = z \cdot F \cdot U_{\text{rev}}$ where $z=2$ is the number of moles of electrons (e^-) transferred per mole of H_2 and $F=96,485.3 \text{ C/mol}_{e^-}$ is the Faraday constant

$U_{\text{rev}} = \frac{\Delta G}{z \cdot F}$ Reversible voltage

$U_{\text{tn}} = \frac{\Delta H}{z \cdot F}$ Thermoneutral voltage

Operational cell voltage $U_{\text{cell}} = U_{\text{rev}} + \eta_{\text{act}}^v + \eta_{\text{ohm}}^v + \eta_{\text{conc}}^v$

Activation overpotential Ohmic overpotential Concentration overpotential

Electrical and Thermal Demands	Main Variables of Influence
U_{rev}	Liquid water/steam, operating temperature, pressure, water activity (Nernst Equation)
η_{act}^v	Half-reactions, catalysts, operating temperature, pressure, current density
η_{ohm}^v	Operating temperature, pressure, current density, components' materials, morphology, and dimensions, thus electrical and ionic conductivity, gases' bubbles, components' assembly
η_{conc}^v	Operating temperature, pressure, current density, products' removal rate, gases' bubbles, electrolyte ion concentration/ionic conductivity, electrodes' porosity, and ionic conductivity
Process heat, steam (only SO technology)	Operating temperature, thermal source of process heat, heat transfer mechanisms, components' conductive, convective, and radiative properties, steam properties

Fig. 2. Main constant values and equations for water electrolysis.

Water electrolysis for hydrogen production: main technologies

Low-temperature technologies have an average electricity consumption of around 55–60 kWh per kg of hydrogen, while the leading high-temperature technology may reduce the electrical consumption to about 40–42 kWh/kg_{H₂}.

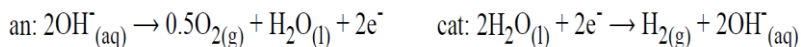
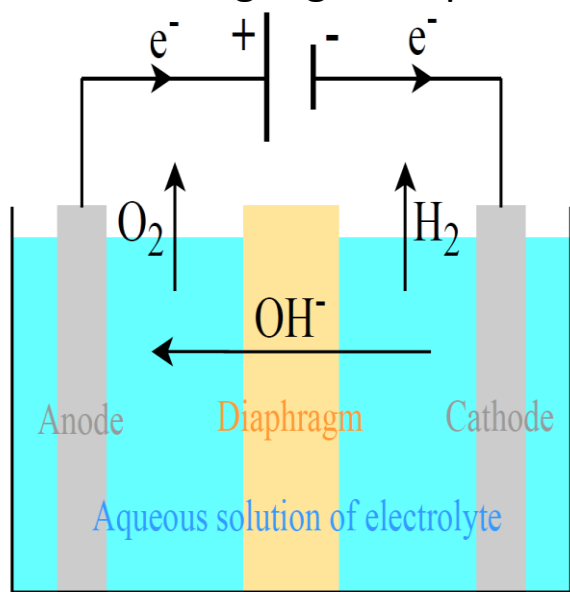


Fig. 3. Simplified alkaline electrolysis cell.

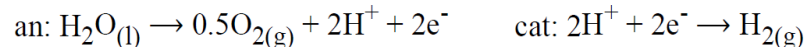
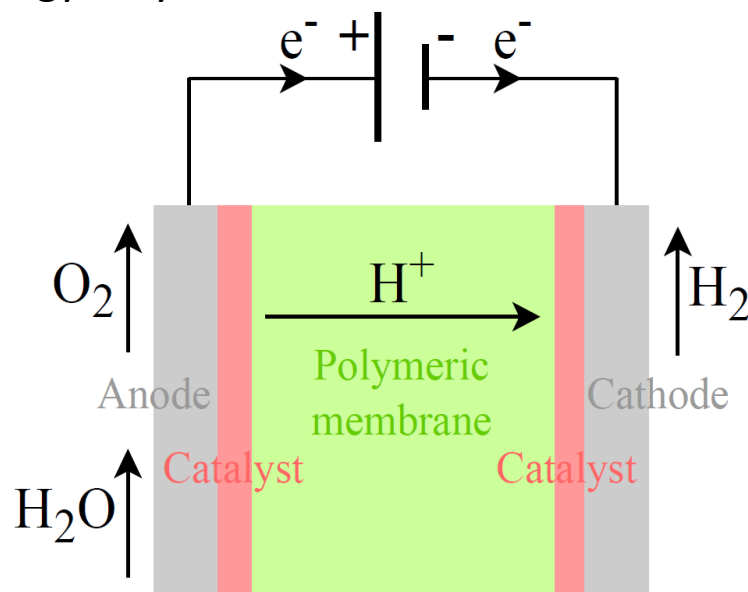


Fig. 4. Proton exchange membrane cell.

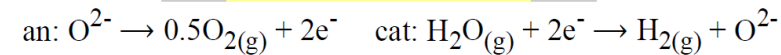
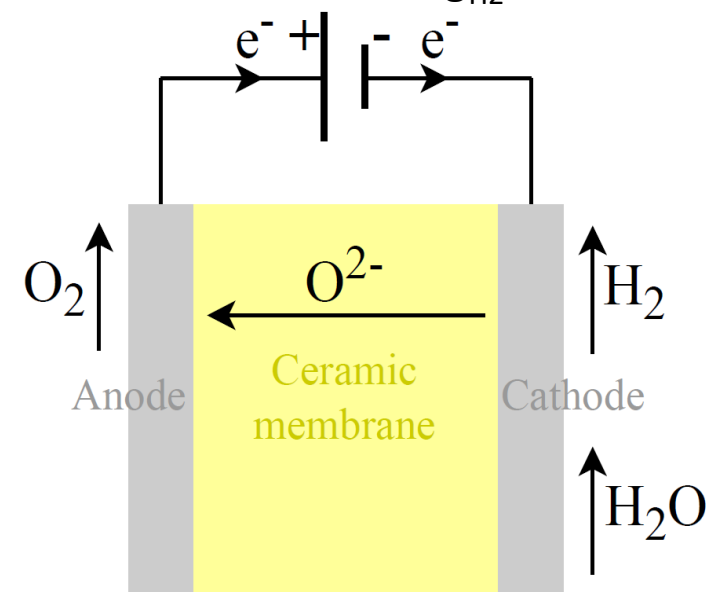


Fig. 5. Solid oxide electrolysis cell.

Tab. 2. Main advantages and disadvantages of water electrolysis technologies.

	Alkaline technology	Proton exchange membrane technology	Solid oxide technology
Main Advantages	Well-tested technology; Lower costs; Condensation recovery.	Higher current density; Smaller volume; Heat recovery from cooling.	Higher electrical efficiency; RES- or industrial waste-heat usable; Reversible devices.
Main Disadvantages	Corrosive electrolyte; H ₂ purification necessary; Lower current density; Bigger Volume.	Higher costs; Greater water requirement; Smaller application experience.	Thermal energy needed (steam); Long warming up; Limited lifetime.

Water electrolysis: energy analysis at cell, stack and system level

A first analysis based on mass and energy balances (in blue boxes) at cell, stack (N cells in series) and system level of electrolysis technologies was carried out to evaluate the necessary electrical and thermal power.

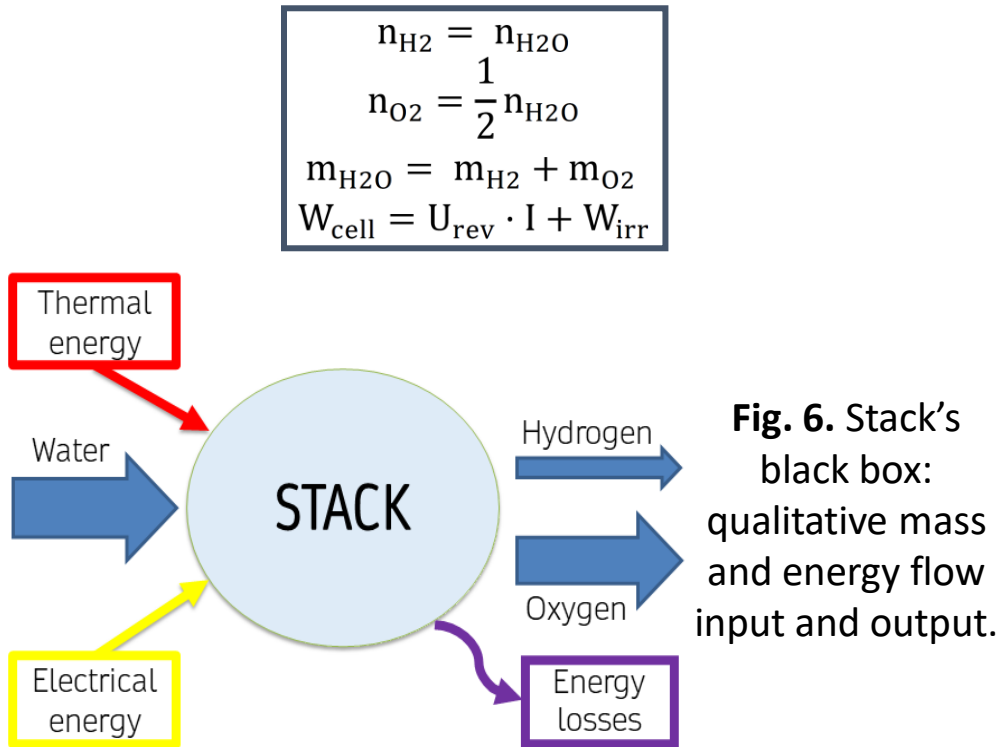


Fig. 6. Stack's black box: qualitative mass and energy flow input and output.

$$\begin{aligned} n_{\text{H}_2} &= n_{\text{H}_2\text{O}} \\ n_{\text{O}_2} &= \frac{1}{2} n_{\text{H}_2\text{O}} \\ m_{\text{H}_2\text{O}} &= m_{\text{H}_2} + m_{\text{O}_2} \\ W_{\text{cell}} &= U_{\text{rev}} \cdot I + W_{\text{irr}} \end{aligned}$$

$$\begin{aligned} U_{\text{stack}} &= N \cdot U_{\text{cell}} \\ I_{\text{stack}} &= I_{\text{cell}} \\ W_{\text{stack}} &= N \cdot U_{\text{rev}} \cdot I + W_{\text{irr,stack}} \\ W_{\text{irr,assembly}} &= W_{\text{irr,stack}} - N \cdot W_{\text{irr,cell}} \\ Q_{\text{gen}} &= N \cdot (U_{\text{cell}} - U_{\text{rev}}) \cdot I - N \cdot \frac{T \cdot \Delta S}{z \cdot F} \cdot I \end{aligned}$$

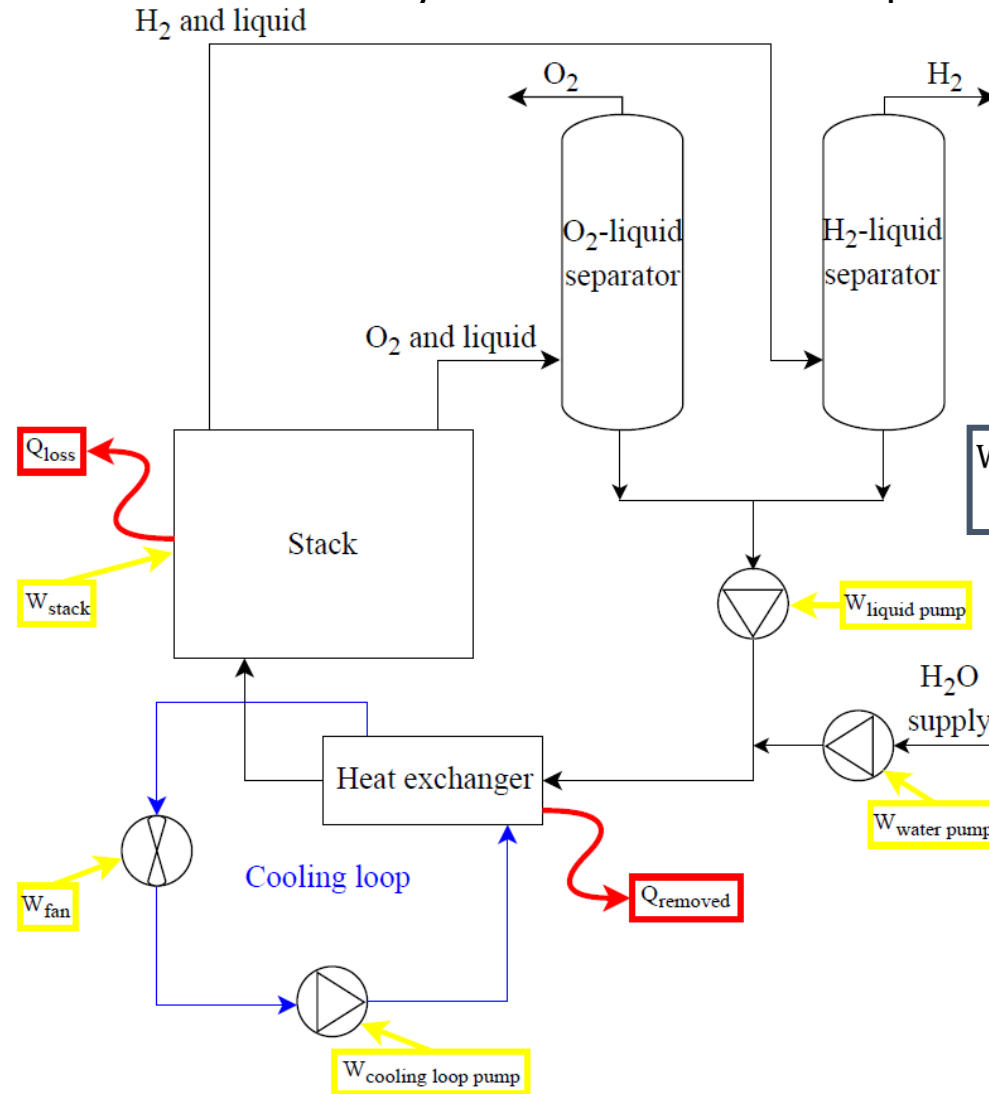


Fig. 7. Simplified low-temperature system (alkaline technology: liquid is electrolyte solution; proton exchange membrane: liquid is water).

$$\begin{aligned} W_{\text{input}} &= W_{\text{stack}} + W_{\text{pumps}} + W_{\text{fan}} \\ Q_{\text{rem}} &= Q_{\text{gen}} - Q_{\text{loss}} \end{aligned}$$

Electrolyser efficiency

$$\eta_I = \frac{\text{LHV}_{\text{H}_2} \cdot \dot{m}_{\text{H}_2}}{W_{\text{input}} + Q_{\text{input}}}$$

$$\eta_{\text{el}} = \frac{\Delta G_{\text{electrolysis}}}{\text{ASEC}_{\text{electrolyser}}}$$

Storage of hydrogen in compressed gaseous form at ambient temperature

Multistage compression with intercooling for storage of hydrogen in compressed gaseous form at ambient temperature was investigated. The storage pressures (p_{st}) of interest range from 2 to 100 MPa. Assuming a constant value of isentropic efficiency (η_{is}) for all the stages, the specific compression work was minimized as the storage pressure and the number of stages vary with constraints on the pressure ratio and the maximum temperature reached in compression. When compressing H_2 produced at atmospheric pressure, the optimized work is 8–9% of the hydrogen energy content for industrial storage ($p_{st}=20\text{--}30$ MPa).

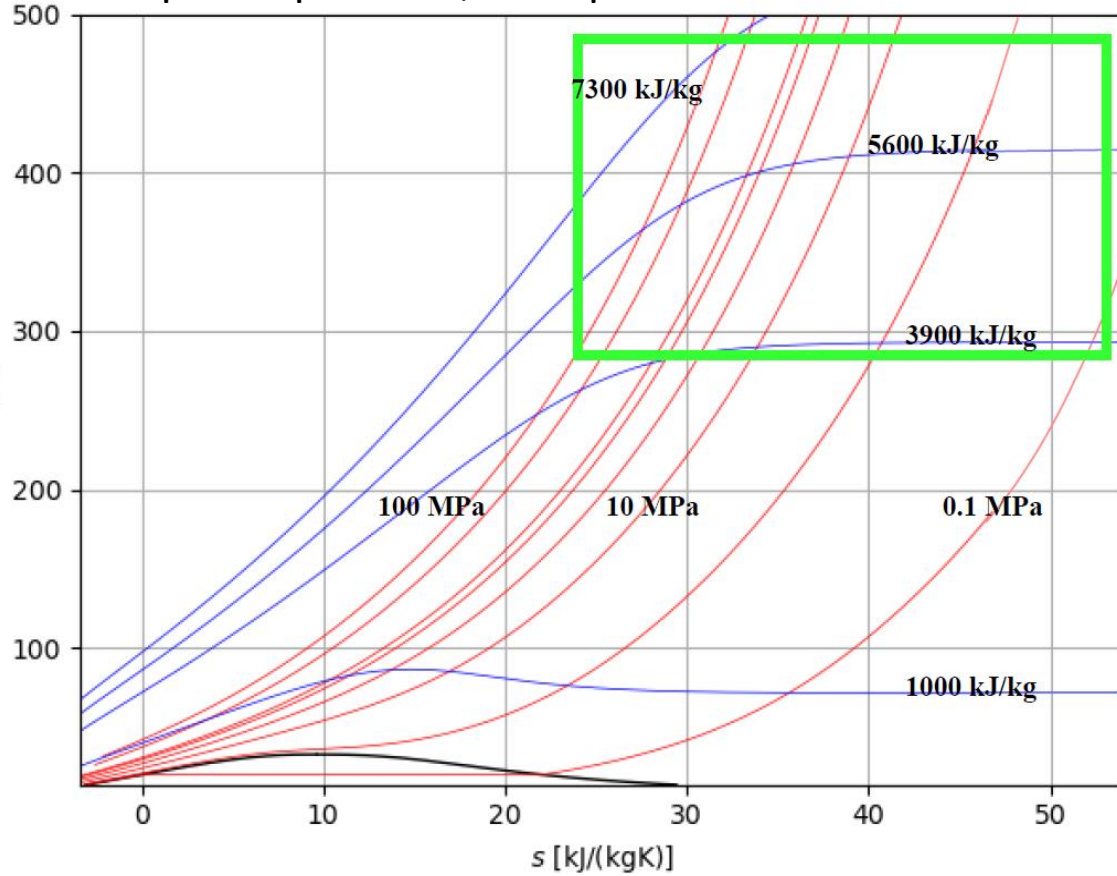


Fig. 8. Zone of interest (green box) for the storage of H_2 in compressed gaseous form at ambient temperature.

Tab. 3. Multistage intercooled compression ($\eta_{is}=0.80$) from 20 °C and 0.1 MPa: evaluable number of stages for storage pressures of interest and maximum temperature of the optimized configuration. Comparison of the optimized specific work (w_{m-s}) with the Lower Heating Value of hydrogen and corresponding ideal isothermal work of compression ($w_{iT,id}$).

p_{st} [MPa]	Number of stages	T_{max} [°C]	Optimized w_{m-s} [MJ/kg $_{H_2}$]	$w_{m-s}/LHV_{H_2} * 100$ [%]	$w_{iT,id}/w_{m-s}$ []
2	3	143	5.3	4.4	0.69
10	4	165	8.3	7.0	0.67
20	5	151	9.6	8.0	0.67
30	5	163	10.5	8.7	0.66
35	5	168	10.9	9.1	0.65

Storage of hydrogen in compressed gaseous form at ambient temperature

The value of the hydrogen production pressure, the isentropic efficiency and the ambient temperature were varied to estimate the change in the optimum work of compression. For industrial applications ($p_{st}=20\text{--}30$ MPa), large electrolyzers producing hydrogen at 3 MPa can reduce compression work by 60–65%, compression stages from 5 to 3, and the maximum temperature reached in compression by about 50 °C.

Tab. 4. Optimized work of compression from 20 °C and 0.1 or 3 MPa ($\eta_{is}=0.80$). Comparison of the cases analysed for p_{st} of 20 and 30 MPa.

p_{st} [MPa]	From 0.1 MPa, 5 stages		From 3 MPa, 3 stages	
	T_{max} [°C]	w_{m-s} [MJ/kg]	T_{max} [°C]	w_{m-s} [MJ/kg]
20	151	9.6	94	3.3
30	163	10.5	112	4.2

Fig. 9. Multistage compression with intercooling from 3 MPa: optimized configuration for p_{st} of 30 MPa with three stages of compression.

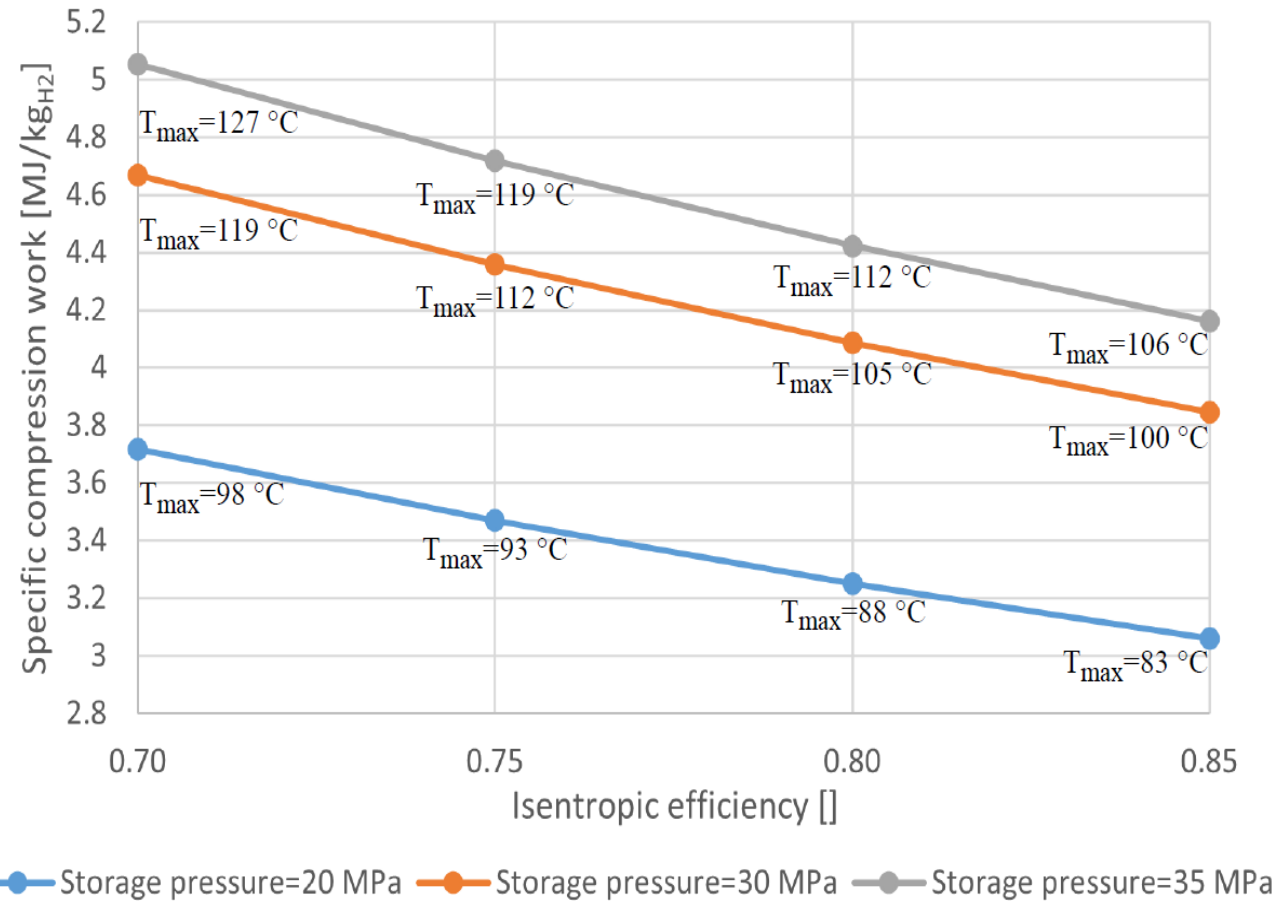
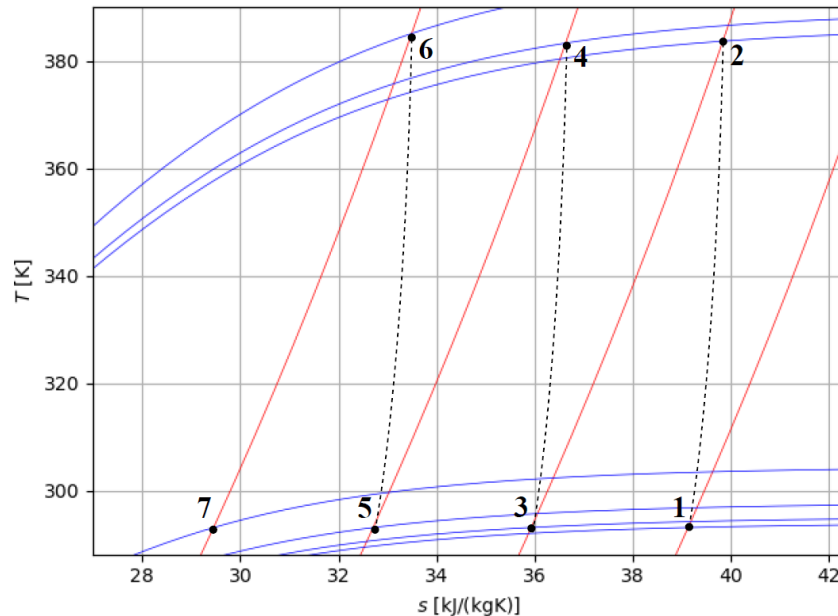


Fig. 10. Optimized specific work of compression from 15 °C and 3.0 MPa as p_{st} and η_{is} vary, with 3 stages of compression.

Hydrogen uses in hard-to-abate industrial sectors

Some examples of hard-to-abate industries include iron and steel, cement, chemicals, paper and glass production. In the chemical, petrochemical and steel sectors, hydrogen is already used as a feedstock or process agent. Hydrogen can also be used as an alternative fuel in high-temperature processes. An estimate was made of the non-renewable primary energy savings achievable through the blended combustion of hydrogen and natural gas (Tab. 5).

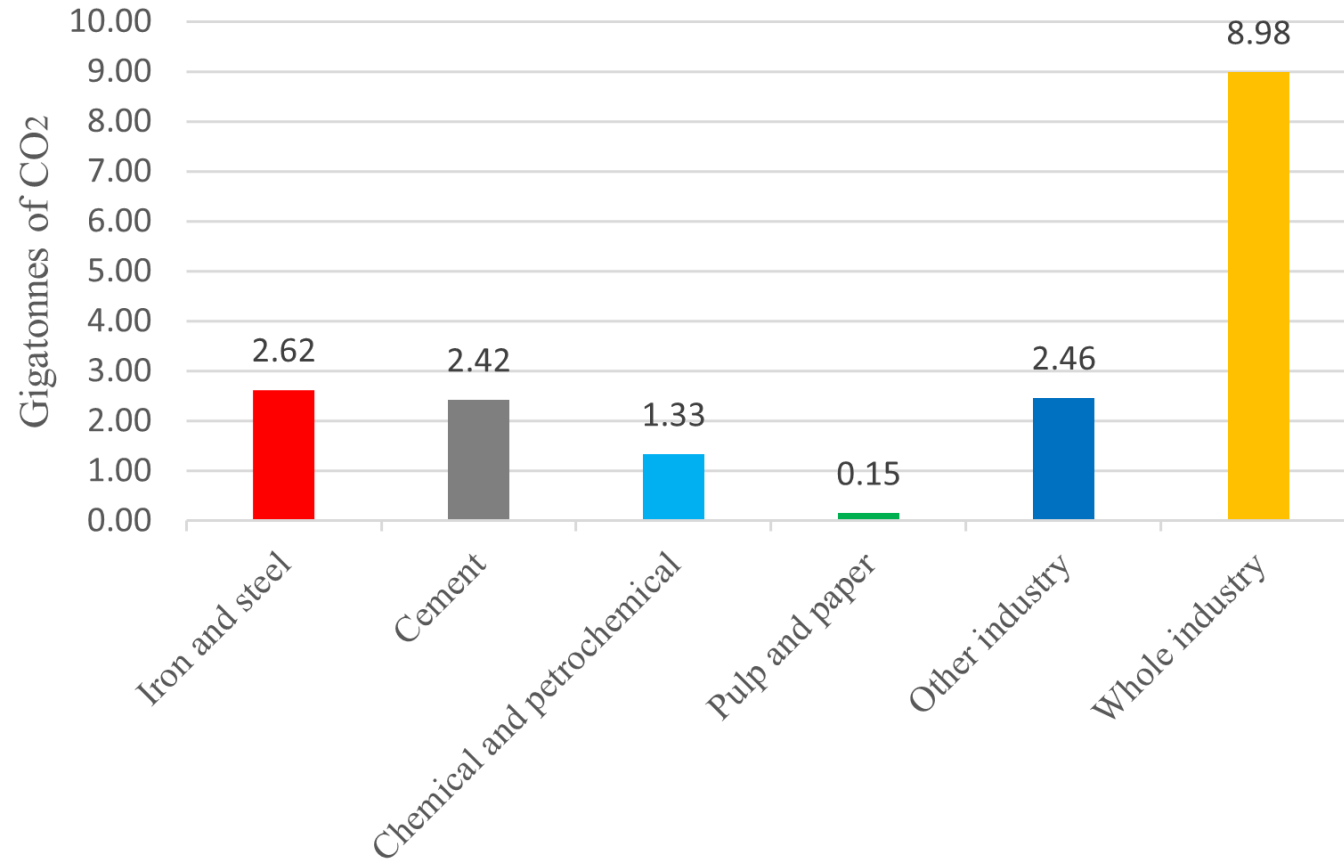


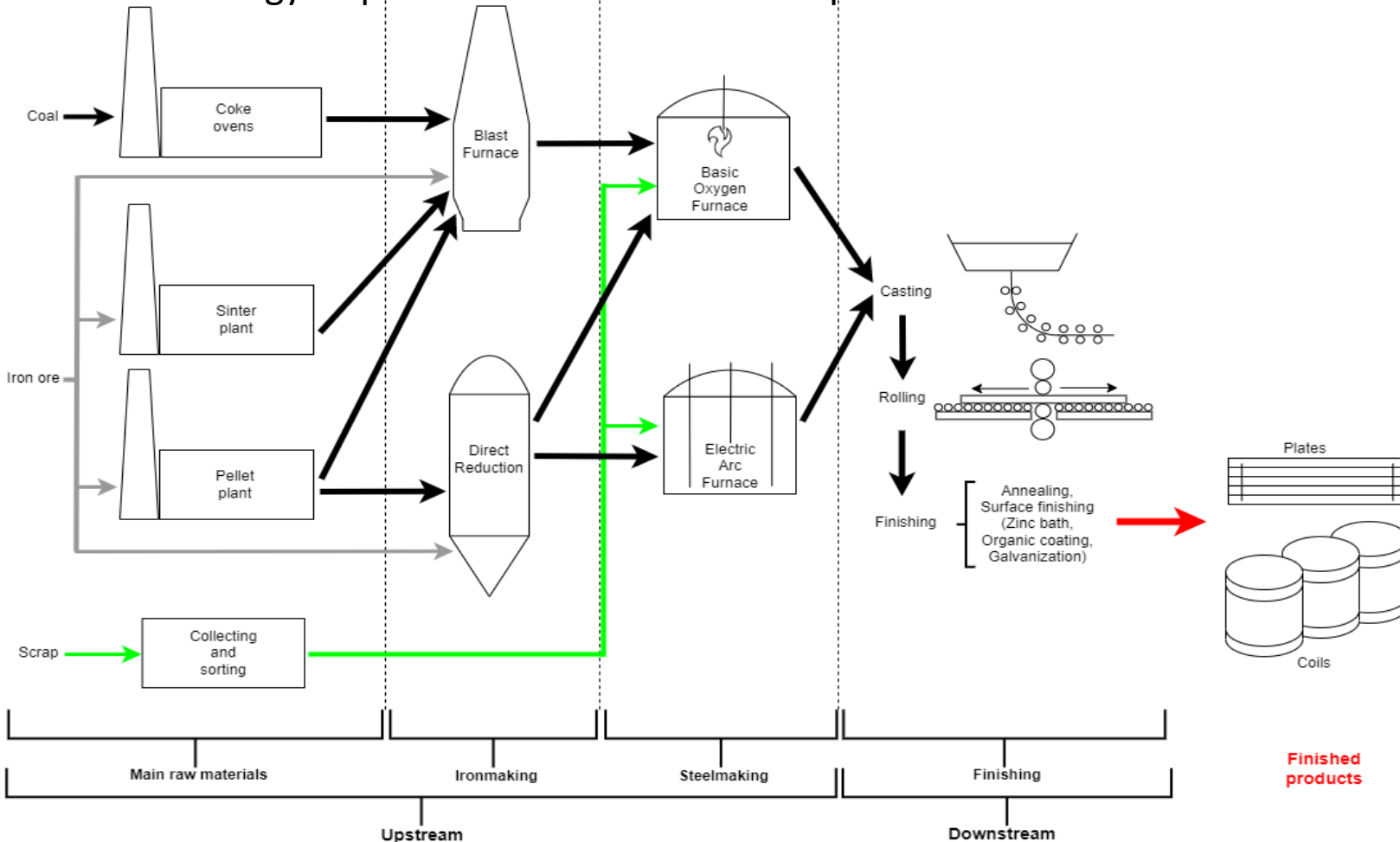
Fig. 11. CO₂ emitted by hard-to-abate industries in 2022.

Tab. 5. Heat requirement coverage (HRC) by hydrogen, i.e. non-renewable primary energy saving, of 1 MW thermal varying the percentage in weight of H₂ in the combustible blend natural gas-hydrogen. The average efficiency of the combustion system was assumed equal to 0.85–0.86.

H ₂ [%]	LHV _{blend} [MJ/kg]	\dot{m}_{blend} [kg/h]	\dot{m}_{H_2} [kg/h]	\dot{q}_{H_2} [Nm ³ /h]	HRC [%]
0	50.0	84.2	0	0	0
2	51.4	81.9	1.6	18.2	4.7
4	52.8	79.7	3.2	35.5	9.1
4.4	53.1	79.3	3.5	38.9	10.0
6.8	54.8	76.9	5.2	58.4	15.0
9.4	56.6	74.4	7.0	77.9	20.0

Hydrogen uses in steel production

In steel production, hydrogen is evaluated as an alternative fuel (e.g., in blast furnaces, hot finishing and reheating furnaces) and as a reducing agent in the H₂-based Direct Reduced Iron process. In the latter case, around 60 kg of H₂ are necessary per tonne of crude steel produced, therefore over 3 MW of low-temperature electrolysers would be needed to produce 1 tonne/h of crude steel. The energy requirement of the main steel production routes was reconstructed and compared with the literature (Tab. 6).



Tab. 6. Summary of average energy requirements of the steel production technologies analyzed.

Process Type	Energy Requirement [GJ/tonne]	Share of Electricity
Blast Furnace – Basic Oxygen Furnace	18–22	<5%
Natural gas-based Direct Reduced Iron – Electric Arc Furnace	14–18	13–17%
Hydrogen-based Direct Reduced Iron – Electric Arc Furnace	15–18	90–94%

Fig. 12. Scheme of steel production by main process routes.

From: Franco, A., & Giovannini, C. (2023). Routes for Hydrogen Introduction in the Industrial Hard-to-Abate Sectors for Promoting Energy Transition. *Energies*, 16(16), 6098. <https://doi.org/10.3390/en16166098>

Conclusions and future activities

The electrical efficiency of water electrolysis is around 60% for low-temperature technologies and about 80% for high-temperature technologies. Further improvements are needed in the performance, lifetime extension and flexibility to operating conditions of electrolyzers, also with a view to integration with renewable energy sources.

Storage of hydrogen in compressed gaseous form at ambient temperature can be achieved with energy requirements around or below 10% of the Lower Heating Value of hydrogen.

The uses of hydrogen in hard-to-abate industries as an alternative fuel or process agent are under experimentation and have great potential for decarbonization.

The research will be continued on the use of hydrogen as an alternative fuel in hard-to-abate industrial sectors and on electrolytic hydrogen production.