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TRANSITIONING TOWARDS LOW-CARBON HYDROGEN PRODUCTION (part 1)

Gregory de Temmerman, Boigontier Thomas

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Gregory de Temmerman, Boigontier Thomas. TRANSITIONING TOWARDS LOW-CARBON HYDROGEN PRODUCTION (part 1): LOW-CARBON HYDROGEN PRODUCTION TECHNOLOGIES: VARIOUS BUT NOT EQUIVALENT OPTIONS. Mines Paris. 2023, pp.40. hal-04093939

HAL Id: hal-04093939

<https://hal.science/hal-04093939>

Submitted on 10 May 2023

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THE HYDROGEN SERIES – PART 1
REPORT
MAY 2023

TRANSITIONING TOWARDS LOW-CARBON HYDROGEN PRODUCTION

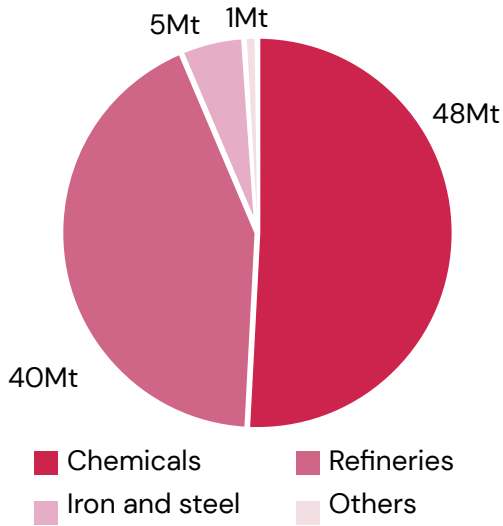
LOW-CARBON HYDROGEN PRODUCTION TECHNOLOGIES:
VARIOUS BUT NOT EQUIVALENT OPTIONS

Hydrogen (H₂) has long been considered a key for the future energy system – the concept of “H₂ key economy” was first coined at the beginning of the 1970s¹. This is because H₂ can in principle be used for many applications such as fuel, steel production, energy storage etc². This has led to a renewed interest in H₂ in the context of the energy transition³. This means that the demand for H₂ will increase in the future, although scenarios differ about the extent of this demand for 2050⁴. This poses a double challenge. First, to comply with climate pledges, the current production of H₂ needs to be decarbonised as quickly as possible. At the same time, the production will need to increase sharply to allow the development of new end-uses technologies, and this additional H₂ will also need to be low-carbon.

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Current hydrogen production: a carbon-intensive industry



About **94 Mt** of hydrogen (H₂) are produced every year in the world, currently used for different purposes dominated by **chemicals** (70% for methanol and 30% for ammonia production) and **refineries**. Today's production is dominated by processes based on **fossil fuels**: steam methane reforming (SMR, using natural gas), and coal gasification (CG). Those two processes are particularly **carbon-intensive**: the production of 1 kg of H₂ emits on average 9 kg CO₂e/kgH₂ for SMR, and 20 kg CO₂e for CG¹¹. **Less than 1%** of the total H₂ demand is currently met by low-carbon production technologies (mostly fossil fuels with carbon capture)⁵.



Navigating the variety of H₂ production methods

Hydrogen production methods are usually referred to by **colours**. 'Green H₂' from water electrolysis, one of the most mature processes, in which water is decomposed into H₂ and oxygen using renewable electricity, is considered in **most net-zero scenarios**. There is, however, a **large variety of methods** at various stages of development.

Key characteristics

Energy/feedstock	Technology	Color	2021 global production ⁵	2020 EU production capacity ⁶	
Fossil fuels or biofuels	Natural gas	Steam methane reforming (SMR) or autothermal reforming (ATR)	Gray	58 Mt (62%)	10 Mt (91%)
		Methane/biogas pyrolysis	Turquoise	-	
	Black coal	Coal gasification (CG) or partial oxidation (PO)	Black	18 Mt (19%)	
	Brown coal		Brown		
	Fossil fuels	SMR, ATR, CG or PO with carbon capture and storage (CCUS)	Blue	660 kt (0.7%)	58 kt (0.5%)
Electricity	Nuclear	Water electrolysis	Pink	35 kt (0.04%)	12 kt (0.1%)
	Mixed-origin grid		Yellow		
	Renewable		Green		
Natural H ₂	Water	Natural resource	White	-	-

Table 1: Hydrogen colours and their characteristics⁹.

By-product H₂ is the missing part of the total H₂ production in the table⁷.

Although H₂ colours depict an apparent simplicity, they fail to represent the **physical processes** and how they might be related from one colour to another due to the lack of a **consistent methodology** for their attribution. Indeed, they can either refer to the type of feedstock, the energy used or the technology without real logic. Another more rigorous classification has been proposed by The Royal Society⁸, based on the type of physical/chemical processes and feedstocks, making it simpler to compare the different technologies. **Five production routes**, in addition to natural H₂, can be identified: thermochemical, electrolytic, pyrolytic, photolytic, biological. Each of these routes include multiple technologies at different levels of maturity.

This report aims at exploring the different routes and individual technologies in terms of their working principles, CO₂ emissions, current maturity and evolutions perspectives.

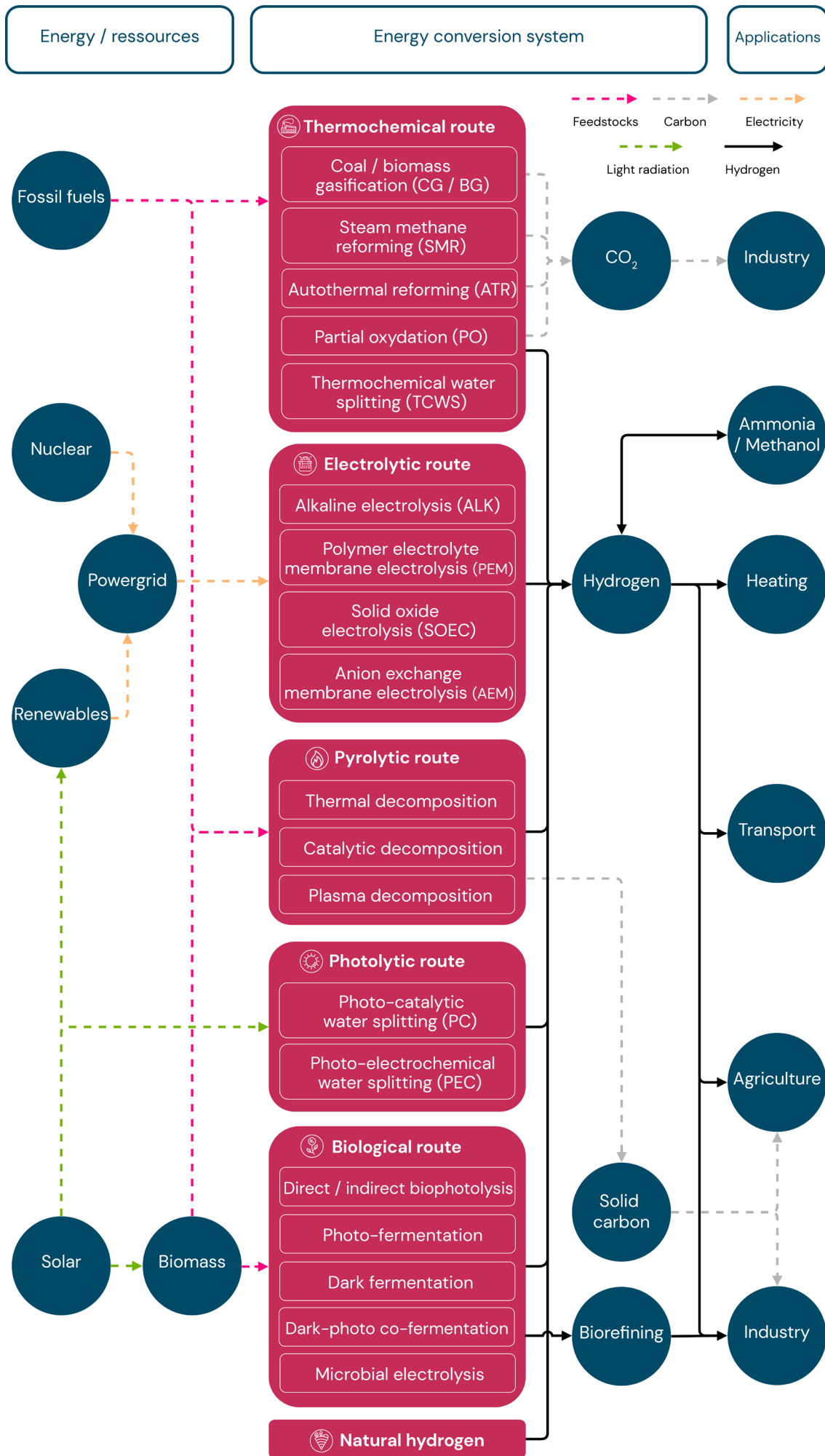


Figure 1: Hydrogen routes and technologies classification⁸



THERMOCHEMICAL ROUTE

Thermochemical production of hydrogen (H_2) encompasses a very broad range of processes involving **chemical reactions that occur when applying a certain amount of heat to an H-containing feedstock**.

This route includes the two most common methods for producing H_2 today, namely **Steam Methane Reforming (SMR)** and **Coal Gasification (CG)**, but also other techniques such as **Autothermal Reforming (ATR)**, **Partial Oxidation (PO)**, **Biomass Gasification (BG)** and finally **Thermochemical Water Splitting (TCWS)**. Apart from TCWS, all of these pathways generate CO_2 directly – coupling them with carbon capture utilisation and storage (CCUS) is therefore necessary for such processes to produce H_2 in a low-carbon way (or even carbon-negative, in the case of BG).

Below is a simplified flow diagram that applies for all thermochemical technologies except TCWS.

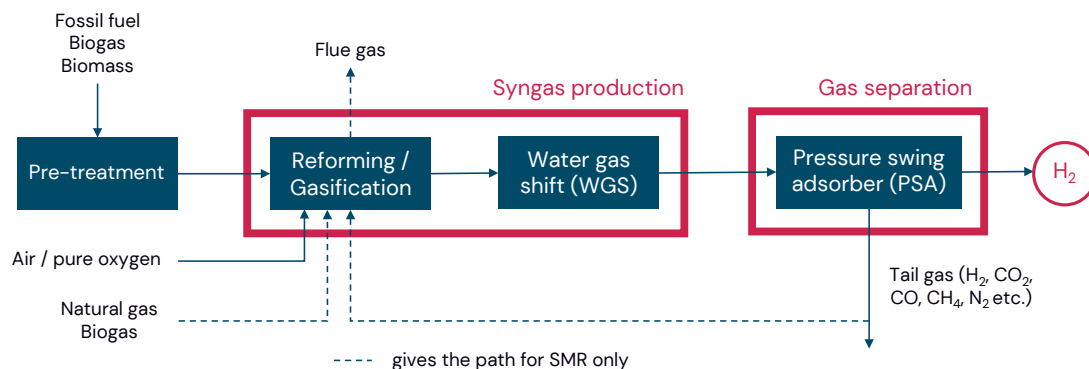


Figure 2 : Simplified flow diagram of thermochemical production processes (except TCWS)⁹

These diverse processes share some fundamental steps. First, the fuel is **pre-treated** (depending on its type: de-sulfuration, pre-heating...) and fed into the reformer or gasifier. The **heat** necessary for oxidation and gasification is provided either by the fuel itself or by an external heat source in the case of reforming. These reactions produce a **syngas** composed of CO , H_2 , CH_4 and CO_2 which then enters a water gas shift unit (WGS) where it reacts with water at lower temperatures to generate more H_2 and CO_2 . The mixture is then flowed into the **pressure swing adsorption unit (PSA)** where calcium oxide (CaO) is combined with CO_2 to form calcium carbonate ($CaCO_3$). A high purity, high-pressure flow of H_2 is obtained, along with another low-pressure stream after the desorption phase, called **"tail gas"**, containing the impurities and some of the H_2 . In the case of SMR, the tail gas is then fed to the reformer and burnt with natural gas to provide heat for the reforming process. Eventually, burned gasses are vented into the atmosphere at the end of the reformer (**flue gas**)⁹.

Steam Methane Reforming (SMR)

Steam methane reforming is a catalytic reaction where **methane (CH₄)** reacts with high temperature **steam** (700–900°C) at pressures of 3–35 bar to generate H₂ and **syngas (CO)**. The reaction is endothermic and thus requires the input of **external heat** provided by steam and/or the burning of some of the natural gas along with the tail gas.

Historically, SMR has imposed itself as the most attractive way to produce H₂, due to a number of key factors:

- SMR has long benefited from the development of the **natural gas industry**, with cheap prices and widespread infrastructure, making it a very cost-competitive method – despite recent fluctuations in Europe due to the war in Ukraine^A;
- SMR is very **efficient** (57–75%)¹⁰, which contributed to a low Levelized Cost of Hydrogen (LCOH) and rapid market adoption;
- Hydrogen **yield** is important since the molar ratio of H₂ with SMR is 4:1, meaning that for every mole of methane, 4 moles of H₂ are produced⁵⁹;
- SMR can produce H₂ **continuously**, making it suitable for industrial applications such as ammonia production or fossil fuel refining.

However, SMR is **very carbon intensive**. The process itself emits ~9 kg CO₂e/kg H₂ and ~10.5 kg CO₂e/kg H₂ when taking supply chain emissions into account (100 years GWP^B, standard IPCC natural gas leakage rate of 1.7%)¹¹. Hence, carbon capture technologies are particularly adapted to these fossil fuels technologies.



Air Liquide's Cryocap CO₂-capture technology is in use at its hydrogen plant in France – Credit Air Liquide

A. The war in Ukraine that has resulted in rapidly rising cost for natural gas in Europe (from <30€/MWh before May 2021 to as high as 343€/MWh in August 2022). But prices are gradually coming down (56€/MWh on January 25th 2023) and prices in the US and in Russia are still low, respectively USD\$10/MWh on January 25th 2023 and USD\$9/MWh for businesses in June 2022, so these two countries can still produce hydrogen at a low cost.

B. Global warming potential (GWP) is defined as the cumulative radiative forcing, both direct and indirect effects, over a specified time horizon resulting from the emission of a unit mass of gas related to some reference gas (CO₂).

Coal Gasification (CG)

Coal and biomass gasification are very similar in the process and only differ on the **pre-treatment step**. Depending on the type of biomass, it is first washed, dried, sieved, leached or thermally pre-treated while coal is only dried and grounded before being fed into a **gasifier**, where they react with oxygen and steam under **high temperature conditions** (usually $>900^{\circ}\text{C}$), producing a gas mixture containing H_2 , CO and CO_2 . This reaction is also **endothermic** – heat being often provided by the (partial) combustion of coal. The H_2 content of the gas mixture is then increased using a **water gas shift process (WGS)**, converting the remaining CO into CO_2 as for SMR. Finally, H_2 is separated from the CO_2 via the **pressure swing adsorption unit (PSA)**¹³.

Coal gasification is generally **less efficient** (50–80%) and **more expensive** than SMR¹⁰. This is why this method is mostly used in countries with abundant coal reserves like China. This process is also the **most carbon intensive** one, producing as much as 20.4 kg $\text{CO}_2\text{e}/\text{kg H}_2$ (brown coal), double the emissions of SMR¹¹.

Biomass gasification is one of the **most efficient processes** of biomass conversion to H_2 (40–60%)¹⁰. It can convert a **variety of biomass sources** (sometimes with a high moisture content) into H_2 with a relatively **high yield** depending on the feedstock (0.068 to 0.080 kg H_2/kg -feedstock)¹². However, it still needs to solve **H_2 separation** issues as well as **catalyst corrosion** and **tar formation** issues before becoming a competitive production route.

Partial Oxidation (PO)

Partial oxidation (PO) is another **commercial pathway** to produce H_2 from **natural gas**. The difference with SMR is that the oxidation process is done using oxygen instead of steam. Oxygen is supplied in proportions lower than the stoichiometric ratio, inducing an **incomplete oxidation of methane** which as a result gives a CO and H_2 mixture¹³. Compared to SMR, PO does not require external heat supply since the reaction is **exothermic**, thus reducing energy consumption. PO reaction does not necessarily require **catalysts** contrary to SMR thus decreasing the cost of the process. It also has a better tolerance to impurities towards sulphur generally present in fossil fuels and the **efficiency** of the process generally reaches 55–75%¹³. However, the current H_2 **yield** of PO is not comparable to that of SMR making it difficult to compete with SMR (SMR produces 4 moles of H_2 for every mole of CH_4 while PO produces only 2 moles)¹⁴.

Autothermal Reforming (ATR)

Autothermal reforming (ATR) combines the advantages of SMR and PO processes by connecting the devices of the **two processes** in series: the heat produced by the partial oxidation step is used to power the reforming process. Given the **high thermal efficiency** of this process, it requires **less energy** than SMR or PO individually¹⁵. However, ATR is characterized by a **higher H_2 yield** than PO but lower than SMR. The efficiency of ATR is generally 60–75%¹³.

CARBON CAPTURE, UTILISATION AND STORAGE (CCUS) FOR THERMOCHEMICAL PROCESSES

Carbon capture, utilisation and storage (CCUS) can help mitigate the emissions of H₂ production routes described above and lead to H₂ certified as **low-carbon**¹⁶. Considering that most of the current production is from fossil fuel, implementing CCUS can make use of **existing infrastructure** of natural gas in Europe and “only” require installing CCUS units on existing facilities, with minimal changes to **consumption patterns**.

Production routes with carbon capture

In the case of CG, PO and ATR, the fuel is oxidized **inside the reactor** that provides the heat⁹. As for SMR, the reactor is **externally heated** by a furnace burning fossil fuels (usually natural gas) and thus produces a flue gas stream containing CO₂. Hence, about **60% of the total CO₂** generated by SMR is contained in the syngas or tail gas and **the other 40%** is produced during the combustion process in the furnace. A carbon capture unit can then be positioned after the reformer to prevent the remaining 40% from entering the atmosphere.

A general diagram for fossil fuel H₂ production + CCUS is given below:

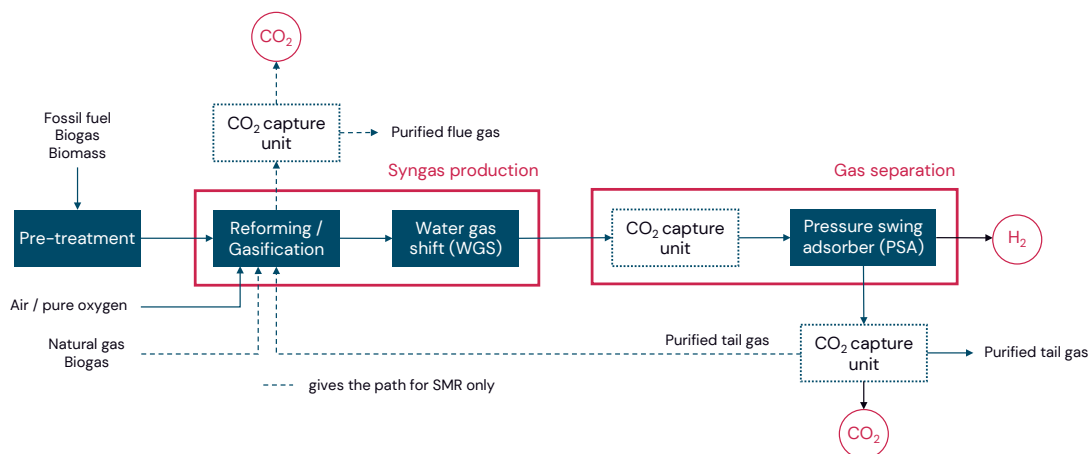


Figure 3 : Simplified flow diagram of fossil fuel with CCS H₂ production process⁹

Carbon capture rates

Usually, **carbon capture rates** as high as 90% can be achieved for CG, PO and ATR with one unit positioned either after the WGS or after the PSA. Other studies even mention a **maximum of 99.9%**¹⁰ and some ATR projects have reported 95% capture rates¹⁷.

The current practice for SMR is also to install the unit after the WGS or the PSA as the stream has a **high concentration of CO₂**, making it easier and cheaper to capture. By doing so, 56% of the total CO₂ of the whole process can be captured. The option that has the **biggest potential** for carbon capture is after the reformer, where 90% capture rates can usually be achieved.

However, as the stream is **less concentrated** and contains more pollutants and impurities, this option is the most expensive, potentially doubling the cost of the other two options, which is significant because CCUS already represents a significant portion of the cost of low-carbon H₂ production^{10 18}.

Energy and carbon footprint

Another important aspect of implementing CCUS is its energy consumption. From a whole plant perspective, the **energy efficiency** of a SMR plant with CO₂ capture **drops by 14%** compared with a reference SMR plant without CO₂ capture¹⁹. Depending on the carbon intensity of the electricity used, the emission reduction offered by CCUS facilities could be lower than expected.

It is crucial to evaluate the carbon footprint of the **whole value chain** and not only **process emissions**. For example, fugitive emissions associated with natural gas extraction, transport, storage and distribution cannot be mitigated by CCUS technology.

The emissions of the SMR process itself is 74 kg CO₂e/GJ or **~9 kg CO₂e/kg H₂** and range between **9.6 and 12.1 kg CO₂e/kg H₂** for the whole value chain depending on the level of fugitive emissions¹¹. The warming effect from these emissions is even higher when considering a **20 years period**, as CH₄ is a potent greenhouse gas whose half-life in the atmosphere is about 9 years (while that of CO₂ is 100 years). Fugitive emissions are also higher, thus reducing the impact of CCUS on the process total emissions.

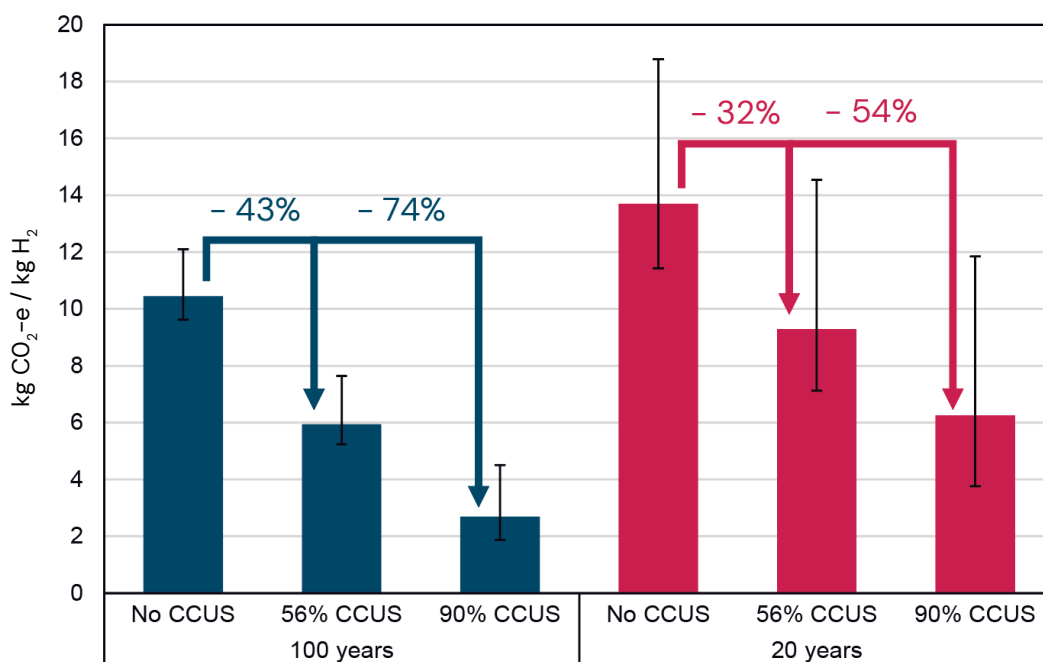


Figure 4 : Well-to-gate emissions of SMR using different fugitive emissions levels (kg CO₂e/kg H₂)

Three levels of fugitive emissions are shown with the brackets, based on the paper of Longden et al. (2021)¹¹. The global warming effect of the emissions was studied on a 100 years and a 20 years period. The lower bound was calculated using the IPCC low value of 0.9%, the middle value used the IPCC default level of 1.70% and the upper bound used the 3.50% conservative value found in Howarth & Jacobson (2021) paper^{20,21}.

CCUS is also effective for production based on coal gasification, but the emissions are still high compared to SMR with CCUS or other low-carbon production methods, respectively 7.8 and 5.2 kg CO₂e/kg H₂ for black and brown coal gasification with 90% capture rates and IPCC default fugitive emissions levels¹¹.

Thermochemical Water Splitting (TCWS)

Thermochemical water splitting is a process that relies on **high temperature heat** to drive **chemical reaction cycles** which as an output produce H_2 and oxygen. The minimum temperature to generate H_2 from water is 1700°C for partial dissociation and 4000°C for total dissociation, which is hard to reach for most heat sources, hence the use of cycles to reduce the temperature needed for the reaction²². Between 2000 and 3000 **thermochemical cycles** have been studied in the literature, of which only about 10% are available for large-scale H_2 production.

The most promising thermochemical cycle is the **sulphur-iodine cycle** because of its prospects for high efficiency. It consists of three chemical reactions that results in the dissociation of water. First, sulphur oxide and iodine combine with water at temperatures of $20\text{--}100^\circ\text{C}$ during an exothermic reaction called Bunsen reaction, forming two separated acids: sulfuric acid and hydriodic acid. Sulfuric acid is then fed into a Gibbs reactor where it is decomposed under temperatures of $600\text{--}900^\circ\text{C}$ with a catalyst forming oxygen and sulphur oxide. This reaction is endothermic, so heat must be provided by another source (e.g. concentrated solar or nuclear heat). At the same time, the hydriodic acid goes into the equilibrium reactor where it is decomposed under temperatures of $300\text{--}450^\circ\text{C}$ (endothermic) forming H_2 and iodine. The sulphur oxide from the Gibbs reactor and the iodine from the equilibrium reactor are then fed into the Bunsen reactor to close the loop. The net reactant is water and the net products of this cycle are oxygen and H_2 ¹³.

The **copper-chlorine cycle** is also very promising, as it operates at lower temperatures than the sulphur-iodine cycle, allowing it to be integrated with a wider range of heat sources.

A simplified flow diagram of a sulphur-iodine thermochemical cycle is given below:

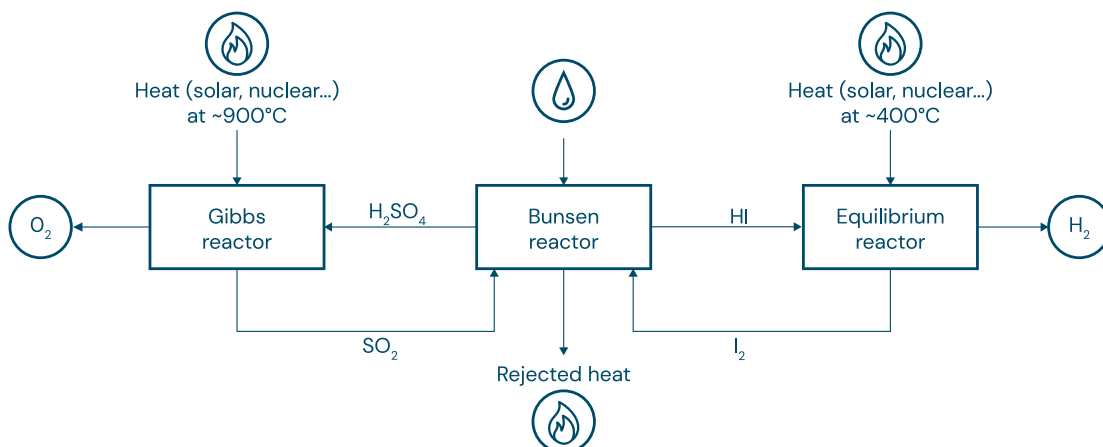


Figure 5 : Simplified flow diagram of a Sulphur-iodine thermochemical cycle for H_2 production¹³

High efficiencies of 20–45% for thermochemical water splitting have been reached under lab conditions and the advantage of this thermochemical technology is that it doesn't produce any carbon dioxide²².

Thermochemical Routes: maturity and projects

Route	TRL	Insights
SMR	11	Currently dominates H ₂ production (62% of global and 96% of European production) ^{5,23} .
SMR + CCUS	5-9	High capture rates (>90%) are less mature than moderate ones (~56%). Some projects ongoing in Europe.
CG	11	Currently 19% of the world's H ₂ production ⁵ . Only a few operational CG plants in Europe, none is fitted with a CCUS unit.
CG + CCUS	5-9	High capture rates (>90%) are less mature than moderate ones (~56%).
BG	8	
BG + CCUS	5-7	High capture rates are less mature than moderate ones (~56%). ¹²
PO & ATR	9	Mature, yet currently a very limited share of H ₂ production.
PO & ATR + CCUS	5	Because of their design, only high capture rates are foreseen. Some projects with 95% capture rates have been announced in the EU.
TCWS	6	Large prototypes are being built (50 kW demonstrator for kerosene production using CO ₂ and water currently under construction) ²⁴ .

Announced projects	Technology	Description
FerroSilva (Sweden)	BG + CCUS	Aims at showing the feasibility of producing fossil-free sponge iron for green steelmaking out of H ₂ produced from biomass ²⁵ .
H ₂ morrow (Germany)	SMR + CCUS	Launched by Equinor and OGE. Aims at decarbonizing current SMR H ₂ production for the industry and other end-users in North Rine-Westphalia ²⁶ . Plans to produce 8.6 TWh/year by 2030, capturing about 1.9 MtCO ₂ /year (capture rates 95%), and storing it in saline aquifers in the North Sea.
H ₂ BE (Belgium)	ATR + CCUS	Announced by ENGIE and Equinor in February 2021. Aims to produce low-carbon H ₂ at gigawatt scale before 2030. Capture rates: 95% ²⁷ .
H-Vision (Rotterdam)	ATR + CCUS	Plans to produce 300 ktH ₂ /year and capture 2.7 MtCO ₂ /year before 2030 using residual gases from the industry and a small amount of natural gas ²⁸ .



ELECTROLYTIC ROUTE

Water electrolysis for hydrogen (H_2) production was discovered as early as 1789 by van Troostwijk and Deiman and electrolyzers began producing H_2 for the industry by the end of the 19th century^{29,30}. The principle is very simple: **a direct electric current decomposes water into H_2 (forming at the anode) and oxygen (at the cathode)**.

There are currently four main electrolyser technologies based on the type of electrolyte used (charge carriers): **Alkaline (ALK)**, **Proton Exchange Membrane (PEM)**, **Solid Oxide (SOEC)** and **Anion Exchange Membrane (AEM)**.

Alkaline Electrolysis (ALK)

In ALK, two electrodes are immersed in a **concentrated alkaline solution**, typically KOH or NaOH. Negatively charged hydroxide ions (OH^-) act as charge carriers and cross an **anion-selective porous diaphragm**, transfer from the cathode to the anode in solution, and then generate water with the H_2 ions produced at the anode. Oxygen is thus produced at the cathode and H_2 at the anode, allowing for easy separation of the gasses. The porous diaphragm assumes a very important role, separating the H_2 and oxygen produced. It must be durable and highly wettable in alkaline electrolytes, otherwise gas bubbles would be produced and increase resistance, affecting the purity of gas products. ALK efficiency is usually 58% to 65%²⁹.

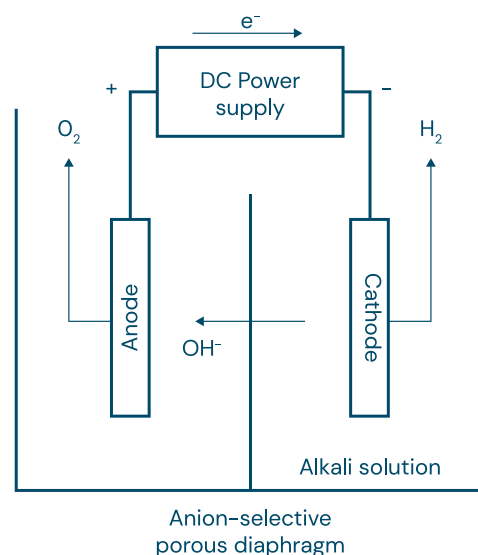


Figure 6 : Simplified representation of an ALK electrolyser

Thanks to continuous improvements, it is currently the **cheapest option** (CAPEX 800 - 1500 USD/kW) and offers the **longest lifetime** (~100,000h)²⁹. However, it generally has a **low operating pressure** (<10 bars)¹³ which necessitates an additional compression step for transport and/or storage. Compressing H_2 from 1 to 30 bar results in a 3.5%-4% increase of the energy consumption of H_2 production based on H_2 LHV^C. Increasing the operating pressure to 30 bar is also technically possible and would raise its price by ~\$USD 50/kW³¹, which is quite low compared to the total price of the electrolyser.

^C Lower Heating Value (LHV): The LHV of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25 °C or another reference state) and returning the temperature of the combustion products to 150 °C. The LHV assumes that the latent heat of vaporization of water in the fuel and the reaction products is not recovered. By contrast, the higher heating value (HHV) includes the heat of condensation of water in the combustion products³⁴

Proton Exchange Membrane Electrolysis (PEM)

The chemical reaction is the same as ALK but the technology differs in the electrolyte. PEM efficiency is usually 59 to 68%²⁹. It uses a **solid acidic electrolyte membrane** where the charge carriers are H_2 ions (protons) instead of hydroxide ions (anions). The **advantages of PEM** are its higher flexibility, higher operating pressure (lower need for compression), smaller footprint (relevant for coupling with offshore wind), higher current densities, faster response and lower degradation rate with load changes, making it particularly suitable for renewable energy integration (see Table 2).

However, PEM uses noble metal catalysts like palladium and iridium (which increases the total cost of the system), has a **shorter lifetime** than ALK (50,000 – 90,000 h) because of the harsh oxidative environment, high voltages, and oxygen evolution at the anode³⁵. State-of-the-art PEM electrolyser **efficiencies** are currently lower than ALK electrolyser but there is great potential for improvement and cost reduction, as small improvements around the cell design or in reducing the membrane thickness would greatly increase the current density³³.

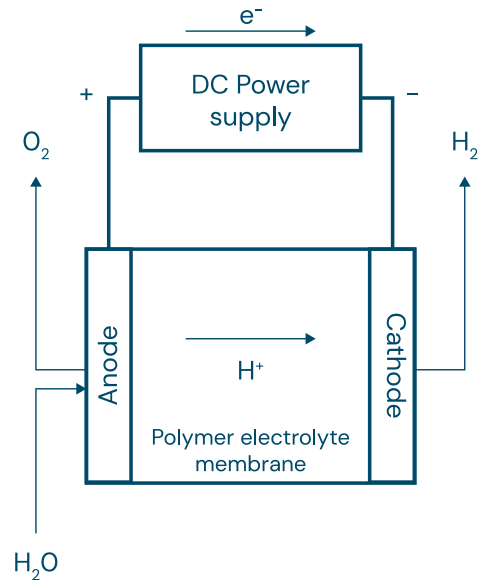


Figure 7: Simplified representation of a PEM electrolyser

Anion Exchange Membrane Electrolysis (AEM)

AEM uses a **low concentration alkaline membrane**, where OH^- ions serve as charge carriers, which allows to avoid the high concentration corrosive electrolytes used in ALK (see Table 2). Also, contrary to PEM electrolyser, AEM does not use noble metal catalysts but rather **cheap and abundant transition metals**, reducing the cost. It shares the high flexibility, compact cell design, high operating pressure and a leakage-free design with PEM and the low cost and high durability with ALK.

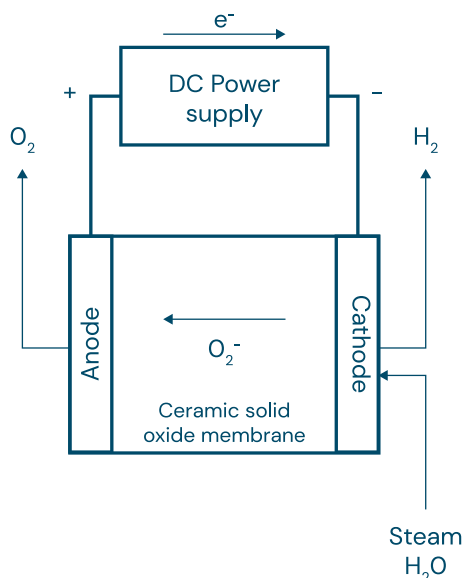


Figure 9: Simplified representation of an AEM electrolyser

But it also suffers from membrane degradation, low current densities compared to PEM ($200-1000 \text{ mA/cm}^2$) and excessive catalyst loading (amount of catalyst per unit amount of reactant). The IRENA reported LHV efficiencies of 48%–58% for AEM in 2020³³. Hence, some improvements around the efficiency, membrane design and catalyst stability, ease of handling as well as reduction of cell cost are still required for AEM to become a **competitive technology in the future**³⁶.

Solid Oxide Electrolysis (SOEC)

SOEC is quite different in its design because it doesn't use a liquid electrolyte. Instead, it uses **high temperature steam water** (650–1000°C) as an electrolyte and a **ceramic solid oxide membrane** to make the bridge between the cathode and the anode.

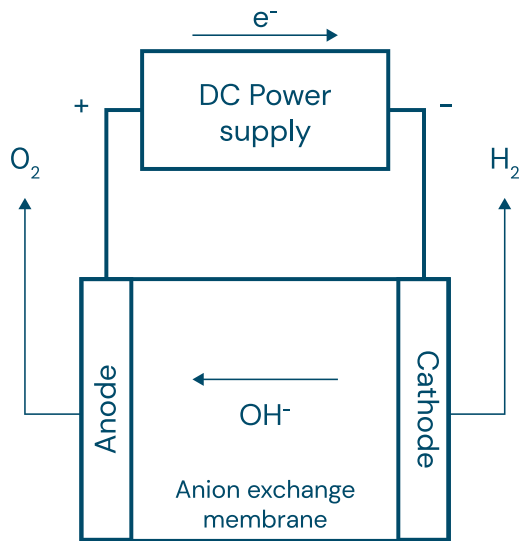


Figure 8 : Simplified representation of a SOEC electrolyser

O₂⁻ ions and H₂ are formed at the cathode and transported towards the anode to complete the electrolysis process. Using high temperature steam, generated by **industrial waste heat** for example, greatly decreases the **power consumption** needed for the reaction. SOEC is thus the **most efficient** electrolysis process, with an efficiency of 68% to 77%²⁹ and may produce the **cheapest H₂** in the future. However, SOEC is **less flexible and stable** than PEM and has a **shorter lifetime** because of the high working temperatures.



MultiPHLY project in Rotterdam, Netherlands. Multi megawatt SOEC electrolyser for the production of green hydrogen – Courtesy of Sunfire.

ELECTROLYTIC ROUTE: MATURITY AND PROJECTS

ALK & PEM

TRL
9

ALK electrolysis is the **oldest** and **most mature** production technology²⁹ (TRL 9³²) and also the **most used** today (59% of market shares in 2021³⁷). PEM electrolysis is also a mature technology (TRL 9³²) which was developed during the 60's³³ to replace ALK. It has for the moment a **lower market share** (27% of market shares in 2021³⁷) although it is expected to grow very fast in the **next decade**. **NEL** (Norway) is the leading ALK and PEM electrolyser manufacturer, with more than 3,500 units installed around the globe (2023)³⁸. **Thyssenkrupp** (Germany), is also one of the biggest suppliers of electrolysers, with over 10 GW of installed power in 2019³⁹.

Concerning the biggest operating electrolysers in Europe, the 20 MW alkaline electrolyser of the **HySynergy** project in Denmark began producing H₂ in December 2022 and Iberdrola also started up its 20 MW PEM electrolyser in Spain in May 2022³². **Gigawatt scale projects** have also been announced for the mid-2020s like the **Green Marlin** project in Bantry Bay, southwest Ireland, planned for 2026 with its 3.2GW electrolyser powered by a 4GW offshore wind farm, or the 1GW electrolyser project planned for 2024 in Esbjerg, Denmark^{40 41}.

SOEC

TRL
7

Contrary to the first two electrolyser technologies, SOEC (solid oxide electrolyser cell) has not yet reached commercial scale (TRL 7³²). A company in France, **Genvia**, is developing **high-performance SOEC** systems to decarbonize the industrial processes in the cement, steel and chemical sectors⁴². The company is part of the European Hy2Tech IPCEI supported by France 2030 that grants public funding for innovative projects around low-carbon H₂^{43 44}. Genvia plans to deliver its first commercial units in 2027. **Elcogen**, in Estonia, is a manufacturer of SOEC that has also developed a **reversible cell** that can be used as a fuel cell or an electrolyser depending on the needs. It received €24 Million of investment from HydrogenOne in mid-2022 to scale-up their production line and to continue the development of its technology⁴⁵.

AEM

TRL
6

The AEM concept was only introduced at the beginning of the 21st century¹³, and this technology is still at the lab stage (TRL 6). In Europe, the German company **Enapter** is developing solutions based on the AEM technology, betting on the **modular aspect** of electrolysers to progressively scale-up the size of the H₂ production plants by stacking modules⁴⁶. In July 2022, Enapter raised \$USD 53 million to support the construction of its electrolyser factory, with the goal to produce **10,000 AEM electrolysers per month**⁴⁷. In France, **Gen-hy** is working on a new high efficiency H₂ production system that also uses AEM technology, reaching **record efficiencies** comparable to those of SOEC electrolysers (72% LHV efficiency)⁴⁸. It will also be the first company to fully control the **value chain** of their electrolysers⁴⁹. Gen-hy announced in May 2022 it invested 15 M€ for a new factory with 3 production lines that will come in operation mid-2023.

ELECTROLYTIC ROUTE: GENERAL CONSIDERATIONS

9-24
kgH₂O/kgH₂

Water requirements

From a pure stoichiometric perspective, producing 1 kg of H₂ requires **9 kg of water**. Some electrolyser technologies like PEM require high purity demineralised water and along with the system inefficiencies, the water consumption can reach between **18 kg and 24 kg** of water per kg of H₂⁵⁰. Using electrolysis to produce the 94 Mt of H₂ produced in 2021 would consume between **1.7 and 2.26 billion cubic meters** of water. For comparison, this represents less than 0.06% of the **global freshwater use** (2014 figures)⁵¹. Hence the water consumption may be a **local issue**, depending on where electrolysers are installed, but is not a **resource problem**. In regions where freshwater is scarce, using seawater could provide an interesting alternative, as it represents 96.5% of the Earth water resources⁵².

This normally require desalinating it first but some new technologies allow for directly feeding it to the electrolyser. The former is not a technical challenge as many **desalination plants** are already operating around the world and would only induce a marginal increase of the overall energy consumption (+0.06-0.13%) and of the cost of H₂ produced (+\$0.01/kg H₂)⁵³. The latter is much less attractive as it less developed (TRL 3) and show multiple issues such as catalyst degradation, low current densities, lower efficiency⁵⁴... Hence desalination is by far the preferred option where freshwater is scarce.

Shares of H₂ production

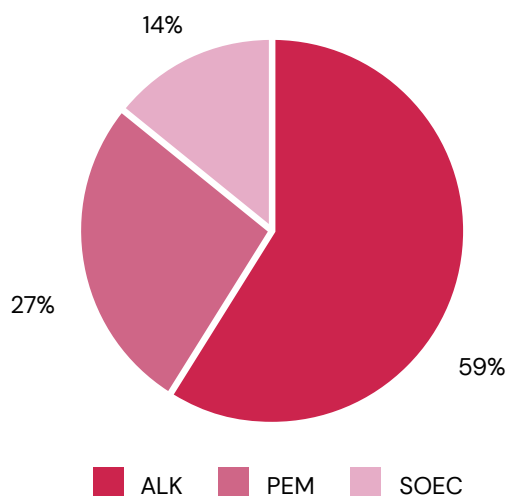


Figure 10 : Electrolyser technologies market shares in 2021⁵⁷.

Further R&D efforts on those technologies may induce significant evolutions in terms of their relative importance in the global electrolysers industry in the upcoming years.

Key characteristics

	ALK	PEM	AEM	SOEC
TRL ³²	9	9	6	7
Temperature ^{13 55}	60–90°C	50–90°C	50–70°C	500–1000°C
Pressure ^{13 55}	2–10 bar	15–30 bar	30 bar	< 30 bar
Charge carriers ^{13 55}	OH-	H+	OH-	O ²⁻
Most common electrolyte/membrane ²⁹	20–40% aqueous KOH or Na-	Proton conductive polymer membrane	Anion exchange ionomer (e.g. AS-4) + optional dilute caustic solution	Ceramic: solid, nonporous metal oxide (Y ₂ O ₃ -stabilized ZrO ₂)
Most common electrode materials ¹³	Ni and Ni alloys	Ni and Ni alloys	Transition metal-based materials	Cermet and doped metal composites
Most common catalyst ²⁹	Pt and Ru	Pt black, Ir, Ru, Rh	Pt and Ru	ZrO ₂
Current density ^{13 55}	0.2–0.5 A/cm ²	0.8–2.5 A/cm ²	0.2–0.5 A/cm ²	0.3–1 A/cm ²
Load range ^{13 56 50}	15–100% nominal load	0–160% nominal load	5–100% nominal load	20–100% nominal load
Start-up (cold) ^{13 50}	10 minutes	5 minutes	< 20 minutes	> 600 minutes
Energy consumption ²⁹	50–78 kWh/kg H ₂	50–83 kWh/kg H ₂	57–69 kWh/kg H ₂	45–55 kWh/kg H ₂
Stack lifetime ²⁹	60,000–100,000 h	50,000–90,000 h	~30,000 h	20,000–90,000 h
CAPEX ²⁹	\$800–1,500/kW	\$1,400–2,100/kW	Unknown	> \$2,000/kW
Project scale ³²	Hundreds of MW	Tens of MW	kW	Hundreds of kW to MW
Advantages	<ul style="list-style-type: none"> • Cheapest option today • No rare materials • Long lifetime • High maturity • Tolerance to impurities 	<ul style="list-style-type: none"> • High flexibility (adapted to renewable energy) • High current density • Quick response time • Compact cell design • Low minimal load 	<ul style="list-style-type: none"> • No rare materials • Non-corrosive electrolyte • Compact cell design • No leaking • High operating pressure 	<ul style="list-style-type: none"> • Low power consumption needs (fatal heat) • High energy efficiency • Feasible reversible operation • Low expected cost • Combination with other technologies • Low minimal load
Disadvantages	<ul style="list-style-type: none"> • Low current density • Corrosive electrolyte • Mixing of gases • High minimal load • Electrolyte leakage 	<ul style="list-style-type: none"> • Rare materials (more expensive) • High membrane cost • Acidic corrosive components • CO poisoning 	<ul style="list-style-type: none"> • Low technological maturity • Low current densities • Medium durability • Membrane degradation • Excessive catalyst loading • High minimal load 	<ul style="list-style-type: none"> • Short lifetime (ceramic membrane) • Severe environment (high temperatures) • Unstable electrodes • Sealing issues

Table 2: Summary of electrolyser technologies characteristics



PYROLYTIC ROUTE

Pyrolysis is the process of chemical decomposition of an organic compound that happens when elevating its temperature higher than 200°C in the absence of oxygen, which as a result produces other gasses and compounds depending on the reaction conditions.

Producing hydrogen (H_2) through the pyrolytic route relies on the pyrolysis of methane or biomass, also referred to as **methane/biomass decomposition**, producing gaseous H_2 and **solid elemental carbon**. This reaction is **highly endothermic**, thus requiring external heat supply.

As for SMR, methane is supplied in the form of natural gas or biogas but pyrolysis requires **2 times more natural gas than SMR** to produce 1 kg of H_2 , due to the molar ratio of H_2 to CH_4 being 2:1 instead of 4:1 for SMR. Indeed, in SMR, the steam provides another source of H_2 atoms contrary to methane pyrolysis (MP). The yield is even lower with biomass due to its low H_2 to carbon ratio compared to methane (0.04 kg H_2 /kg-biomass as opposed to 0.3 kg H_2 /kg CH_4)³². However, the upside is that pyrolysis **does not produce CO_2** but only solid carbon that can be used for diverse applications depending on its structure. Consequently, utilizing the carbon by-product will be crucial for economic feasibility as well as environmental performance of the process.



Monolith's Olive Creek 1 (OC1) commercial-scale facility - Courtesy of Monolith Corp

Some companies like **Monolith** even built their business model on the production of **carbon black**, a very pure and valuable form of carbon used for diverse applications such as rubber reinforcement, paints & coatings, plastics, battery electrodes, inks & toners and soil enhancers⁵⁷. The carbon black market was estimated at \$18.6Bn in 2020 and is expected to continue to grow because of its increasing use in tires⁵⁸. But considering the expected consumption of H_2 in the future, one should also be careful not to saturate the carbon black market. The worldwide annual carbon black consumption in 2025 is forecasted to grow beyond 15 Mt/a. In comparison, meeting the current annual demand of pure H_2 of around 70 Mt⁵⁶ by methane pyrolysis would lead to approximately 210 Mt/a of carbon by-product and, thus, exceed the estimated market demand for carbon black by a factor of 14⁵⁹. This should not happen as some technologies are currently being developed with the goal of producing **other carbon compounds** like graphene, which have many other applications and whose demand is expected to grow particularly because of its increasing use in batteries⁶¹.

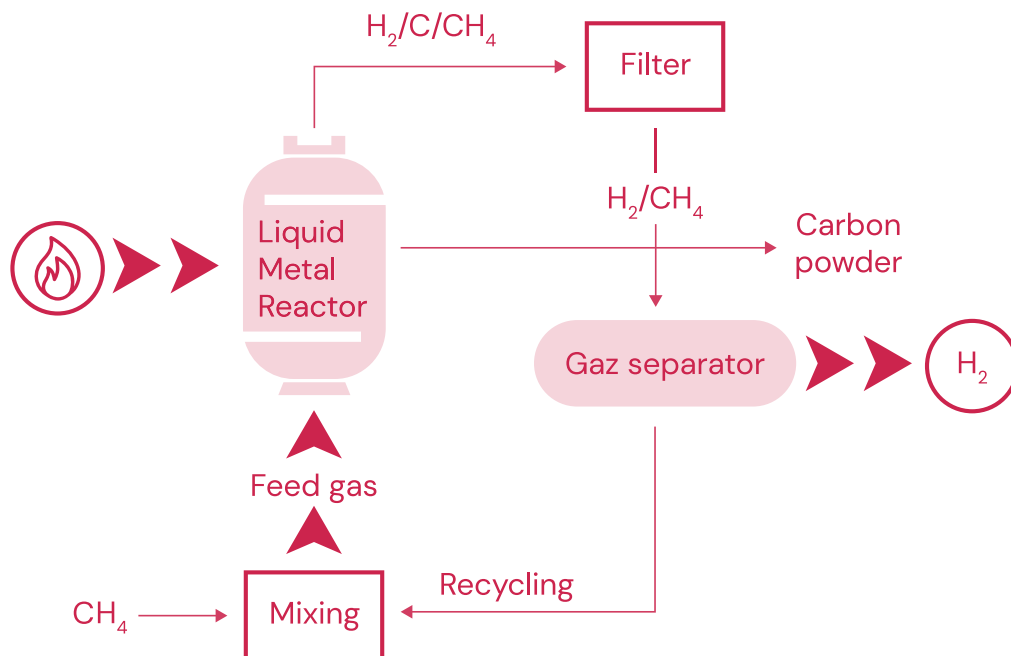


Figure 11: Simplified methane pyrolysis with liquid metal reactor diagram

The other upside of methane pyrolysis compared to SMR is that it is **thermodynamically less energy intensive**: 37.8 kJ/mol H_2 compared to 63 kJ/mol H_2 respectively. Compared to water splitting, it is even **8 times less energy intensive**, although the feedstock is different.

There are 3 main methane pyrolysis technologies at different development stages. They differ from each other by the way methane is decomposed in the reactor and how the energy needed for the decomposition is provided³².

Thermal & Catalytic Decomposition

In **thermal pyrolysis**, methane breaks down into H_2 and carbon in reactors that reach temperatures of **1,000–1,500°C**. Catalytic decomposition is often preferred because it reduces the operating temperature and thus the energy required for the process.

In **catalytic pyrolysis**, methane breaks down into H_2 and carbon over a metal catalyst, which is typically **nickel- or iron-based**, at temperatures typically **under 1,000°C**⁶², making it more suitable for coupling with renewable energy systems like concentrated solar.

Biomass pyrolysis is usually performed at temperatures between **200–600°C** in presence of a catalyst. The energy efficiency of this process is usually 56%–64%¹². Contrary to methane pyrolysis, biomass pyrolysis does not produce pure solid carbon but rather **solid biochar**, **liquid bio-oil** and other non-condensable gas products along H_2 . The type of biomass as well as operational conditions (heating rate, solid residence time) have a great influence on the quantity and the type of products. A **fast pyrolysis** (high temperature, short residence time) targets **liquid fuel** as the output, whereas **slow pyrolysis** (low temperature, long residence time) targets **solid biochar**. Biomass pyrolysis, however, faces several issues such as tar formation (10–35%), high corrosiveness, low heat stability and low H_2 concentration in the gaseous products¹².

Plasma Decomposition

In thermal-plasma pyrolysis processes, the energy demand of the pyrolysis is supplied by electricity. The electric energy ignites the plasma (an ionised gas), which reaches temperatures in the range of **1,000– 2,000°C** and splits CH_4 into its elements. Two types of plasma are applied for methane decomposition⁶³:

- 1) In a **thermal plasma** or a **“hot” plasma** the temperature is homogeneously distributed. The chemical decomposition process of methane is observed within a high-temperature environment allowing it to reach chemical equilibrium.
- 2) In a **non-thermal** or **“cold” plasma**, the electrons show a much higher temperature than the heavier species such as neutrals and electrons. The electrons can have temperatures of several 10,000°K whereas the gas is much colder (e.g. room temperature).

Based on these two plasma types, plasma applications for methane decomposition are classified into **cold (less than 1,000 K)** and **hot (>1,000 K)** processes. Cold plasma processes typically show lower conversion efficiencies compared to hot plasma processes. However, cold plasma processes show a higher selectivity. Possible by-products of the methane decomposition reaction include **ethyne**, **benzene**, and **ethane**. Most plasma systems operate without a catalyst.

PYROLYTIC ROUTE: MATURITY AND PROJECTS

Thermal decomposition

TRL
3-4

Molten Industries, a startup based in Oakland CA, plans to produce H₂ by heating up methane using renewable electricity and resistive heating⁶³. It is currently developing a new type of reactor that **fluidizes** the carbon produced so that it does not clog during operation one of the major issues with methane decomposition.

Catalytic decomposition

TRL
6

Startups like **C-Zero** in Santa Barbara (CA) and **Hycamite** in Finland are developing H₂ production processes based on methane catalytic decomposition^{65 66}. **C-Zero** recently raised \$USD 34 million to build a **first pilot plant** capable of producing 400 kg of H₂ per day, expecting to come online as soon as Q1 2023⁶⁷. **Hycamite** also secured a \$USD 3 million investment round to build an industrial pilot plant next to their **small test facility** in Kokkola Industrial Park (KIP), although the operation date has not been disclosed⁶⁸.

Biomass pyrolysis

TRL
6

SoCalGas and **Kore Infrastructure** have been testing and demonstrating their carbon-negative, **waste-to-energy** modular system based on biomass waste pyrolysis technology in Los Angeles (CA) since July 2022⁶⁹. The facility can process 24 t/day of organic feedstock and produce up to 1 t H₂/day dedicated to fuel cell electric vehicles.

Plasma decomposition

TRL
3-8

Plasma decomposition is the only methane pyrolysis technology that has reached **commercial scale** (TRL 8), others still being at the stage of development with some demonstration plants on the way.

Monolith produces 600 kg/hr of H₂ using its plasma decomposition technology at their Olive Creek 1 facility since 2020 and has recently received a conditional approval from the US Department of Energy for a \$USD 1 billion guaranteed loan to expand the plant which will make Olive Creek the **US's largest carbon black production facility** with a production capacity of around 194,000 tonnes/year⁷⁰. Although Monolith's economic model is for the moment only based on carbon black, it shows that producing H₂ at a **commercial scale** is already possible.

Other plasma decomposition technologies are **less mature**. In Europe, many startups are working on this technology, such as **Sakowin** (microwave plasma technology, TRL 3), **Spark Cleantech** (cold nanopulsed plasma, TRL 4), **Hiiroc** (hot plasma, TRL 7) or **Levidian** (microwave plasma, TRL 8), although they have not reached commercial scale production yet^{71 72 60}. They also focus on the **technology as a product** rather than H₂ or carbon as a product like Monolith does.



PHOTOLYTIC ROUTE

Photolytic production of hydrogen (H_2), sometimes called 'artificial photosynthesis', consists in directly using photons from sunlight to trigger a water splitting reaction.

There are two main photolytic processes: **particulate photocatalysis (PC)** and **photo-electrochemical catalysis (PEC)**⁷³. Both use **photocatalysts**, a substance that absorbs photons and generates excited states, which then cause photophysical and photochemical processes as they return to their original ground states⁷⁴. They are most often coupled with **electrocatalysts** that induce the redox reactions. In essence, the same steps occur for both methods, but for PC all processes take place in single particles in an electrolytic solution, while the different components are separated for PEC. Photolytic methods generate no CO_2 and could hence play a role in the long term as a low-carbon H_2 source, but only if their efficiency and the durability of the catalytic materials improves rapidly.

Photo-Electrochemical Catalysis (PEC)

Photo-electrochemical cells could be considered as the combination of an **electrolyser** and a **PV module** in a single device, thus having the potential to reduce capital costs and energy losses (direct photo-chemical conversion). In PEC systems, semiconductors are immersed in a **water-based electrolyte**, where sunlight drives the process of splitting H_2O into H_2 and O_2 – oxidation occurs at the photoanode and reduction at the photocathode, similar to alkaline electrolysis.

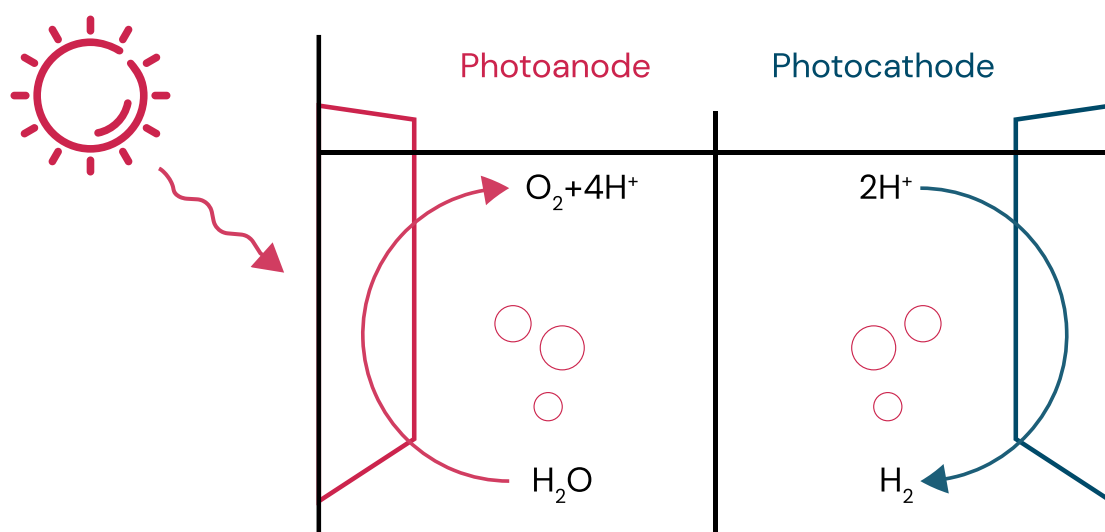


Figure 12 : Simplified representation of a PEC unit⁷⁶

Current PEC efficiencies range between 14 and 40% but systems quickly increase in complexity along with increased efficiency, where current electrolyzers are already twice as efficient from 58% to 77% (if the efficiency of electricity production is not taken into account)^{75,29}. However, it has the advantage of operating at **near ambient temperatures**, between 25 and 65°C, and does not need any noble metal catalysts. The real challenge with these systems lies in the scale up part, as bigger modules can have **more spatial defects**, require different fabrication methods and also **increase total ohmic resistance** thus greatly reducing the overall efficiency.

Particulate Photocatalysis (PC)

In this process, the photocatalyst is in the form of a **powder dispersed in an aqueous solution**. These particles are composed of a photocatalyst, an oxidation electrocatalyst, and a reduction electrocatalyst. The charge carriers thus have a shorter pathway compared to PEC or electrolysis, reducing the **power losses** of the process. As photocatalysts produce H₂ and O₂ at the same place, a **gas separator** is needed.

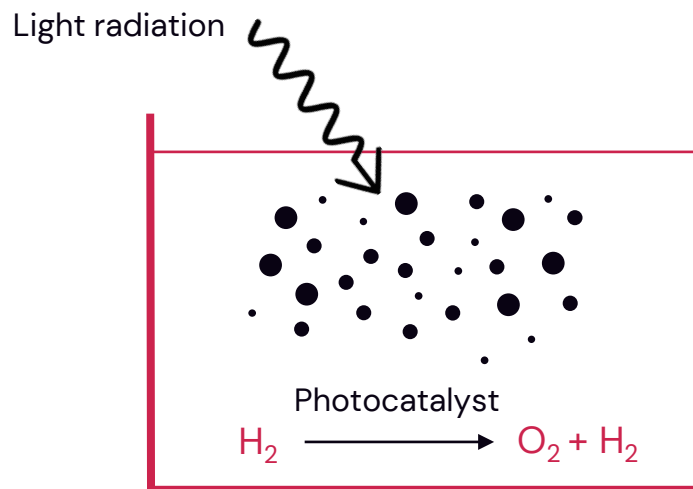
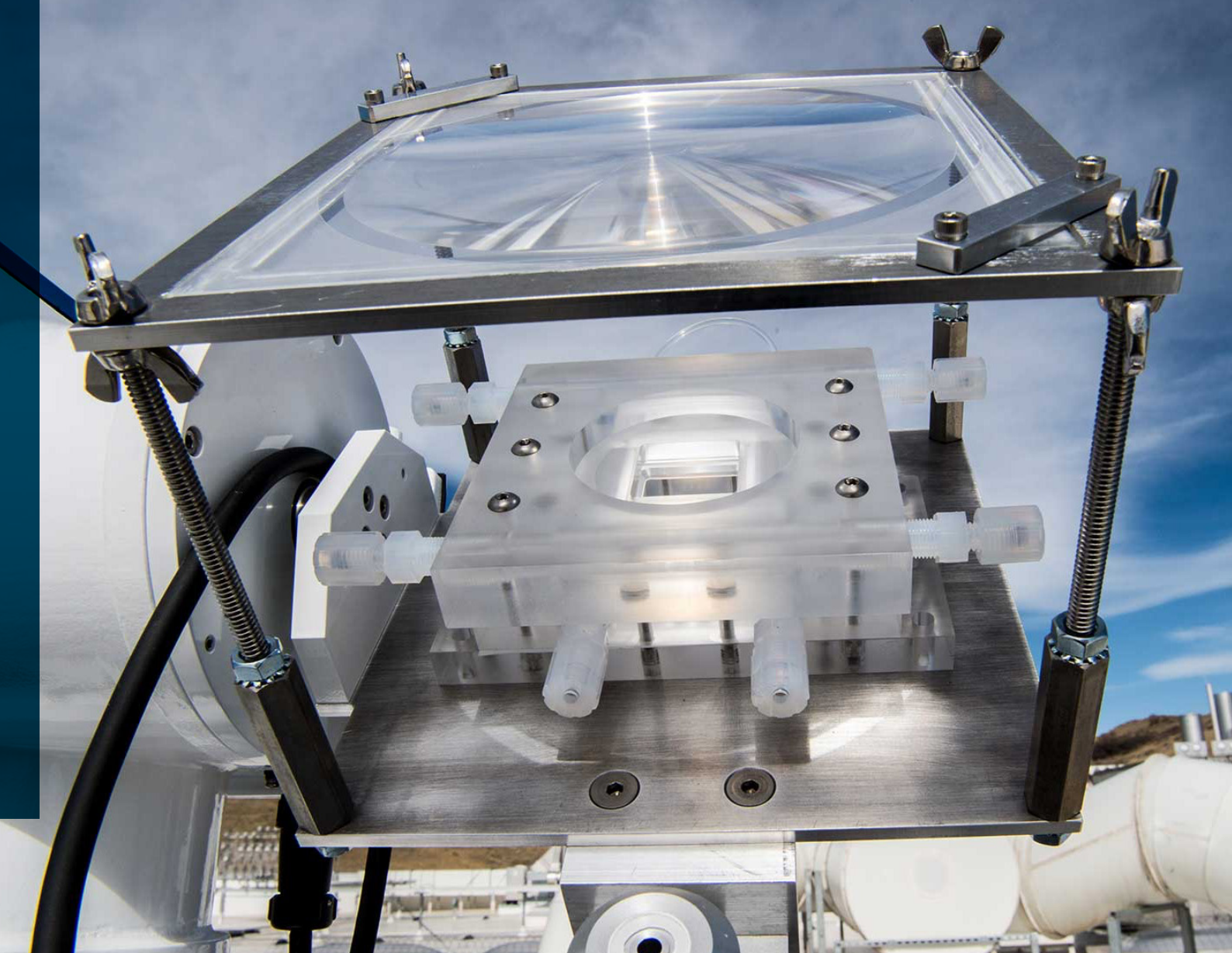


Figure 13 : Simplified representation of a PC unit⁷⁶

Although PC is the simplest solar to H₂ process, main challenges need to be overcome. It proves very difficult to find **light absorbers** with a proper band gap, band edge potentials, and to maintain their stability in the aqueous medium. In addition, it is difficult to control the **charge carriers** since there is no applied bias. Hence, the **solar to H₂ efficiency** of these kind of systems has only reached maximum values of around ~5% under lab conditions⁷⁶.



Solar water splitting device from HydroGEN Advanced Water Splitting Materials consortium - Courtesy of NREL

Photolytic routes: maturity and projects

TRL
5-6

Solar fuel production was rated at a low TRL of 1–3 in 2018⁸, but this field is evolving **very rapidly** as the technology was reported to be at TRL 5 in 2021 as multiple prototypes have been built since then⁷⁷. Recently, a PEC pilot plant was built by **Sunrgyze** in 2021⁷⁸, a company owned by Repsol and Enagas, and has been operating for more than 4,000 hours in real conditions reaching **>20% solar-to-H₂ (STH) efficiency**⁷⁹. This technology can hence now be considered at TRL 6. Sunrgyze is also planning to build a first pre-demonstration plant funded by the European Innovation fund which will be operational in 2025, with the goal to produce 100 kg of H₂ per day (efficiency >13%).



Biological hydrogen (H_2) production uses microorganisms that contain enzymes able to synthesize H_2 through biochemical reactions.

Such technologies can perform at or close to room temperature and atmospheric pressure. There are two types of biohydrogen production processes: sunlight-driven ones relying on **photosynthesis**, and pathways using **fermentation** of organic substrates. **Hybrid processes** also exist, combining the advantages of each category¹³. Involved microorganisms differ depending on the type of process: sunlight-driven methods use microalgae, cyanobacteria or photosynthetic bacteria, whereas fermentation-based ones use fermentative bacteria.

Biophotolytic Processes

In biophotolysis, **microorganisms** use light radiation to decompose water and produce H_2 and oxygen. It generates no CO_2 and consumes only water to produce H_2 .

Direct biophotolysis relies on photosynthesis: microorganisms containing chlorophyll (green algae, cyanobacteria) are placed under sufficient light intensity, producing oxygen with a **tenfold solar conversion efficiency** compared to plants. Under sunlight energy, **enzymes** (hydrogenases) convert surplus electrons and protons (H_2 ions) from water into gaseous H_2 . Although this enzyme can theoretically convert sunlight to H_2 with 12–14% efficiency⁸⁰, laboratory experiences based on green microalgae have not exceeded values of 3–4%⁸¹. Direct biophotolysis could become cost-effective once it reaches 5% conversion efficiency in microalgae.

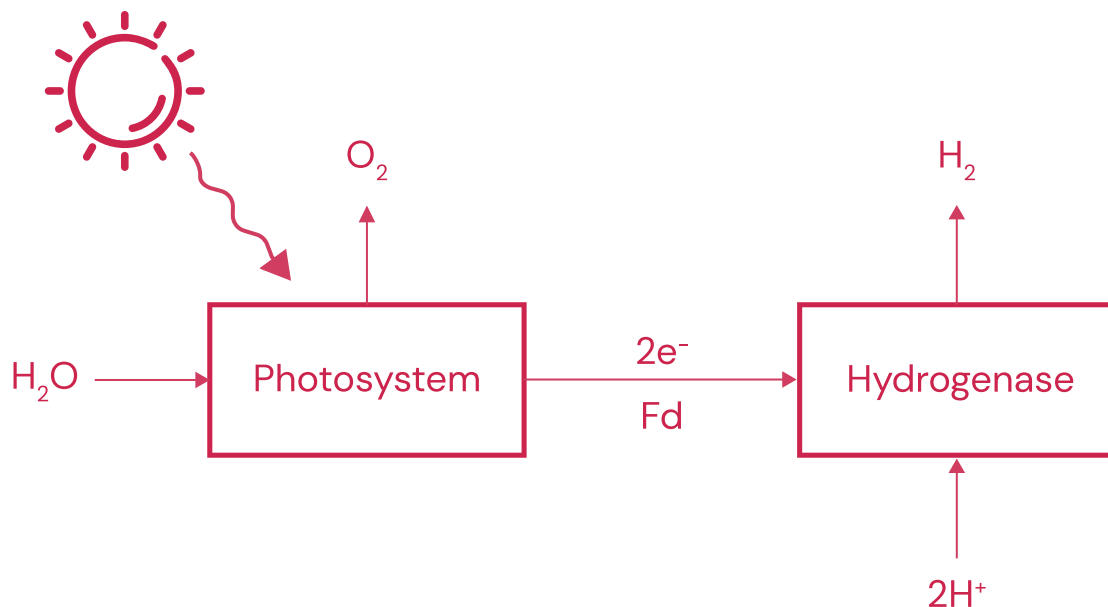


Figure 14 : Simplified direct biophotolysis process⁸²

Indirect biophotolysis is a **two-step process** where CO_2 is first fixed as carbohydrates by **cyanobacteria** using sunlight, which are then broken down by the **hydrogenase enzyme** to produce H_2 . The advantage of indirect biophotolysis is that oxygen production is separated from H_2 production. Indeed, oxygen has an inhibitory effect on the hydrogenase enzyme which is a major issue for direct biophotolysis systems. Cyanobacteria could in principle achieve a maximum 16.3% light conversion efficiency but the actual process efficiency is much lower.

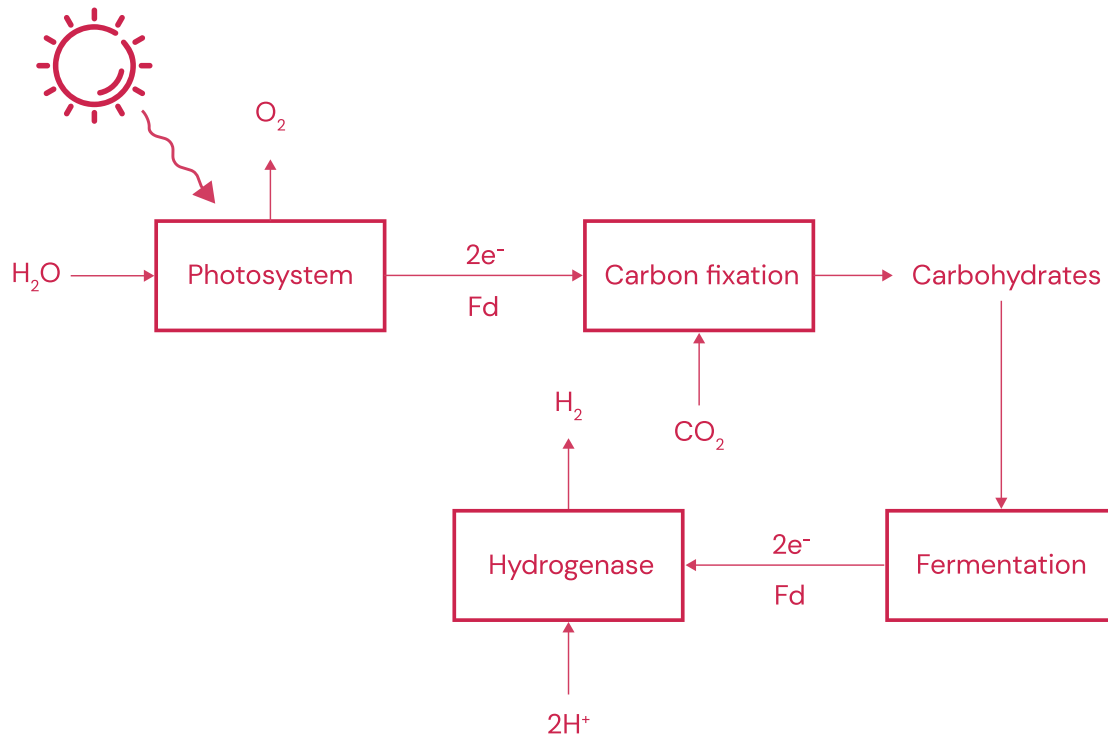


Figure 15 : Simplified indirect biophotolysis process⁸²

Fermentation-based Processes

Fermentation is a process where microorganisms use **sugar-containing organic matter** as carbon source and break it down into simpler compounds, producing chemical energy along with H_2 and carbon dioxide. These processes can be classified into two types depending on whether the microorganisms need light to process the organic matter or not.

Fermentation processes that need light to occur are called **photo-fermentative**. Contrary to bio-photolysis, photo-fermentation takes place in **anaerobic conditions**. This process can consume **carbohydrate-rich waste** (effluents from the food and beverage industry, household and municipal organic waste, waste water) to produce a valuable energy vector. The downside is that the reaction requires strictly-controlled conditions, which makes bioreactors very expensive. Light conversion efficiency is also quite low compared to other H_2 production methods (1-5%⁸³).

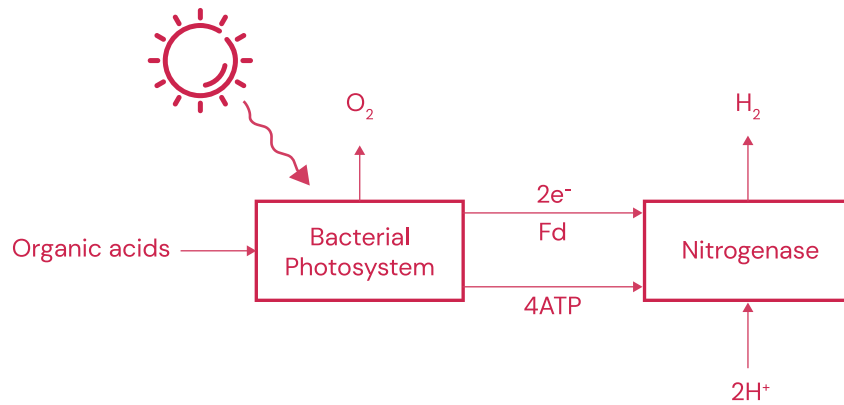


Figure 16 : Simplified photo-fermentation process²¹

In **dark fermentation**, bacteria and microalgae degrade **complex organic compounds** under **anaerobic conditions** with **no light radiation** and produce H_2 among other molecules. This process can also use **waste** as an input. The overall efficiency of dark fermentation ranges between 19% and 28%, which is quite low compared to biomass-waste gasification or pyrolysis⁸⁶. Low yields are also observed, with a theoretical maximum of 12 mol H_2 /mol glucose reduced to 4 mol H_2 /mol glucose in practice due to the co-production of organic acids. Dark fermentation also produces CO_2 , between 0.96 and 8.6 kg CO_2 /kg H_2 depending on the feedstock which reduces the environmental benefits of the process¹². However, an advantage of such reactors is their overall reduced complexity, which makes them cheaper to build and operate.

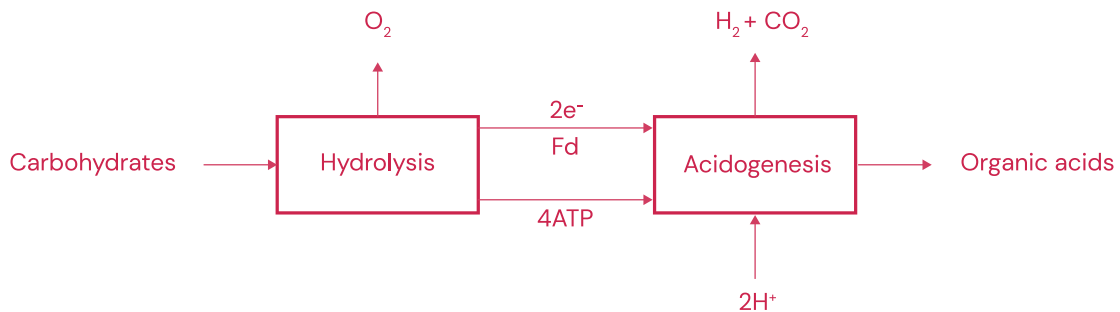


Figure 17 : Simplified dark fermentation process^{21 23}

Hybrid Processes

Dark-photo co-fermentation makes use of photo fermentation to further decompose the carbohydrates produced by dark fermentation, thus **improving H_2 yields** and **minimizing waste production**⁸⁷. Another process that has gained popularity in recent years is **Microbial Electrolysis Cells (MEC)**, in which electrons are generated by the oxidation of organic matter in the anode and transported to the cathode where they combine with protons, generating H_2 . This method can reach very high efficiencies but suffers from the same issues as biophotolysis.



EQTEC Plc 1.1 MWe Market Development Center (MDC) turning biomass waste into hydrogen energy, biofuel and electricity (Italy) – Credit: energynews

Biological route: maturity and projects

TRL
1-7

Despite the environmental advantages of biological methods, their low H₂ yield – about 0.01 kg H₂/kg-feedstock for biophotolysis and between 0.01 and 0.07 kg H₂/kg-feedstock for fermentation processes – makes **scale-up** and **industrial applications** difficult¹². Comparatively, steam methane reforming has a H₂ yield of about 0.25 kg H₂/kg-feedstock. For the moment, most of these technologies are still at the **lab level** (TRL 1-3) and will only be able to get to **demonstration** if their efficiency and H₂ production yield are improved.

A key issue common to all biological routes is that microorganisms are **highly sensitive** to light intensity and wavelength, which can lead to substantial disparities between experiments under optimal conditions in laboratories and **real-life situations**. Dark fermentation is more mature and was rated at TRL 7 in 2021 as multiple **pilot projects** have demonstrated good yields and rates of H₂ production, with some problems still to be addressed, such as process stability.



NATURAL HYDROGEN

Natural hydrogen (H_2) was discovered a long time ago although the topic has clearly been overlooked in recent years.

For example, continuously burning gas seep near Antalya in Turkey with concentrations 7.5–11.3% of H_2 have been **known for 2,500 years** and “Los Fuegos Eternos” (the eternal flames) in the Philippines were discovered more than two centuries ago with concentrations ranging from 41.4 to 44.5%⁸⁸.

Unlike oil and gas, natural H_2 is **not a fossil resource**: it is continuously produced inside Earth’s crust. Two main processes are currently favoured by scientists. The first one, a water–rock interaction called **serpentinization**, produces H_2 through the oxidation of Fe(II) or magnesium minerals by seawater. Serpentinization is most effective in the temperature range 200 to 310°C. The reaction rate becomes limited at lower temperatures. The second one is the **radiolysis of water**, where the radioactivity of Earth’s crust dissociates water molecules due to ionizing radiation⁸⁸.

H_2 properties have made measurements very difficult. H_2 is very volatile and diffusive so it cannot be retained for long periods of time in geological formations. It is also rapidly consumed by microorganisms and reacts with oxygen to form water when arriving in the atmosphere, which makes it even more **difficult to detect**⁸⁸.

While today’s estimations on resources are not very precise due to insufficient exploration and data, the **latest estimates** from 2019 give an annual production of 23 Mt⁸⁸, much more than the previous ones of 6 Mt/y in 2005⁸⁹. Historical records show that estimates have been increasing by an order of magnitude every one or two decades, implying that even these are likely to **underestimate the resource**⁸⁸. Some argue that the situation is similar to the **beginnings of oil exploration** at the end of the 19th century⁹⁰. By improving exploration techniques, the potential reserves might increase and their exploitation will allow us to better understand the underlying formation mechanisms.



First U.S hydrogen well drilled in 2019 by Natural Hydrogen Energy – Credit: Viacheslav Zgonnik

Natural hydrogen: maturity and projects

TRL
3

For the moment, natural H₂ extraction is considered by the IEA to be at TRL 3³², meaning that the concept has been formulated but the solution still needs to be **prototyped** and **applied**.

However, there is already an example of a commercial exploitation of natural H₂ in Mali since 2016 from a well that has produced continuously without a drop in pressure, implying a **continuous recharging** of the reservoir. In 2011, a company named **Petroma (now Hydroma)** acquired the rights to exploit the initial well and eighteen other small ones. The gases from these wells (98% H₂ purity, 1400 m³/day) have been fuelling an **internal combustion engine** supplying the nearby village with clean electricity since 2018^{91,92}.

A startup named **45-8 Energy** in France is also working on natural H₂ and is currently estimating the potential for natural H₂ in the Pyrenees, along with other energy companies like Engie or Total Energies. Some permits have also been granted in Australia where the resource seems to be more available than elsewhere⁹¹.

COMPARISON OF HYDROGEN PRODUCTION TECHNOLOGIES

As shown previously, there exists a lot of hydrogen (H₂) production technologies, using different feedstocks, with different maturity levels... What is important for the energy transition is the potential to decarbonize the **current production** of H₂ and to enable **new end-use technologies** based on low-carbon H₂.

COMPARISON OF TECHNOLOGY MATURITIES

Technology innovation takes time. One tool to track the development of a technology is the technology readiness level (TRL). At TRL 9, technologies are commercially ready. Hence, technologies that currently have a TRL lower than 7 (pre-commercial demonstration) are unlikely to play a **major role** during the coming decade but could in the **long term** contribute to achieving climate targets by 2050.

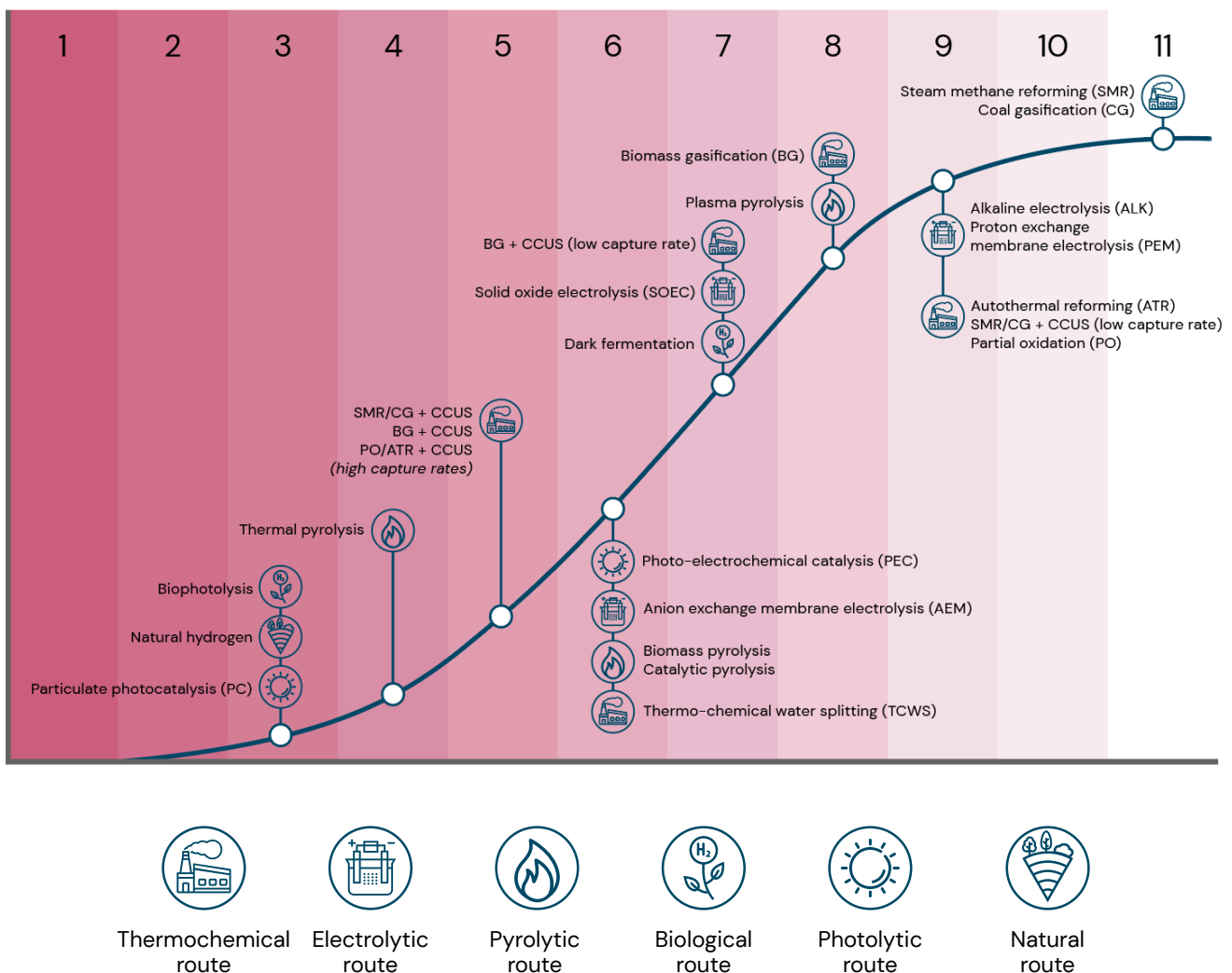
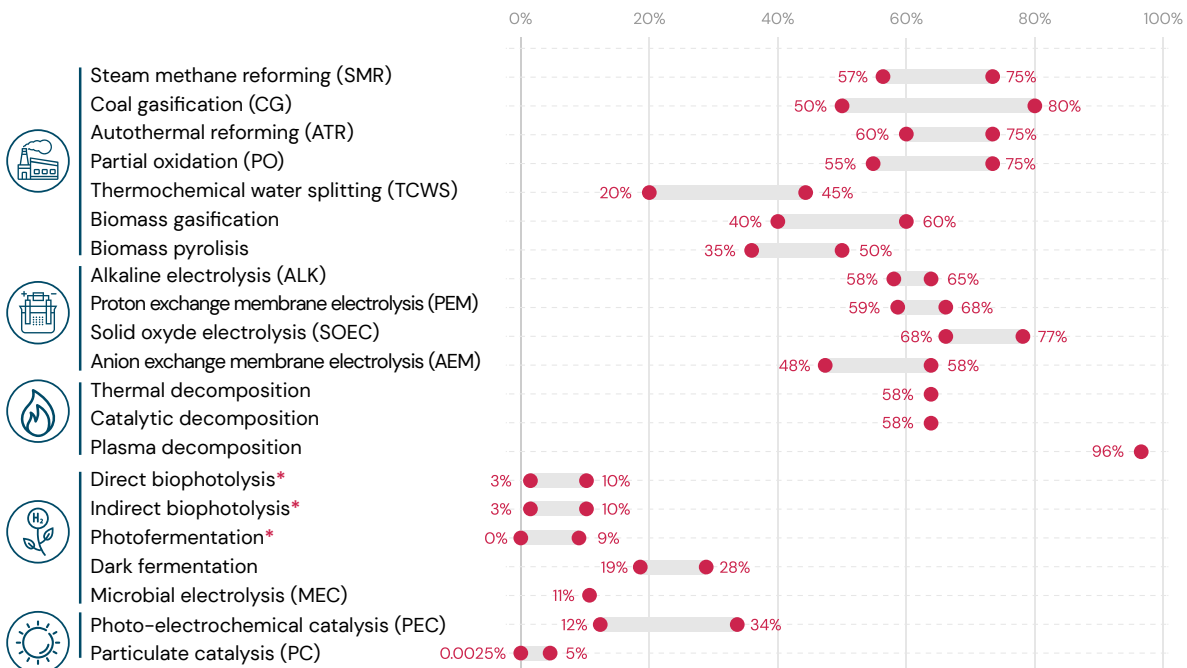


Figure 18 : Classification of H₂ production technologies based on their maturity level (TRL)

Although TRLs give information about the stage of development of a technology, a high TRL (7–8–9) doesn't necessarily mean that the technology will be a **commercial success**. For example, ATR and PO are currently at TRL 9 but don't gain much **market shares** compared to SMR or CG because the market is already saturated and the benefits they bring are not enough to justify a switch. Moreover, there can be **big differences of readiness level** for the same technology as the TRL is determined by the latest and most advanced projects. For example, plasma pyrolysis is at TRL 8 because **Monolith** has been operating its first-of-a-kind commercial plant Olive Creek 1 since 2020, but other companies are still at the development stage (see plasma pyrolysis section).

COMPARISON OF LHV EFFICIENCIES

Efficiency, which is the ratio between the energy input and the energy output of a process, is also an important parameter to consider. The table below compares the energy efficiency of different production methods. The most efficient technologies are **electrolysers** and **current fossil fuel-based methods**. Methane pyrolysis, photo-electrochemical catalysis and thermochemical water splitting are the **second most efficient** methods and could show great potential for H₂ production. In general the most mature technologies appear to have the highest efficiencies among the other technologies. Below are given the efficiency range for each of the technologies presented before. It is important to mention that if electrolysis and direct biophotolysis were to be compared, the efficiency of the electricity generation would have to be considered too (hence taking into account the conversion efficiency of the solar panel if electrolysers are powered by PV).



(*) refers to Solar-to-Hydrogen (STH) efficiencies

Figure 19 : Comparison of H₂ production technologies LHV energy efficiency;

Sources: SMR, CG, biomass gasification and pyrolysis efficiencies¹⁰. Direct and indirect biophotolysis and MEC efficiencies⁸¹. Photofermentation efficiency⁷³. Dark fermentation efficiency⁸⁶. PC efficiency⁷⁶. ALK, PEM, SOEC and PEC efficiencies²⁹. AEM efficiency³³. ATR and PO efficiencies¹³. TCWS efficiency²². Thermal and catalytic decomposition efficiency⁶². Plasma decomposition efficiency calculated based on plant energy balance⁹⁴.

COMPARISON OF GHG EMISSIONS

In terms of climate impact, the level of **process emissions** is a critical parameter. In its REDII directive⁹⁵, the European Union considers a **fossil fuel comparator** for low-carbon fuels like H₂. It corresponds to a 60% reduction of emissions compared to the “well-to-gate” emissions of H₂ produced by natural gas without CCUS.

Moreover, it also launched in 2021 an organism name **CertifHy**¹⁶ whose aim is to certify that the H₂ produced is indeed low-carbon as defined by the REDII directive. The benchmark value given for **well-to-gate emissions** of SMR by CertifHy is 10.9 kg CO₂e/kg H₂ (91 kg CO₂e/MJ). But even more recently, the European Commission set out new rules through **two delegated acts** on February 10th of 2023 to define what constitutes renewable H₂ in the EU⁹⁶.

The first Act clarifies the principle of **“additionality”** for H₂ set out in the EU’s Renewable Energy Directive, by imposing stricter **temporal and geographic correlation** between renewable electricity supply and H₂ production. It also allows the use of grid electricity for renewable H₂ production if the installation is located in a **bidding zone** where the emission intensity of electricity is lower than **65 g CO₂e/kWh** (with certain conditions). The second delegated Act defines the methodology by which to assess the greenhouse gas emissions savings of renewable fuels of non-biological origin (RFNBO), changing the threshold from 60% to **70% of reduction in emissions** compared to the fossil fuel comparator of 11.3 kg CO₂e/kg H₂ (94 g CO₂e/MJ). The European Parliament and the Council have 2 months to scrutinise them and to either accept or reject the proposals. This scrutiny period can be extended by 2 months at their request.

It is thus interesting to look at the **emission reduction potential** of each technology presented here and see if the H₂ produced can be qualified as low-carbon according to the current and the new regulation. Only the most mature technologies that are likely to play a role in the EU H₂ production mix this decade are considered. Figure 20 shows GHG emission associated with the different technologies described in this report, taking into account **fugitive emissions** of the fossil fuels supply chains, when applicable:

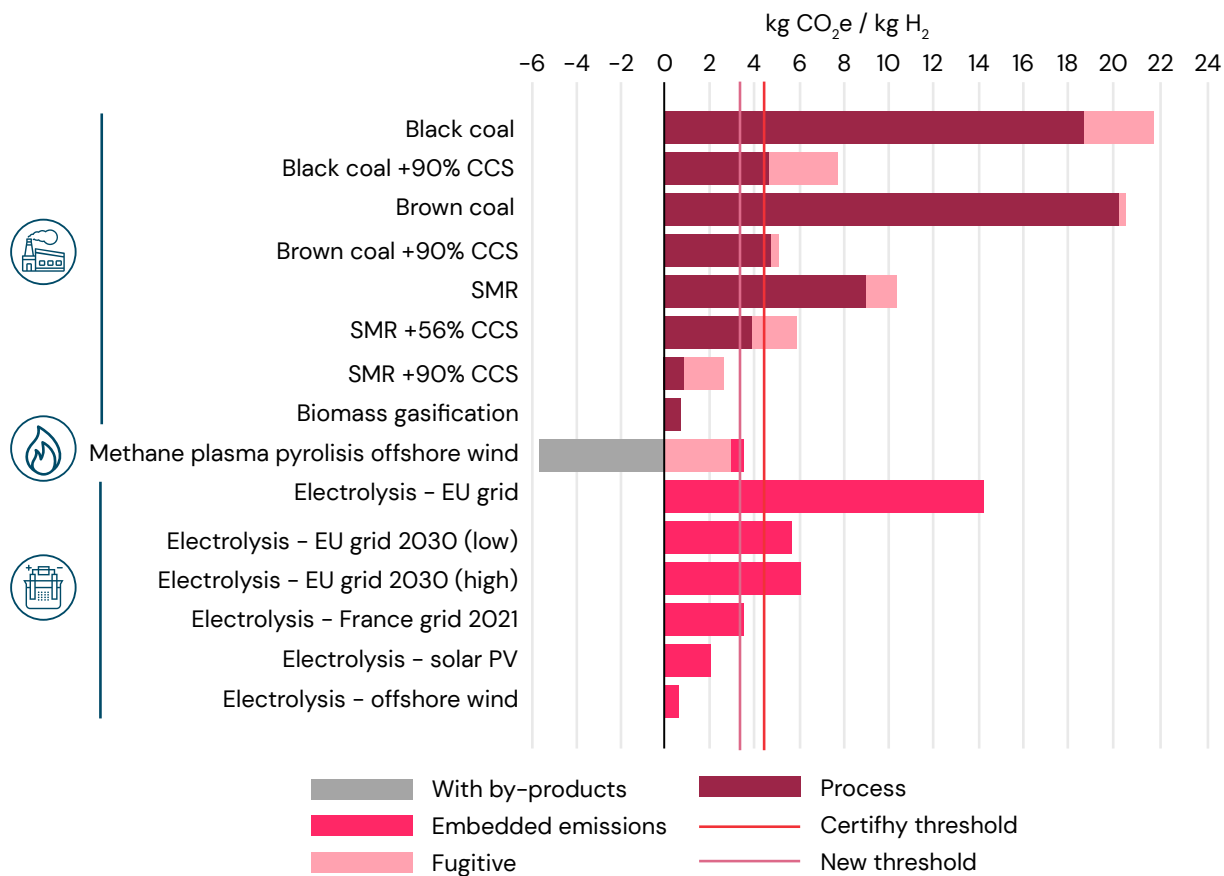


Figure 20 : GHGs emissions comparison of the most mature H₂ production technologies

Black coal, brown coal and SMR process (with CCS) and fugitive emissions were extracted from calculations made by Longen et al. (2021)¹¹ based on data provided by the IPCC. Biomass gasification emissions were obtained from the ICCT white paper on biomethane and H₂ emissions in Europe of October 2021¹⁰. Methane pyrolysis fugitive and embedded emissions as well as the amount of carbon stored under solid form come from calculations made by Hermesmann and Müller (2022)⁵⁹. (The one showed here is the best-case scenario where the heat for the process is provided by German offshore wind electricity). For electrolysis embedded emissions, a 64% average LHV efficiency was chosen for the ALK electrolyser. Life-cycle emissions of the EU and France electricity generation were taken from the European Environment Agency⁹⁷, from ADEME INCER-ACV⁹⁸ for EU solar PV and from Carbon Neutrality in the UNECE Region 2022 report⁹⁹ for EU offshore wind. Values showed here don't take into account the emissions associated with manufacturing, transport, construction and end-of-life of hydrogen production technologies.

First, it is clear that H₂ produced from either **black or brown coal** is far too carbon emissive to be considered low-carbon even with a 90% capture rate and considering that there are no associated fugitive emissions. In the end, among the fossil fuel-based methods, only **natural gas-based** ones with high capture rates above 90% and standard fugitive emissions could be considered as low-carbon by the EU. This is also true when considering that carbon dioxide is stored permanently after being captured without generating too much fugitive emissions during transport. In comparison, **biomass gasification** is already very low-carbon and could become carbon negative if CCS is added to the process.

Methane pyrolysis produces no carbon emissions directly but has a **high level of fugitive emissions**, as it needs more natural gas than SMR for the same quantity of H₂ produced. According to the IEA, a significant share of these emissions could be abated at **no net cost**, because the value of the captured methane is sufficient to cover the cost of the abatement measure¹⁰⁰. The precise share of emissions that can be avoided at no net cost is highly dependent on natural gas prices and on geographical location.

Depending on the type of energy used for the provision of heat, methane pyrolysis embedded emissions can vary but are still **lower than 1 kg CO₂e/kg H₂** even with natural gas, because the carbon produced is stored or used under solid form. However, the carbon intensity of the electricity used is important because emissions can for example raise to **4.4 kg CO₂e/kg H₂** when using **German grid electricity**. Hence, to be qualified as low-carbon, this technology should be powered by renewable electricity. Using **biogas** instead of natural gas will also be crucial later as this technology has the advantage of being able to store carbon under a solid form and thus balance the emissions and even make the process **carbon negative**.

What is also interesting is that **SMR with 90% capture rates** is better on a climate standpoint than electrolysis powered by grid electricity, even in 2030, when considering the average carbon intensity of the EU power sector (275 g CO₂e/kWh)⁹⁷. However, countries whose power sector has a low-carbon intensity (<85 g CO₂e/kWh) could produce low-carbon H₂ using grid electricity directly. Only countries like Sweden, France, Luxembourg and Finland had an electricity mix with a carbon intensity **lower than 85 g CO₂e/kWh** in 2021. However, emissions decrease a lot when using renewable electricity from solar PV or offshore wind, coming down as low as **0.62 kg CO₂e/kg H₂** and every country could install dedicated renewable power or buy renewable electricity through PPA.

KEY TAKEAWAYS

There is a **wide range of methods** to produce low-carbon H₂

1

• **SMR** and **CG** are the most mature H₂ production technologies. H₂ produced by **natural gas** (without CCUS) represented **62%** of the global H₂ production in 2021, with SMR being the most used technology. **19%** of the global H₂ production was attributed to **coal** (without CCUS) in 2021, with CG being the most used technology.

2

• There are **4 main electrolyser technologies**. Among them, **ALK** is currently the **cheapest** and **most mature** technology, followed by **PEM** which is particularly suitable for **REN integration**. **SOEC** and **AEM** are still at the **pre-commercial stage** but could become **cost-competitive** in the near future due to their characteristics, respectively **industrial heat coupling** and use of **abundant materials**.

3

• **Methane pyrolysis** is a **promising technology** that could compliment the low-carbon H₂ production in the 2030s as it **doesn't generate CO₂** but only valuable co-products such as **carbon black** and **graphene** (depending on the type of process) which have numerous applications in the industry. Its economic model could hence not only rely on H₂ alone but also on its **co-products**.

4

• **Thermochemical route technologies** with **partial CCUS** are already available but do not sufficiently reduce the emissions of processes based on fossil-fuels to make them qualify as **low-carbon** by the EU. Several projects announced that they planned to install CCUS with **high capture rates**, which could turn some fossil fuel-based production routes into low-carbon ones, but the technology has not yet been proven **at scale**.

5

• **Other H₂** production technologies have some potential as low-carbon alternatives but won't be available **at scale** until at least **the 2030s**.

6

• Producing H₂ via **electrolysis** is only low-carbon when it is powered by **renewables**. The average carbon intensity of EU electricity is **too high** and will stay so in 2030 for low-carbon H₂ to be produced using electricity from the grid, except for **some countries** which had an average electricity carbon intensity **lower than 65 gCO₂e/kWh** (18 gCO₂e/MJ) during the past calendar year, like France or Norway.

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AUTHORS

- **Greg De Temmerman**
Zenon Research
Mines Paris PSL, IHEIE
- **Julien Lamarque-Lacoste**
Archery Strategy Consulting
- **Manon de la Motte Saint Pierre**
Archery Strategy Consulting
- **Thomas Boigontier**
Zenon Research
Mines Paris PSL, IHEIE
- **Anouck Dubois**
Archery Strategy Consulting

This note should be cited as:

Zenon Research, Archery Strategy Consulting (2023),
Low-carbon hydrogen production technologies: various
but not equivalent options

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