

Sources and technologies for green hydrogen production: a review

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1 Introduction

For decades, hydrogen has been used primarily by the chemical and petrochemical industries. For example, in Finland, approximately 150,000 tons (5 TWh) of hydrogen is used annually in oil refining and biofuel production, in the chemical industry for hydrogen peroxide production, and in the mining and ore refining sectors (Laurikko et al., 2020). Globally, ammonia production for urea and other fertilizers is the largest hydrogen consumer, accounting for approximately 50 % of the total industrial hydrogen demand (Dincer & Acar, 2017).

The energy transition and route to net zero emissions has also led to new potential roles for hydrogen. Indeed, hydrogen is recognized as the key contributor to the clean energy transition. By replacing fossil fuels, low-CO₂ hydrogen has enormous potential for reducing carbon emissions in sectors where other alternatives might be unfeasible or more expensive. Hydrogen can replace fossil-based hydrogen for industrial processes and start new industrial products, such as green fertilizers (EC, 2023). Other notable growth areas include transportation (mainly shipping, long-haul road transportation, and aviation), steelmaking and cement industries, food processing, and electronics manufacturing. Hydrogen is also one of the leading options for storing renewable energy. Thus, hydrogen may play an essential role in balancing renewable intermittent electricity production, electricity demand, and grid stability (EC, 2023). Furthermore, hydrogen plays an important role in the development of new strategies for converting industrial CO₂ emissions into valuable chemicals such as synthetic fuels (Sánchez-Bastardo et al., 2021).

Today, hydrogen is framed not only in terms of decarbonization but also in energy security. The EU has doubled its target for clean hydrogen use to 20 million tons by 2030, half of which is expected to come from domestic hydrogen production (EC, 2023). Hydrogen can be produced from various resources using different feedstocks, pathways, and technologies, including fossil fuels and renewable energy resources. Currently, most hydrogen is produced from fossil fuels, typically natural gas. In Finland, 99 % of the dedicated hydrogen is produced via either steam reforming or partial oxidation of fossil fuels, and less than 1 % via water electrolysis (Laurikko et al., 2020). Still, fossil fuel-based methods neither lower emissions nor tackle the limited fossil fuel supplies issue. Hence, there is a strong need to identify clean, low-cost, and abundant sources for hydrogen production. From a cradle-to-grave perspective, renewable energy sources offer the best opportunity to lower the carbon footprint of this substance and reduce dependence on fossil fuels (Dincer & Acar 2017; Karaca et al., 2023).

The primary objective of this report is to provide a comprehensive review of sustainable hydrogen production systems, that could guide energy companies, various industries, food chain companies and entrepreneurs, landowners, start-up companies, regional developers, experts, and other organizations in South Ostrobothnia.

The report is organized as follows: Chapter 2 outlines the main hydrogen production methods, classified by the raw material used. The different hydrogen production processes and their technology readiness levels (TRLs) are then described in more detail in Chapters 3, 4, and 5: Chapter 3 focuses on traditional methane-based hydrogen production processes, biomass-based technologies are described in Chapter 4, and water-splitting technologies in Chapter 5. Finally, Chapter 6 summarizes the key findings.

2 Overview of hydrogen production pathways

Fig. 1 shows the main methods to produce hydrogen, classified by the raw material used. Hydrogen colour codes, referring to the energy source employed to produce hydrogen, are used to identify different hydrogen production pathways. For fossil fuels, steam reforming and partial oxidation of hydrocarbons, primarily methane from natural gas, are the dominant technologies worldwide, although coal gasification is also used in countries rich in this resource (Ursua et al., 2012). Hydrogen from natural gas is coded as "grey", "blue", or "turquoise". Grey hydrogen is produced from natural gas without capturing the greenhouse gases originating from the process; almost 10 kg of CO₂ is emitted into the atmosphere per kg of hydrogen produced (Giovannini, 2021). Grey hydrogen is considered blue when more than 90 % of the emitted CO₂ is captured and sequestered via carbon capture and storage (CCS) (AuroraHydrogen, 2021). Turquoise hydrogen refers to hydrogen produced via natural gas pyrolysis. The most significant benefit of the pyrolysis method is that all carbon is recovered in solid form. The solid carbon by-product can be sequestered more easily than the gaseous CO₂, and the solid carbon can even be used in other applications, such as a soil improver or manufacturing goods. If the electricity driving the pyrolysis comes from renewable resources, the process is considered zero-carbon (AuroraHydrogen, 2021).

Although fossil fuels are currently the primary raw material for H₂ production, interest in "green" hydrogen production from renewable resources is growing. The traditional, mature natural gas-based technologies above can also be applied to hydrogen production from biomethane, resulting in renewable green hydrogen. Using biomethane instead of natural gas as a feedstock and combining it with CCS would even lead to a net removal of CO₂ from the atmosphere, so-called negative emissions (Antonini et al., 2020). Green hydrogen can also be obtained from various biomass sources through thermochemical and biochemical processes. The main thermochemical processes are pyrolysis and gasification. Biochemical processes employing microorganisms for hydrogen production are less mature but may have long-term potential for sustainable hydrogen production with low environmental impact. Hydrogen production from biomass through a well-established anaerobic digestion process combined with CO₂ reforming, also called dry reforming, of raw biogas has also emerged as an attractive technological solution for green hydrogen production. Integrated anaerobic digestion and CO₂ reforming can take full advantage of both CH₄ and CO₂ in biogas, eliminating the need for CO₂ removal from biogas and its release into the atmosphere. A co-benefit of all biomass-based methods is the possibility of solving the dual problem of waste disposal and energy generation.

Water is widely thought to be the most promising source of green hydrogen in the future. Electrolysis, a process that uses electricity to split water into hydrogen and oxygen, is currently the most mature method to obtain hydrogen from water. When renewable electricity sources are used, green hydrogen is obtained. Some use the "yellow" colour code to refer to hydrogen made through electrolysis with solar power, while others, like this study, consider it as electrolysed hydrogen made using power of mixed origin. i.e., a mix of renewable and fossil power flowing through the grid. In addition to water electrolysis, thermal, photocatalytic and photobiological water decompositions are also attracting attention (Ursua et al., 2012). Thermochemical water splitting uses high temperatures, e.g. from concentrated solar power, and chemical reactions to produce hydrogen and oxygen from water. In photoelectrochemical water splitting, hydrogen is produced from water using sunlight and specialized semiconductors that use light energy to dissociate water molecules into hydrogen and oxygen. The photobiological hydrogen production process uses microorganisms and sunlight to turn water into hydrogen. Technologies based on solar energy are expected to be viable in the medium to long term. (EERE, 2023).

“Black” and “brown” hydrogen, produced by coal or lignite gasification, were excluded in this study since the fossil coal-based H₂ production was not considered relevant for South Ostrobothnia. Fossil coal-based processes are also the most polluting.

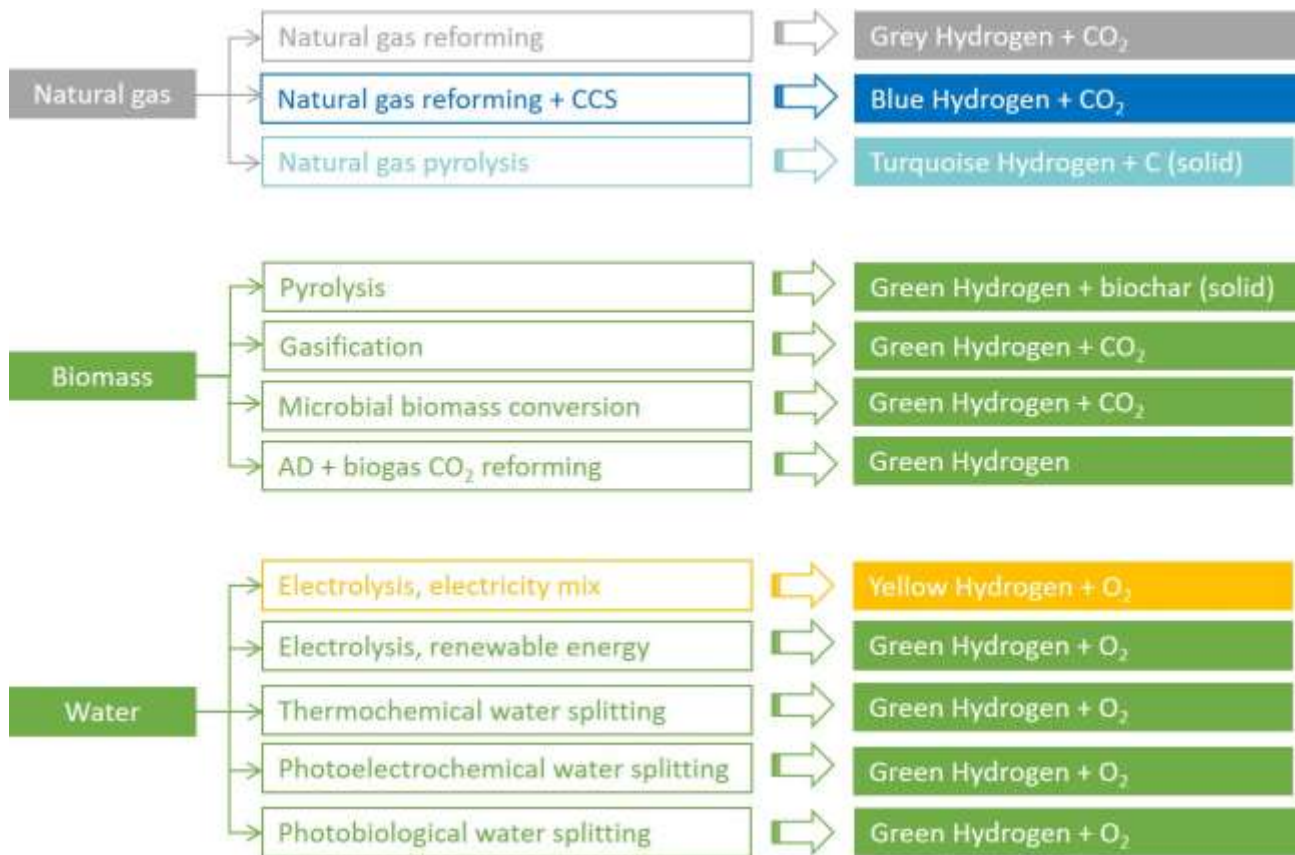


Figure 1. Overview of possible hydrogen production pathways, modified from (Ringsgwandl et al., 2022).

The following chapters (Chapters 3–5) describe the different production processes and the respective technology readiness levels in more detail.

3 Conventional hydrogen production technologies

Around 96 % of the hydrogen produced globally is generated from fossil fuels. The most used process is natural gas (48 %) and oil (30 %) reforming, followed by coal gasification (18 %) (Arregi et al., 2018). This report focuses on sustainable hydrogen production, so only conventional natural gas-based technologies are reviewed since the same technologies can also be applied to hydrogen production from renewable methane (biomethane).

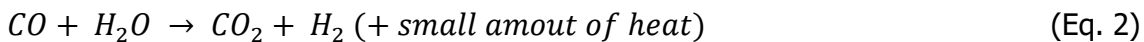
Hydrogen generation from methane can be through reforming and methane pyrolysis processes, of which reforming is the most important process of industrial bulk hydrogen production (Baeyens et al., 2020). Based on the reactant, methane reforming can be classified as steam reforming, partial oxidation, or autothermal reforming (Abdin et al., 2020).

3.1 Steam methane reforming

Steam methane reforming (TRL 9) is today’s standard in large-scale hydrogen production (Ringsgwandl et al., 2022). The steam methane reforming (SMR) method involves a catalytic conversion of methane, predominantly available in natural gas, and steam to hydrogen and carbon oxides. The main steps of the process are illustrated in Fig. 2. First, natural gas is cleaned to remove impurities and sulphur compounds to avoid poisoning the reforming catalyst, leaving a pure methane stream. In the reformation step (Eq. 1), methane is thermally decomposed into CO and H₂ by hot (800–950 °C), pressurized water steam in the presence of a suitable catalyst, usually nickel.



After the reformer, the CO and H₂ mixture, called syngas, passes through a heat recovery step and is fed into a water-gas shift reactor (WGSR). In the WGSR, CO reacts with steam, again assisted by a catalyst, to produce additional H₂ (Eq. 2):



After WGSR, the mixture of H₂ and CO₂ (plus small amounts of unconverted CH₄ and CO) passes through a pressure swing adsorption (PSA) process, leaving H₂ with high purity of nearly 100 % (Nikolaidis & Poullikas, 2017).

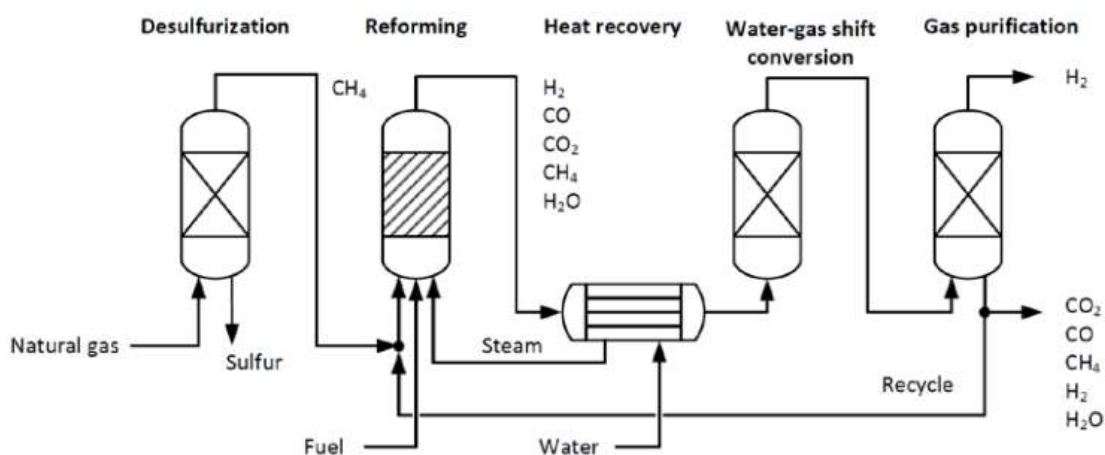


Figure 2. Hydrogen production using the SMR process with its process steps (Binder et al, 2018)

A major concern associated with natural gas reforming is high CO₂ emission. To achieve even partial carbon neutrality, an effective carbon capture and utilization or storage (CCUS) should be added in the process. However, CO₂ capture, transport, and utilization options that are currently available are associated with high costs, which hinders the implementation of CCUS. In addition, technical barriers to large-scale deployment still exist and are yet to be addressed, along with the chicken-and-egg problem of infrastructure (CCUS SET-Plan, 2020).

The efficiency of hydrogen production from steam methane reforming on an industrial scale (150–300 MW) is 70–85 % (IEA, 2015; Abdin et al., 2020). The addition of CCUS in the SMR process, needed to decrease GHG emissions if natural gas is used as a feedstock, results in a significant ~15 % decrease in the energy efficiency (Sánchez-Bastardo et al., 2021). In small-scale applications (<15 MW, without CCUS), the energy efficiency is considerably lower compared to large scale application, around 51–63 % (IEA, 2015; Schreiber et al., 2020).

SMR has the advantages of extensive commercialization and high H₂ to CO ratios relative to the other hydrocarbon reforming methods (Pinsky et al., 2020). The main detriment of this process is that steam reforming is highly endothermic and demands enormous heat input (63.3 kJ/mol H₂) to the process for the reaction to proceed. The heat required for the SMR reaction is usually supplied by the combustion of natural gas and waste gas from hydrogen purification. Up to 30 % of the total natural gas consumption of the plant is used as a process fuel (Nikolaidis & Poullikas, 2017). The heat requirement of the SMR could also be supplied by concentrated solar thermal energy. Solar thermal reforming was one of the first solar-derived fuel routes investigated since the early 80s in the U.S. (Abdin et al., 2020).

In the past years, most of the research related to SMR has focused on catalyst performance to increase hydrogen yield through improving catalyst sintering resistance and minimizing the effect of carbon deposition and sulphur poisoning (Abdin et al., 2020). In addition, much research has been done to find alternative solutions to conventional reformers to increase energy efficiency and save costs. Membrane reactors offer a promising solution. A hydrogen perm-selective membrane inside a reactor allows the chemical reaction and hydrogen separation to be combined in only one unit. As a result, hydrogen production is enhanced. In addition, the SMR reaction is possible at a lower temperature (450–550 °C as opposed to ~850–900 °C of traditional SMR). (Nikolaidis & Poullikas, 2017)

In the IEA (2019) report, hydrogen production costs using natural gas SMR (large-scale) without CCSU were 1.73 USD/kg of H₂ and, with CCSU, 2.32 USD/kg of H₂. Adding CCUS to SMR plants led, on average, to cost increase of 50 % for CAPEX (from 500–900 USD/kW_{H2} to 900–1600 USD/kW_{H2}). In addition, OPEX was doubled due to CO₂ transport and storage costs.

The capital costs of steam reformers are considered prohibitive for small and medium-sized applications. The costs of these complex facilities do not scale down well: based on IEA (2015), the specific investment cost in €/kW_{H2} for small-scale applications (<15 MW) may be up to ten times that of large-scale applications.

3.2 Partial oxidation of methane

Partial oxidation (POX) of methane, also a commercially available technology (Pinsky et al., 2020), is an alternative technology to steam methane reforming. In partial oxidation, methane reacts with a limited amount of oxygen – typically sourced from the air through a cryogenic air separation unit – not enough to completely oxidize CH₄ to CO₂ and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and carbon monoxide (Eq. 3):



The produced syngas is further treated in WGSR in the same manner as the product gas of the SMR process to increase the hydrogen yield. The main process steps are depicted in Fig. 3. In contrast to steam reforming, partial oxidation is an exothermic process – it gives off heat. Heat released from this exothermic reaction can be used to generate steam for downstream water-gas-shift process and for more general pre-heating of other processes (Walden, 2022).

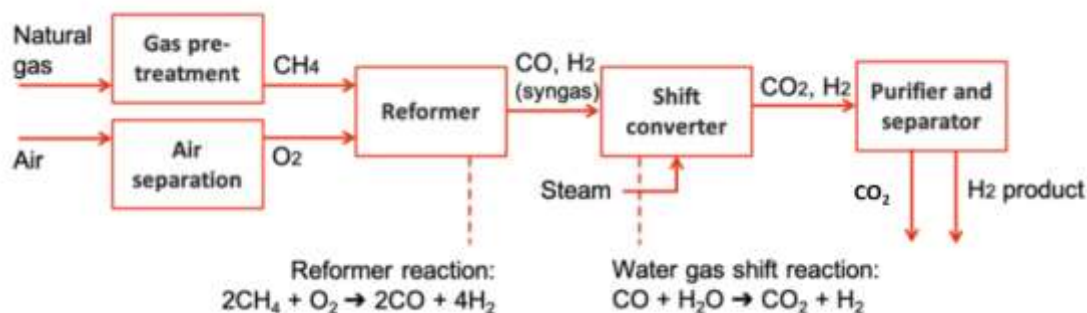


Figure 3. Hydrogen production using the POX process. Modified from (Broadleaf, 2021)

Partial oxidation units can be designed as thermal partial oxidation or catalytic partial oxidation reactors. The main difference between the two is the operating temperature. In the thermal partial oxidation process, the hydrocarbon feedstock is converted to syngas at 1300–1500 °C, while the catalytic partial oxidation process operates at 700–1000 °C, offering a potential solution to overcome high external heat energy consumption problems experienced in reforming technologies (Abdin et al., 2020).

Catalytic partial oxidation (CPOX) reactions are usually carried out using nickel or rhodium catalysts. CPOX is much faster than steam reforming and requires a smaller reactor vessel. This, and the relatively mild conditions (<1000 °C, 2.5–3.5 MPa), make it possible to implement CPOX on a small-scale application (Makaryan et al., 2023). However, CPOX still faces certain technical difficulties. The catalytic partial oxidation of methane to syngas is challenging because the selectivity of the reaction towards total combustion is difficult to control (Alvarez-Galvan et al., 2019); the catalyst must overcome not only the stability of the CH₄ C–H bond, but also the probability of overoxidation of CH₄ to CO₂ and H₂O. In addition, since partial oxidation consists of a reforming reaction that is exothermic, there is a risk for local overheating in the reactor and intensive soot formation, which contribute to catalyst sintering and deactivation (Pinsky et al., 2020). In thermal POX units, soot formation is tolerated in the reactor to a degree determined by downstream equipment (Walden, 2022).

Partial oxidation technology avoids the need for large amounts of costly superheated steam. On the other hand, it requires the use of expensive oxygen, which can be up to 50 % of the total costs of synthesis gas (Makaryan et al., 2023). In addition, the high cost of the air separation unit makes such plants very capital-intensive (Abdin et al., 2020).

Compared with SMR, partial oxidation has a slightly lower thermal efficiency; without CCUS the POX efficiency is 60–75 % (Makaryan et al., 2023). The hydrogen yield in catalytic partial oxidation process varies significantly with the choice of catalyst (Abdin et al., 2020).

3.3 Autothermal methane reforming

Autothermal reforming (ATR) combines exothermic partial oxidation and endothermic steam methane reforming reactions in one reactor. Basically, steam and oxygen are injected into the reformer, causing the oxidation and reforming reactions to occur simultaneously, as shown in Eq. 4.



ATR takes place in two zones: a partial oxidation zone, which generates the heat needed for the subsequent endothermic steam reforming stage, and a catalytic steam reforming zone, where the final synthesis gas composition is reached (Makaryan et al., 2023). The core benefit of this system is that, by properly selecting the oxygen/fuel ratio, no external heat is required (Martino et al., 2021). Operating temperatures of the process range from 850–1500 °C, with a sharp increase in temperature in the oxidation zone and a uniform decrease in the endothermic catalytic transformation zone (Makaryan et al., 2023).

A simplified flow diagram of the autothermal reforming of natural gas, combined with carbon capture, is shown in Fig. 4. Oxygen, produced in the air separation unit, steam, and methane react in an ATR reactor to produce syngas. As with SMR or POX systems, a water gas shift reactor and a hydrogen purification stage are needed. After ATR, the syngas is cooled and led to the WGSR, where CO reacts with steam to produce additional H₂ and CO₂. The shifted gas is then sent to the carbon capture unit, where the CO₂ is separated. The separated CO₂ is compressed and stored, while the hydrogen-rich gas (with unconverted CO and CH₄ and some trace gases) is sent to the PSA unit, leaving high-purity "blue" hydrogen. In the case of no carbon capture ("grey" H₂), the shifted gas from the WGSR is sent directly to the PSA unit, and the separated CO₂ is released into the atmosphere.

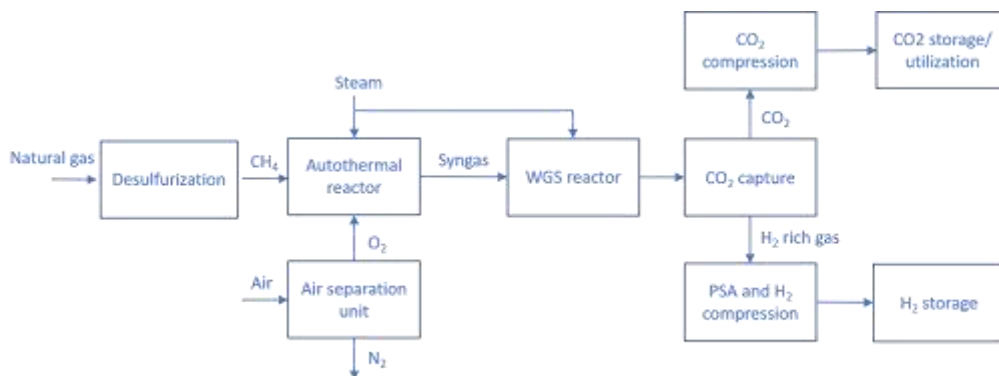


Figure 4. Simplified flow diagram of autothermal reforming of methane process with CCUS. Modified from (Oni et al, 2022; Nikolaidis & Poulikas, 2017)

The thermal efficiency of autothermal methane reforming is 60–75 % (without CCUS) (Nikolaidis & Poulikas, 2017). As in SMR or CPOX, the catalyst choice plays a crucial role in the overall performance. Nickel-based catalysts are most commonly used due to their efficiency and low cost (Megia et al, 2021).

The ATR reaction has several advantages over SMR: improved energy efficiency as all the heat generated by the partial oxidation reaction is fully utilized to drive the steam reforming reaction. Moreover, ATR has faster start-up times, faster response time to transient operation, and less coking tendency (Assabumrungrat & Laosiripojana, 2009). Independent control of the steam-to-carbon and

air-to-fuel ratios allows effective heat management (Brett et al., 2012). However, the major drawback of ATR is the large investment needed for an oxygen production plant, which may only become cost-effective at high production capacities (Assabumrungrat & Laosiripojana, 2009).

3.4 Methane pyrolysis

Although reforming processes are the most commercialised processes for producing hydrogen from natural gas, they have the disadvantage of negative environmental effects due to excessive CO₂ emissions. Even with CCS, not all CO₂ can be captured; for example, the maximum for SMR is seen between 85–90 % (van Cappellen et al., 2018). Hence, cleaner technologies are needed to be developed and implemented industrially. In this context, natural gas pyrolysis has recently gained particular attention due to its ability to produce H₂ without CO₂ emission.

Methane pyrolysis involves heating methane to high temperatures, usually in the presence of a catalyst, in an air- and water-free environment. Hence, the only source of hydrogen is methane itself, which undergoes thermal decomposition into its components, hydrogen and carbon (Eq. 5). The most significant benefit is that no CO₂ is produced; all carbon is recovered in solid form.



Technological variants of methane pyrolysis are divided into three categories, depending on the energy exposure method and reaction conditions: 1) thermal decomposition, 2) plasma decomposition, and 3) catalytic decomposition. Since the process is endothermic, heat must be added. To achieve appropriate reaction rates and CH₄ conversion rates, the temperature requirement for catalytic processes is above 800 °C, for thermal processes above 1000 °C, and when plasma torches are used, up to 2000 °C (Schneider et al., 2020). Plasma technologies for methane pyrolysis are probably the least close to industrial implementation (Ringsgwandl et al., 2022). Fig. 5 illustrates a simplified flow diagram of the catalytic methane pyrolysis process.

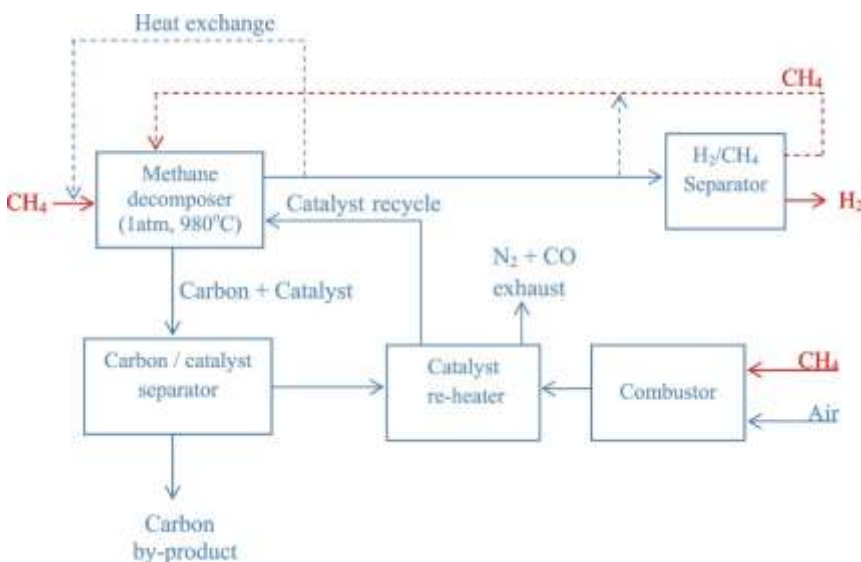


Figure 5. Flow diagram of the methane pyrolysis process (Nikolaidis & Poullikas, 2017)

The energy requirement per mole of H₂ produced is 37.6 kJ/mol, hence considerably lower than that for the SMR method (63.3 kJ/mol). The thermal energy demand could be covered by combustion of approximately 15–20 % of hydrogen produced in the process (Nikolaidis & Poullikas, 2017). In

addition, methane pyrolysis does not include water-gas-shift and CO₂ removal steps, and the energy-intensive CCUS is replaced by solid carbon management. As a result, capital investments for large plants are expected become lower than that for the SMR or POX processes, allowing for 25–30 % lower hydrogen production costs (Nikolaidis & Poullikas, 2017). Another advantage of pyrolysis is that the elemental carbon by-product may possess an economic value; the resulting carbon can be used as an important industrial raw material in the aluminium, steel or construction industries, as a graphite substitute for battery materials, in the semiconductor, wind and solar industries, or for soil amendment and environmental remediation (Mauthner & Malkamäki, 2022; Sánchez-Bastardo et al., 2021).

The achievable energy efficiency at the commercial scale is estimated at 58 % (Sánchez-Bastardo et al., 2022), so less hydrogen per mole of methane is produced compared to SMR. However, when the implementation of CCS systems in SMR is considered, the net energy efficiency of both processes becomes quite similar.

From an environmental point of view, natural gas pyrolysis can be considered emission-free at the point of hydrogen production if the energy for the process is from renewable sources. However, some GHGs are still emitted during natural gas extraction, processing, and transportation. In any case, the CO₂ emissions associated with natural gas pyrolysis are considerably lower than those of fossil fuel-based reforming technologies. (Sánchez-Bastardo et al. 2021). A special case is "super green" hydrogen from biomethane. During the pyrolysis of biomethane and the subsequent solid carbon storage, the CO₂ previously removed from the atmosphere through biomass growth is not rereleased but is bound to solid carbon (Mauthner & Malkamäki, 2022). Hence, pyrolysis of biomethane can be considered a negative emissions technology.

Although methane pyrolysis is a well-known technical process applied to produce, e.g., carbon black (Schneider et al., 2020) for the rubber industry, using this chemistry for large-scale hydrogen production is still an early stage. For example, BASF is developing thermal methane pyrolysis process to produce hydrogen in large quantities. A pilot reactor has been built in Ludwigshafen. The scale-up of the process is currently being developed in an ongoing research project (Schneider et al., 2020). In Finland, Hycamite has a catalytic methane pyrolysis pilot plant already in operation and is preparing to begin constructing an industrial-scale demonstration plant in Kokkola. The industrial-scale demonstration plant will have two functions: First, to produce and demonstrate the technology for producing clean hydrogen, and second, to provide carbon allotropes for high-value carbon customers. The plant will have an annual nominal capacity of 2,000 tons (67 GWh) of clean hydrogen (comparable to a 20 MW electrolyser with 5,500 hrs annual operation). Similarly, the plant can produce 6,000 tons of solid carbon. As the plant will use biomethane as feedstock, it will act as a carbon sink; almost 22,000 tons of CO₂ are stored when only the hydrogen use is counted. In addition, solid carbon can further reduce the carbon footprint of other products. Hence, depending on the application, the total CO₂ removal can be significantly more, in most cases up to 100,000 t/year. (Mauthner & Malkamäki, 2022; Hycamite, 2021)

4 Hydrogen production from biomass

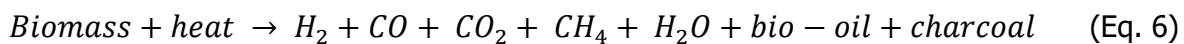
Biomass is a renewable, abundant primary energy resource derived from plants and animal materials such as agricultural residue and waste, forestry residues, municipal solid waste, waste from food processing, aquatic plants and algae, and animal by-products. The methods available for hydrogen production from biomass can be divided into two main categories: thermochemical and biological routes. Comparing these two methods, thermochemical routes basically have higher hydrogen production rate than biological ones (Aziz et al., 2021). Biochemical methods are also more selective about feedstocks. Biochemical methods require feedstocks rich in starch and sugar and cannot treat lignocellulosic stuffs, whereas thermochemical methods allow an extensive range of feedstocks (Parthasarathy & Narayanan, 2014). These reasons have led research to focus more on thermochemical routes for hydrogen production from biomass. In addition, there is a growing interest in hydrogen production through the well-established anaerobic digestion process combined with CO₂ reforming of raw biogas. Although the method has not yet been commercialized, CO₂ reforming is definitely a promising process for producing H₂ from biogas, especially considering that the process can fully utilize both CH₄ and CO₂ from the biogas.

4.1 Thermochemical processes

The most developed thermochemical routes for producing hydrogen from biomass are pyrolysis and gasification. These technologies are considered mature and ready for application (Aziz et al., 2021). Also, other, less mature technologies exist. For example, in recent years, extensive research has been conducted to evaluate the possibilities of supercritical water gasification for hydrogen production from wet biomasses. However, the technology has only progressed to a pilot stage (Lepage et al., 2021).

4.1.1 Biomass pyrolysis

Biomass pyrolysis is heating organic material in the absence of oxygen to convert it into liquid fuel (bio-oil), solid char (biochar), and gaseous compounds, including CO, CO₂, CH₄, and H₂ (Eq. 6). The proportion of liquid, solid and gaseous products depends on several factors, including the type of feedstock, the type of catalyst used, the temperature, and the residence time (Nikolaidis & Poullikas, 2017).



According to operating conditions, pyrolysis can be further categorized into slow and fast pyrolysis. In a slow pyrolysis process, with low temperature (<450 °C) and high residence time, pyrolysis will yield mainly biochar (Megía et al., 2021). Therefore, it is not considered appropriate for hydrogen production. Fast pyrolysis is the rapid heating of biomass to peak temperature of 500–800 °C (Megía et al., 2021) before the decomposition of the biomass. Fast pyrolysis process generates mostly vapor, i.e., bio-oil and gases, which can be further processed for hydrogen production. Some tar and charcoal are also generated. (Pandey et al., 2019)

A promising alternative to direct H₂ production from biomass is the two-stage operation with fast biomass pyrolysis in series with steam reforming (Fig. 6). The pyrolysis gases and bio-oil vapours from the first reactor are directly fed to the second reactor, where the reforming reactions take place (Lopez et al., 2022).



Figure 6. Schematic representation of biomass pyrolysis with in-line reforming for H₂ production

At first, to ensure efficient heat transfer in fast pyrolysis, biomass pre-treatment is performed. Pre-treatment involves biomass grinding and drying to reduce particle size and moisture content. The second step, biomass pyrolysis, leads to three fractions: bio-oil (60–75 wt%), non-condensable gases (10–20 wt%), and biochar (15–25 wt%) (Santamaria et al., 2021; Lopez et al., 2022). In the reforming step, the volatile stream (bio-oil + gases) from the pyrolysis reaches the reformer and reacts with steam on the catalyst active sites to yield an H₂-rich gaseous product. CO can be further oxidized to CO₂ + H₂ via the water-gas-shift reaction. (Santamaria et al., 2021) Finally, the gas stream produced from the WGSR is cooled to condense the steam fraction. The dried gas is then compressed and fed to the PSA module to separate H₂ and CO₂. The solid biochar fraction can be utilized to generate heat for the process or used for other applications such as carbon sequestration, soil remediation, and wastewater treatment.

Pyrolysis with in-line reforming has shown a considerable capacity for H₂ production; regarding biomass conversion, values of around 10 wt% (0.1 kg H₂/kg biomass, dry and ash-free basis) have been reported under optimal conditions and catalysts (Santamaria et al., 2021).

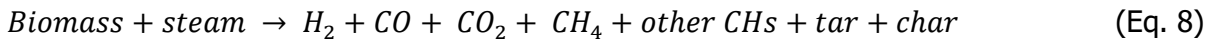
Biomass pyrolysis (TRL 7) has been successfully demonstrated at small-scale, and several pilot plants or demonstration projects (up to 200 ton/day biomass) are in operation (Motola et al., 2022). Critical challenges are related to H₂ variation due to biomass complexity and composition variation, tar formation, the need for catalyst regeneration, and high reactor cost. However, biomass pyrolysis for green hydrogen production is expected to mature to reach a TRL of up to 9 in the next two decades (Lepage et al., 2021). The production cost of H₂ from biomass pyrolysis is estimated to be 1.25–2.20 USD/kg, depending on the plant's size and the biomass type. (Nikolaidis & Poullikas, 2017; Lepage et al., 2021).

4.1.2 Biomass gasification

Biomass gasification is a thermal process in which organic carbonaceous materials are converted into gaseous products, so-called product gas, and small quantities of char (Hosseini & Wahid, 2016). The fundamental difference between gasification and pyrolysis is that the main target of gasification is to obtain gaseous products, whereas the primary product from fast pyrolysis is bio-oil.

Virtually any carbonaceous feedstock can be gasified to product gas, including lignocellulosic biomass such as agricultural and forestry residues. Prior to entering the gasification reactor, the feedstock is typically pre-treated. This may include, e.g., milling to reach a homogeneous feedstock in terms of size (ETIP, 2021). Gasification occurs in a reactor, the so-called gasifier, at temperatures between 700 and 1200 °C in the presence of an oxidizing agent that may be air, pure oxygen, steam, or combinations of these. For biomass, operating pressure of 4–5 bar is often considered optimal (Szul et al., 2021). The gas-phase product obtained mainly consists of H₂, CO, CO₂, and CH₄, plus

low quantities of other hydrocarbons and contaminants, such as tar and ash (Couto et al., 2013). The ratio of these products is influenced by the biomass type and the processing technology. Equations 7 and 8 represent the transformation of biomass into product gas when it reacts with air or steam.



Using steam as an oxidizing agent enhances hydrogen formation and produces a high heating value gas with no nitrogen (Arregi et al., 2018), therefore considered the preferred method for H₂ production. The main steps in biomass steam gasification are; drying, thermochemical decomposition (pyrolysis), and char conversion (gasification or combustion). The pyrolysis step can be further divided into two stages; in the first step, the biomass is thermally decomposed into gases (H₂, CO, CO₂, CH₄), tar, and char. In the second stage, tar cracking occurs, producing CO, CO₂, H₂, heavier hydrocarbons, and inert tar (Karlbrink, 2015). A schematic representation of the biomass steam gasification process for H₂ production is illustrated in Fig. 7.

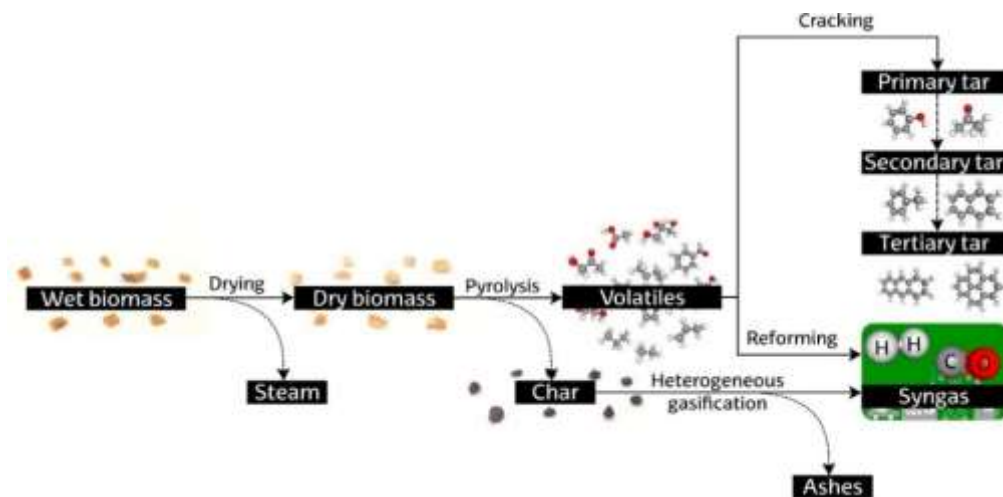


Figure 7. Schematic representation of the biomass steam gasification process (Arregi et al., 2018)

Gasification reactors are typically classified into entrained flow, fluidized bed, and moving or fixed bed systems. The dual fluidized bed (DFB) process has recently received great attention both in academia and the industry. This gasification system consists of two fluidized bed reactors, a gasifier and a combustor, interconnected by the bed material circulating between them (Fig. 8). The pre-treated biomass is fed into the gasifier, where it is devolatilized and partially gasified with steam. The unconverted fraction of biomass, i.e., the unreacted char, is transported together with bed material from the gasifier to the combustion reactor, where it burns, producing heat. The hot bed material is then transported from the combustor to the gasifier, providing heat for the endothermic gasification reactions. Fluidized loop seals ensure that the product gas from gasification and flue gas from combustion remain separated (Binder et al., 2018). Depending on the desired conditions, this can be the only fuel source for the combustor, or additional fuel can be fed to the combustor to increase the temperature level of the process (Myöhänen et al., 2018).

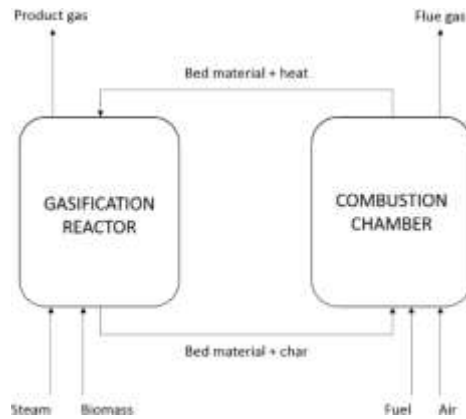


Figure 8. Principle of the dual fluidized bed process (Karlbrink, 2015)

The typical product gas composition of the DFB gasification from woody biomass is 35–45 vol% H₂, 22–25 vol% CO, 20–25 vol% CO₂, 10 vol% CH₄, and tar 20–30 g/m³. Hence, gas upgrading and cleaning unit operations, such as WGSR, scrubbers, and PSA unit, are necessary to enhance H₂ yield and remove bulk CO₂ and trace components like H₂S, HCl, and tar. (Binder et al., 2018). Hydrogen yield up to 0.14 kg per kg of biomass (dry and ash-free basis) have been reported for biomass gasification combined with catalytic steam reforming and water-gas-shift reactors (Corella et al., 2008).

Despite the high maturity of single units, such as dual fluidized bed reactors, WGSR, and PSA units, complete process chains for hydrogen production have yet to be demonstrated on a commercial scale. The complete process chains are evaluated at TRL 5–7 (Binder et al., 2018; Nikolaidis & Poullikas, 2017). However, several gasification plants producing syngas for heat and power production (e.g., Vaasan Voima, former Vaskiluodon Voima) or to be used for producing biofuels (e.g., GoBiGas in Gothenburg, Sweden) have been built and started operation and can provide best practices and lessons learned for hydrogen production as well. Moreover, the process chain is based on the utilization of developed and technologically proven operation units (TRLs of 8 and above for DFB gasification, gas cleaning, and upgrading), so the development of the process chain to market maturity could be achieved in the near future (Binder et al., 2018).

Of all biomass thermochemical processes, steam gasification provides the highest stoichiometric yield of hydrogen (Parthasarathy & Narayanan, 2014). The production cost of H₂ via biomass gasification is estimated between 1.2 and 2.4 USD/kg (Parthasarathy & Narayanan, 2014), depending on the facility size and biomass type.

4.1.3 Supercritical water gasification

One of the main problems related to the conventional thermochemical processes described above is the difficulty of using biomass with high moisture content. For example, steam gasification technology is best suited for biomass having a moisture content of less than 35 % (Parthasarathy & Narayanan, 2014). Supercritical water gasification (SCWG) is a promising technology platform for processing biomass feedstocks and residues with high moisture content, including manures, sewage sludge, food waste, and aquatic biomass such as algae (Adams et al., 2018). Supercritical water gasification can directly use the wet biomass without an energy-intensive drying process since the reaction takes place in the water phase.

SCWG involves the decomposition of organic compounds using water as the conversion medium (Adams et al., 2018). At supercritical conditions ($T \geq 374$ °C and $P \geq 22.1$ MPa), the properties of water, such as density, dielectric constant, viscosity, and solvating power, are quite different from those of liquid water or steam. In the supercritical region, water behaves like a non-polar organic solvent. Organic compounds that are only sparingly soluble in normal liquid water become completely miscible with supercritical water. (GA, 1997) In addition, thanks to the aqueous environment, SCWG can boost steam reforming and water-gas shift reactions, thus allowing to obtain a syngas very rich in hydrogen (Castello, 2013).

SCWG mainly involves three reactions; steam reforming, water-gas shift, and methanation reactions. In steam reforming, supercritical water reacts with organic feedstock and produces gaseous mixtures of H_2 and CO. The CO generated in the first reaction then reacts with water producing H_2 and CO_2 via the water-gas shift reaction. In the methanation reaction, CO from steam reforming and H_2 from water-gas shift react to produce CH_4 and water as end products. (Hosseini & Wahid, 2016) The syngas produced is rich in hydrogen or methane, depending on the reaction conditions. At temperatures near to the critical point of water, methane is the preferred product (Correa & Kruse, 2018), while hydrogen production increases at temperatures above 600 °C. Thus, hydrogen production typically occurs at 600–700 °C (Motola et al., 2022).

The gaseous products obtained from SCWG are mainly H_2 , CO_2 and small amounts of CH_4 and other hydrocarbons. CO content is low, since CO is partially consumed by the water shift reaction. The H_2 productions reported in the literature vary widely, between 0.1 and 11 wt%, depending on the biomass type and loading, operating conditions, and catalysts used (Arregi et al., 2018).

The main advantage of SCWG is high thermal efficiency for very wet biomass and the ability to produce H_2 -rich gas with low CO and low tar in one step (Motola et al., 2022). However, the process still has severe challenges in terms of large-scale feasibility. The high energy consumption of the process is one of the most critical factors, as water has to be maintained at supercritical conditions, which increases costs (Arregi et al., 2018). In addition, SCWG still faces issues related to the lack of deep knowledge of operation with different feedstocks. A wide range of potential process designs and the optimal process parameters still need to be established together with advanced materials to avoid corrosion in severe operating conditions (Motola et al., 2022). As a result, the technology has only been investigated at pilot scale, and although promising results have been obtained, the TRL is 4–5 (Lepage et al., 2021).

4.2 Microbial processes

Microbial biomass conversion processes utilize the ability of microorganisms to consume and digest biomass and release hydrogen (EERE, 2023). Microbial biomass conversion is particularly interesting in waste management and enables the conversion of, e.g., agricultural waste and agri-food effluents. In addition, investigations on sewage sludge have recently increased because the nature of the material is favourable to its conversion through biological processes (Lepage et al., 2021). The main advantages of biological processes compared to thermochemical routes are lower operating temperatures (30–60 °C) and pressures (1 atm) (Lepage et al., 2021), which reduce energy costs. In addition, the microorganisms used can be easily regenerated by replication, decreasing the turnover frequency compared with chemical catalysts, which are easily deactivated during thermochemical conversions (Abdalla et al., 2018).

There are two main pathways: applying anaerobic microorganisms, referred to as dark fermentation, or applying photosynthetic microorganisms, referred to as photo fermentation. The principal difference between the two pathways is the energy source for biomass-decomposing bacteria. In

photo fermentation, the bacteria take up energy from sunlight, whereas in dark fermentation, the bacteria take up energy from biomass (EERE, 2023).

4.2.1 Dark fermentation

Dark fermentation is the best-understood biotechnological H₂ production method. It is also considered the most attractive process for biological H₂ production due to low net energy input, the low demand for light (unlike the photosynthetic routes), versatile substrate utilization, including lower-value waste as raw materials (Dzulkarnain et al., 2022; Abdalla et al., 2018), and the possibility of integrating it with other processes, e.g., methane production processes (Łukajtis et al., 2018).

Dark fermentation produces biohydrogen using anaerobic bacteria on carbohydrate-rich substrates under anoxic conditions in the absence of light. The process converts organic matter in two stages; hydrolysis, where molecules are broken down, and acidogenesis, where the hydrolysis products are converted into H₂, CO₂, alcohols, and organic acids (Bastidas-Oyanedel et al., 2015). Pre-treatment processes needed to improve substrate bio-degradability include various physical (e.g., heat), chemical (e.g., acids), physicochemical (e.g., steam explosion), and biological (e.g., use of enzymes) techniques (Bundhoo et al., 2015). In addition, a separation step is required to produce high purity hydrogen. The main process steps of dark fermentation for H₂ production are described in Fig. 9.

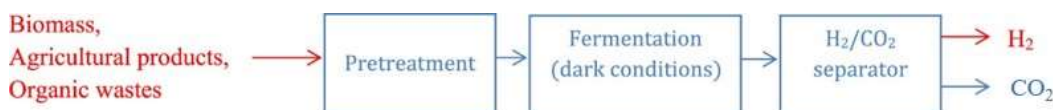


Figure 9. Flow diagram of the dark fermentation process (Nikolaidis & Poullikas, 2017)

The H₂ yield of the process depends on a series of factors: pH, temperature, pressure, the hydraulic retention time for continuous process, partial pressure of hydrogen, substrate composition, and the kind of microorganisms used (Łukajtis et al., 2018). Furthermore, the fermentation process produces organic acids (volatile fatty acids), which can depress hydrogen yield by diverting the metabolic pathway toward organic chemical production. In addition, these by-products require subsequent wastewater treatment, adding system complexity and costs. The volatile fatty acids pathway needs to be eliminated to maximize H₂ production and simplify the process, or it needs to be taken advantage of by integrating fermentation with other systems. (Holladay et al., 2009) Organic acids recovered from the fermentation process could be further converted into biofuels or serve as an inexpensive and sustainable carbon substrate for, e.g., fine chemicals or bioplastics production.

Dark fermentation has the potential to integrate waste management into energy production. Several pilot facilities are in operation, but no commercial-scaled plants have been constructed (ETIP, 2021). The main factor limiting its development on an industrial scale is the low H₂ yield and production rate compared to thermochemical processes. Hydrogen yield for dark fermentation varies from 0.004 to 0.044 kg H₂/kg of feedstock (Lepage et al., 2021), which is low compared to, e.g., biomass steam gasification with H₂ yield of up to 0.14 kg H₂/kg biomass. Today, the technology has a TRL of around 5 (ETIP, 2021). Valorisation of fermentation by-products could enhance the energetic gains and increase the economic profitability of dark fermentation, leading to an improved industrial potential of this technology (Baeyens et al., 2020).

4.2.2 Photo fermentation

The second microbial biomass conversion process is photo fermentation. As the name suggests, photo fermentation is a light-dependent process. In photo fermentation, the carbon source is converted to biohydrogen using photosynthetic bacteria, typically purple non-sulphur bacteria. The key addition to the whole process is light energy. Under anaerobic conditions, photosynthetic bacteria utilize light energy to break organic acids into H^+ , CO_2 , and electrons. The nitrogenase enzyme, synthesized by purple non-sulphur bacteria, then combines the electrons with a proton to produce molecular hydrogen. (Melitos et al., 2021) Fig. 10 illustrates a schematic diagram representing the H_2 production by photo fermentation. As with dark fermentation, various pre-treatment processes are used to improve hydrogen production.

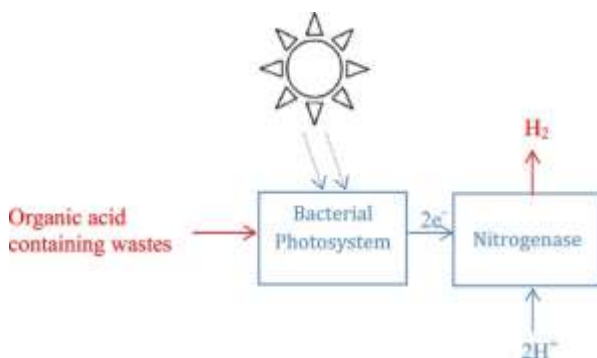


Figure 10. Flow diagram of the photo fermentation process (Nikolaidis & Poullikas, 2017)

The photo fermentation process is an attractive clean energy production approach due to the mild reaction conditions (ambient temperature and pressure) and the use of solar energy. In addition, purple non-sulphur bacteria can utilize a wide range of substrates, such as agricultural and forestry residues, forestry, industrial and domestic waste, algae, and animal manure (Hitam & Jalil, 2020). However, several difficulties have been identified. For example, photosynthetic bacteria have limitations in capturing sunlight energy, which may result in low light conversion efficiency. In addition, the cell shadowing effect, and if industrial effluents are used as a feedstock, the colour of wastewaters reduces light penetration inside the photoreactor, diminishing the light intensity and hydrogen production capacity. Consequently, a huge surface area exposed to the light source would be essential for large-scale applications to realize an efficient anaerobic photobioreactor. (Hitam & Jalil, 2020; Nikolaidis & Poullikas, 2017; Melitos et al., 2021) In addition, the unstable output of biohydrogen in continuous operation, the slow productivity and low hydrogen yield compared to thermochemical processes, and the high cost hinder the commercial application of photo-fermentative biohydrogen production (Zhang et al., 2021).

The research on biohydrogen production by photo fermentation is still at the laboratory level, and the technology's TRL is estimated at 4 (Zhang et al., 2021; ETIP, 2021). Intense R&D efforts are still needed to improve its performance and applicability in practical applications. In general, the hydrogen yields of photo fermentation are in the same range as in dark fermentation. However, due to higher costs, photo-fermentation is considered economically less competitive than dark fermentation (ETIP, 2021).

4.2.3 Two-stage fermentation

Higher hydrogen production yields and reduced light energy demand can be obtained using a two-stage fermentation process consisting of sequential dark and photo-fermentation periods. In the first step, carbohydrate-rich biomass is decomposed by anaerobic bacteria by dark fermentation to

produce H_2 and organic acids. The organic acids formed in the dark fermentation step are then further degraded by photosynthetic bacteria to produce additional hydrogen (Fig. 11). (Nikolaidis & Poullikas, 2017; Lepage et al., 2021)

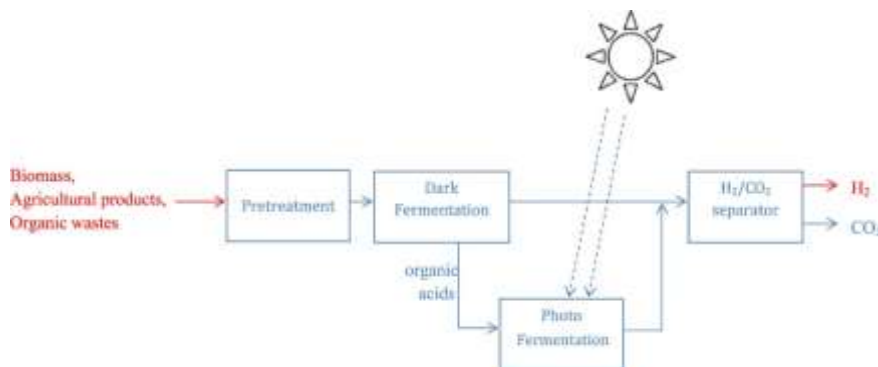


Figure 11. Flow diagram of the sequential dark and photo fermentation process (Nikolaidis & Poullikas, 2017)

An integrated dark and photo fermentation system can lead to higher biohydrogen production than a single process. However, the difficult operations to control the different bacteria and the parameters between the separate stages pose significant challenges (Lepage et al., 2021). Therefore, more detailed studies are needed to evaluate the viability of industrial biohydrogen production through two-stage fermentation.

In summary, although biological processes are considered more environmentally friendly and less energy intensive than thermochemical processes, they provide relatively low hydrogen yields, requiring large reactor volumes. Thermochemical conversion processes are also much faster than the biochemical methods (Nikolaidis & Poullikas, 2017; Abdin et al., 2020). Therefore, the possibilities of biomass in large-scale H_2 production are seen mainly via thermochemical routes, whereas the potential of biological processes is more in small-scale hydrogen production or centralized waste recycling and processing (Nikolaidis & Poullikas, 2017).

4.3 Combination of anaerobic digestion and biogas CO_2 reforming

Chapter 3 introduced technologies suitable for hydrogen production from pure biomethane. However, hydrogen could be produced from raw biogas as well. The high levels of CO_2 (35–55%) in raw biogas enable biogas conversion to synthesis gas (H_2 and CO) via CO_2 reforming, also called dry reforming, avoiding the high cost of the purification process to separate CO_2 from CH_4 (Kalai et al., 2018).

Biogas dry reforming takes advantage of the CO_2 in the biogas stream. CO_2 , the completely oxidized form of carbon, is used as an oxidizing agent for methane conversion to syngas. The main reaction of biogas dry reforming is shown in Eq. 9. Since CO_2 is very stable, getting it to interact as an oxidant requires a significant amount of energy (Balaji et al., 2020) and high temperatures, usually in the range of 800–1000 °C (Kalai et al., 2018), are required to achieve high reagent conversions. High temperatures are also needed to minimize the coke formation on the catalyst. Before being transferred to the reforming reactor, biogas should be scrubbed of impurities, including siloxanes and sulphur species, as they may cause catalyst poisoning (Zhao et al., 2020). The water vapor, naturally present in the biogas, does not need to be removed as it favours the occurrence of water-gas-shift reaction, improving H_2/CO ratio (Balaji et al., 2020). To enhance H_2 yield, the syngas can

be further treated in a water-gas-shift reactor. The H₂ content in the syngas reaches its highest amount when equal moles of CH₄ and CO₂ are present in the reformer feed (Hajizadeh et al., 2022).



Hajizadeh et al. (2022) demonstrated that 150 m³/d of cow manure (6 % total solids and 80 % volatile solids) fed to the anaerobic digester operating at 20 °C could produce 553.5 m³/d biogas. From the produced biogas, 195 kg of H₂/d could be obtained through CO₂ reforming + WGS reaction.

CO₂ reforming is definitely a promising process for producing H₂ from biogas, especially considering that the process can take full advantage of both CH₄ and CO₂ in biogas. However, some serious problems are involved in biogas dry reforming, hindering its commercialisation. For example, the high temperatures required for endothermic dry reforming reaction may lead to catalyst support collapse or metal sintering. In addition, a significant problem related to the dry reforming reaction of methane is the coke generation. This process can destroy the catalyst or block the reactor quickly. Catalyst nature affects the coke formation rate, so current research efforts have focused on developing highly stable catalysts with low carbon production (Kalai et al., 2018). Bimetallic Ni-Co is usually employed to take advantage of both metals in controlling coke and catalyst deactivation (Hajizadeh et al., 2022).

In addition to catalyst development, carbon deposition can be significantly inhibited by adding steam in the dry reforming process (Zhao et al., 2020). With steam addition, CO₂ reforming is coupled with steam methane reforming, described above in Chapter 3. Combined CO₂ and steam reforming of methane is referred to as bi-reforming. Methane tri-reforming, a combination of three methane reforming processes, i.e., CO₂ reforming, SMR, and partial oxidation reforming, has also been investigated. Theoretically, the tri-reforming process could avoid the main disadvantages mentioned for biogas dry reforming. The presence of H₂O and O₂ reduces the possible coke generation on the catalyst surface. In addition, WGS reaction also occurs, contributing to higher H₂ yields. Furthermore, adding O₂ leads to an exothermic partial oxidation reaction, significantly reducing energy requirements. (Izquierdo et al., 2013) However, most studies on tri-reforming reactors are still of a theoretical nature. Compared to other methane reforming processes, the implementation of the tri-reforming process has more technical challenges and requires a thorough understanding of the effects of different parameters individually and in interaction with each other during this process (Soleimani & Lehner, 2022).

The role of CO₂ reforming in the future large-scale H₂ production is still debatable as there are still many questions on how to improve the catalyst performance and selectivity to H₂ (de Medeiros et al., 2022). However, a few examples were found. One example of commercialized CO₂ reforming processes is CALCOR™ (Caloric, 2023). The primary target of the CALCOR™ process is to produce synthesis gas with a high CO content. The SPARG™ process, designed by Haldor-Topsoe and commercialised by Sterling Chemical Inc., is a bi-reforming process capable of delivering syngas with an H₂/CO ratio of 1.8-3.0 (Mortensen & Dybkjær, 2015). Another example of bi-reforming technology is the DRYREF™ technology developed by Linde and BASF (Linde, 2023). This process produces syngas with H₂/CO ratio of 1.0–3.0, suitable for several downstream processes, such as methanol and acids synthesis (de Medeiros et al., 2022). The DRYREF™ technology is currently in commercial demonstration. As such, none of these targets the production of H₂ as the final product. However, they can provide valuable information about the advantages and limitations of CO₂ reforming technology.

5 Hydrogen production via water splitting

Water is the most abundant resource for hydrogen production. Water can be split into hydrogen and oxygen if enough energy is provided. Water splitting in its simplest form uses an electric current through two electrodes to split water into hydrogen and oxygen. The process is known as electrolysis. However, water can also be split with other energy sources, such as thermal energy (thermochemical water splitting) and photon energy (photoelectrochemical water splitting), or through photobiological methods using microorganisms (Megia et al., 2021). These processes all utilize some method to split water according to the following reaction (Eq. 10):



5.1 Electrolysis of water

The basic principle of electrolysis is to split H₂O into oxygen and hydrogen with the help of electricity. It is a well-established technology that has been used for almost a century for various applications in the industry, such as food processing and metallurgy. Nowadays, it is also considered a key process for producing hydrogen from water and renewable energy sources (Ursua et al., 2012). The conversion is fast and straightforward and the hydrogen obtained with this technology has a high purity that can reach 99.999 vol.%, which is suitable for a wide range of applications, including fuel cells and chemical production. In addition, there are no carbon, sulphur, or nitrogen by-product compounds (Lepage et al. 2021), which simplifies the purification step compared with those of, e.g., gasification processes. Hydrogen produced via electrolysis can result in zero greenhouse gas emissions, depending on the source of the electricity used.

The core of an electrolyser is the electrolytic cells. Electrolytic cells are composed of two electrodes – a positively charged anode and a negatively charged cathode – immersed in a liquid electrolyte or adjacent to a solid electrolyte membrane (Irena, 2020). When voltage is supplied, water splits and hydrogen is produced at the cathode while oxygen is evolved on the anode side. The electrolyte is needed to provide the necessary conductivity for the electrical current to flow through the water. In addition, a membrane or diaphragm between the electrodes is needed to spatially separate the two reactions and prevent the product gases from mixing. Catalysts are used in order to increase current density and rate of electrolysis reactions (Dincer & Acar, 2015).

Electrolysers are typically divided into three main technologies: alkaline electrolysers (AEL), proton exchange membrane (PEM) electrolysers, and solid oxide electrolysers (SOEL). These methods differ mainly according to the ion transport method or the type of electrolyte used. While the low-temperature technologies, AEL and PEM, both provide high technology readiness levels, the high-temperature SOEL technology is still in the development stage and not yet widely commercialised (Tenhumberg & Bükler, 2020). Table 1 summarises the parameters of state-of-the-art AEL, PEM and SOEL water electrolysis. The principle layout, reactions, and related properties of these technologies are then discussed in more detail in subsections 5.1.1.-5.1.3. In addition, the latest technology, anion exchange membrane (AEM) water electrolysis, is briefly described in section 5.1.4. Finally, subsection 5.1.5 presents an overview of the leading electrolysis equipment manufacturers.

In practice, electrolyser devices consist of several interconnected electrolysis cells, called stacks. At the systemic level, the electrolysis process also comprises the power supply (e.g., transformer and rectifier) and possibly electricity buffers, water supply and purification (e.g., deionization), hydrogen

processing (e.g., purification, drying, and compression), and possible hydrogen storage, etc. (Irena, 2020).

Table 1. Summary of parameters of state-of-the-art water electrolysis (Tenhumberg & B ker, 2020; Irena, 2020; Buttler & Spliethoff, 2018)

Technology	AEL	PEM	SOEL
Electrolyte	20–40 wt% KOH	PFSA membranes	Solid ceramic (YSZ)
Operating temperature (�C)	60–90	50–80	700–900
Typical operating pressure (bar)	10–30	20–50	1–15
Current density (A/cm ²)	0.2–0.8	0.6–2.0	0.3–2.0
Specific energy consumption, stack (kWh _{el} /Nm ³ H ₂)	4.2–4.8	4.4–5.0	>3.0
Specific energy consumption, system (kWh _{el} /Nm ³ H ₂)	5.0–5.9	5.0–6.5	3.7–4.7
Gas purity (%)	> 99.95	99.99	99.90
Load flexibility (% of nominal load)	15–100	0–100	–100/+100
Cold start-up time (min)	60	<20	>600
Warm start-up time (s)	60–300	< 10 s	900
System response	seconds	milliseconds	seconds
Stack lifetime (h)	60 000–90 000	20 000–60 000	<20 000
Stack unit size	up to 6 MW	up to 2 MW	5 kW
Maturity	mature	commercial	demonstration
Capital cost, stack (1 MW) (USD/kW)	270	400	<2000
Capital cost, system (>10 MW) (USD/kW)	500–1000	700–1400	unknown

5.1.1 Alkaline electrolysis

Of the different water electrolysis technologies, alkaline electrolysis is the most established and mature (TRL 9). AEL plants of up to 160 MW are already operating on an industrial scale (Tenhumberg & B ker, 2020).

Fig. 12 depicts a scheme of an alkaline electrolysis cell. The two electrodes (anode and cathode) are immersed in a liquid alkaline solution, typically potassium hydroxide (KOH) in a concentration between 20 wt% and 40 wt% (Tenhumberg & B ker, 2020). The two electrodes are separated by a porous diaphragm that allows ionic transport but is impermeable to gases. When sufficient voltage is applied, water is split at the cathode to form H₂ and release negatively charged hydroxide anions (OH⁻). The OH⁻ ions then cross through the diaphragm and combine to form O₂ at the anode.

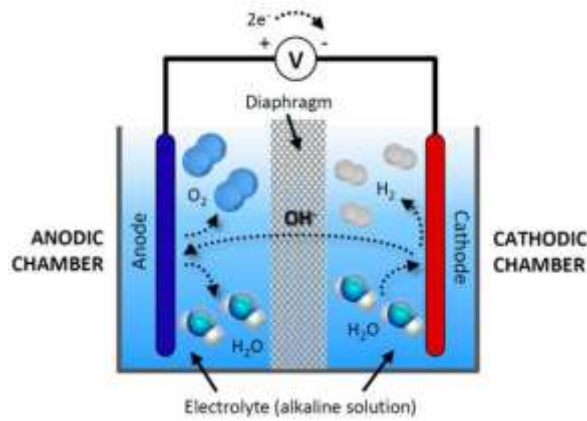


Figure 12. General scheme and operation of an alkaline electrolysis cell (Rodriguez & Amores, 2020).

The two-phase liquid electrolyte and product gas mixture leave the electrolysis cell and enter subsequent gas separators. The product gas is demisted, dried, and prepared for usage, and the liquid electrolyte leaving the gas separator is pumped back to the electrolysis stack (Brauns & Turek, 2020). Neglecting physical losses, the liquid electrolyte is not consumed. Instead, water is consumed in the process and has to be supplied continuously.

AEL units generally work between 60 and 90 °C and deliver high-purity hydrogen up to >99.95 % purity (Tenhumberg & Bükér, 2020). The system temperature has to be in an optimal range to maintain an efficient operation. Temperatures above 90 °C should be avoided with a suitable cooling system to prevent degradation issues of the electrolysis cells and material restrictions (Buttler & Spliethoff, 2018). A typical operating pressure is 10–30 bar (Tenhumberg & Bükér, 2020).

Rated efficiency and specific energy consumption of AEL electrolysis stacks are in the range of 63–71 % LHV and 4.2–4.8 kWh/Nm³ of H₂ (Buttler & Spliethoff, 2018). However, the system comprises not only the electrolyser unit but also auxiliaries, such as feed water preparation, the power supply system, heat management, pressure control, and hydrogen gas treatment (Fig. 13). The additional consumption of auxiliaries and losses by rectification lies typically in the range of 0.4–0.8 kWh/Nm³ of H₂, giving the specific energy consumption of the entire AEL electrolysis system in the range of 5.0–5.9 kWh/Nm³ of H₂ (system efficiency 51–60 %) (Buttler & Spliethoff, 2018).

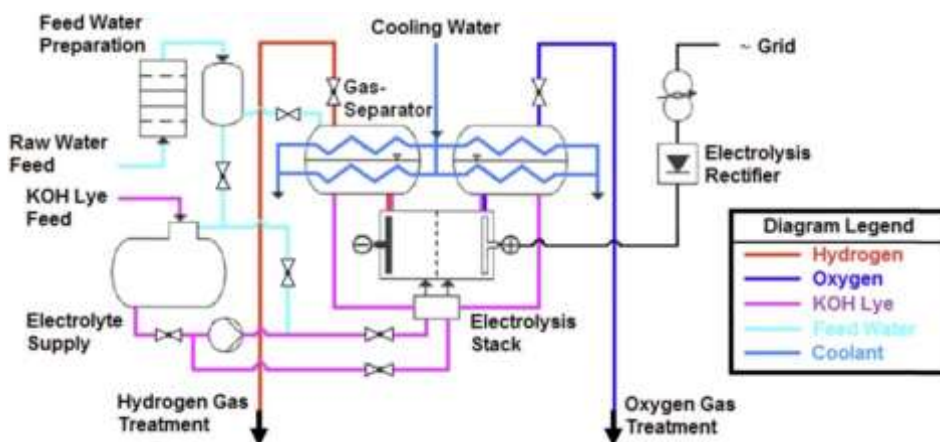


Figure 13. Layout of an alkaline electrolysis system (Buttler & Spliethoff, 2018).

One of the main advantages of AEL is its scalability. AEL cells are highly stackable, providing highly scalable technology (Anwar et al., 2021). Alkaline electrolysis can be scaled up or down depending on the size of the hydrogen production plant needed. This makes it suitable for a wide range of applications, from small-scale hydrogen production for fuel cells to megawatt-scale industrial hydrogen production. Robust alkaline water electrolysis systems also offer the longest stack lifetime of existing electrolysis technologies. Another advantage of AEL systems over other water electrolysis technologies is their lower cost, as they do not require expensive noble materials, which is a limitation of PEM technology, and can be operated at relatively low temperatures, hence not requiring high temperature resistant construction materials such as SOEL technology (de Groot et al., 2022).

Traditionally, the major weakness of alkaline technology has been its relatively low current densities (0.2–0.4 A/cm²), leading to low performance profiles (Anwar et al., 2021) and making these electrolyzers large and heavy compared to other technologies for similar production rates (de Groot et al., 2022). The low current density is caused by the poor current-voltage curve, which primarily results from a high ohmic resistance. This high ohmic resistance was almost unavoidable in old alkaline electrolyzers when only thick asbestos diaphragms were sufficiently stable in the strongly alkaline environment (de Groot et al., 2022). However, with new and thinner diaphragm materials, developing AEL systems that can operate at significantly higher current densities is now possible. A vast amount of research has also been devoted to searching for new, more efficient electrocatalysts and improved cell concepts. An example of improved cell concepts is the zero-gap concept, where the electrodes are directly pressed onto the diaphragm to minimize ohmic losses due to the electrolyte (Brauns & Turek, 2020). Advanced zero-gap AEL can be operated at a significantly higher current density, thus more efficiently, than conventional alkaline electrolyzers (de Groot et al., 2022).

Another weakness of alkaline electrolysis is that the minimum load of the AEL is typically limited to 15–25 % of the nominal hydrogen production due to the lateral diffusion of hydrogen through the diaphragm to the oxygen side, resulting in the formation of a combustible mixture at low production. In practice, safety stops occur with 1–2 % hydrogen contamination in the oxygen stream (Buttler et al., 2018). A novel approach under investigation is modifying the AEL technique using anion exchange membranes instead of diaphragm membranes (Anwar et al., 2021), to eliminate the gas crossover between the anodic and cathodic sides (see section 5.1.4.).

Alkaline electrolyzers also suffer from slow system response to dynamic operations. This slow response is due to the liquid electrolyte used, slowing down the movement of the hydroxide ions from the cathode to the anode (Yodwong et al., 2020). Indeed, most recent AEL technology improvements are focused on dynamic operation with intermittent renewable energies (Tenhumberg & B ker, 2020). In this context, the most important development targets are 1) high ramp speed, 2) low minimum turndown, and 3) improved start-up times after periodical shutdowns (L ke & Zschocke, 2020).

Moreover, much research regarding alkaline electrolysis has been devoted to searching for new highly active electrocatalyst materials. Nickel is the most commonly used catalyst material due to its accessibility with low cost (Anwar et al., 2021). In addition to good electrocatalytic activity, nickel has a good corrosion resistance under alkaline conditions. However, due to the lower electrocatalytic activity of nickel compared to noble metals, combining it with other metals to form alloys such as molybdenum, iron, or aluminium is often necessary. For example, MoO₂-Ni arrays have recently been reported to exhibit a platinum-like activity at low temperatures (Martino et al., 2021). Another common approach is to increase the surface area of the catalyst that remains exposed to the electrochemical reactants. This can be accomplished by, e.g., nanoengineering the catalyst morphology and structure (Karacan et al., 2022).

Two examples of ongoing AEL projects in the Nordic countries are HySynergy (Denmark) and HYBRIT (Sweden/Finland). The purpose of HySynergy, a collaborative project between hydrogen fuel company Everfuel and Shell Denmark, is to establish a large-scale production and storage facility of green hydrogen. The first phase of HySynergy involves the installation of a 20 MW alkali electrolysis plant in 2022–2023 in Fredericia, Denmark – but the partners eventually aim to expand the plant up to 1 GW by 2030 (Everfuel, 2023). HYBRIT (Hydrogen Breakthrough Ironmaking Technology) is an initiative between steel producer SSAB, mining company LKAB, and Vattenfall, intending to develop the world's first fossil-free ore-based steelmaking technology, where coal will be replaced by fossil-free hydrogen. The pilot plant in Luleå was commissioned in August 2020. The 4.5 MW alkaline electrolyser to the pilot plant was delivered by Nel ASA. The next step is planned for 2026 with a demonstration plant for fossil-free steel production on an industrial scale in Gällivare, using approximately 500 MW electrolyser capacity powered by fossil-free electricity (Hybrit, 2023).

5.1.2 Proton exchange membrane electrolysis

Another commercially available electrolysis technology is proton exchange membrane electrolysis. PEM-based water electrolysis has gained popularity in recent years due to its high performance and the ability to work under variable power feeding regimes (Sood et al., 2020). Short start-up and fast response times make PEM electrolysis the most suitable technology for dynamic operation associated with intermittent energy sources.

The structure of the PEM electrolyser is similar to that of the alkaline electrolyser. The main difference is the use of a solid polymer electrolyte membrane (a thin plastic film), which is responsible for transporting ions from one electrode to the other and, at the same time, physically separating the produced gases. In the PEM electrolysis process, only deionized water is injected into the cell; there is no need to add a liquid electrolyte solution as the ion transport happens within the proton-conducting membrane component (Irena, 2020). The reaction principle of the PEM electrolyser is shown in Fig. 14. Water is fed to the anode side of the cell, where it is split into oxygen, protons (H^+), and electrons (e^-). The O_2 formed during this half-cell reaction is removed with the unconsumed water, and the H^+ pass through the proton-conducting membrane towards the cathode. The electrons exit from the anode through an external power circuit. At the cathode side, the protons combine with the electrons from the external circuit to form hydrogen gas. The water feed to the cathode side is optional, as it is only there to facilitate the efficient removal of hydrogen (Sood et al., 2020).

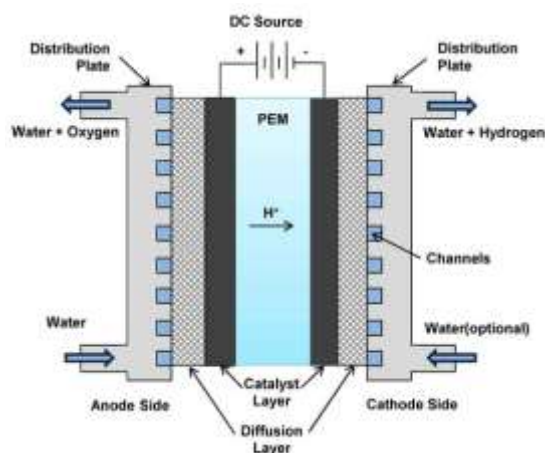


Figure 14. Schematics of PEM electrolyser cell (Sood et al., 2020)

The reactions take place at the catalyst layers coated on electrodes. The diffusion layer on each side ensures efficient current distribution and connects the membrane electrode assembly to the bipolar plates (distribution plates). Bipolar plates contribute to the structural integrity of the cells. They also separate one cell from the other when cells are assembled together as a stack to deliver the required hydrogen flow rate. In addition to the cell/stack, an electrolyser has auxiliary components to ensure the proper functioning of the stack. These include, e.g., the power supply/voltage controller, inlet water conditioning system, water circulation system, water–gas separators, heat exchanger, and safety devices. (Sood et al., 2020)

PEM features a very low cross-permeation, yielding hydrogen with higher purity than AEL, typically greater than 99.99 % H₂ after hydrogen drying (Buttler & Spliethoff, 2018). In addition, the very low gaseous permeability of the polymeric membranes lowers the risk of the formation of flammable mixtures; hence, operating at the full load range (0–100 %) is possible (Ursua et al., 2012). Another significant advantage of PEM over AEL is that it can perfectly deal with load fluctuation due to its rapid response (milliseconds). Further advantages of PEM electrolysis include high current density due to the low ionic resistance of polymer membranes, compact module design due to the solid electrolyte, small footprint, fast start-up, and low operating temperatures (Buttler & Spliethoff, 2018; Kumar & Himabindu, 2019).

The rated efficiency and specific energy consumption of commercial PEM electrolysis stacks are 60–68 % LHV and 4.4–5.0 kWh/Nm³ of H₂. The specific energy consumption of the entire PEM electrolysis system, including power consumption of auxiliaries and losses by rectification, is in the range of 5.0–6.5 kWh/Nm³ of H₂, corresponding to system efficiency of 46–60 %. (Buttler & Spliethoff, 2018)

The main problem of PEM electrolysers is the high investment cost; PEM systems for water electrolysis are generally 50–60 % more expensive than alkaline ones. High costs are mainly associated with the noble materials used inside the electrolyser. The acidic environment provided by the proton exchange membrane, high voltages, and oxygen evolution in the anode creates a harsh oxidative environment, demanding the use of materials that can withstand these conditions. Titanium-based materials, noble metal catalysts and protective coatings are necessary, not only to provide long-term stability to cell components, but also to provide optimal electron conductivity and cell efficiency. (Irena, 2020)

The corrosive acidic regime provided by PEM requires the use of noble metal catalysts like iridium (Ir) for the oxygen evolution reaction at the anode and platinum (Pt) for hydrogen evolution reaction at the cathode (Buttler & Spliethoff, 2018; Anwar et al., 2021). These are expensive and with low availability, which inhibits their practical application. For example, iridium is one of the rarest elements on earth, costing 4,200 EUR per ounce (nearly 150,000 EUR/kg) at today's market prices. With 1–2kg of iridium required for standard PEM electrolyser stacks, the catalyst cost alone for a 1 MW electrolyser can add up to 300,000 EUR (Hydrogen Insight, 2022). Therefore, a central goal of R&D efforts is a drastic decrease of noble metal-based catalyst loadings.

Other key materials for PEM water electrolysis are the membrane itself, current collectors, and bipolar plates. A commercial membrane must have high mechanical strength and proton conductivity, as well as outstanding oxidative and thermal stability. At present, membranes are mainly focused on perfluorosulfonic acid (PFSA) polymer membranes. The most commonly used are Nafion membranes due to the advantages of high proton conductivity and high durability at higher current densities. However, the high price and complex disposal after the end of use restrict its development. Research efforts have been devoted to reducing the cost of these polymer membranes and simultaneously optimizing the ion exchange characteristics and stability. (Wang et al., 2022)

Current collectors, commonly referred to as a gas diffusion layer at both sides of the electrodes, are used to transfer electrons from the catalyst layer to bipolar plates and to eliminate the gases (i.e., H₂, O₂) from the catalyst layer (Yodwong et al., 2020). The porous titanium plates are the most used current collectors due to their good conductivity, excellent mechanical stability, and corrosion resistance (Wang et al., 2022). Bipolar plates are a significant cost component for PEM stacks, as they are often built to provide multiple functions, such as conducting electrons, connecting single cells to realize a stack, arranging a flow path for pure water-sharing over the current collectors, isolating hydrogen and oxygen, supporting the membrane and electrodes, and bringing thermal conduction to handle the PEM temperature (Yodwong et al., 2020). As such, they require advanced materials such as gold or platinum coated titanium. This is one of the areas where innovation can play an important role in reducing costs. Research is ongoing to replace titanium with cheaper materials (Irena, 2020).

Examples of large-scale PEM projects in Europe are the Energiepark Mainz, commissioned in 2015, and HyBalance project in Denmark. The research facility Energiepark Mainz was built to provide ancillary services for a local power grid and to explore the possibilities of the PEM electrolysis technology on a large scale. Three electrolysis skids with a peak power of 6 MW_{el} and an output of 1000 Nm³ hydrogen per hour were designed by Siemens. The plant is located in Mainz, Germany, grid-connected to an 8 MW wind farm (Kopp et al., 2017). The HyBalance plant in Hobro, Denmark, is another example of Europe's first facilities to produce hydrogen by PEM electrolysis on an industrial scale. It has successfully produced and delivered hydrogen since 2018. The plant has also demonstrated its ability to accommodate the intermittency of renewable energy production, thus stabilizing the Danish electric grid. (Air Liquide, 2020). The 1.2 MW HyBalance electrolyser was supplied by Hydrogenics.

In May 2023, US-based Plug Power Inc. announced plans to build three green hydrogen production plants in Finland with a total electrolysis capacity of 2.2 GW. The plants are expected to produce 850 tons per day (TPD) of green hydrogen by the end of the decade. The Kokkola facility will see 1 GW of electrolytic capacity installed to produce 85 TPD of green hydrogen and 700 kilotons of green ammonia per year. These will be both used locally and exported across Europe. The Kristiinankaupunki facility will create a further 1 GW of electrolytic capacity. Based in the vicinity of a decommissioned coal plant, the green hydrogen produced will be earmarked for use in green steel production. Porvoo site will produce another 100 tons per day by 2030. The hydrogen will be used for local mobility and exported through pipeline injection to Western Europe. All three plants are intended to use Plug's PEM electrolysis technology. The final investment decision is scheduled for 2025/2026. (Hydrogen Insight, 2023)

5.1.3 Solid oxide electrolysis

Apart from alkaline and PEM hydrogen production technologies, solid oxide electrolysers are widely expected to become the third main water electrolysis technology in the foreseeable future (OIES, 2022). SOEL constitutes an advanced concept enabling water, or rather, steam electrolysis at high temperatures (700–900 °C), which enables conversion efficiencies of around 80–90 % (OIES, 2022), surpassing the efficiency of all currently existing electrolyser options. The high electricity-to-hydrogen conversion efficiency is caused by the increased possibility of supplying energy in the form of heat instead of electricity. This makes using SOEL of particular interest in situations in which a high-temperature heat source is available (Brynolf et al., 2018).

In solid oxide electrolysis, a solid oxide electrolyte, typically made of ceramic materials such as yttria-stabilized zirconia (YSZ), is used as the electrolyte. This material exhibits good ionic conductivity at

the prevailing high operating temperatures. The cathode is usually a porous YSZ-nickel cermet, while the anode is commonly a composite of YSZ and perovskites, such as lanthanum manganite or ferrites, substituted with strontium to enhance the electrocatalytic activity. (Ursua et al., 2012) The operating principle of a SOEL cell is shown in Fig. 15. The steam at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions (O_2^-). The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

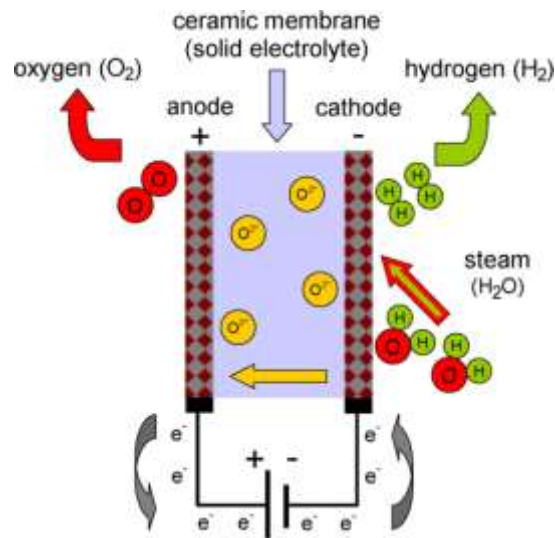


Figure 15. Scheme of the operating principle of a solid oxide electrolysis cell (Ursua et al., 2012).

The advantage of SOEL over traditional water electrolysis methods is the high electricity-to-hydrogen efficiency. The solid oxide electrolyte also eliminates the need for a liquid electrolyte, which reduces corrosion and other issues associated with liquid electrolytes. Additionally, the high operating temperature enables the utilization of waste heat or renewable energy sources such as geothermal energy.

Despite these advantages, some of its disadvantages have limited its commercialisation and broader use. Its most remarkable feature – high operating temperature – appears to be one of its main challenges as well, as it increases start-up and break-in times. This may hamper the system's coupling with intermittent renewables (OIES, 2022). The high-temperature operation also leads to mechanical compatibility issues, such as concerns about the thermal stability of brittle ceramic materials and sealing issues (Ursua et al., 2012). Consequently, solid oxide electrolyzers currently have lower durability and shorter lifetime than AEL or PEM (OIES, 2022). Moreover, the stream leaving the cathode is a mixture of hydrogen and steam that requires further processing, resulting in higher capital costs than conventional liquid water electrolysis (Ursua et al., 2012). Bulky system design and small available production scale also leave space for further improvements.

Although SOEL is considered a promising technology and has been extensively researched, it has not yet been widely commercialised. However, some examples were found. In April 2023, Germany-based company Sunfire installed a 2.6 MW electrolyser, consisting of twelve SOEL modules, in Rotterdam, the Netherlands. According to Sunfire, it is the first multi-megawatt high-temperature electrolyser installed to produce green hydrogen in an industrial environment. Sunfire's electrolyser will be integrated into Neste's refinery processes and will become part of the on-site production of renewable products. Once operational, the electrolyser will produce more than 60 kg of green hydrogen per hour. (Sunfire, 2023) Moreover, Topsoe is constructing the world's first industrial-scale

SOEL manufacturing facility in Herning, Denmark. The factory will have an initial 500 MW/year manufacturing capacity. The factory is expected to be in operation by 2025. (Topsoe, 2023)

5.1.4 Anion exchange membrane electrolysis

Anion exchange membrane water electrolysis is the latest technology, with only a few companies commercialising it. AEM's potential lies in combining the less harsh environment of alkaline electrolyzers with the simplicity and efficiency of PEM electrolyzers (Irena, 2020).

AEM water electrolysis can sometimes be considered a subcategory of alkaline water electrolysis technology. The main difference between conventional alkaline electrolysis and AEM is the replacement of the porous diaphragm in AEL with a thin, dense, non-porous membrane, as in PEM. However, charges are transferred over the membrane by hydroxide ions, as in AEL water electrolysis. (Risbud et al., 2023). Replacing the traditional diaphragm in alkaline electrolysis with the polymeric anion exchange membrane allows low ohmic resistance and high gas purity as in PEM, while the alkaline working environment allows the use of inexpensive non-noble materials (Hua et al., 2023). In addition, AEM can largely eliminate the gas crossover between the anodic and cathodic sides, making it a safer and more energy-efficient solution than traditional AEL. Distilled water or a low concentration of alkaline solution can be used as an electrolyte instead of concentrated KOH. The absence of a corrosive liquid electrolyte offers advantages such as the absence of leaking and ease of handling (Vincent & Bessarabov, 2018).

Compared to PEM electrolysis, where noble metal electrocatalysts are required due to the strongly acidic environment, the operation of AEM in alkaline conditions allows cheap and abundant transition metal catalysts like nickel in the electrodes, making them more cost-effective compared to PEM electrolyzers. Moreover, the high pH of the system reduces corrosion problems of the components: titanium in the transport layers and bipolar plates can be replaced by steel. (Risbud et al., 2023) Furthermore, the quaternary ammonium ion-exchange-group-containing membranes used in AEM electrolysis are less expensive than the Nafion-based membranes in PEMs (Vincent & Bessarabov, 2018). As a result, AEM promises cheap, compact systems with fast response times.

However, the AEM technology is relatively new and faces many issues that must be solved before it realises its full potential. The OH^- ion is inherently three-fold slower (lower conductivity) than H^+ protons within PEM, forcing AEM developers to make thinner membranes or ones with higher charge density. Consequently, the AEM membrane has chemical and mechanical stability issues, leading to unstable lifetime profiles. In addition, the performance is still not as good as expected, primarily due to low AEM conductivity, poor electrode architecture, and slow catalyst kinetics. Performance enhancement is typically achieved by tuning membrane conductivity properties or adding a supporting electrolyte, e.g., KOH or sodium bicarbonate. However, such tuning could lead to decreased durability. Another major limitation of AEM is the degradation of the polymer due to KOH attack, which rapidly reduces the conductivity of the membrane. (Irena, 2020)

Examples of pioneering industrial-scale AEM manufacturers include Alchemr and Enapter. The US company Alchemr has a readily available kilowatt-scale AEM electrolyser (Alchemr, 2023). Enapter's AEM Multicore is the world's first megawatt-class anion exchange membrane electrolyser. The prototype of this MW-scale electrolyser is running in Saerbeck, Germany. On-going testing aims to optimise its operating concept during 2023. At the same time, Enapter focuses on constructing the first commercial AEM Multicore systems (Enapter, 2023).

5.1.4 Electrolyser manufacturers

Table 2 lists some of the leading European and US hydrogen electrolyser manufacturers (non-exhaustive). More information on electrolyser capacities and their technical data can be found on the companies' websites.

Table 2. Electrolyser manufacturers

Manufacturer (location)	Technology
Green Hydrogen Systems (Denmark)	Alkaline
HydrogenPro ASA (Norway)	Alkaline
John Cockerill Hydrogen (Belgium)	Alkaline
McPhy (France)	Alkaline
thyssenkrupp nucera (Germany)	Alkaline
Cummins (US)	Alkaline Proton exchange membrane
Nel ASA (Norway)	Alkaline Proton exchange membrane
Sunfire GmbH (Germany)	Alkaline Solid oxide
Elogen (France)	Proton exchange membrane
H-Tec Systems (Germany)	Proton exchange membrane
ITM Power PLC (UK)	Proton exchange membrane
Plug Power Inc. (US)	Proton exchange membrane
Siemens Energy AG (Germany)	Proton exchange membrane
Topsoe (Denmark)	Solid oxide
Enapter (Germany)	Anion exchange membrane

5.2 Thermochemical water splitting

Thermal decomposition, or thermolysis, is a chemical decomposition caused by heat. Theoretically, if we simply heat up enough, we can split water into its components, H₂ and O₂ (Torre, 2022). However, direct thermal water splitting requires very high temperatures, generally over 2500 °C (Nikolaidis & Poullikas, 2017), which makes it unsuitable for real-life applications (Torre, 2022). This main problem is solved by employing chemical reagents and dividing the water decompositions into several steps (Torre, 2022). The multi-step thermochemical water-splitting proceeds at considerably lower operating temperatures (Megía et al., 2021). In addition, thanks to a multi-step process, hydrogen and oxygen are produced in different steps, eliminating the need for costly high-temperature downstream gas separation.

A thermochemical cycle can involve 2–5 steps with operating temperatures between 500 °C and 2000 °C (Torre, 2022). In general, increasing the number of cycles lowers the temperature required to split water. Two-step thermochemical water-splitting composed of metal oxides redox pairs, such as ZnO/Zn and CeO/Ce, are attractive for hydrogen production only at high temperatures (1600–1800 °C) (Fraile et al., 2016), and they suffer from low efficiencies (Boretti, 2022). Two-step solutions also have an extremely low technology readiness level compared to those with three or four steps (Boretti, 2022).

The most developed thermochemical cycle, with TRL 4–5 (Pinsky et al., 2020; Fraile et al., 2016), is the three-step sulfur–iodine (S–I) cycle (Fig. 16). In the S–I cycle, sulfuric acid (H_2SO_4) acts as the oxygen carrier, while hydrogen iodide (HI) carries hydrogen. Both decomposition reactions are endothermic, so heat must be added to the reactants to allow the reaction to occur. On contrary, the Bunsen reaction is exothermic. The limiting reaction is the H_2SO_4 reaction due to its high-temperature requirements ($>800\text{ }^\circ\text{C}$). Chemicals are recycled throughout the system, so the inputs and outputs consist solely of water and water products. (Pinsky et al., 2020)

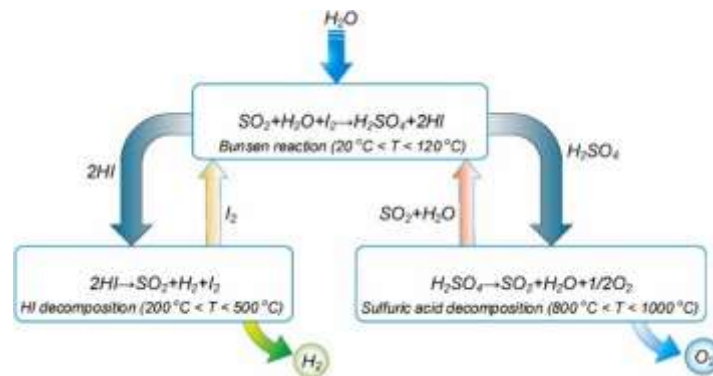


Figure 16. Three-step S–I thermochemical cycle (Karaca et al., 2023)

For S–I cycle, around 30–45 % efficiencies are reported (Nikolaidis & Poullikas, 2017; Pinsky et al., 2020, Li et al., 2022). However, with peak process temperatures above $880\text{ }^\circ\text{C}$, efficiencies above 50 % are possible (Boretti, 2022). This means that 240–400 MJ of heat, plus approximately 9 kg of water, are needed to produce 1 kg of H_2 .

Although the sulfur–iodine thermochemical cycle requires relatively high temperature, it is considered the most promising thermochemical cycle (Megía et al., 2021). Lower-temperature cycles are also under research. These include, e.g., copper–chlorine (Cu–Cl), iron–chlorine (Fe–Cl), and magnesium–chlorine (Mg–Cl) cycles (Torre, 2022). Many of these cycles can also be implemented as hybrid thermochemical cycles, meaning that the hydrogen-generating reaction is supported by at least one electrochemical step. This enables the temperature to be lowered even further but also increases the complexity of the overall system (Torre, 2022).

The major advantage of thermochemical water-splitting cycles is that they do not require catalysis to drive individual chemical reactions. Except water, all chemicals used in the thermochemical cycle can be recycled. Other advantages of thermochemical water splitting cycles include low, even zero electrical energy requirement, and no need for O_2 – H_2 separation membranes (Dincer & Acar, 2015). The main disadvantages include complex reaction kinetics (Karaca et al., 2023), slow response rates and large reactor sizes (Pinsky et al., 2020), and large inventories of highly hazardous or corrosive materials (Dincer & Acar, 2015).

The technological developments achieved in solar energy collectors and concentrators make coupling thermochemical water-splitting cycles with concentrated solar energy an attractive alternative to produce green hydrogen (Fig. 17). Furthermore, in addition to solar energy, thermochemical water-splitting can utilize industrial waste heat, offering great opportunities for decentralized hydrogen production in the vicinity of industry or power plants. (Torre, 2022)

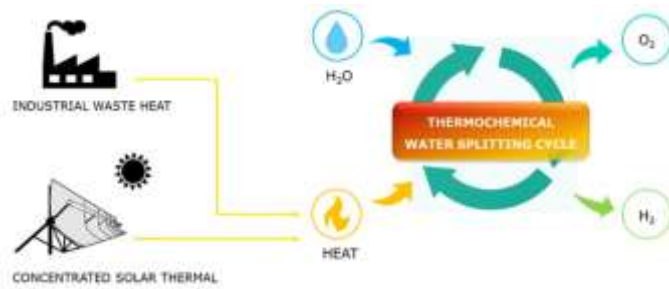


Figure 17. Thermochemical water splitting cycles for green H₂ production (Torre, 2022)

5.3 Photoelectrochemical water splitting

The conventional way of producing hydrogen from solar energy comprises two individual process steps: First, electricity is generated via photovoltaic cells, and second, the electricity drives an electrolyser that splits water into oxygen and hydrogen. Photoelectrochemical hydrogen production, also known as photo-electrolysis, combines photovoltaic electricity generation and electrolysis in a single process (Fraile et al., 2016), eliminating the need for a separate power generator and electrolyser.

Fig. 18 shows the basic components of a photoelectrochemical hydrogen production unit, including a sunlight-absorbing electrode, typically made of or coated with a semiconductor, and a counter electrode, which are immersed in an aqueous electrolyte. The photoelectrolytic hydrogen production mechanism includes the following steps: 1) generation of an electron-hole pair with the help of a photon that has sufficiently high energy, 2) flow of electrons from the anode to the cathode generating electric current, 3) decomposition of water into hydrogen ions and gaseous oxygen, 4) reduction of hydrogen ions at the cathode to form hydrogen in gas form, and 5) separation of the product gases, processing, and storage. (Dincer & Acar, 2015)

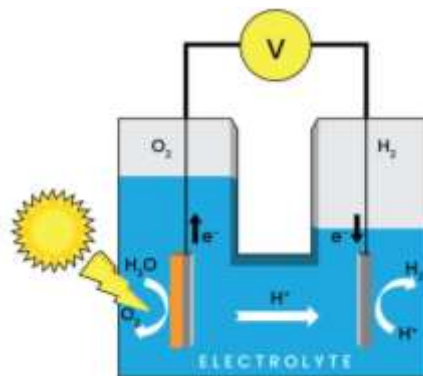


Figure 18. Photoelectrochemical cell (SinoVoltaics, 2023)

The performance of a photoelectrochemical system depends on the type of photon-absorbing material, its crystalline structure, corrosion resistance, and reactivity. Usually, there is a trade-off between photoelectrode stability and photon energy-to-hydrogen conversion efficiency: high-efficiency photoelectrodes often have poor stability in aqueous electrolytes, while chemically stable photoelectrodes generally have poor water-splitting efficiency. (Dincer & Acar, 2015) Among semiconductor materials, titanium dioxide (TiO₂) is one of the earliest and most widely studied

candidates for water splitting due to its high stability and low cost. However, a severe limitation of TiO_2 is that it can absorb only ultraviolet light (small fraction of solar spectrum), resulting in very low efficiency. Thus, various emerging semiconductors with excellent visible light response have been developed for photoelectrochemical water splitting, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$), tungsten oxide (WO_3), copper oxide (Cu_2O), etc. (Chen et al., 2020). Fraile et al. (2016) reported the highest efficiencies demonstrated for laboratory-scale devices to be only around 4 %. However, significantly higher efficiencies of 12–16 % have also been commonly reported (e.g., Megía et al., 2021; Pinsky et al., 2020; Chen et al., 2020).

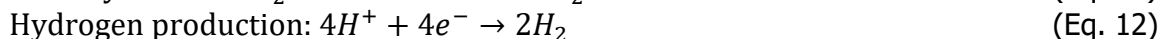
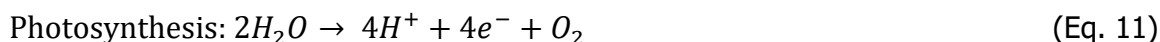
The major strengths of photoelectrochemical-based hydrogen production pathways include the possibility of diversifying the energy base by using solar energy, the advantages of a low-temperature process (20–60 °C) compared to the thermochemical process, and high scalability to build plants at virtually all scales (Fraile et al., 2016). However, continued efficiency, durability, and cost improvements are still needed for market viability.

The current TRL for this technology is estimated at between 2 and 5 (Fraile et al., 2016). Within this technology, the semiconductor device is immersed in an aqueous environment. Consequently, corrosion and device durability are significant problems. In addition, due to the relatively low efficiency of solar hydrogen production pathways, large-scale photoelectrochemical hydrogen production would require huge land areas and large amounts of construction materials for collecting the necessary solar energy, resulting in significant capital costs. Hence, maximizing conversion efficiency to reduce the system footprint remains critical to cost reduction. Furthermore, identifying and developing new active materials to improve corrosion resistance and increase the durability and lifetime are key factors for the future success of this technology. (Fraile et al., 2016)

5.4 Photobiological water splitting

Photobiological water splitting, also called bio-photolysis, uses specialized microorganisms, such as green algae or cyanobacteria, to produce hydrogen from water. An important factor is the sunlight, essential to drive the system. Bio-photolytic processes can be categorized into two main categories: direct bio-photolysis and indirect bio-photolysis (Melitos et al., 2021).

Direct bio-photolysis occurs in two basic steps: splitting of water molecules into hydrogen ions and oxygen via photosynthesis (Eq. 11), and hydrogen production by converting the produced hydrogen ions with the help of hydrogenase enzyme, present in green algae and cyanobacteria (Eq. 12) (Show et al., 2018).



The merit of this H_2 production pathway is that the primary feed is water, and the driver energy is derived from sunlight, both of which are readily available (Show et al., 2018). However, although this technique offers significant potential, it also faces tremendous challenges. A particular challenge is that splitting water also produces oxygen, which quickly inhibits the hydrogen production reaction (EERE, 2023): the natural hydrogenase only functions in anaerobic conditions, and it is eventually deactivated as O_2 is continuously produced during photosynthetic processes (Aslam et al., 2023). Consequently, the process is stable only for short periods (Fraile et al., 2016). Oxygen can also be a safety issue when mixed with hydrogen in certain concentrations (EERE, 2023).

So far, bio-photolysis solar-to-hydrogen conversion rates are very low, less than 1 % (Fraile et al., 2016). However, it is argued that by successfully overcoming oxygen inhibition and engineering the

organisms to utilize solar power better, 10–13 % could be achievable (Holladay et al., 2016; NREL, 2007). To tackle the oxygen inhibition problem in particular, the current research attempts to identify or engineer less oxygen-sensitive microorganisms and/or change the ratio of photosynthesis (oxygen production) to respiration (oxygen consumption) to prevent oxygen buildup (Show et al., 2018).

Another strategy to overcome oxygen inhibition is to spatially separate the hydrogen and oxygen cycles. In indirect bio-photolysis, oxygen generation is separated from the hydrogen evolution stage, so oxygen does not inhibit the H₂ evolution (Melitos et al., 2021). Indirect bio-photolysis involves two consecutive bioreactors, one for each reaction step. In the first reactor, photosystems within microorganisms trap sunlight, leading to water splitting and the production of photons and O₂. Simultaneously, they convert CO₂ into endogenous reserve carbohydrates, specifically glycogen in cyanobacteria and starch in green microalgae (Aslam et al., 2023). These intracellular reserves (starch and glycogen) are then utilized as substrates for H₂ production in the second reactor. (Aslam et al., 2023) This second stage has some similarities with anaerobic fermentation processes described in Chapter 4.

The theoretical solar-to-H₂ conversion efficiency of indirect bio-photolysis is estimated to be around 16 % (Pilon & Berberoğlu, 2014). However, practical applications of indirect bio-photolysis have been limited, possibly due to the system's complexity (Aslam et al., 2023).

In summary, photobiological hydrogen production technologies are still in the fundamental research phase, representing a TRL of 1 (Fraile et al., 2016). In the long term, photobiological production technologies may provide economical hydrogen production from sunlight with net-zero carbon emissions. The algae and bacteria could be grown in water that cannot be used for drinking or for agriculture and could potentially even use wastewater (EERE, 2023). However, further research is needed to improve the activity of the hydrogen-producing enzymes and the metabolic pathways needed for the reactions to increase the H₂ production rates. (EERE, 2023)

6 Summary

Hydrogen is recognized as the key contributor to the clean energy transition. However, its sustainability depends on the cleanness of the hydrogen production pathway and the energy used during its production. Currently, the most developed and used technology is the reforming of hydrocarbon fuels, primarily natural gas. As a result, significant CO₂ emissions are produced. To face this problem and to decrease the dependence on fossil fuels, various hydrogen generation technologies from renewable resources, such as biomass and water, have been developed. Table 3 summarizes the hydrogen production technologies discussed in this report, along with their feedstocks, reaction conditions, technology readiness levels, advantages and disadvantages, and H₂ yields.

The most cost-effective process for large-scale H₂ production today is steam methane reforming. From natural gas, low-carbon hydrogen can be obtained by coupling SMR, or other reforming processes, with carbon capture and storage. Pyrolysis of natural gas is also considered a low-emission pathway; during the process, no CO₂ is produced as all carbon is recovered in solid form. Traditional natural gas-based technologies can also be applied to hydrogen production from biomethane, resulting in renewable green hydrogen.

Water splitting coupled with renewable electricity is the most discussed alternative for sustainable hydrogen production. Water can also be split into hydrogen and oxygen using solar energy. Water electrolysis is the most developed technology for making hydrogen from water, with many commercial systems available for small and large-scale applications. Water electrolysis is already responsible for around 4 % of the world's hydrogen production. Among water electrolysis technologies, alkaline electrolysis is the most established and mature, while PEM is often considered as the most flexible and most suitable technology for dynamic operation associated with intermittent energy sources. SOEL technology is still under development but quickly approaching commercialisation. AEM technology is also at earlier stages of development: they are produced, but still at very small scale. Longer-term water splitting technologies include thermochemical, photo-electrochemical, and photo-biological water splitting. These processes are currently in various early stages of research but may offer long-term potential for sustainable hydrogen production with low environmental impact.

Hydrogen production from biomass might be attractive in cases where biomass is locally abundant. Regarding biomass, the pyrolysis and gasification pathways have the highest technology readiness levels and production yields. In addition, studies have been conducted to use microorganisms that allow the biological conversion of biomass to hydrogen, using sunlight or organic matter as an energy source. Biological biomass processes are in the research and development stage, with pilot demonstrations being conducted, but in the long term have the potential for sustainable, low-carbon hydrogen production. The key advantage of these processes is the mild conditions used. The main limitations are the slow conversion rate and the low H₂ yields. Thus, much R&D remains before biological processes can be considered attractive from a commercial perspective. In addition, hydrogen production through a well-established anaerobic digestion process combined with CO₂ reforming of raw biogas has recently gained growing interest. However, commercial hydrogen production from raw biogas through CO₂ reforming would require further research efforts to develop catalysts with strong resistance to sintering and carbon deposition.

Although significant progress has been made in developing alternative hydrogen production systems, further technical development and cost reductions are needed to compete with traditional large-scale reforming technologies. However, for smaller-scale hydrogen production in decentralized plants, alternative technologies may be cost-competitive.

Table 3. Technology summary table

Process	Inputs	Reaction conditions	Maturity	Advantages	Disadvantages	H ₂ yield
Steam reforming	CH ₄ + H ₂ O + heat	800–950°C, 3–25 bar	TRL 9/ Commercial	Most developed technology, existing industrial design, no expensive oxygen source required	High CO ₂ emissions (if natural gas is used), high operating temperature and high energy need, need for catalysts regeneration	0.29–0.35 kg H ₂ /kg feedstock
Partial oxidation	CH ₄ + O ₂	700–1000°C (catalytic), 1300–1500 °C (thermal) 30-80 bar	TRL 9/ Commercial	Proven technology, existing industrial design	High cost of oxygen, difficult process control, risk for local overheating (exothermic reaction) and catalyst deactivation	0.25–0.31 kg H ₂ /kg feedstock
Autothermal reforming	CH ₄ + H ₂ O + O ₂	850–1500°C, 100 bar	TRL 9/ Commercial	Existing industrial design, improved energy efficiency compared to SMR, improved reactor temperature control compared to POX	Limited commercial experience, air/oxygen requirement	0.25–0.31 kg H ₂ /kg feedstock
Methane pyrolysis	CH ₄ + heat	700–800°C (catalytic), atmospheric pressure	TRL 7/ Pilot plant	Carbon is recovered in solid form (low emissions), one-step process (no need for WGS or CO ₂ separation steps)	Large-scale hydrogen production is still an early stage, high operating temperature, need for catalysts regeneration	0.24 kg H ₂ /kg feedstock
Biomass pyrolysis	Biomass + heat	500–800 °C 1–5 bar	TRL 7/ Pilot plant	CO ₂ neutral, existing industrial design, forest residue and industrial waste recycling, versatile conversion of biomass (gas, bio-oil, biochar), simple process	Tar formation, varying H ₂ content due to seasonal availability and feedstock impurities, need for catalysts regeneration, need was feedstock pretreatment	0.1 kg H ₂ /kg feedstock
Biomass gasification	Biomass + H ₂ O + heat	700–1200 °C 1–5 bar	TRL 7/ Pilot plant	CO ₂ neutral, existing industrial design, forest residue and industrial waste recycling, high biomass conversion efficiency, cheap feedstock	H ₂ variation due to biomass composition variations, tar formation leading to catalyst deactivation, need for catalysts regeneration, need for feedstock pretreatment	0.04–0.14 kg H ₂ /kg feedstock
SCWG	Biomass + H ₂ O	600–700 °C, 250–400 bar	TRL 4-5/ Lab/pilot scale	CO ₂ neutral, suitable on biomass with very high moisture content, no costly drying process needed, cheap feedstock, one-step process, low tar formation	High pressure, high energy consumption and high capital costs, lack of knowledge of operation with different biomass feedstocks, corrosion	0.1–11 wt%
Dark fermentation	Biomass	30–60 °C, atmospheric pressure	TRL 5/ Pilot scale	CO ₂ neutral, various suitable carbon sources, contributes to waste recycling, mild operating conditions, simple reactor technology	Low H ₂ yield and production rate, need large reactor volume, large amounts of by-products (wastewater treatment needed), need for feedstock pretreatment	0.004–0.044 kg H ₂ /kg feedstock
Photo fermentation	Biomass + sunlight	30–35 °C, atmospheric pressure	TRL 4/ Under research	CO ₂ neutral, various suitable carbon sources, contributes to waste recycling, mild operating conditions	Low H ₂ yield and production rate, high energy demand for enzymes, low solar energy conversion efficiency, high surface area requirement, need to control the bacteria, need for feedstock pretreatment	0.009–0.049 kg H ₂ /kg feedstock

Process	Inputs	Reaction conditions	Maturity	Advantages	Disadvantages	H ₂ yield
Anaerobic digestion (AD) + Biogas dry reforming (DBF)	Biomass	AD: 35–45°C, ambient pressure DBF: 800–1000°C, ambient pressure	AD: TRL 9 DBF: under research	CO ₂ negative, both CH ₄ and CO ₂ are available from a single source, various suitable carbon sources, contributes to waste recycling	High energy consumption, variability associated with biomass composition and availability, adjustment of CH ₄ /CO ₂ ratio in feed may be needed, coking of catalyst, need for catalyst regeneration, possibility of catalyst poisoning due H ₂ S and other trace substances in biogas	e.g. for cow manure 0.0013 kg H ₂ /kg feedstock
Alkaline electrolysis	H ₂ O + electricity	60–90 °C, 10–30 bar	TRL 9	No pollution with renewable sources, proven technology, abundant feedstock, O ₂ is the only byproduct, highly scalable, large stack size, long-term stability, non-noble materials	Corrosion susceptible electrolyte, low current densities, limited load range	Stack: 0.63–0.71 kWh H ₂ /kWh el. System: 0.51–0.60 kWh H ₂ /kWh el.
PEM electrolysis	H ₂ O + electricity	50–80 °C, 20–50 bar	TRL 8–9	No pollution with renewable sources, abundant feedstock, O ₂ is the only byproduct, high current density, compact design, high H ₂ purity, quick response, high dynamic operation, low maintenance	High cost of components, high-cost catalysts (hard to replace noble catalysts), acidic environment, less durable, medium system size	Stack: 0.60–0.68 kWh H ₂ /kWh el. System: 0.46–0.60 kWh H ₂ /kWh el.
Solid oxide electrolysis	H ₂ O + electricity + heat	700–900 °C, 1–15 bar	TRL 6–7	No pollution with renewable sources, abundant feedstock, O ₂ is the only byproduct, high energy efficiency, non-noble materials, possibility to utilize waste heat streams	Bulky system design, low durability (brittle ceramics), sealing issues, small available production scale	Stack: 0.9–1.0 kWh H ₂ /kWh el. System: 0.70–0.89 kWh H ₂ /kWh el.
Water thermolysis (sulphur–iodine cycle)	H ₂ O + heat	800–1000°C	TRL 4–5	Use of thermal energy from various sources including solar, low environmental impacts, no need for catalysts, no need for downstream H ₂ –O ₂ separation, high thermal efficiency	Large inventories of highly corrosive materials, large reactor sizes, high temperature requirement for H ₂ SO ₄ decomposition, complex reaction kinetics	Efficiency 30–50 % (240–400 MJ heat is needed to produce 1 kg of H ₂)
Photo-electrolysis	H ₂ O + sunlight	20–60 °C	TRL 2–5	Emission-free, O ₂ is the only by-product, abundant feedstock, low operating temperature and pressure, high scalability	Low conversion efficiency, vast land area and large amounts of construction materials required, corrosion and device durability problems	Solar-to-H ₂ efficiency 4–16 %
Bio-photolysis	H ₂ O + sunlight + microalgae	Ambient temperature and pressure	TRL 1	Environmentally friendly, operation under mild conditions, inexpensive and widely available reactant	O ₂ sensitivity, low H ₂ yields, large reactor volume, large surface area to collect maximum light, low maturity	Solar-to-H ₂ efficiency 1 %

Abbreviations

AEL	alkaline electrolysis
AEM	anion exchange membrane electrolysis
ATR	autothermal reforming
CCS	carbon capture and storage
CCUS	carbon capture and utilization or storage
CPOX	catalytic partial oxidation
DFB	dual fluidized bed
KOH	potassium hydroxide
PEM	proton exchange membrane electrolysis
PFSA	perfluorosulfonic acid
POX	partial oxidation
PSA	pressure swing adsorption
SCWG	supercritical water gasification
SMR	steam methane reforming
SOEL	solid oxide electrolysis
TRL	technology readiness level
WGSR	water-gas shift reactor
YSZ	yttria-stabilized zirconia

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