Sustainable hydrogen production: Technological advancements and economic analysis

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Abstract

Hydrogen (H_2) is pivotal to phasing out fossil fuel-based energy systems. It can be produced from different sources and using different technologies. Very few studies comprehensively discuss all available state-of-the-art technologies for H_2 production, the challenges facing each process, and their economic feasibility and sustainability. The current study thus addresses these gaps to effectively direct future research towards improving H_2 production techniques. Many conventional methods contribute to large greenhouse gas footprints, with high production costs and low efficiency. Steam methane reforming and coal gasification dominate the supply side of H_2, due to their low production costs (<\$3.50/kg). Water-splitting offers one of the most environmentally benign production methods when integrated with renewable energy sources. However, it is considerably expensive and ridden with the flaw of production of harmful by-products that affect efficiency. Fossil fuel processing technologies remain one of the most efficient forms of H_2 production sources, with yields exceeding 80% and reaching up to 100%, with the lowest cost despite their high reliance on expensive catalysts. Whereas solar-driven power systems cost slightly less than \$10kg^{-1}, coal gasification and steam reforming cost below \$3.05kg^{-1}. Future research thus needs to be directed towards cost reduction of renewable energy-based H_2 production systems, as well as in their decarbonization and designing more robust H_2 storage systems that are compatible with long-distance distribution networks with adequate fuelling stations.

Keywords: Hydrogen production; hydrogen economy; sustainability; water splitting; pyrolysis; electrolysis

Symbols

n_h	Amount of water molecules in gaseous states
n_f	Amount of water molecules in liquid states
m	Mass (g)
n	Quantity (mole)
y	Year
h	Hour
s	Second
M	Million
η	Electrolysis efficiency
kW	Kilowatt
E_{out}	Wind power input
MH_2	Mass of generated H_2

Abbreviations

APAMEC	Artificial photo-assisted microbial electrolysis cell
CCS	Carbon capture and storage
Ce-Cl	Cerium-chlorine
CG	Coal gasification
CO	Carbon monoxide
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CuCl	Copper chloride

Cu-Cl	Copper-chlorine
Cu-SO_4	Copper-sulphate
DC	Direct current
EED	Electro-electrodialysis
EFG	Entrained flow gasifier
Fe-Cl	Iron-chlorine
GHG	Greenhouse gas
H_2	Hydrogen
H_2O	Water
HCl	Hydrochloride
HTGR	High-temperature gas-cooled reactor
HydS	Hydrogen Square
HyS	Hybrid Sulphur
IS	Iodine-sulphur
I-S	Iodine-sulphur
JAEA	Japan Atomic Energy Agency
KOH	Potassium hydroxide
Mg-Cl	Magnesium-chlorine
Mg-I	Magnesium-iodine
N_2O	Nitrous oxide
NaCl	Sodium chloride
NaOH	Sodium hydroxide
O_2	Oxygen
OH-	Hydroxide ions
PEM	Proton exchange membrane
PV	Photovoltaic
REF	Residue electric field
SMR	Steam methane reforming
SO_2	Sulphur dioxide
SOEC	Solid oxide electrolysis cells
STH	Solar-to-hydrogen

TDM	Decomposition of methane
V-Cl	Vanadium-chlorine
WGS	Water-gas shift

1. Introduction

The continuous expansion of the world's population, growing economies, and rapid urbanization is leading to a huge increase in energy demand [1,2]. Currently, fossil fuels supply about 80% of the primary energy used globally [3]. Particularly developing nations demonstrate high energy requirements [4] to ensure sustainable investments [5] that promote economic growth. With the consistently increasing global energy demand, current trends of global energy consumption are projected to increase 50% by 2050 [6]. In the present world, our overreliance on fossil fuels for energy has resulted in two of the most daunting issues: a threat to global energy security because of the non-renewable nature of fossil fuels [7], and accelerating rates of global warming with increasing numbers of intense natural disasters [8–12]. Consequently, driven by concerns of energy and climate security and unequal economic development, there is an urgent need to phase out fossil fuels [13]. Therefore, there is tremendous interest in the decarbonization of energy supply systems using sustainable, clean, and renewable sources of energy to mitigate the impacts of greenhouse gases [12,14].

Renewable energy sources are integral to promoting this transition towards clean and sustainable energy systems [15,16]. However, there is a huge need for technical solutions to effectively exploit the benefits of renewable energy [17], as renewable energy sources are highly variable and intermittent in terms of supply [18–20]. Proper penetration of renewable energy into current energy facilities depends on the availability of large-scale sophisticated energy storage systems that can overcome these issues [21], by capturing and releasing energy during different periods [20,22,23]. Hydrogen (H_2) as a fuel plays a key role in this energy transition because, as an energy-efficient, socially beneficial, and economically promising solution to the increasing global energy demand, it alleviates many of the issues of the contemporary world [24,25].

Hydrogen offers numerous advantages as a clean fuel, such as its high energy density, the absence of polluting by-products when combusted, and its renewable nature [26,27]. Moreover, the liquefaction of H_2 makes it relatively easy to store and transport long distances [27,28]. Therefore, H_2 serves as a promising energy carrier to serve as a cost-effective, large-scale renewable energy storage system [12,16,29,30]. The incorporation of H_2 into energy policies is crucial to the speeding up of the energy transition away from conventional energy systems [31–33]. It has further been reported that H_2 can facilitate extensive use and full market penetration of renewable energy sources [34]. Dincer and Acar [35] highlighted that H_2's key roles in initiating the energy transition lie in the provision of accessible, safe, clean, reliable, and affordable energy across all regions, and the possibility to build a resilient and efficient multigenerational energy system with the widespread integration of renewable energy sources. H_2 has the potential to not only reduce six gigatonnes of carbon dioxide emissions but can also meet 18% of the final energy demand [36]. Furthermore, it can lead to the creation of 30 million new jobs [36] and power 20–25% of the transportation sector [37]. Advancements have been evident in the H_2 energy sector. With a production cost of $2.50/kg, H_2 can unlock 8% of the global energy demand [38]. Further developments are expected to lower production costs to $1.80/kg by 2030 when H_2 would fulfil 15–18% of the energy demand based on current estimates [39]. However, the hydrogen economy cannot yet be fully realized [40–42] because of technological barriers.

As a pivotal component of the hydrogen fuel cell, H_2 has the potential to revolutionize and transform the energy sector by lowering greenhouse gas emissions [43–45]. H_2 can be generated from a wide range of different sources using different production technologies, including the use of renewable energy sources and fossil fuels [12,46]. However, many of the current methods of hydrogen production are highly unsustainable. The most commonly used method is reforming or cracking fossil fuels for industrial usage, which is anticipated to consume more than 600 Billion Nm^3y^{-1} [12]. The industrial use of H_2 ranges from the food processing sectors [47–50] to fertilizer production [47], semiconductor production [51], petrochemical refining [52], and use in metalwork [53]. Several socio-economic and environmental challenges accompany conventional techniques [54]. In addition to transportation and storage issues, one of the major drawbacks in the scaling-up of H_2 in the energy economy is sustainable H_2 production [55]. The source of H_2 production is essential as sustainability can only be ensured if H_2 is obtained through clean, cost-effective, renewable, and reliable sources [56]. Therefore, sustainable sources of H_2 production are increasingly being investigated, particularly the highly advantageous renewable sources [57]. For instance, solar-driven H_2 production systems have been found to display the most favorable environmental performance compared to others [48]. The fossil fuel phase-out will become more rapid when H_2 systems integrating renewable production sources become available at large scales [31].

With increasing attention and efforts to drive H_2 as a dominant fuel for a smooth transition towards cleaner and more sustainable energy systems, H_2 production methods have garnered monumental research interest from scientists over the years (Fig. 1). As a result of this, several review papers have compiled knowledge on the state-of-the-art technologies used to produce H_2 to direct future research on improving techniques and addressing limitations. Most of the recent articles review the production of H_2 with specific techniques, namely, using renewable sources such as biomass [58–60] and electrochemical systems [62–64] in addition to other methods [64–67]. Furthermore, there is much buzz around the production of H_2 specifically using biological methods as they are known to address the limitations of conventional methods [69–77]. Others [22,29] have also particularly focused on hydrogen storage systems, as storage remains one of the major current challenges hindering the realization of a complete hydrogen economy. As a highly energy-intensive process relying on inefficient equipment and processes, hydrogen liquefaction has also been the subject of many recent reviews [77,78].

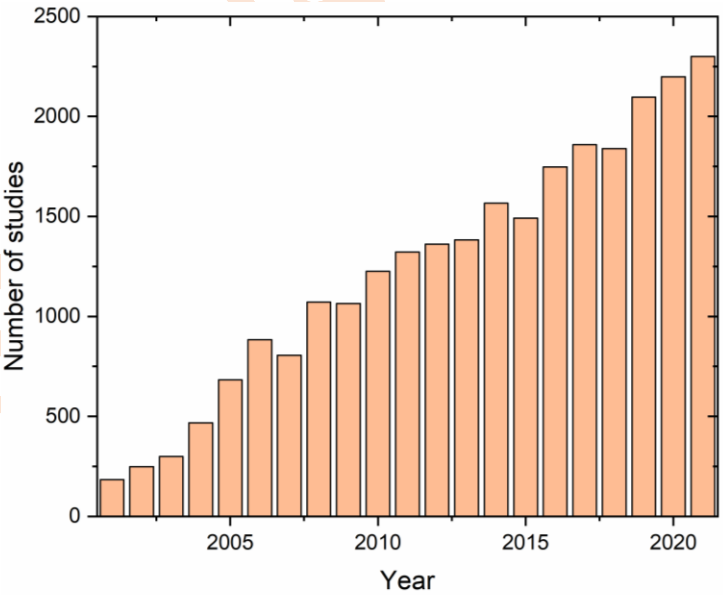

Fig. 1. Studies carried out on hydrogen production/generation since 2000. Research increased because of technological advancements and increased environmental concerns.

Very few reviews, however, report comprehensively on all of the available state-of-the-art technologies for H_2 production. Moreover, they also do not adequately discuss the storage and transportation methods for H_2, its industrial applications, or the current challenges and benefits of producing H_2. Most importantly, crucial insights into the economic and long-term feasibility of production techniques are largely excluded from discussions in recent works. These knowledge gaps significantly impede progress and development in the realization of the hydrogen economy. Therefore, this review paper attempts to address these gaps by compiling information on the recent advances in H_2 production routes and technologies, current storage, transportation, and application systems of H_2, and the economics and long-term feasibility of production technologies. Then, by discussing the benefits and challenges facing the production techniques, this paper aims to lead future research towards advancing H_2 production techniques along a path that can facilitate the emergence of a hydrogen economy. Table 1 displays the topics discussed in this study and those explored by review papers published in the last five years.

Table 1. Comparison of the current review article with relevant recent review articles (2017-2021) that comprehensively review H_2 production technologies

Review study	H_2 production routes	Storage, transport, and use	Technological advancements in H_2 production	Economics of H_2 production	Sustainability analysis of H_2 production	Advantages and challenges of H_2 production technologies	Future directions
This study	√	√	√	√	√	√	√
Yukesh et al. [79]	×	×	√	√	×	×	×
Sazali [80]	√	√ (application only)	√	×	×	×	×
Dawood et al. [51]	×	×	√	×	√	×	×
Acar & Dincer [48]	×	√ (storage only)	√	×	√	×	√
El-Emam & Özcan [49]	×	×	√	√	√	×	×
Abdalla et al. [50]	√	√	√	×	×	√	×

Sinigaglia et al. [81]	×	√	√	√	×	×	×
Nikolaidis & Poullikkas [82]	×	√	√	√	×	×	×

√: adequate information present; ×: inadequate information present

2. Hydrogen production routes

Hydrogen is widely regarded as an ecologically friendly secondary source of renewable energy since it contains a huge amount of energy and comes with a zero-carbon footprint. A broad range of methods is available for H_2 generation which can be categorized into two primary groups: renewable technologies and non-renewable technologies [82]. Hydrogen production via renewable energy has two main branches, as shown in Fig. 2. Processes that use biomass as the raw material fall into two further sub-categories: thermochemical technologies such as gasification, pyrolysis, combustion, and liquefaction; and biological processes comprising fermentation and biophotolysis stages. The other main branch using renewable technology covers water-splitting processes such as electrolysis, photo-electrolysis, and thermolysis where water is the feedstock. Non-renewable technologies that use fossil fuels to produce hydrogen are described in two branches, hydrocarbon reforming and pyrolysis [82]. The chart below depicts the many techniques available for generating hydrogen from renewable and non-renewable sources.

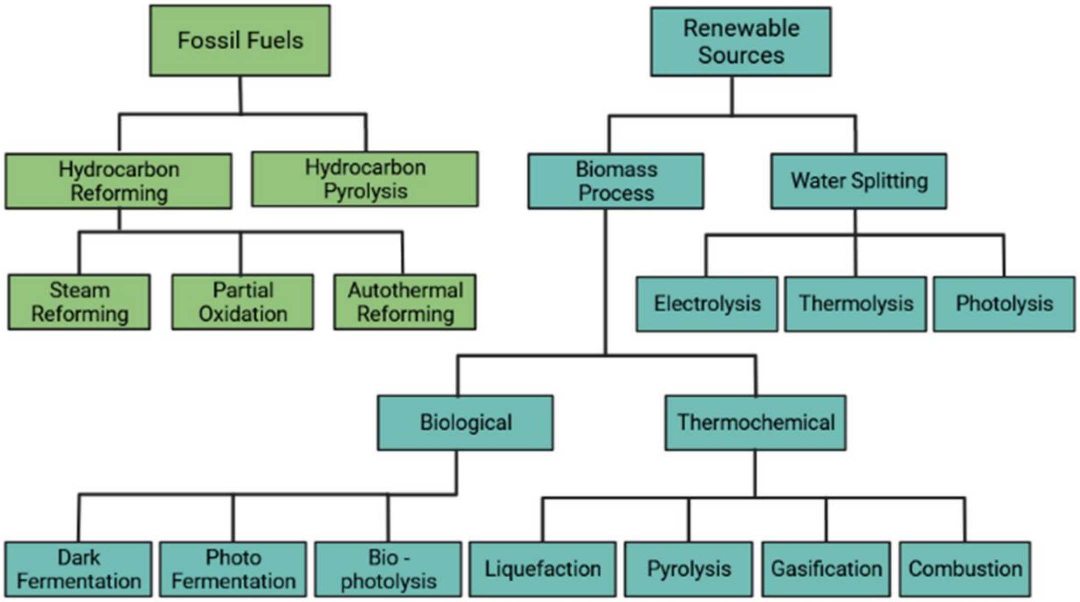

Fig. 2. Hydrogen production routes [82]

Several researchers have proposed hydrogen-based energy models to provide insights into the development of an accomplished hydrogen economy [48]. To build a successful hydrogen economy, it is necessary to ensure the cleanliness standard throughout the overall production system. As a result, there must be a well-developed model in place which will ensure the cleanliness standard for the whole hydrogen-based energy system. Besides, from the literature, it is clear that the long-term potential of hydrogen production systems can be fully realized if a well-planned roadmap is developed from the production route to the end-use point [51].

A model named Hydrogen Square (HydS) was proposed by Dawood et al. [51] to demonstrate the importance of integrating all four stages of hydrogen production, storage, safety, and utilization when deciding on a certain hydrogen production method. The model consists of four corners, each of which represents a separate stage of hydrogen-based energy systems. The HydS model depicts the interdependence of these four corners (Fig. 3) highlighting the cleanliness standard of the overall system. Moreover, hydrogen purification and compression, two extra sub-stages, can fill in any of the corners of the HydS model. Hence, the paper raises awareness about the importance of planning hydrogen production infrastructure while keeping the four corners of the HydS model in mind.

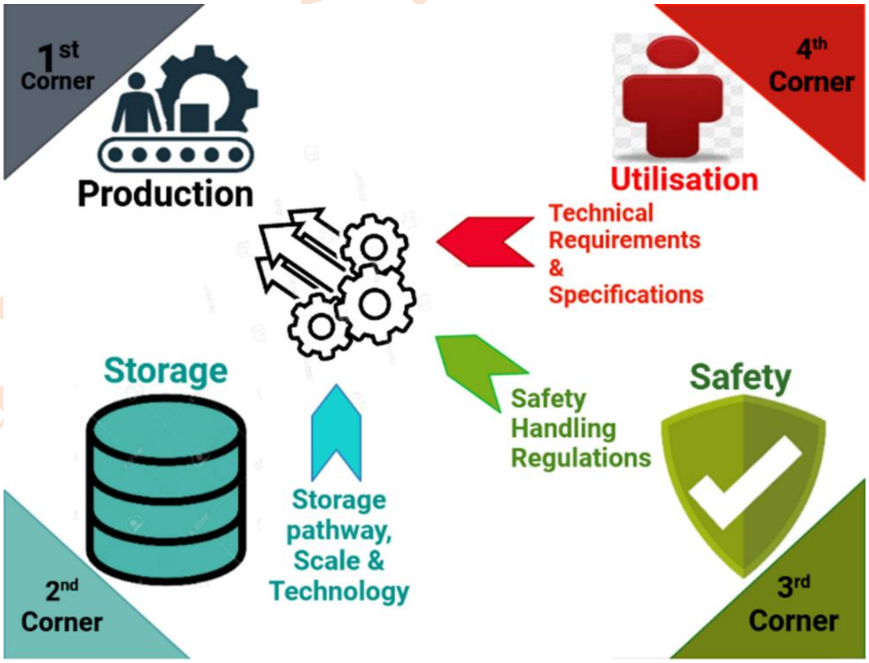

Fig. 3. Hydrogen Square model [51]

The interconnection of the stages of a hydrogen-based energy system must be considered to preserve the overall cleanliness quality of the entire hydrogen economy. That said, a successful hydrogen economy cannot be developed by assuring zero carbon emissions solely at the end-use applications, instead, all stages of the total hydrogen production system, including production routes, storage, usage, and safety must also be carbon-free.

3. Storage, transportation, and utilization of hydrogen

3.1. Storage of hydrogen

Due to the growing demand for hydrogen energy, it is critical to design a dependable and long-lasting storage framework for each hydrogen application. To avoid a significant interaction between hydrogen and the material used for H_2 storage, the material's quality must be thoroughly assessed [50].

3.1.1. Compressed H_2 storage

Hydrogen storage tanks come in a variety of forms and sizes. Each of these types has a pressure tolerance capacity and thus, the storage option is selected depending on the eventual use, which necessitates a trade-off between technical performance and cost competitiveness. [50,83,84]. The different kinds of hydrogen storage options are discussed below.

The type I vessel is made entirely of metals (i.e., aluminum or steel) and weighs around 3.0 lb=L. One of the complications of this vessel type is it can only hold around 1% of H_2, resulting in limited storage capacity. Additionally, there is a possibility of metal embrittlement owing to hydrogen-metal interaction. These container types are incapable of withstanding pressures greater than 50 MPa [50,83]. The type II vessel comprises both metal and composite materials and is a pressure vessel with the greatest pressure tolerance. However, although being 30–40% lighter, type II vessel production expenses are regarded as greater than for type I [50,84]. The type III vessel is made up of a composite frame and a liner. The metal liner bears approximately 5% of the structural load and the composite structure the remaining load. One of the drawbacks of this storage system is that, when considering the composite wrapping, damage build-up might occur due to pressure loads and environmental effects during operation. However, this form of pressure vessel has demonstrated efficiency at 45 MPa working pressure [82]. Lastly, the type IV vessel is entirely made of composite materials. Composites bear most of the weight of the carrier. They are known to be light in weight, but their price is higher compared to the other storage vessels. Pressures of up to 100 MPa can be handled by type IV pressure vessels. Due to their greater cost, composite pressure vessels have a far smaller market share than metallic pressure vessels [83].

3.1.2. Liquid/cryogenic H_2 storage

Cryogenic containers have been serving the storage sector for over 40 years. The density of liquid contributes to the systemic storage of hydrogen. Besides, the quality of H_2 has secured its place in space technology. On the contrary, the disadvantage of this system arises from the fact that the liquefaction of hydrogen takes place at 253 °C which takes a long time and requires significant energy [83]. High efficiency (vacuum) insulated containers are used to handle storage at 253 °C. These vessels are made up of an interior pressure vessel and an outside protective jacket [85]. However, this technique is not considered suitable for long-term use because of the risk of hydrogen evaporation. Therefore, it is more commonly utilized for gas distribution via trucks with capacities exceeding 60,000 L [50]. Further, there is a possibility of experiencing 40% energy loss during the process whereas for compressed hydrogen storage it is only 10% [83].

3.1.3. Cryo-compressed H_2 storage

This technology is a combination of compressed and cryogenic storage systems. Cryo-compressed storage offers a storage density of 80 g/L, which is a considerably higher storage capacity than cryogenic storage. This kind of storage is equipped to allow a reduction in the hydrogen vaporization rate. Further, to store hydrogen at a cryogenic temperature of 20 K and a pressure of 30 mph or more, hydrogen is stocked up in an insulated tank. The tanks considerably prolong the period before evaporative losses begin, increasing storage autonomy [83]. Apart from withstanding the high-pressure efficiency, the cryo-compressed storage system also provides a higher degree of safety owing to the presence of a vacuum enclosure.

3.2. Transportation of hydrogen

Hydrogen distribution is a critical component of the hydrogen-based energy system, contributing to the costs, energy consumption, and emissions connected with hydrogen routes. There are two options for H_2 transportation and distribution. Firstly, truck trailers, large containers, and railway tank cars are used for the transportation of liquid hydrogen. Secondly, pipelines are used for the transport of gaseous hydrogen to refueling stations. In general, when hydrogen is compressed to a pressure of 200 bar into long cylinders and carried in a truck trailer for transportation purposes, it can deliver modest amounts of hydrogen across short distances of up to 200 km.

Liquid hydrogen trailers are more cost-effective for delivering small amounts over long distances but the insulation of cryogenic liquids and the high-energy liquefaction procedure come at a significant expense [86]. Further, the best techniques for optimizing large-scale and economically feasible liquefaction operations are explored by [87,88]. Efforts were made to build more efficient techniques, and eventually, an innovative largescale liquefaction process was proposed with an energy consumption of 7.69 kWh/(kgLH_2), whereas conventional facilities spend between 12.5 and 15 kWh/(kgLH_2) [89].

3.3. Utilization of hydrogen

Hydrogen has the potential to become the alternative energy source required to tackle greenhouse gas (GHG) emissions and other challenges associated with existing energy sources. The ability of hydrogen to store energy creates potential benefits in terms of decarbonization and ensures the stability of the energy supply network [90]. By using hydrogen, the renewable energy share in the power grid could be promoted. Although renewable energy sources are inexhaustible, the energy supply from them is inconsistent owing to fluctuating weather patterns. H_2 becomes a temporary carrier for renewables if it is initially created from renewables, and it will also allow electricity to be generated using fuel cells [91]. This will help to preserve the power grid's resilience by preventing imbalanced supply, which would otherwise occur due to the intermittent nature of renewable energy supply.

Hydrogen is mainly utilized as a reactant for petroleum processing, petrochemical synthesis, and ammonia manufacture. As ammonia is the primary basic material used in fertilizer production, it uses almost half of all hydrogen generated globally [50]. In automobiles, hydrogen can be applied in two ways: internal combustion engines and fuel cells. The aerospace sector makes the most use of hydrogen by utilizing it as a rocket propellent [50]. Fuel cells are of significant importance in terms of power production, heating, and transportation due to their flexible use and environmental friendliness. Moreover, substantial amounts of hydrogen are used as feedstock in methanol refinement and manufacturing, and the iron and steel sector [50].

4. Technological advancements in hydrogen production

4.1. Water splitting technologies

4.1.1. Thermolysis

The process of thermolysis involves the breakdown of molecules. But in the case of thermolysis, the application of heat is involved in breaking down water molecules, and as such is a method of chemical decomposition by heating [92]. The main mechanism of this process is to apply the heat of high temperature, around 500–2000 °C, to power a sequence of reactions that leads to the production of hydrogen [93]. The feedstock to produce hydrogen via thermolysis requires materials that contain hydrocarbons or non-hydrocarbons [51]. Recently, there have been studies on thermochemical cycles like iodine-sulfur (I-S), magnesium-chlorine (Mg-Cl), cerium-chlorine (Ce-Cl), hybrid sulfur (HyS), copper-chlorine (Cu-Cl), magnesium-iodine (Mg-I), iron-chlorine (Fe-Cl), vanadium-chlorine (V-Cl), hybrid chlorine, and copper-sulfate (Cu-SO_4) [49,94]. These processes have been demonstrated to be technically feasible. One major drawback of most of the mentioned cycles is their requirement for high process heat which can be around 800 °C except for the Cu-Cl cycle which requires much less (540 °C) [94]. Cu-Cl cycle includes a series of four principal steps in the following sequence: hydrolysis (water-splitting) → thermolysis (oxygen production) → electrolysis (hydrogen production) → separation of water via crystallization or spray drying [95]. The steps are as follows:

- Hydrolysis (endothermic):

  $$2CuCl_2 \cdot n_h\, H_2O\ (l) + H_2O\ (g) \leftrightarrow CuOCuCl_2\ (s) + 2HCl\ (g) + n_hH_2O\ (g) \qquad (1)$$

  In this reaction, $n_h = 0\text{-}4$ at 400°C, $\Delta H = 27.9$ kcal/mol

- Thermolysis (endothermic):

  $$CuOCuCl_2\ (s) \leftrightarrow 2CuCl\ (l) + 0.5O_2\ (g) \qquad (2)$$

  at temperature of 530 °C, $\Delta H = 30.9$ kcal/mol

- Electrolysis:

  $$2CuCl\ (aq) + 2HCl\ (aq) \leftrightarrow 2CuCl_2\ (aq) + H_2\ (g) \qquad (3)$$

  This reaction occurs in HCl in an aqueous solution, at a temperature of 90 °C, $\Delta H = 22.4$ kcal/mol

- Water Separation (endothermic):

  $$CuCl_2\ (aq) + n_fH_2O\ (l) \leftrightarrow CuCl_2 \cdot n_hH_2O\ (s) + (n_f - n_h)H_2O\ (g/L) \qquad (4)$$

In this reaction, n_h and n_f denote the amounts of water molecules in gaseous and liquid states, respectively, where n_h = 0-4 and $n_f > 7.5$ at a temperature range of 30–80 °C for crystallization or 100–260°C for spray drying [95].

A comparison among the water splitting processes for hydrogen production is shown in Table 2. The process of water-splitting starts with the entry of water into the thermochemical plant. Here, water recovers heat to form steam and passes into the hydrolysis reactor where it undergoes a reaction with copper(II) chloride, in its solid form, to produce solid copper oxychloride and gaseous hydrogen chloride [95]. The two gases produced, H_2O and HCl, flow out of the hydrolysis reactor, undergo condensation to turn into an aqueous solution and enter an electrolysis reactor. Particles of $CuOCuCl_2$ exit the hydrolysis reactor and are moved to the thermolysis reactor for decomposition to produce oxygen gas and molten CuCl. The thermolysis reactor becomes overfilled with the molten CuCl which pours into a water bath, becoming solidified and releasing steam in the process to create a slurry of water and CuCl. Through a dissolution cell, the slurry is transported to the electrolyzer where CuCl becomes dissolved in HCl (aq) and a ternary aqueous solution of H_2O/HCl/CuCl is created. Afterwards, this solution is driven towards the electrolyzer anode where HCl and CuCl dissociate into their ions as shown by the following reactions and Fig. 4 [95]:

Dissociation:

$$CuCl(s) \Leftrightarrow Cu^{+}\,(aq) + Cl^{-}\,(aq) \tag{5}$$

Dissociation:

$$HCl(l) \Leftrightarrow H^{+}(aq) + Cl^{-}(aq) \tag{6}$$

Oxidation:

$$Cu^{+}(aq) \Leftrightarrow Cu^{+2}(aq) + e^{-} \tag{7}$$

Precipitation:

$$Cu^{+2}\,(aq) + 2Cl^{-} \Leftrightarrow CuCl_2(aq) \tag{8}$$

Reduction:

$$H^{+}(aq) + e^{-} \Leftrightarrow 0.5H_2(g) \tag{9}$$

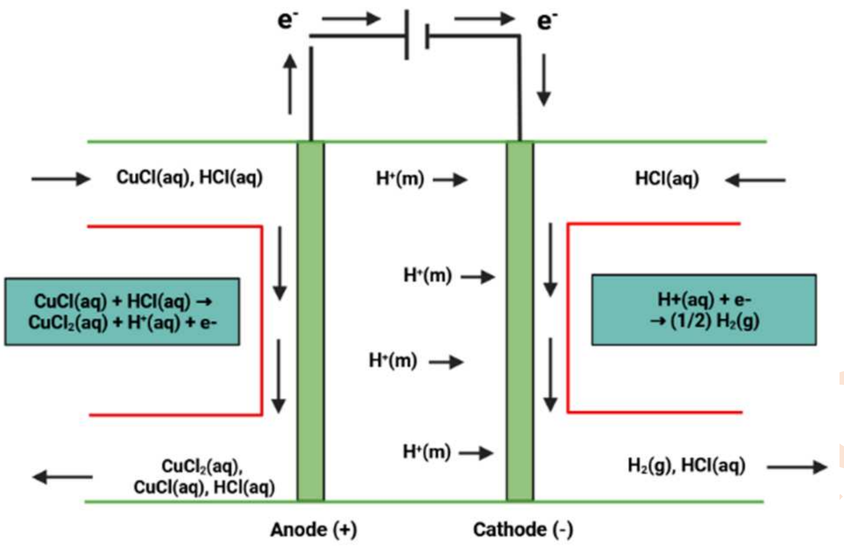

Fig. 4. Schematic illustration of the Cu-Cl cycle [95]

There has been ongoing research by the Japan Atomic Energy Agency (JAEA) on a nuclear reactor called the high-temperature gas-cooled reactor (HTGR) and its application in the iodine-sulfur (IS) process as the source of heat energy. The high thermal energy of 950 °C is acquired from the HTGR for the IS process to proceed and perform the water-splitting reaction [94, 95]. Iodine and sulfur compounds are used in the IS as presented by Fig. 5, and the following chemical reactions occur [96]:

Bunsen reaction:

$$SO_2\ (g) + I_2\ (aq) + 2H_2O\ (aq) \rightarrow 2HI\ (aq) + H_2SO_4\ (aq) \tag{10}$$

Hydrogen iodide (HI) decomposition:

$$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g) \tag{11}$$

Sulphuric acid (H_2SO_4) decomposition:

$$H_2SO_4\ (g) \rightarrow H_2O\ (g) + SO_2\ (g) + 0.5O_2\ (g) \tag{12}$$

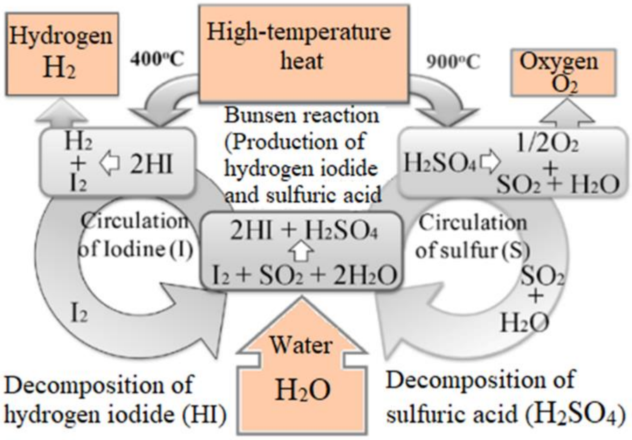

Fig. 5. Schematic illustration of the IS cycle [96]

As seen from the reactions, the products of the Bunsen reaction are hydroiodic acid and sulphuric acid when sulfur dioxide (SO_2), iodine (I_2), and water (H_2O) react together, which occurs at 100 °C [96]. During the decomposition of HI, gaseous HI is thermally decomposed at around 400 °C to give out hydrogen (H_2) and I_2 with the application of heat. At temperatures of up to 900 °C via heat absorption, gaseous H_2SO_4 is thermally decomposed in sulphuric acid decomposition generating oxygen (O_2) and SO_2. The Institute of Nuclear and New Energy Technology of Tsinghua University in China has also been performing research since 2005 for the advancement of hydrogen production via nuclear means involving the IS process [97]. According to INET, the unit operations involved in this process that have a key influence on the closed-cycle operation or process efficiency are the Bunsen reaction and separation of products, the purification of HI_x (the mixture of HI, I_2, and H_2O), and the phases of H_2SO_4 produced during the Bunsen reaction, HI_x preconcentration, and the type of catalysts used in the decomposition of HI and SO_3. This research studied the Bunsen reaction and the separation characteristics of the $HI/I_2/H_2SO_4/H_2O$ system in terms of phase equilibrium. It also identified the main factors that influence the purification efficiency for the purification of HI_x and sulphuric acid phases and attempted to find appropriate parameters for operation [97]. The development of the electro-electrodialysis (EED) stack was a success and it was implemented in the close-cycled operation. Catalysts were required in the decomposition process of HI and SO_3 and Pt–Ir/AC and $CuCr_2O_4$ were recommended.

4.1.2 Electrolysis

Electrolysis is a technique for decomposing ionic compounds into their respective ions. The electrolysis of water occurs when a direct current (DC) is used to drive water decomposition to generate its constituent elements, oxygen, and hydrogen [98]. A DC electrical power source is put into connection with two electrodes and placed in water. These electrodes are usually comprised of inert metals like stainless steel, platinum, or iridium. Fig. 6 illustrates a typical electrolysis unit or electrolyzer. Water splits with the application of current, generating H_2 at the cathode while O_2 is generated at the anode through the following reaction [82]:

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (13)$$

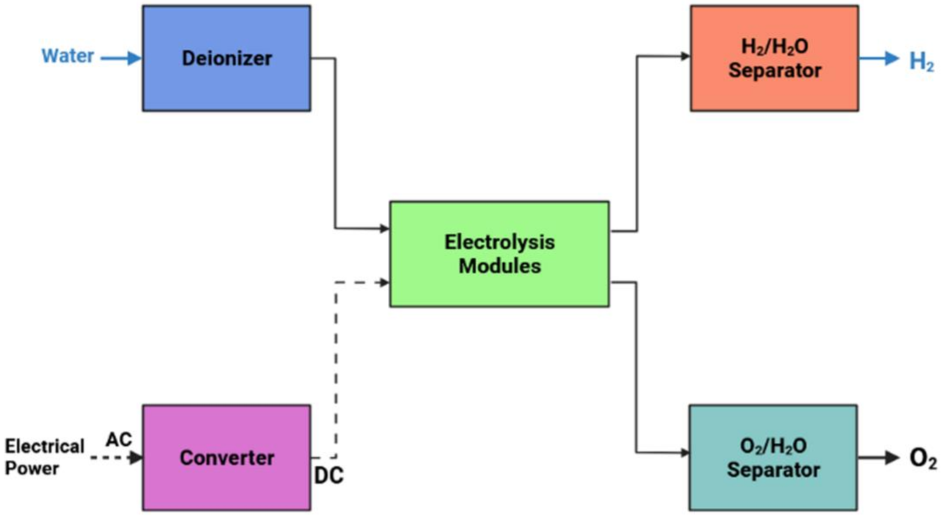

Fig. 6. Flow diagram of the water electrolysis process [82]

The type of electrolyzer varies depending on the kind of electrolyte being used. The most developed hydrogen production technologies which involve electrolysis are solid oxide electrolysis cells (SOEC), alkaline, and proton exchange membrane (PEM). The PEM electrolyzer technology has the anode placed in the water after which the water splits into protons (hydrogen ions, H^+) [82]. The H^+ ions are transported through the membrane and towards the cathode where they combine to form H_2. Oxygen (O_2) remains in the anode chamber in water. The following reactions show how the dissociation occurs:

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (14)$$

Cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{15}$$

The alkaline electrolyzer uses sodium hydroxide (NaOH) or potassium hydroxide (KOH) in liquid form as the electrolyte [49]. It functions at lower temperatures of around 30–80 °C, the diaphragm is asbestos, and the electrodes are made of nickel materials [62,99]. In the cathode area, water splits to form H_2. This is separated from the water via an external unit and the hydroxide ions (OH^-) are transported through the aqueous electrolyte where they move towards the anode to produce O_2. The dissociation reaction of the alkaline electrolyzer and a diagram of alkaline water electrolysis is given in Fig. 7.

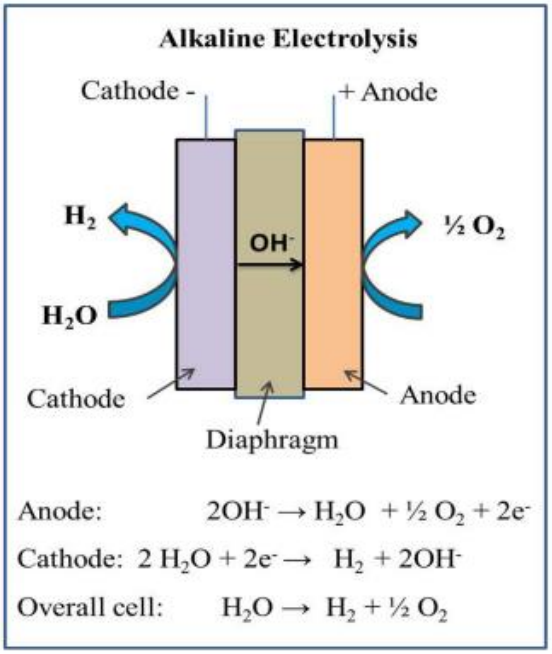

Fig. 7. Schematic illustration and dissociation reactions of the alkaline water electrolysis, reprinted with the permission of Elsevier from [62]

The solid oxide electrolysis cell (SOEC) uses O^{2-} as conductors that are primarily nickel or yttria-stabilized zirconia [62]. Ceramic in solid form is also used in SOEC due to its superior ionic conductivity and high efficiency which surpasses that of O^{2-} conductors at an operating temperature range between 500–700 °C [62]. This technique displays a high energy efficiency and with the application of heat, the efficiency reaches more than 90% [99]. Fig. 8 shows a schematic illustration of SOEC and the dissociation reactions in the electrodes.

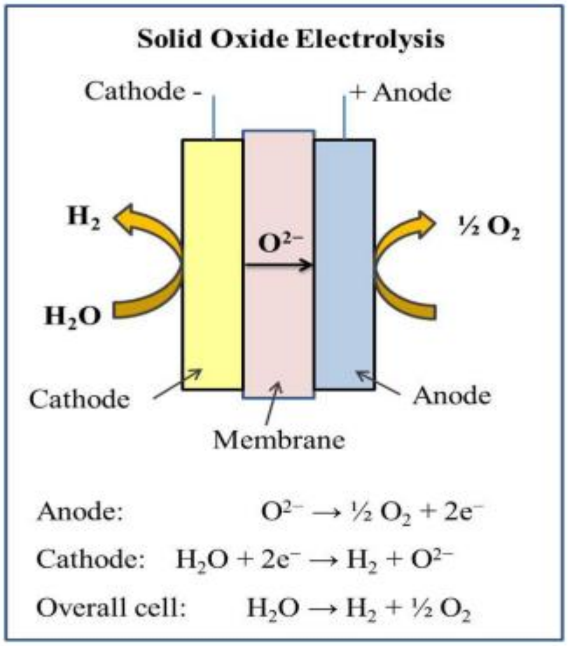

Fig. 8. Schematic illustration and dissociation reactions of SOEC, solid oxide electrolysis cell, reprinted with the permission of Elsevier from [62]

Pure hydrogen can be formed by using the electrolysis process, but the electrolyzers consume a high amount of energy, thus increasing the production cost. If alternative and renewable energy sources are implemented, like solar, wind, and hydro, the cleanest energy carrier could be the H_2 that has been produced via electrolysis [82]. Alkaline electrolysis has some negative features like low energy efficiency, less current densities (below 400 mA/cm^2), slow loading response, and low operating pressure [62,99]. SOEC has stability and degradation issues at high temperatures and therefore cannot be implemented on a large scale [62].

The H_2 production technologies can be distinguished using different colour codes. The majority of the H_2 produced nowadays is grey. Yellow H_2 refers to hydrogen produced by nuclear electrolysis in some cases [100], whereas yellow H_2 sometimes refers to hydrogen produced by solar electrolysis [101]. In this scenario, nuclear electrolysis produces pink H_2. Finally, electrolysis is used to produce green H_2 using renewable electricity such as solar or wind [102][103]. In today's world, it produces only 0.1% of all hydrogen produced. As the costs of renewable electricity and electrolysis technology are declining, green hydrogen may be the next best investment in the world of clean energy in the coming years.

Worth to mention, the direct use of solar thermal energy to produce hydrogen in thermochemical plants with feedstock of water (white hydrogen [104]) with oxygen as a by-product, or methane (aquamarine hydrogen [104]), in this latter case with carbon black as a by-product, may in principle deliver better than green hydrogen environmental and economic costs.

4.1.3 Photo-electrolysis

Photo-electrolysis is a process performed in a photo electrochemical cell where sunlight is used to produce H_2 from water [105]. Radiation from the sun is converted by photovoltaic (PV) cells into energy used to drive separate electrolyzers in the generation of hydrogen from water as shown in Fig. 9.

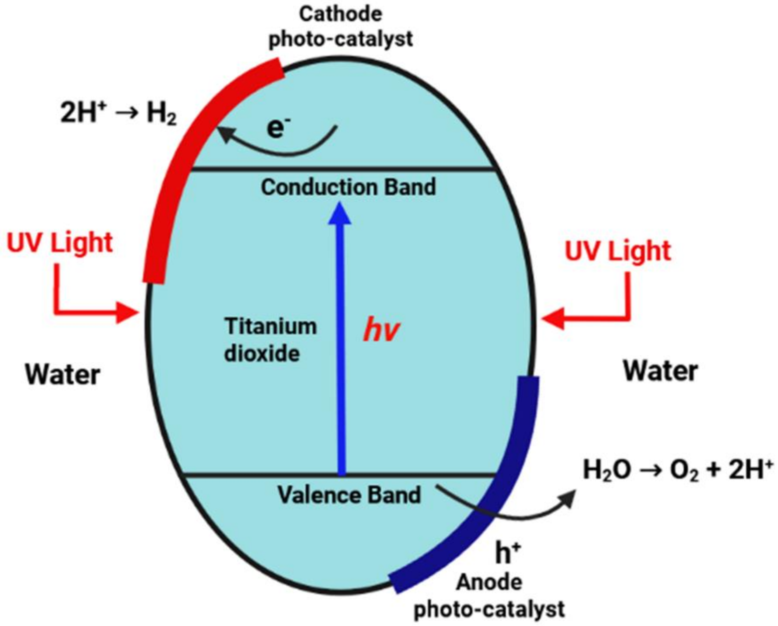

Fig. 9. Photo-electrochemical hydrogen production [105]

The study of Bidin et al. [106] explored how sunlight affects the production of hydrogen via the water electrolysis process and made an attempt to increase the efficiency of water electrolysis. Three experiments were performed with three different scenarios and results showed that by utilizing collimated sunlight, the generation of improved hydrogen can be produced (around 53%) than using conventional light or dark field (16%). The electrolysis chamber used graphite rod electrodes with a DC electricity supply. The chamber consisted of 100 mL distilled water, 1.0476 mg of sodium chloride (NaCl) as a catalyst, and 7 mL ethanol to supplement partial oxidation. The strength in this technique lies in the abundance and polarizability of sunlight which made the electric field stronger and improved the water splitting. However, clashes in the electric fields are a disadvantage. Electric fields were induced by the ionic compound of Na^+ and Cl^- and the electric dipole of water that is in the opposite direction of the external electric field created by the DC power supply. This phenomenon resulted in a weakened residue electric field (REF) in the electrolysis which negatively influenced hydrogen generation [106].

The experiment by [107] created a PV-electrolysis system that had the highest solar-to-hydrogen (STH) efficiency to date. The system was composed of a high-efficiency triple-junction solar cell connected in series with two PEMs. This system was able to produce H_2 with an average STH efficiency of 30% in 48 h. The strength of this system lies in its efficiency and low production costs but there is a downside in terms of optical loss in the lenses or mirrors that are required for focusing the incident sunlight onto the PV cell. Keruthiga et al. [108] investigated biohydrogen production from wastewater generated by rice mills using an artificial photo-assisted microbial electrolysis cell (APAMEC). This system has an inexpensive anode and is created from carbonaceous material which is considered waste by the sugar industry (carbon cloth that has a char coating acquired from low-cost filter cake). The best results were observed on the 5th day of fermentation with maximum hydrogen production of 220mL. The rate of production was 3.6 ± 0.4 mL/l/h on that day. While examining the impact of acid concentration and pH for acid hydrolysis of wastewater derived from the rice mill, the optimum acid concentration, and pH was found to be 1.5% and 6, respectively, as it resulted in enhanced biohydrogen production and removal of chemical oxygen demand (COD). A biocatalyst called *Rhodobacter sp.* was used in this process which helped in the production of hydrogen and also in reducing COD.

Table 2. Comparison of water splitting technologies for hydrogen production

Process Category	Technology	Objective	Feedstock	Reactor	H_2 production	Strengths	Weaknesses	Ref.
Thermolysis	Partial oxidation pyrolysis	Investigate H_2S thermolysis for direct hydrogen and sulfur production	Hydrogen sulfide (H_2S)	Perfectly stirred reactor Plug flow reactor	48.8%	Almost ideal conversion of H_2S to H_2 and S_2	Formation of intermediate species like SH, HS_2, H, and S during the chemical processes in the reactor	[109]
	Copper-chlorine (Cu-Cl) cycle of thermochemical water splitting	Present the advancements in each operation of CuCl, Cu-Cl cycle, and HCl electrolysis	Copper chloride (CuCl) and water (H_2O)	Hydrolysis reactor Electrolysis reactor	0.89 kg H_2/s	- Lower temperature required for operation - Can effectively use substandard waste heat for an endothermic process	- Finding appropriate corrosion-resistant coatings at high temperatures	[95]
	Iodine-sulphur water-splitting	Presenting the status of research and development in thermochemical water-splitting processes for hydrogen production	Compounds of iodine and sulfur	High-temperature gas-cooled reactor (HTGR) Bunsen reactor	10 L/h in 8hrs	- Can be implemented on a large scale - Materials and equipment are workable since the temperature is less than 1,000 °C	Formation of SO_2 that needs to be disposed of or utilized in an effective way such as to prevent negative environmental impacts	[96]

		Reporting the advancement of nuclear hydrogen production via IS process performed by INET for the past decade	Compounds of iodine and sulfur	High-temperature gas-cooled reactor (HTGR) Bunsen reactor	60 NL/h	- CO_2 emission does not occur - Efficient hydrogen production	- Maintaining the stable and ongoing operation of the closed-cycle IS process is challenging	[97]
Electrolysis	Alkaline electrolysis Proton exchange membrane electrolysis	To conduct a techno-economic study for producing large-scale hydrogen plants	Water	Electrolyzers	(4000–40,000 kgH_2/d	- Carbon-free - Uses renewable resources	- Expensive	[110]
	Solid oxide electrolysis	SOEC was employed to split untreated seawater, and the electrochemical performance was investigated	Seawater	Electrolyzers	183 mL/min	- High energy conversion efficiency - Less electricity required	Sea salt in the seawater could potentially damage the electrolyzers	[111]
		Producing hydrogen via steam electrolysis	Steam	Electrolyzers	80%	High efficiency	- Carbonaceous materials become oxidized to CO_2	[112]

							- Expensive	
Photo-electrolysis	Solar to water electrolysis	Exploring how sunlight affects hydrogen production from water electrolysis	Water	Photovoltaic electrolysers	53%	The polarizability and abundance of sunlight strengthened the electric field in the electrolysis of water and enhanced the splitting of water	- Clash in electric fields leads to a reduction in hydrogen production	[106]
		Creating a photovoltaic-electrolysis system with the highest solar-to-hydrogen efficiency	Water	Photovoltaic electrolysers	30%	Comparatively cheap	- Optical losses occurred in the lenses or mirrors utilized for focusing the incident light on the PV cell	[107]
		Investigation of biohydrogen production from rice mill wastewater employing an APAMEC	Rice mill wastewater	Photo-assisted microbial electrolysis cell	220 mL	- Cheap anode		[108]

4.2. Biomass technologies

Apart from water splitting technologies, hydrogen may be generated in a variety of ways. This section includes a brief overview of some of the biomass-based methods. The critical need to meet increasing energy use has prompted plenty of studies focusing on the development of biomass-based technologies because of their waste-to-energy application. It is the most likely potential strategy to ensure energy sustainability and reduce CO_2 emissions. Animal food, municipal and industrial waste, energy crops, agricultural residues and waste, and waste paper are all biomass sources [113][114]. These renewable resources are abundant, carbon-neutral, and easy to use. Current hydrogen-generating biomass techniques are divided into two broad categories—thermochemical processes and biological processes—which are briefly discussed below.

4.2.1. Thermochemical

Thermochemical technology includes the production of hydrogen and hydrogen-rich gases from biomass [108,109]. This is a crucial technique for sustainable development and reducing greenhouse gas emissions. Gasification and pyrolysis are two significant thermochemical techniques. The pyrolysis process involves the decomposition of hydrocarbon without the presence of water or O_2 [117], except in producing thermal energy where partial combustion is required. This process can produce liquid oils, solid char, and gaseous products from biomass in specified conditions (300–600° C and at a pressure of 0.1–0.5 MPa) [118]. The water-gas shift (WGS) process can generate more hydrogen and other hydrocarbons including methane which can be purified further by steam [119]. The reactions can be demonstrated in the following way:

$$\text{Pyrolysis} \rightarrow H_2 + CO + CO_2 + \text{hydrocarbon gases} + \text{tar} + \text{char} \tag{16}$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{1}{2m}\right)H_2 \tag{17}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{18}$$

Several factors influence pyrolysis product yield such as temperature, pressure, reaction time, feedstock type, reactor, facility size, and the type of catalyst used [120]. Because the production of CO/CO_2 is prevented and only solid carbon is produced as a reaction by-product, methane pyrolysis is a more ecologically friendly technique that could be a potential way to lighten the burden of waste disposal [114,115]. The gasification technique is extremely mature, commercially used. In a specified environment and with controlled amounts of oxygen, steam, or supercritical water, it converts biological waste to H_2, CO_2, CO_2, and CH_4 [123]. H_2 and CO are the main by-products generated by gasification due to steam reforming. The resulting syngas may be fed into the Fischer-Tropsch process to transform into hydrocarbons and green diesel [124].

$$\text{Biomass} + \text{Air} \rightarrow H_2 + CO_2 + CO + N_2 + CH_4 + \text{other CHs} + \text{tar} + H_2O + \text{char} \quad (19)$$

Following the conversion of biomass into syngas, the gas combination is handled in the same manner as the pyrolysis process's product gas. However, the key factors influencing hydrogen yield are temperature, type of catalyst, and biomass particle size [125]. To generate pure hydrogen, a WGS method can be utilized to raise the hydrogen concentration. Various methods have been employed to reduce tar formation and several feasible and affordable catalysts can be used.[126]. Downdraft gasification is advantageous for hydrogen production. The use of steam instead of air as the gasification source can increase hydrogen production [120]. Research put forward by Dogru et al. [127] discovered a set of downdraft gasifier gasification rates, air-fuel, and other operational settings that resulted in high-quality gas. Gasification reactors are often developed on a huge scale and nowadays the products are to be supplied continually. They can attain efficiencies of 35–50% [128] and steam gasification is more efficient than fast pyrolysis [129]. One of the challenges with this technology is that it requires a massive amount of resources so increased operational costs might be a concern.

4.2.2. Biological

Because of the growing emphasis on sustainable development, research into biological hydrogen generation has risen significantly in recent years. Most of the biological activity under investigation functions at pressure and room temperature, using less energy. Furthermore, the studies make use of the infinite supply of renewable energy and contribute to waste reduction and recycling by using a variety of waste items as feedstock [130]. Both direct and indirect biophotolysis have different functions in the hydrogen production processes. The biophotolysis process occurs via reduction and oxidation reactions in the presence of sunlight [131]. Different photosynthetic microorganisms (for example, cyanobacteria and green algae) decrease ferredoxin by transferring electrons to the hydrogenase enzyme. Because this enzyme is extremely sensitive to oxygen, it must be kept at a low level of less than 0.1% [132]. The hydrogenase enzyme generates hydrogen by reducing protons first and then oxidizing water [73].

$$2H_2O + \text{Light} \rightarrow O_2\uparrow + 4H^+ + \text{FD (reduced)} + 4e^- \rightarrow 4H^+ + \text{FD (reduced)} + 4e^- \rightarrow \text{FD (oxidized)} + 2H_2 \quad (20)$$

In indirect photolysis, hydrogen production from water occurs by blue-green algae or heterocystous cyanobacteria [133]. The process takes place in anoxic conditions when direct biophotolysis cannot be performed owing to a sulfur-deficient environment. The process can take place in a one-stage or two-stage response mechanism, depending on the presence of the PS II stage. A general reaction is:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3CH_2COOH + 4H_2 \qquad (21)$$

No practical implications have been presented for indirect biophotolysis due to its need for a large surface area to gather enough light and complexity of reactions. Using the indirect biophotolysis process, the capital cost of hydrogen production is predicted to be $135/m^2 [82] which can be viewed as a cost-effective and environmentally friendly technique of utilizing water as a renewable resource.

Fermentation is a biochemical process that can be performed with or without the presence of oxygen. This process uses waste materials as feedstock and contributes to minimizing energy consumption. The quantity of biohydrogen generated by this method is determined by the cellulose structures of the microalgae used [134]. Photosynthetic bacteria decompose complex organic microalgal biomass into relatively simpler organic or inorganic components in the presence of light, a process known as photo fermentation. Typically, the light fermentation process produces alcohols, organic acids, carbon dioxide, and hydrogen [135]. Photosynthetic and gram-negative organisms are often more useful for hydrogen generation [67]. Some photosynthetic bacteria may convert organic acids into carbon dioxide and hydrogen due to the presence of nitrogenase enzymes. The following describes the general process:

$$CH_3COOH + 2H_2O + \text{Light} \rightarrow 4H_2 + 2CO_2 \qquad (22)$$

To minimize accidental usage and contamination, the light penetration rate should be carefully assessed when building an appropriate photo fermentation reactor [134]. Dark fermentation can be processed in the absence of light unlike photo fermentation; thus, it is not necessary to construct customized reactors with complex light penetration control. The dark fermentation process is less complex and the reaction rate and mechanism aspects are also very desirable. Photo fermentation produces more hydrogen than dark fermentation, the low conversion efficiency in solar energy, and the scarcity of organic acids are the main obstacles to photo fermentation, obstacles which are much easier to overcome in dark fermentation [82]. Dark fermentation facilitates resource recovery through the process of by-products, acetic acid, and butyric acid. In several recent technical advancements, dark fermentation is combined with photo fermentation to enhance hydrogen output, resulting in a hybrid system with numerous phases. This is still a prospective technique as there have not yet been many large established implementations of such systems. A comparison of this technology with other biomass technologies for hydrogen production is tabulated in Table 3.

Table 3. Comparison of biomass technologies for hydrogen production

Process Category	Technology	Objective	Feedstock	Reactor	H_2 yield/ Gas yield (Nm^3/kg biomass)	Strengths	Weaknesses	Ref.
Thermochemical	Biomass steam gasification	An experimental setup study that provides different gasification temperatures and steam flow rates of pine molding particles	Pine sawdust	Downdraft fixed bed	6.2 H_2 wt%, 1.4 Gas	- To understand the physical and chemical mechanism of high-temperature steam gasification of biomass - Apparent advantages over air gasification because it improves the combustible gases and hydrogen in biomass gasification	Less energy efficient	[136]
		Presents a better understanding of steam gasification showing the effect on hydrogen yield and thermal and hydrogen efficiency	Wood residue	Fluidized bed	5.9 H_2 wt%, 1.22 Gas	- A research-scale fluidized bed gasifier which exhibits uniform temperature distribution and accepts a wide range of particles - Yields results accurately	Large bubble sizes may cause gas to bypass the bed	[137]

	The feasibility of using waste biomass as a fuel for the gasification process, such as manure sewage or sludge, was experimentally investigated	Wood pellets	Dual fluidized bed	1.8 H_2 wt%, 0.82 Gas	- High availability of fuels - Low operating costs - Enables new applications, such as disposal applications - Can be implemented on a large scale	- Finding relevant impurities and identifying ways to reduce them - Recovery of nutrients from ashes due to gasification	[138]
Pyrolysis	Demonstrates the effect of Zn for the catalytic behavior including C deposition and its activity of pyrolysis catalytic steam reforming	Wood sawdust	Fixed bed/fixed bed	1.9 wt%	For biomass thermochemical processing, Zn promoted Fe nano catalysts made from abundant and cheaper metals using a quicker method	Possible sintering might have been observed	[139]
	A laboratory study to understand the impact of volatile K with a	Cellulose	Fixed bed/fixed bed	5.9 wt%	- Carbon-free - Uses renewable resources	Expensive	[140]

		Ni/Al2O3 catalyst in terms of hydrogen generation and catalyst stability						
		Tire char used as a catalyst for producing hydrogen during reforming of pyrolysis of biomass was studied	Wood pellets	Fixed bed/fixed bed	6.1wt%	High energy conversion efficiency	Char production	
Biological	Bio photolysis (indirect photolysis)	Investigate hydrogen production by immobilized *Synechocystis sp.* cells using indirect photolysis	*Synechocystis* sp. PCC 6803	photobioreactor	40.6 ± 4.9 mmol H_2 mg chl^{-1} hr $^{-1}$	- Production of hydrogen was carried out in a short time effectively. - Cells immobilized in an alginate-containing culture media were able to persist for more than 30 days.	Leakage problem in cells immobilized in a culture medium	[141]
		Develop a practical and scalable photolytic H_2 production process using a purpose-built	*C. reinhardtii* CC-124	Custom made flat-plate photobioreactor	1.13 mL H_2 l-1 h^{-1}	This photobioreactor is capable of producing H_2 and biomass on a continuous and cost-effective basis utilizing green algae		[142]

	flat-plate photobioreactor						
Dark fermentation	Controlling homoacetogenesis and methanogenesis in a packed bed reactor and an up-flow anaerobic sludge blanket reactor	*Clostridiaceae*	Up-flow anaerobic sludge blanket	1.47 mol H_2	UASB and PBR are low cost and ecologically friendly reactors to successfully suppress methanogenesis and homoacetogenesis	Hydrogen-consuming microbes from high-rate reactors were not completely removed	[143]
Photo fermentation	Utilize molasses for photo fermentative hydrogen production in a fed-batch mode	*Rhodobacter capsulatus*	Tubular photobioreactor	0.31 mol H_2/m^3 h			[144]

4.3. Fossil fuel processing technologies

Fossil fuel processing technologies offer low-cost and easily adaptable alternatives to the non-conventional hydrogen extraction mechanisms and lead to a significantly higher yield of hydrogen. Table 4 compares fossil fuel processing technologies for their hydrogen production capability. Such technologies utilize the high hydrogen content of fossil fuels and break down the hydrocarbons in multiple ways to extract hydrogen and other by-products. Such processes can be categorized under two major classes depending on the stages followed during hydrogen extraction. Extractions occur either by reforming the molecular structure of the compounds or by imposing the thermal decomposition of hydrocarbons at extremely high temperatures [62]. Thermal reformation of the hydrocarbons can be initiated in multiple ways—by partial oxidation, by auto-thermal reformation, or by steam reformation technologies [82]. On the other hand, thermal decomposition commonly occurs during the pyrolysis of fossil fuels. In most cases, these processes need to be catalyzed to assure hydrogen selectivity during extraction. Also, optimum conditions are needed for maximum yield and the highest process efficiency. The following subsections of the paper address the major mechanisms related to these processes.

4.3.1. Hydrocarbon pyrolysis

Hydrocarbon pyrolysis is one of the most popular processes to produce hydrogen by thermal decomposition. In this process, the light liquid hydrocarbons (i.e., methane, ethane, etc.) are decomposed through a thermo-catalytic process that produces elemental carbon and hydrogen [48]. The general reaction of the process is as follows:

$$C_n H_m \rightarrow nC + 0.5\ mH_2 \qquad (23)$$

During pyrolysis, natural gas produces hydrogen and carbon in an endothermic reaction. The reaction starts at 700 °C and the reaction temperature can be reduced using suitable catalysts [145]. The reaction for methane is given by:

$$CH_4 \rightarrow C + 2H_2;\ \Delta_g H^o = 74.91\ \text{KJ/mol} \qquad (24)$$

In conducting this pyrolysis process, the temperature should be higher than the corresponding boiling point of the hydrocarbons. Hydrogasification and cracking of hydrocarbons are the two stages of the pyrolysis reaction process [82]. The process can be accelerated through the interactions of catalysts. The type of decomposition mechanism used during pyrolysis falls into three major categories: thermal decomposition, plasma decomposition, and catalytic decomposition [145]. All these decomposition mechanisms take place in suitable reactors and their applications vary in scale from the laboratory to the industrial level. Using cheaper feedstocks with no significant evidence of GHG emission is the major reason behind the popularity of pyrolysis. Also, the produced hydrogen contains barely any impurities, eliminating the need for contaminant removal stages. However, conversion efficiency does reduce drastically based on the number of impurities in the feedstock [62].

Despite being a well-known process, pyrolysis is extremely energy inefficient. Even the efficiency of fossil fuel pyrolysis is quite a lot lower than pyrolysis using renewable resources [145]. Although pyrolysis does not produce any greenhouse gases (GHGs), it is a direct decarbonization process that has other environmental drawbacks via indirect pathways. Such limitations are often minimized by introducing certain modifications to the pyrolysis process. Molten metal technology can be considered as a modern alternative to the traditional pyrolysis mechanism where natural gas pyrolysis is conducted in molten metal bubble columns [146]. Interactions between bubbles and feedstocks reduce the energy barrier for pyrolysis initiation. However, this study assessed the techno-economic feasibility of the process and considered it economically impractical unless its by-products are sold, or carbon tax is deducted. This indicates that the adoption of this process will be more practical for some developing countries where carbon taxes are not yet introduced on a large scale.

Despite assuring impurity-free production of hydrogen utilizing molten metal-based catalysts, the high cost associated with the process discourages industrial scale implementation. Another study used metal oxides as catalysts where the hydrocarbons were diluted with argon to reduce the high conversion temperature [147]. In this way, the optimum temperature was halved in comparison to the previous study. The cost was relatively low, yet to avoid soot formation during the process, extra investments are often required. Another cost-effective application of fossil fuel pyrolysis used molten mixtures of Ni and Bi to assess and compare the H_2 production potential of multiple feedstocks. The conversion efficiency of propane is higher than that of methane and ethane due to the comparatively weaker chemical bonds present in propane [148]. Therefore, conversion using propane can be considered as a techno-economically feasible process due to the better availability and cheaper accessibility of the required catalysts and reactors. However, in many cases impurity is found caused by nickel contamination or due to the difficulties associated with using heavier hydrocarbons. Thus, extra treatment should be embedded within the production process. In many cases, carbon-salt separation might be cheaper, however, impurity analyses comparing this process with the discussed metal-based extraction strategies should be undertaken.

4.3.2. Partial oxidization technology

Partial oxidation refers to a catalytic or non-catalytic conversion process used for the extraction of carbon dioxide and hydrogen as the by-products of steam, oxygen, and hydrocarbons. In this process, if any sulfur is present in the hydrocarbon, it is removed initially and then the feedstock comes into contact with O_2 so that the hydrocarbon becomes partially oxidized. The produced syngas is then treated using steam reformation techniques. The process is very similar to steam reformation technology. The major difference is the initial oxidization step. The process might be catalytic or non-catalytic. Corresponding reactions of the process are as below [82]:

(a) Reformer:

$$\text{Catalytic reaction: } C_nH_m + 0.5\ nO_2 \rightarrow nCO + 0.5\ m\ H_2 \tag{25}$$

$$\text{Non-catalytic reaction: } C_nH_m + nH_2O \rightarrow nCO + (n + 0.5\ m)\ H_2 \tag{26}$$

(b) $CO + H_2O \rightarrow CO_2 + H_2$ (27)

(c) Methanation: $CO + eH_2 \rightarrow CH_4 + H_2O$ (28)

The process is highly applicable for heavy oil residues and coal substances since the low H_2 and carbon ratio of such feedstock assures easier oxidation [149]. Therefore, the process is sometimes known as coal gasification. Also, since the steam reforming technology is combined with the partial oxidation process, a huge volume of H_2 is produced from the steam. Carbon capture and sequestration technology can also be combined with the process to limit carbon emission into the environment. Industrial applications of this type of partial oxidation process are quite common in developed countries. However, high capital and operational cost often reduce the popularity of partial oxidation-mediated hydrogen production. Also, frequent cleaning, prevention of coke formation, and handling of reaction conditions are some of the challenges associated with this process.

Studies found higher popularity of catalytic partial oxidation for fossil fuel-mediated hydrogen production, while non-catalytic partial oxidation is more applicable for biomass processing. It is the interaction barriers associated with fossil fuels that cause catalysis for easier interactions. Therefore, research on partial oxidation is highly associated with the discovery of bedding components and catalytic regulations. Metal-supported beds and metal-containing catalysts are so far the most popular set up to produce hydrogen from light hydrocarbons. Metallic components provide surface area for hydrocarbon molecules at high temperatures, and thus the catalysis occurs to break down the intramolecular bonds. A nickel-catalyzed partial oxidation process calcinated the catalysts in the presence of alumina and zirconia to assure the highest stability of the catalysts during partial oxidation [149]. X-ray diffraction measurements denote higher process efficacy of the combined catalysis over regular metallic catalysis mechanisms. In this study, the presence of aluminum in the modified catalysts showed the maximum conversion efficiency. Also, temperature oscillation is a contributing factor behind fluctuations in the catalysts' surface area for which, at a higher temperature, smaller and high-affinity potentials of the catalyst surfaces could increase the reaction rate and process efficiency. During partial oxidation of methanol, temperature oscillations also obtained variance in the flow rate [150]. Therefore, for industrial applications, temperature oscillation can be considered a suitable mechanism for determining the optimum conditions associated with partial oxidation mediated hydrogen production.

In addition to the catalysis and temperature variables, other factors can also be adjusted to increase recovery efficiency and yields. The type of fluidized beds used contributes drastically to the hydrogen yield level. A variety of bedding conditions are being experimented with to facilitate the selection of the most suitable option for certain contexts. Since oxidization is the basic reaction mechanism in this technology, suitable oxygen donors are needed to initiate the process. As mentioned in the former examples, in most cases metallic oxides worked as oxidation agents. Another study used nitrous oxide (N_2O) as an oxygen donor in the fluidized bed and found it to be an environment-friendly alternative to traditionally used oxidizing agents [151]. Yet, the high carbon dioxide yield (89%) of this process necessitates the adoption of carbon capture and storage setup. Although high hydrogen yield has been noted in this study, the impurity content has not yet been assessed. Another proposition for bedding conditions is the utilization of sprays that are not commonly practiced. However, methanol's partial oxidation under sprays resulted in satisfactory efficiency and yield [152]. Particle size and kinetics can be flexibly manipulated under spray conditions, indicating the need for more research to validate the advantages and limitations of the use of sprays. This study was able to detect an intensification of the yield in the presence of Pt catalyst. If commercial applications of spray-based partial oxidation are designed, then a good amount of heat energy will also be saved since Pt activated the process at close to room temperature, though maximum efficiency was not found at room temperature. However, its techno-economic feasibility is yet to be tested.

4.3.3. Autothermal reforming technology

The auto-thermal reforming technique combines exothermic partial oxidation with an endothermic steam reforming process to promote hydrogen production. Here, unlike the partial oxidation process, both oxygen and steam are injected into the reactor at the same time, and reforming and oxidation reactions occur simultaneously in the reactor. The combined reaction of the process is as follows [82]:

$$C_nH_m + 0.5\ nH_2O + 0.25\ nO_2 \rightarrow nCO + (o.5\ n + 0.5\ m)\ H_2 \tag{29}$$

The process incorporates a series of reactions commonly found in the steam reforming and partial oxidation process, but most of these reactions happen simultaneously. Like the other mechanisms, any sulfur present in the hydrocarbons should be eliminated at the initial stage, and later, using optimum pressure and temperature, hydrogen is extracted along with other gaseous by-products. Subsequently, selective extraction of hydrogen, or membrane-based adsorption, is conducted to assure pure hydrogen is extracted from the gaseous mixture [51]. In this way, pure elemental hydrogen can be obtained. Due to technological limitations, the commercial implications of this technique have not yet been fully explored.

Nickel catalysis is the most common methodology to enhance the reaction rate for auto-thermal processing. Multiple percentage ratios of nickel associated with other catalytic metals showed significant promotion of hydrogen yield. Bioethanol is one of the most common biofuels that can be considered for the large-scale production of hydrogen in various parts of the world. One study used multiple Ni-associated catalysts for bioethanol-mediated hydrogen production and found the surface area of the catalysts to be one of the major contributors to the hydrogen yield and reaction time [153]. Also, despite obtaining maximum efficiency at a lower temperature, the optimum temperature of the reaction to assure efficient removal of hydrogen from the gaseous mixture was much higher. The higher amount of catalysts used also indicated higher process performance. Another study on methane processing for hydrogen production found similar trends in process efficiency enhancement where the reducibility of Ni^{2+} acted as the contributing factor in terms of reaction rate [154]. Depending on feedstock type, the elemental ratio can also be considered as a factor contributing to process efficiency and hydrogen yield determination. This ratio regulates the carbon-carbon cleavage rate under certain conditions which alter the bond strengths [155]. Also, modification of catalysts through calcination showed 4.8% higher conversion efficiency under certain process conditions. However, the process operating cost should be carefully reviewed since these factors are taken together to assist in determining appropriate reforming conditions.

4.3.3. Steam reforming technology

Steam reforming is a well-developed catalytic conversion technology that converts hydrocarbons and steam into hydrogen gas and carbon oxides through multiple reforming steps.

The reforming process includes synthesized gas production, water-gas shift (WGS), gas purification, and other stages [82]. The process involves a wide variety of feedstocks, e.g. light hydrocarbons and heavy naphtha, without any requirement for an oxygen source. Since multiple gaseous substances are produced in this process, several purification stages are required. There is also the chance of coke forming on the corresponding catalysts' surfaces that can be prevented under optimum conditions and frequent cleaning. Also, a major drawback of this process is the carbon dioxide emissions caused by the lack of support to include a carbon capture stage.

In steam reforming technology, there are two different sources of produced hydrogen—hydrocarbons and steam. Initially, hydrogen is produced from hydrocarbons and the mixed products pass through the WGS reactor where the carbon monoxide (CO) produced during the initial stage reacts with the steam, extracts hydrogen, and thus converts it into carbon dioxide (CO_2). The product contains multiple gases, but mostly H_2 and CO_2 that can be purified, using CO_2 removal mechanisms for which a pressure swing adsorption (PSA) technique should be applied. Thus, only H_2 gases can be removed [82]. Carbon capture and storage techniques are also being implemented these days to reduce the environmental emissions of GHGs from steam reforming technology. The ocean can be used as a natural reservoir for GHGs in this context [145]. Reactions that occur in different stages of steam reforming technology are:

(a) Reformer: $C_nH_m + nH_2O \rightarrow nCO + (n + 0.5m)\,H_2$ (30)

(b) WGS reactor: $CO + H_2O \rightarrow CO_2 + H_2$ (31)

(c) Carbon oxides removal: $CO + 3H_2 \rightarrow CH_4 + H_2O$ (32)

The steam reforming technology can also be catalyzed using nickel particles. This is often preferred over any other fossil fuel-based hydrogen production techniques due to the low capital and maintenance cost. Similarly, high purity and the positive environmental impact of the process are also reasons behind its popularity. Further, combining this technology with other technologies illustrates a promising area for development from an economic point of view. For instance, combining membrane reactors with steam reforming technology assures selective adsorption of the hydrogen gas, drastically, reducing the carbon-removal cost [48].

Steam reforming technology extracts hydrogen from fossil fuels under multiple conditions and a wide range of catalysts and feedstocks are used in this technology. Nickel-based catalysis is the most common form of catalysis and it is often incorporated with other types of catalysts to increase the process efficiency and yield. Nickel catalysts are incorporated with other metallic oxides or alloys to increase their efficiency in the reaction processes [156]. However, in many cases, coke formation occurs on the catalysts' surface which is a process disruption only avoided with an excessively high temperature. Research shows that though the highest efficiency is achieved at a lower temperature, sometimes the temperature is doubled to avoid coke formation on the catalyst surface [156,157]. In addition, the type of fossil fuel used plays an important role in terms of hydrogen yield.

One study found that the conditions applied for maximum hydrogen yield from methane failed to obtain the same yield from glycerol [157]. Also, different combinations of alloys as catalysts showed different yields and efficiencies. It has been found that Pd-Zn alloy could assure high stability in hydrogen production from steam reforming that cannot be obtained by either of these two metals on their own [158]. This process also has limitations since the slightest amount of carbon monoxide can hinder the activities of this catalyst. This can be prevented by the constant separation of carbon compounds produced as by-products in the reactors. Taken together, there is hope that different aspects associated with the process will enhance efficiency and yield.

Table 4. Comparison of fossil fuel processing technologies used for hydrogen production

Technology	**Feedstock**	**Conditions for maximum conversion**	**Catalysts**	**H_2 yield**	**Conversion efficiency**	**Production costs**	**Ref.**
Hydrogen pyrolysis	Methane	1,175 °C temperature and ambient pressure, residence time of bubbles = 0.5 s	Quartz bubble column using molten gallium	78%	91%	6 M€ (Fixed) 200 M€ (Variable – includes feedstock (€/kg), water (€/m^3), electricity (€/MWh), gallium (€/kg), tax (€/kg))	[146]
	Ethane	473 K temperature, 1 bar pressure, an argon dilution of 93 mol%,	Metal oxides and Argon dilution	70%	80%	1.7 \$/kg of H_2	[147]
	Propane	> 950 °C temperature, residence time in reactor ≈ 1 secone	Molten mixture of 73 mol % Bi and 27 mol % Ni in a bubble column reactor	60%	100%	1.98 \$/kg of H_2	[148]
Partial oxidation technology	Methane	650 °C temperature, catalysis time on stream ≈ 7 h, alumina and zirconia surface	Wet-impregnation method using Ni-Al-H-600 or 10% Ni supported Al_2O_3 and zirconia catalysts	72%	90%	Low cost (around 1.5 \$/kg) for Ni catalysis High cost for Rh, Ru, and Pt catalysts	[149]

	Methanol	Around 500 °C temperature, reaction time ≈ 20 min	Ultra-low Pt and Pd contents and Al_2O_3	91.3%	99%	High cost due to expensive catalysis	[152]
	Methanol	350 °C temperature, relative range of pressure ratio 0.05 – 0.015, N_2O utilized in fluidized bed	Iron-chromium catalyst	95%	90%	High cost due to expensive catalysis	[151]
Autothermal technology	Crude glycerol	550 °C temperature, steam to carbon ratio = 2.6, oxygen to carbon ratio = 0.5, reaction time > 2 h	5 wt% Nickle catalyst	83%	85%	~ 1.5 $/kg of H_2	[155]
	Methane	850 °C temperature, nearly atmospheric pressure	10Ni - 0.9Re/$Ce_{0.5}$ $Zr_{0.5}$ O_2 /Al_2O_3	70%	100%	Very expensive catalysts	[154]
	Ethanol	600 °C temperature and atmospheric pressure	10Ni-0.4Re catalyst	65%	100%	Very expensive catalysts	[153]
Steam reforming technology	Methane	850 °C temperature, reaction time = 20 h to	10% Ni supported on SiC modified CA_x/Al_2O_3	75%	81%	-	[156]

		avoid coke formation on catalysts	(NASC)				
	Glycerol	650 °C temperature, atmospheric pressure, conducted in quartz microreactor	Unreduced 20% Nickel	55%	80%	-	[157]
	Methanol	300 °C temperature, 0.1 MPa pressure, water : glycerol = 1.2 : 1, time = 2 h	Pd-Zn alloy based catalysts	86.3%	98%	2.3 \$/kg of H_2	[158]

5. Economy of hydrogen production

Since hydrogen is not widely accessible in nature, the energy conversion routes highly influence the overall cost of hydrogen production. Thermal or electric input from energy sources is necessary for the majority of hydrogen production techniques which are undertaken in facilities powered by the conversion plants, resulting in a rise in the total cost [49]. Therefore, it is essential to perform a cost analysis for each production route to understand their respective feasibility. Economic assessments of each of the H_2 production routes are therefore included in the following discussion, based on the raw materials, conversion technique, and other contributing factors.

5.1 Thermochemical

Due to its high energy density and broad availability, the thermochemical conversion method is highly utilized for carbon-based fuels. [79]. The processes that fall within the category of thermochemical conversion are explored in the following.

The thermal decomposition of methane (TDM) has shown feasibility in hydrogen generating operations ranging from small to medium-sized on-site projects [159][160]. Parkinson et al. (2017) stated that the TDM will take precedence over steam methane reforming (SMR) if a tax of $78 is levied on 1t CO_2 along with a market price of $200/tC [161]. Although concentrated H_2 production through SMR is a low-cost technology, the inclusion of transportation would result in greater required investment. In addition to the techno-economic study, Keipi et al. (2018) assessed CO_2 emissions for three techniques—TDM, SMR, and electrolysis—and concluded that TDM-produced H_2 accounts for 40 kg per MWh of CO_2 and H_2 emissions which are considered the lowest emission result of all. [159]. Nevertheless, the emission quantity for SMR technology is already three times greater than TDM-induced emissions, accounting for additional costs to lower emission levels. As a result, when compared to SMR and electrolysis, the TDM method becomes the most cost-effective alternative [159]. However, in the case of renewable hydrogen generation, the cost of biomass pyrolysis was calculated to be $1.25–$2.20 /kg [82]. Additionally, the authors evaluated the price difference between biomass pyrolysis and CH_4 pyrolysis and revealed that the price of hydrogen produced from CH_4 pyrolysis was more than from biomass pyrolysis.

The three major reactors used for biomass gasification include fluidized beds, fixed beds, and indirect gasifiers. When biomass interacts with either air or steam, it is converted into syngas and the reactions are as follows [82]:

Biomass+Air→ H_2+CO_2+CO+N_2+CH_4+other CHs+tar+H_2O+char (I)

Biomass+Steam→H_2+CO+CO_2+CH_4+other CHs+tar+char (II)

According to Nikolaidis & Poullikkas [82], a typical biomass gasification-steam reforming-PSA method is projected to need 2.4 TJ per TJ hydrogen. Therefore, with an average hydrogen yield of 139,700 kg/d and a biomass cost of \$46–\$80 /dry-ton onboard, the generation cost of such a plant is \$\$2.05 /kg. However, the quantity of produced H_2 for steam gasification is remarkably larger than the rapid pyrolysis process, with a total efficiency of up to 52% [82].

Wang et al. [162] conducted techno-economic research using an entrained flow gasifier (EFG) in which they evaluated hydrogen generation from biomass gasification and coal gasification in terms of total capital investment, material consumption, manufacturing costs, energy efficiency, and carbon tax. The biomass gasification approach has been considered as the best alternative since it outperforms the coal gasification process in a market where the carbon price must be addressed. The study revealed the energy efficiency rates of both these processes which are estimated to be 37.88% for biomass gasification and 37.82% for coal gasification. Although the energy efficiency rate of these two processes is comparable, coal gasification requires a higher feedstock cost than capital cost due to raw material price fluctuations. In addition to increased production costs, coal gasification is coupled with huge GHG emissions, preventing it from becoming a viable hydrogen generation technique.

5.2 Water splitting

Grid electrolysis is a more efficient and cost-effective method of generating H_2 using conventional energy, which benefits the H_2 economy. Despite being an advanced and commercially viable technology, this approach is associated with a greater quantity of GHG emissions [163]. That said, to overcome the problem, wind electrolysis was suggested and consequently, GHG emissions were reduced by integrating a renewable source into the electricity grid. Another study by [164] presents a technique for assessing hydrogen produced through wind energy utilizing various wind turbines. The Weibull function was used to determine the wind energy distribution. The quantity of hydrogen mass generated by wind energy is shown below:

$$MH_2 = \frac{\eta_{el}E_{out}}{LHVH_2} \tag{33}$$

where η is electrolysis efficiency and the wind power input is denoted by E_{out}, the mass of generated H_2 is denoted by MH_2, and the lower heating value of H_2 is denoted by $LHVH_2$. It was clear from the findings that H_2 production is highly dependent on turbine selection. In addition, the study found that the GE 1.5sle turbine had the best productivity rate in terms of H_2 production [164].

Water-splitting technology is an advanced technology that is also cost-effective with sustainable energy production potential [99]. This sort of technology has demonstrated efficiency in terms of storage and transportation, and it does not emit any harmful compounds during manufacture. Besides, the paper discusses the prospect of significant electrolyzer price reductions in the coming years if hydrogen output exceeds 1,000 kg per day. The production scale is currently restricted to 10 kg per day. According to the study, it is possible to reduce the price of the electrolyzer to one-quarter of its present level if large-scale hydrogen production is implemented [99]. On the other hand, to understand the potential of solar photovoltaic (PV) powered electrolysis, a two-dimensional electrolyzer model was used for the PEM fuel system using photovoltaic multi-junction solar cells. Consequently, the authors revealed that this model has shown promise by improving hydrogen production [165].

5.3 Biochemical conversion

The production of hydrogen from biomass via biological processes has been praised for its commercial viability and environmentally friendly nature. Therefore, the cost assessment of fermentation and biophotolysis processes for H_2 generation are addressed in the following discussion. The fermentation method provides a clean hydrogen production route as it does not rely on carbon fuels. Therefore, it is thought to be a favorable option that holds the promise of a fossil fuel-free future. There are two discreet types of fermentation process: photo fermentation and dark fermentation [166]. While examining the overall costs of hydrogen generation using photo fermentation and dark fermentation, Rensick (2004) concluded that the use of a Tredeci-style reactor led to a higher capital cost of \$1.41 GJ^{-1} y^{-1} for photo fermentation. When comparing the economics of these two fermentation processes, a production cost of \$30.7 GJ^{-1} was found for photo fermentation and the projected annual operating cost exceeded \$193 M. In comparison, for dark fermentation, the capital cost was estimated to be \$0.64 GJ^{-1} y^{-1} and the various associated charges led to an annual operating cost of approximately \$980 M. The study demonstrated that the bioreactor's reduced footprint contributed to the cheaper capital cost for dark fermentation [166].

Another study [82] evaluated the fermentation processes in terms of their manufacturing cost. The cost for photo fermentation and dark fermentation was calculated to be \$2.57 /kg and \$2.83 /kg, respectively. According to the findings of the study, the photo fermentation technique was found to be more expensive than the dark fermentation method. The economic assessment of biophotolysis processes is being studied to develop low-cost photo-bioreactors and also to analyze the current status of micro-algal hydrogen production. Mona et al. [166] reported that the production cost of hydrogen stands at \$10 GJ^{-1} when microalgae are cultivated utilizing an open pond system. This study was carried out on a 140-ha open pond and a 14 ha photobioreactor with an annual operating cost of \$10 M and a capital cost of \$43 M. In addition, the annual production yield reaches 1,200 TJ hydrogen only when the plant runs at 90% of its operational capacity.

Gholkar et al. [167] conducted a cost analysis study of a microalgal hydrogen production plant for which a capital cost of \$144.6 M was determined for the hydrogen production of 1,239 kg/h. The product value was assessed to be \$10 kg^{-1} after an in-depth cost analysis of the whole manufacturing technique. Also, the study revealed that this plant takes only 3.78 years to recover the initial investment with an internal rate of return of 22%. Hence, this method was considered to be cost-effective. Acar et al. [162] analyzed the overall costs for direct and indirect biophotolysis where the direct process generated a capital cost of \$50 m^{-2} and a production cost of \$2.13 kg^{-1}. On the other hand, for the indirect biophotolysis process, the production cost was found to be \$1.42 kg^{-1} with a capital cost of about \$135 m^{-2} [160, 162]. The production costs of different hydrogen production methods are summarised in Table 5.

Table 5. Different H_2 production methods and their costs

H_2 production method	Energy source	Capital cost	H_2 production cost	Ref.
Steam reforming with carbon capture and storage (CCS)	Natural gas	\$226.4M	\$2.27kg^{-1}	[82]
Steam reforming without CCS	Natural gas	\$180.7M	\$2.08kg^{-1}	
Photo-electrolysis	Solar		\$10.36kg^{-1}	
Coal gasification with CCS	Coal	\$545.6M	\$1.63kg^{-1}	

Autothermal reforming with CCS	Natural gas	\$183.8M	\$1.48kg^{-1}	
Thermal gasification of microalgae	Biomass	\$215.3M	\$4.59kg^{-1}	[166]
Supercritical gasification of microalgae	Biomass	\$277.8M	\$5.66kg^{-1}	
Direct bio photolysis	Biomass	\$1220 GJ^{-1}y^{-1}	\$11,170.33 GJ^{-1}	
Indirect bio photolysis	Biomass	\$2.40 GJ^{-1}y^{-1}	\$16.26 GJ^{-1}	
Photo fermentation	Biomass	\$1.41 GJ^{-1}y^{-1}	\$30.7 GJ^{-1}	
Dark fermentation	Biomass	\$0.64 GJ^{-1}y^{-1}	\$155.59 GJ^{-1}	
Coal gasification without CCS	Coal	\$435.9M	\$1.34kg^{-1}	[168]
Dark fermentation	Food waste	\$1,636,560	\$3.20kg^{-1}	[169]
	Waste-water	\$1,615,000	\$2.7 m^{-3}	[170]
Gasification	Lignocellulose biomass	76.9 €	€12.75kg^{-1}	[171]
PEM	Solar PV		\$12.6kg^{-1}	[57]

6. Sustainability analysis of hydrogen production technologies

Hydrogen (H_2) as a fuel has been extolled for offering a greener energy alternative and as a way to address the environmental impacts of energy generated from fossil fuels. However, producing hydrogen requires highly advanced technologies that can also cause widespread environmental degradation during plant construction and production processes [172]. Much of the world's H_2 is produced via coal gasification (CG) and steam methane reforming (SMR) [173]. Particularly, SMR alone contributes to three-quarters of H_2 supply [174] and is accountable for 6% of global natural gas consumption [173,174]. Not surprisingly, SMR is now the most cost-efficient method for producing H_2, followed by CG [82]. H_2 produced by SMR and CG are referred to as "grey hydrogen" and "brown hydrogen", respectively, and are far more competitive than "green hydrogen" that is produced using renewable energy-driven water-splitting [175].

The greenhouse gas footprint resulting from the production of grey hydrogen is significantly large [176,177], with as much as 153 g of carbon dioxide equivalent per megajoule of heat energy produced [55]. Even with the recent advocacy of "blue hydrogen" by the industry, a new concept that comprises the production of H_2 via SMR or CG integrating carbon dioxide capture and storage (CCS) technology [175,178], a recent study revealed that 135 g of carbon dioxide equivalent per megajoule of heat energy is generated even with flue gas capture, causing 20% more emissions than technologies using natural gas or coal for heat and approximately 60% more than those using combusting diesel oil for heat [55]. Therefore, to progress towards climate goals, advancements need to be facilitated in the development of green hydrogen-producing technologies as the supply of green hydrogen to meet a substantial portion of the world's needs has a long way to go [55].

Emissions can also greatly vary depending on the source. For instance, in terms of source, using geothermal power plants to produce H_2 can cause twice the amount of emissions as solar PV applications [179]. This technology is also heavily taxing in terms of technical requirements, such as exergy and energy efficiencies, raw material inputs, and process control is less beneficial in terms of generating employment and training opportunities, and has less favorable health impacts, compared to other renewable sources [48]. In nuclear plants, more than half of the emissions are caused by fuel mining, preparation, and transportation while the rest are contributed by construction, operation, and maintenance [49,180]. Overall, H_2 production through the gasification of biomass creates the highest volume of emissions [48,49,181], with a global warming potential of approximately 4,000 g of carbon dioxide per kilogram of H_2. The most favorable source of H_2 production with the lowest carbon dioxide emissions is wind power [49,182], with a global warming potential of less than 1,500 g of carbon dioxide per kilogram of H_2 [49,181]. Utilizing wind power for H_2 production is also highly beneficial for society, as it has a minimal adverse impact on human health and can lead to the creation of employment opportunities [48]. However, it is not adequately cost-effective [48].

The benefits of using concentrated solar energy to synthesize H_2 can be boosted by synergies with high temperature concentrated solar power [183]. Next to biomass gasification, the different solar-driven H_2 generation methods can result in huge emissions, with the production of up to nearly 3,000 g of carbon dioxide per kilogram of H_2 when utilizing solar thermolysis [49,181].

The construction of photovoltaics (PV) alone results in the highest acidification and emission potentials, exceeding those caused by geothermal and hydropower [184]. Nevertheless, in a sustainability analysis of H_2 production sources incorporating their economic, social, environmental, and technical performance [48], solar power performed the best on average, considering all potential solar-based processes. The major challenge making solar-based production processes less competitive is the associated initial and maintenance costs of solar power plants. In contrast, it has minimal adverse effects on human health and can generate new jobs.

Overall, all renewable pathways for H_2 production are far more environmentally friendly than conventional fossil-based routes. Table 6 exhibits the relative sustainability of different H_2 production technologies based on various sources across different dimensions. In terms of the production system, while nearly all perform adequately in terms of environmental sustainability due to the possibilities of integrating renewable technologies into the process, enhancing the economic feasibility, such as by lowering capital costs, again remains a major bottleneck [48]. Biological methods are also less reliable due to issues with controlling and maintaining cultures and microorganisms and are thus the least likely to be easily scaled up [48]. Biological technologies, often integrated with other systems, such as bio-electrolysis, biolysis, biophotolysis, and biothermolysis, also happen to be non-clean methods of H_2 production with significant emissions [51]. Electric production systems exhibit the best sustainability rating due to their well-rounded performance across various dimensions and the benefits of system advancements related to the use of water electrolysis for extended durations [48]. However, its cleanliness in terms of emissions depends on the process utilized. For instance, the thermolysis of biomass, coal, and fuel can result in significant emissions, but emissions from CG and steam reforming can be reduced using CCS technology [51]. Environmentally, solar-based (photonic) hydrogen production is deemed the most eco-friendly [48].

Table 6. Sustainability of H_2 production sources and systems

Hydrogen production sources	Acidification Potential (g of sulphur dioxide per kg of H_2)* [49,181]	Global Warming Potential (g of carbon dioxide per kg of H_2)* [49,181]	Sustainability rating; calculated based on environmental, social, technical, and economic performance, and reliability (10=most sustainable) [48]

Solar	*solar thermolysis, solar thermal, PV electrolysis, PV photoelectrochemical, photobiological, etc.*	3.5-12	1,200-7,500	7.4
Hydro	*hydraulic electrolysis, etc.*	3.5	1,400	6.0
Wind	*wind electrolysis, etc.*	3.5	750	6.0
Biomass	*biomass gasification, etc.*	32.5	4,000	5.8
Nuclear	*nuclear-pure thermochemical, nuclear hybrid thermochemical, nuclear high-temperature steam electrolysis, etc.*	4.5-5	1,650-2,000	4.6
Geothermal		-	-	4.6

H_2 production systems	Sustainability rating; calculated based on economic, environmental, social, and technical performance, and reliability (10=most sustainable) [48]	Relative cleanness (C= Clean with no emissions; N= Non-clean with emissions; CCS= Quasi-clean by using CCS) [51]
Electrical	7.6	C
Thermal	6.6	C/N/CCS
Photonic (solar-based)	5.4	C/N
Biological	4.8	N

*approximates

7. Advantages and challenges of hydrogen production technologies

Modern technologies have inevitably made promising achievements in hydrogen production. However, several obstacles throughout the process must be overcome Many operational and cost-related obstacles still standing in the way of the effective production of hydrogen. Some major and common challenges for the hydrogen production processes are discussed in the following.

To generate hydrogen, natural gas must undergo steam reforming, which means that hydrogen can never economically outperform natural gas as an energy carrier on a unit energy basis. Furthermore, certain other obstacles hinder an increase in H_2 generation via the natural gas steam reforming process. A substantial amount of energy is lost during the steam reformation process which requires strong capital investment if the hydrogen industry is to meet global needs [68]. If hydrogen is to be used to tackle climate change, cost-effective carbon capture and storage must be developed, which is also challenging.

Many hydrogen generation methods face oxygen sensitivity. Because oxygen molecules are particularly sensitive to hydrogenase during biohydrogen generation from wastewater microalgae and the hydrogenase enzyme's activities are inhibited [185]. As such bonds are completely irreversible, extracting oxygen and hydrogen molecules from this complex combination becomes considerably more challenging [186]. The generation of hydrogen molecules is considerably reduced when these hydrogenase activities are blocked. To address this obstacle, bioengineered oxygen-tolerant microalgal species are required, as well as hydrogenase enzymes capable of overcoming their oxygen sensitivity [178,66]. Many bioreactors are found very expensive in their implementation. Operating cost is another key challenge in producing hydrogen from wastewater-based microalgae on a large scale. Such costs must be reduced to make these technologies acceptable to stakeholders at various levels. Technology-specific challenges and their advantages are illustrated in Table 7.

Table 7. Advantages and challenges of different hydrogen production technologies

Name of the Technology	Advantages	Challenges
Thermolysis	- Maximum conversion	- Significant amount of gas conditioning is needed
Electrolysis	- Opportunities for synergy with renewable energy power generation - Oxygen is generated for space and hydrogen is used for fuel cell	- Operating cost is very expensive and 80% used only for electricity consumption - Difficult to reduce cost because of degradation processes and electrolyzer cell
Photo-electrolysis	- Promising efficiency - Cost-efficient	- Band structure in photocatalyst semiconductor - Noble metals difficult to find

		- Separation of oxygen to achieve hydrogen yield
Thermochemical	- A less complicated and efficient technique was utilized. - Low-cost installation - Various scopes to optimize system configuration by combining efficient technologies	- Production of char/tar - Less energy efficient - Multistage process in pyrolysis so more complex
Biological	- Makes extensive use of solar energy - Simple to install - Produces hydrogen effectively in the short term - Abundant supply - Suitable for nitrogen fixation in the environment - No need for highly sensitive reactors - Less energy required - Sustained supply	- Oxygen hinders hydrogen yield - Rate falls due to macronutrient shortage - Expensive separation equipment is required to extract hydrogen - Water contamination - Low hydrogen yield - Thermodynamic difficulties
Partial oxidation	- Minimal desulphurization needed - No dependence on a catalyst - Reduced methane flow	- Limited H2/CO ratio - Relatively high temperatures - Difficult operating procedure
Hydrocarbon pyrolysis	- High heat degrades harmful components and microorganisms - Decrease water because of operating temperature - Reduce reliance on external fuel sources by utilizing the produced gases as fuel	- Char production - Gases cannot be vented out without treatment because of high CO volume
Autothermal reforming	- More economical	- Insufficient economic skills

	- Less temperature required for processing - Minimum methane leakage	- Necessity for air/oxygen
Steam reforming	- No oxygen requirement for the process - Most advanced industrial process - Minimum operational temperature - Optimal H_2/CO ratio	- Comparatively maximum levels of air pollution

8. Conclusion and future directions

Hydrogen is potentially a huge component of the pathway away from the greenhouse gas-emitting fossil fuels with different kinds of production, storage, and distribution. It has far-reaching applications across various sectors, including industry, transport, and municipal energy systems. But for a sustainable transition, hydrogen as a fuel should be clean, safe, efficient, cost-effective, and reliable. A diverse range of processes can be used to produce H_2. The most polluting methods are also the most cost-effective, making it difficult to mitigate dependence on these techniques. For instance, SMR and coal gasification (CG) produce H_2 for \$3.50/kg, while most technologies' production cost is above this value.

Water-splitting offers one of the most environmentally benign production systems, as it can tap into renewable energy sources to drive the electrical systems. However, it can only emerge as a competitive method if reliance on fossil fuels is curbed using carbon taxes. Currently, high capital costs and low conversion efficiencies result in a high production cost, often exceeding \$8/kg and \$20/kg for thermolysis and electrolysis, respectively. PEMs derive the highest H_2 production cost, while nuclear-based technologies offer the lowest. However, nuclear power can have adverse impacts on the environment and public health and pose challenges in terms of techno-economic feasibility and is therefore not adequately sustainable for H_2 production in the long run. Overall, solar-driven technologies exhibit the greatest promise for H_2 production, as they provide advantages in terms of minimal health impacts and opportunities for job creation. Even though they have a wide range of costs, solar thermochemical processes and electrolysis both result in a cost of less than \$10/kg. Wind power also offers advantages similar to solar power, but it is currently implemented only using electrolysis, which makes it more expensive compared with fossil-based H_2 production technologies, with a cost range of \$5–\$8/kg. Even though biomass and geothermal-based production technologies are feasible, the former has many challenges related to maintenance and reliability, while there is a severe lack of knowledge regarding the economic feasibility of the latter.

To expand the applicability of H_2 and realize the hydrogen economy, several research gaps need to be addressed. These include, but are not limited to:

- Significant attention must be placed on decarbonizing H_2 production systems to truly take advantage of the environmental benefits of the fuel. Thus, the reliance on fossil fuels must be lowered. Moreover, currently, much of the renewable production systems have substantially high investment and production costs, low efficiencies, and are not feasible on a large scale. Production systems need to be designed and developed to be more affordable, reliable, clean, and efficient, with a low threshold for process parameters including pressure and temperature.
- In addition to the research gaps in H_2 production, there are also large bottlenecks in the area of H_2 storage and distribution. These include developing cost-effective storage methods at moderate temperature and pressures, improving the volumetric and gravimetric densities of storage systems, and lowering the time taken to charge and discharge storage systems, and enhancing the lifetime of storage systems. Improvements also need to be made to distribution networks for long-distance transport of H_2 with minimal loss. H_2 is primarily transported as a cryogenic liquid or compressed gas, which is highly inefficient and expensive. Therefore, the benefits of advancements in storage systems will also translate into the H_2 transportation network.
- Cost reductions in storage and distribution are pivotal to the scale-up of hydrogen energy systems across different sectors. For widespread utilization in the transportation sector, research needs to be directed towards developing cost-effective fuel cells and electric vehicles with hydrogen-powered internal combustion engines. Extensive use of hydrogen in the industry is possible only if the cost of H_2 is competitive with fossil fuels. The installation of sufficient and accessible fuelling stations needs to be integrated into distribution networks for rapid uptake by end-users.
- Electrolysis of water with excess wind and solar photovoltaic electricity is the only pathway considered feasible at the present stage to deliver the amounts of hydrogen needed

at an acceptable price. Many of the other technologies here considered suffer from the scale effect – i.e. these pathways simply cannot produce all the hydrogen needed. These pathways may only be considered further contributors to hydrogen production mostly by electrolysis.

- Thermochemical hydrogen production, which may progress CO_2 free from feedstocks not only of water but also CH_4, is potentially the only other large-scale method. This method has not to compete with electrolysis, but to complement electrolysis. In this case, the availability of thermal energy at 1,000-1,100 degrees Celsius from concentrated solar is not a problem, as concentrated solar power is already evolving towards higher temperatures, and synergies between power generation and hydrogen production are possible. Schemes which need higher temperatures are much more troublesome and difficult to transform into an industrial product. Two-step thermochemical cycles for solar hydrogen production from water have a low technology readiness level. Much easier is to develop an industrial product from a three-step thermochemical cycle for solar hydrogen production from water, such as the Sulphur-iodine cycle here discussed, which can be done even more efficiently (it was developed for temperatures about 900-950 ^oC from nuclear thermal energy).
- A net-zero future is only achievable if the hydrogen economy and the electric economy continue to advance, as these two building blocks are synergistic and complementary [187].

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