

Review

A brief review of hydrogen production technologies

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Abstract: As a result of the array of problems arising from the use of fossil fuels, it is necessary to develop and optimize alternative energy technologies. Despite hydrogen being an ideal form of energy, its primary source is still fossil fuels via conventional methods. Therefore, several hydrogen-production resources and techniques have been investigated, providing feasibility for clean and effective hydrogen production. This paper provided a mini-review of hydrogen production technologies, including renewable energy, chemical looping, water electrolysis, photocatalysis, and plasma.

Keywords: hydrogen energy; new energy utilization; hydrogen production technology; renewable energy

1. Introduction

With the growth in the world economy and population, the demand for energy increases continuously. Fossil fuels are still the primary energy resources, but their use results in significant CO₂ emissions [1–3]. The massive release of CO₂ increases the absorption of solar and long-wave radiations from the earth's surface, exacerbating the greenhouse effect, which causes nonuniform heat and cold zones and severely threatens agricultural production and ecosystems [4–6].

Currently, 48% of hydrogen energy comes from natural gas, 30% from petroleum products, and 18% from coal. Given the environmental problems associated with the burning of fossil fuels, obtaining alternative energy resources and efficient production technologies is pressing. Hydrogen energy is considered an ideal energy source due to its high energy efficiency, environmental friendliness, ease of transport, and versatility [7–9]. The development of hydrogen not only helps to solve the energy crisis and reduce greenhouse gas emissions but also helps to promote sustainable economic development, meet global emission reduction targets, and address climate change [10].

Owing to these features, hydrogen energy is widely used in various applications, including power generation and fuel cells in the electricity sector, vehicles and aerospace in the power sector, as well as in chemical and food processing industries [11–13]. Hydrogen is obtained through the reforming or thermal cracking of fossil resources, but these resources are non-renewable. Furthermore, this process leads to the production of pollutants, such as NO_x, SO_x, etc., affecting the environment and human health.

At present, most of the research on clean energy hydrogen production focuses on the use of water electrolysis using renewable energy sources (such as solar, wind, geothermal, tidal, and nuclear energy) to produce hydrogen, as the process of producing hydrogen by these methods is free of greenhouse gas emissions, hence

reducing the impact on the environment and realizing a low-carbon production [14–18].

However, research is still needed to optimize equipment cost and hydrogen production efficiency. Therefore, this review presents state-of-the-art clean hydrogen production technologies: renewable resources, chemical looping, water electrolysis, photocatalytic, and plasma.

2. Renewable-energy hydrogen production

Renewable energy resources refer to resources that can be continuously regenerated and sustainably used. They are environmentally safe, widely distributed, and suitable for local development and utilization. Renewable energy mainly includes solar, wind, water, biomass, geothermal, and ocean energy. The advantages of renewable energy compared with traditional fossil energy are as follows:

- 1) It is inexhaustible, and its resources can be recycled in nature. Compared with fossil energy, the reserves of renewable energy are larger and can meet the long-term needs of mankind.
- 2) It does not produce harmful substances and exhaust gases and has less impact on the environment.
- 3) The use of renewable energy can greatly reduce the dependence on traditional energy, promote the sustainable development of society, and promote the balanced distribution of energy.

Therefore, the production of hydrogen is gradually developing from fossil fuels to renewable energy sources [19]. Compared with fossil fuels, renewable-energy hydrogen production using biomass has the following advantages:

- 1) Its renewable resources are abundant and diverse. The thermal conversion of biomass for hydrogen production is considered an effective transformation method. This technique, due to its simple equipment operation and minimal environmental pollution, is gaining increasing attention.
- 2) Biomass can capture CO₂ from the air through photosynthesis, convert it into stored energy, and release CO₂ when the energy is utilized. Thus, the use of biomass is carbon-neutral.

Currently, there are two main methods of biomass thermal conversion for hydrogen production: biomass gasification and biomass tar reforming.

2.1. Biomass gasification

Biomass gasification for hydrogen production refers to the process of converting hydrocarbon organic matter into hydrogen through a gasifying agent (air, steam, or oxygen). As shown in **Figure 1**, the biomass enters the reactor and first undergoes drying (about 200 °C) and then pyrolysis (200–500 °C). The generated pyrolysis gas reacts with the gasification agent, followed by further oxidation-reduction reactions of the char produced from biomass pyrolysis with the gasifying agent (500–800 °C), ultimately producing hydrogen-rich gas. Depending on the flow of the biomass, reactors are divided into fixed-bed and fluidized-bed reactors.

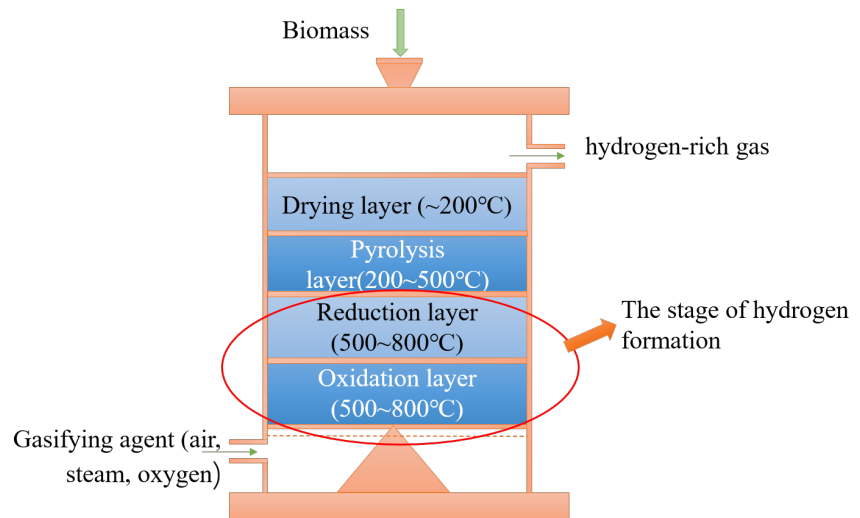


Figure 1. Biomass gasification process.

Each type of reactor has its advantages and disadvantages. For instance, a fixed-bed reactor is an intermittent reactor with simple equipment and easy operation. However, it has low reaction efficiency, and so it is not feasible to employ on a large scale. Conversely, a fluidized-bed reactor has high reaction efficiency and equipment cost. However, the biomass gasification process inevitably produces biomass tar. Biomass tar is a highly viscous and corrosive liquid that can easily block and corrode pipelines, affect operation and equipment, and pose safety hazards [20,21]. Moreover, the presence of tar increases the operating cost of subsequent separation, purification, and refining of product gas. On the other hand, because the energy density of biomass is low, gasification efficiency is limited.

2.2. Biomass tar reforming

Compared with direct biomass gasification for hydrogen production, biomass pyrolysis is a process where biomass is thermally decomposed in an oxygen-free environment to produce pyrolysis gas and pyrolytic oil. As the pyrolysis reaction temperature is relatively low, the biomass tar produced is a mixture containing C_6^+ substances that require higher reaction temperatures for gasification conversion. Through reforming, the high-carbon substance in tar is transformed into a low-carbon substance, which converts to hydrogen under the effect of steam [22], as shown in **Figure 2**. Due to the high energy density of tar, ease of transport, and less environmental influence, it has a higher application value and conversion efficiency compared with direct biomass hydrogen production. Therefore, extensive research is being done to investigate biomass tar's influencing factors and reaction mechanisms for hydrogen production.

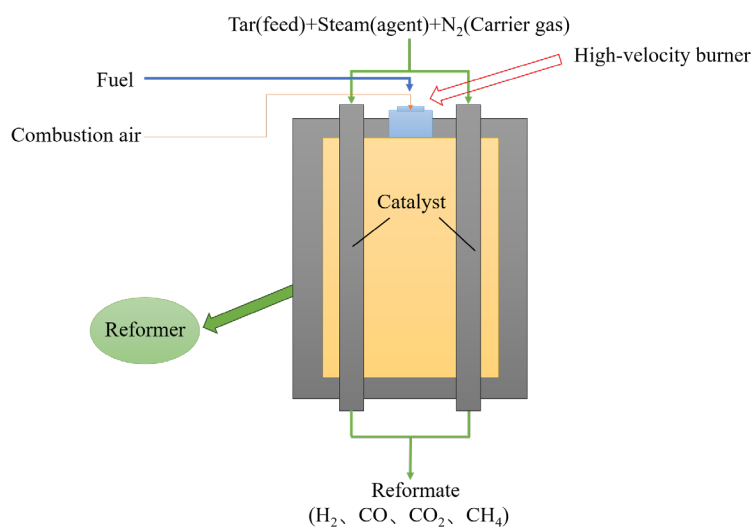


Figure 2. Hydrogen production process of biomass tar reforming.

Biomass tar is a complex mixture consisting of about 300 components that exist in aqueous and oil phases. Oil-phase biomass tar refers to biomass tar that can dissolve in the oil phase, such as benzene, toluene, naphthalene, esters, furans, and other aromatic compounds. Aqueous-phase biomass tar refers to biomass tar that can dissolve in the water phase, such as aldehydes, acids, ketones, ethers, etc. To study the reaction mechanism and potential influencing factors of hydrogen production from biomass tar reforming [23–25], model compounds of tar are chosen.

Toluene accounts for about 22% of oil-phase components [26], so toluene is often used as the model compound for tar. Trinh et al. [27] presented the decomposition steps of toluene on the (111) crystal face of Ni-based catalysts through the density functional theory (DFT) simulation. The result showed that the first step of the decomposition reaction is the breakdown of the C-H bond in the -CH₃ group. Its required activation barrier and reaction energy are 72 kJ/mol and -13 kJ/mol, respectively. This is attributed to the fact that the benzene ring in toluene does not participate in alkyl C-H bond dehydrogenation, and Step 1 results in the dehydrogenation of -CH₃ in toluene to become a -CH₂ group. Then, the process from Step 2 to Step 3 involves further dehydrogenation of the -CH₂ group, ultimately becoming C. Step 4 involves the dissociation of adjacent or distal C-H bonds on the toluene ring. Starting from Step 5, shorter hydrocarbon chains are formed through the breakdown of aromatic C-C bonds, making it possible for the benzene ring in toluene to open up. In the steam reforming of toluene, the role of steam in the opening of the toluene ring also needs to be considered. Mukai et al. [28] conducted a mechanistic study of the catalytic steam-reforming reaction of toluene using a Ni-based La_{0.7}Sr_{0.3}AlO₃ perovskite catalyst via in-situ Fourier transform infrared (FTIR) spectroscopy. The results showed that the impact of water vapor between 1250–1750 cm⁻¹ was small and the intermediate products of the toluene reaction were produced in this wavenumber segment. To identify the produced intermediates, probe molecules, such as benzene, n-heptane, ethylene, and benzaldehyde, were introduced on the surface of the Ni-based catalyst. It was ultimately determined that in the

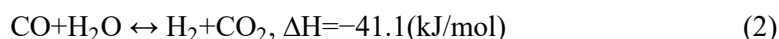
presence of steam, toluene decomposed into C₂-type molecules, thus forming reaction intermediates on the surface of the Ni-based La_{0.7}Sr_{0.3}AlO₃ perovskite catalyst.

Compared with oil-phase biomass tar, hydrogen production by reforming aqueous-phase biomass tar is more valuable. This is because aqueous-phase biomass tar contains less carbon and has a lower utilization value. Acetic acid is a representative of aqueous-phase components, not only because of its high content (about 30%) [29], but because its high flash point makes it easy to transport and store and it is a safe carrier for hydrogen storage. In addition, compared with other aqueous-phase components, acetic acid has a higher hydrogen content (4 moles of hydrogen can be produced from 1 mole of acetic acid). Therefore, acetic acid is one of the best candidates for reforming hydrogen production. The reforming reaction of acetic acid is a complex process that does not only undergo steam reforming but can also undergo pyrolysis, dehydration, polymerization, and other reactions to form organic matter with C₁, C₂, C₃, and more carbon chains [30]. The reactions that occur are shown in Equations (1–16):

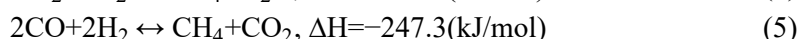
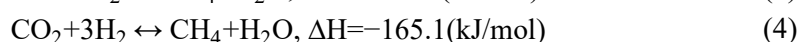
Acetic acid steam reforming reaction:



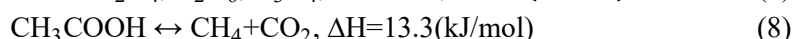
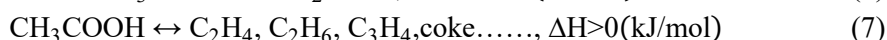
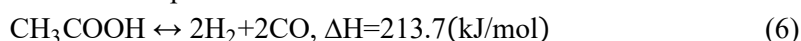
Water vapor transition reaction:



Methanation reaction:



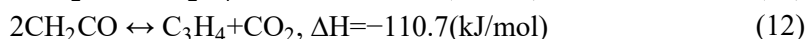
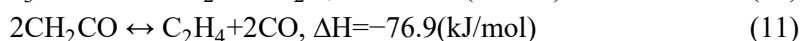
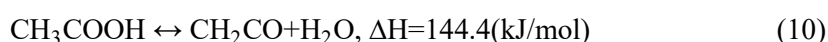
Acetic acid thermal decomposition reaction:



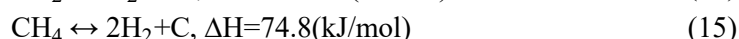
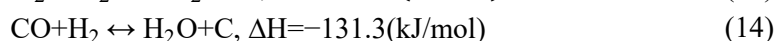
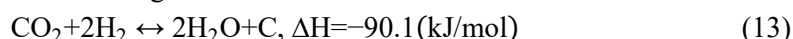
Acetic acid decarboxylation reaction:



Keto-acetic acid reaction:



Carbon deposition forming reaction:



Inverse Boudouard reaction:



Hoang et al. [31] studied the steam-reforming reaction pathway of acetic acid using a Ni-based catalyst and believed that the dissociation of acetic acid was mainly divided into two pathways:

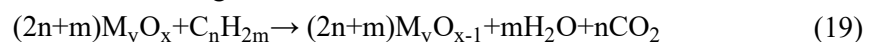


The two different reaction pathways result in different intermediate products in the reforming reaction of acetic acid, which affects the conversion of acetic acid. Wang, Li, et al. [32] used the DFT to simulate and compute the dissociation barrier of acetic acid on the (111) crystal face of a Ni-based catalyst. The results showed that the energy barrier required for acetic acid to dissociate into CH_3COO^* was 0.47 eV, while the energy barrier required for it to dissociate into CH_3CO^* was 1.06 eV. This indicates that acetic acid is more likely to dissociate into CH_3COO^* . Furthermore, the energy barriers needed for CH_3COO^* to lose an O^* and form CH_3CO^* , and for CH_3COO^* to lose COO^* and form CH_3^* , were 1.15 eV and 1.96 eV, respectively. Therefore, CH_3CO^* is the most likely intermediate product.

The main challenge currently facing hydrogen production via biomass thermal-dissolving is that efficient use of biomass is vital in biomass thermolysis processes. Currently, the methods are not very efficient in the production of different high-value products. Therefore, new heating technologies should be considered to improve energy efficiency and quality. In addition, the integration and optimization of biomass thermal solution systems should take into account multiple factors, such as energy efficiency, environmental pollution and carbon dioxide reduction, and economic benefits.

2.3. Chemical-looping hydrogen production

Chemical-looping biomass gasification is a novel method for hydrogen production. The concept originated from chemical-looping combustion proposed by Lewis et al. [33] in 1949. In the process of chemical-looping combustion, as shown in **Figure 3**, there are mainly two reactors, namely, the fuel reactor and the oxygen carrier regenerator [34]. In the fuel reactor, a reduction reaction occurs (Equation (19)). Hydrocarbon fuels combust with the oxygen released by oxygen carriers, generating CO_2 , H_2O , and the reduced oxygen carriers. This process is also a CO_2 capture process, which is conducive to reducing CO_2 emissions.



In the oxygen carrier reoxidation, the reduced oxygen carriers are calcined in an air environment, re-acquiring the oxygen carriers, as described in Equation (20). Since the regeneration process of oxygen carriers requires a high calcination temperature, part of the heat is brought into the oxygen carrier re-generator by the oxygen carriers during the cycle from the combustion furnace. In such a cyclic process, the heat is effectively utilized, and the produced CO_2 is captured.



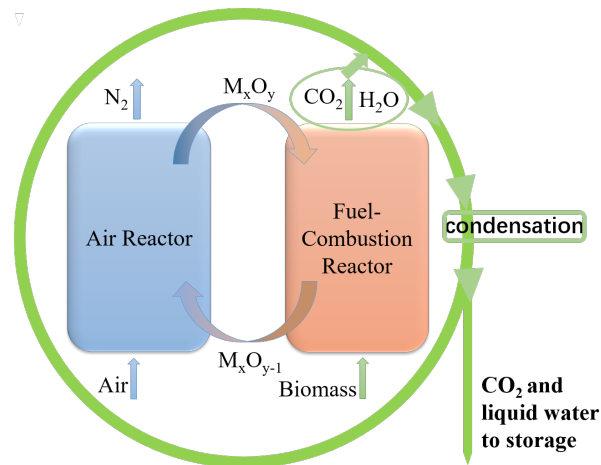


Figure 3. Process of biomass chemical-looping combustion.

This approach can be applied to hydrogen production through biomass gasification by replacing the combustion process with gasification. The main difference is that instead of producing heat, the goal is to produce hydrogen gas. Similar to chemical-looping combustion, the gases produced are separated within the system itself, meaning that there is no need for expensive and energy-intensive gas separation processes. This makes chemical-looping gasification a potentially efficient and cost-effective process for hydrogen production from biomass.

Indeed, in the chemical-looping gasification process, as shown in **Figure 4**, the lattice oxygen of oxygen carriers (MeO_x) oxidizes the biomass in the fuel reactor. The oxygen carriers lose lattice oxygen and transform into oxygen-deficient oxygen carriers (MeO_y), yielding pure CO_2 .

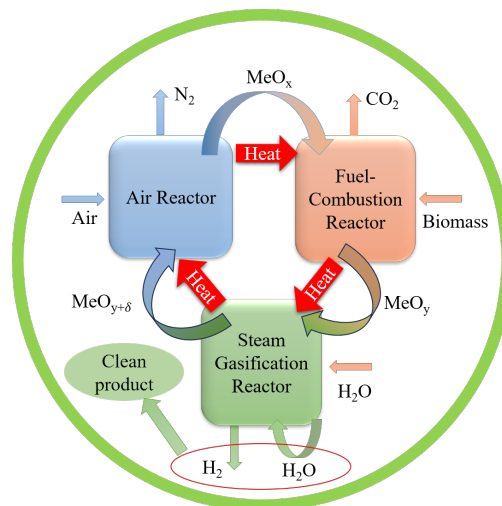


Figure 4. Process of biomass chemical-looping gasification.

In the steam gasification reactor, MeO_y oxygen carriers react with steam to produce H_2 . Also, MeO_y oxygen carriers are partially oxidized to form sub-lattice-state oxygen carriers ($\text{MeO}_{y+\delta}$). Unprocessed water can be condensed to obtain pure H_2 without needing a complex purification system. Finally, $\text{MeO}_{y+\delta}$ oxygen carriers are introduced into the air reactor to replenish lattice oxygen and restore the original oxygen-carrier state (MeO_x) for the next cycle. This gasification method reduces the

dilution of hydrogen-rich gas by N_2 in traditional gasification agents, such as air, making CO_2 easier to enrich and enhancing the quality of hydrogen. It also has the following advantages:

- 1) Since the oxidation and reduction of biomass are separated into two independent steps, this realizes the cascading application of reaction energy and significantly reduces the heat consumption of the fuel reaction.
- 2) The oxidation step is completed through oxygen carriers, avoiding direct contact between biomass and air, thereby reducing the formation of impurities, such as NO_x .
- 3) The oxidation efficiency of lattice oxygen in oxygen carriers is higher than that of gasifying agents, improving the utilization efficiency of biomass. Oxygen carriers play a critical role in this process. Current research on oxygen carriers mainly focuses on single-metal oxide and multi-metal oxide oxygen carriers.

However, with the increase in temperature and with long-term cycles, the performance of oxygen carriers will be affected by sintering, reducing hydrogen production efficiency [35]. Therefore, the future research direction of chemical-looping hydrogen production should be to explore a large number of oxygen carriers with good performance and cheap sources, such as modifying some useful substances in steel industrial slag and mining waste to obtain the best oxygen carriers. Common oxygen carriers are briefly presented below.

a. Monometallic oxygen carriers

Fe_2O_3 is a representative of single-metal oxides. From the perspective of Gibbs free energy change, Fe_2O_3 oxygen carriers react with fuel and undergo reduction reactions with steam for hydrogen production, fulfilling the energy transformation. From the perspective of hydrogen production conversion, Fe_2O_3 oxygen carriers are suitable for use in hydrogen production because Fe_2O_3 has various valence states, such as Fe_3O_4 , FeO , and Fe . In the presence of steam, FeO and Fe have an extremely high ability to produce hydrogen [36]. However, due to its low cost and easy accessibility, Fe_2O_3 is widely used.

Kobayashi et al. [37] studied the oxidation characteristics and pyrolysis performance of Fe_2O_3 oxygen carriers in biomass pyrolysis. The research showed that the volume and composition of the produced gases varied depending on the phase of iron oxide. Among them, Fe_2O_3 exhibited the strongest oxidation capability, while FeO showed a higher tar-cracking ability. The order of carbon deposition on Fe-based oxygen carriers is $FeO > Fe_3O_4 > Fe_2O_3$. However, Fe_2O_3 oxygen carriers cannot satisfy long-term cycle testing, as they lose activity due to sintering. Increasing the specific surface area of Fe_2O_3 is beneficial for improving sintering resistance, increasing lattice oxygen transfer, dispersion of active components, etc. Chang et al. [38] studied the effect of the hierarchical pore structure of Fe_2O_3 oxygen carriers on the performance of biomass chemical-looping hydrogen production. The results showed that Fe_2O_3/Al_2O_3 oxygen carriers prepared with propylene oxide as an additive had a relatively high hydrogen production efficiency of 343 mL H_2/g . The prepared Fe_2O_3/Al_2O_3 oxygen carriers with a hierarchical pore structure can generate more active sites and prolong the contact time between reactants and oxygen carriers,

thereby enhancing hydrogen production activity. In addition, SiO_2 , TiO_2 , MgAl_2O_4 , etc., have also been studied as supports for Fe_2O_3 [39,40].

b. Polymetallic oxygen carriers

Although a support can enhance the stability and reactivity of single-metal oxides, in some cases it reacts with the active phases and reduces the oxygen-transport capacity. Studies have shown that bimetallic or multivalent metal oxides may improve the oxygen-carrying capacity of carriers, especially when they form certain structures, such as spinels or perovskites.

The spinel structure is AB_2O_4 . In this structure, O^{2-} forms a cubic, close-packed structure, creating two types of voids: tetrahedral and octahedral. The A and B metal ions fill these voids. One cation occupies the A site of the tetrahedral spinel, while another cation occupies the B site of the octahedral spinel, as shown in **Figure 5** [41]. The spinel structure can be composed of two or more elements, and it can generate oxygen vacancies. These vacancies play a crucial role in electron conduction and the transfer of lattice oxygen in oxygen carriers. Simultaneously, they act as catalysts in water-gas shift reactions, accelerating hydrogen production. Due to their advantages, CaFe_2O_4 and NiFe_2O_4 are currently the most researched spinels.

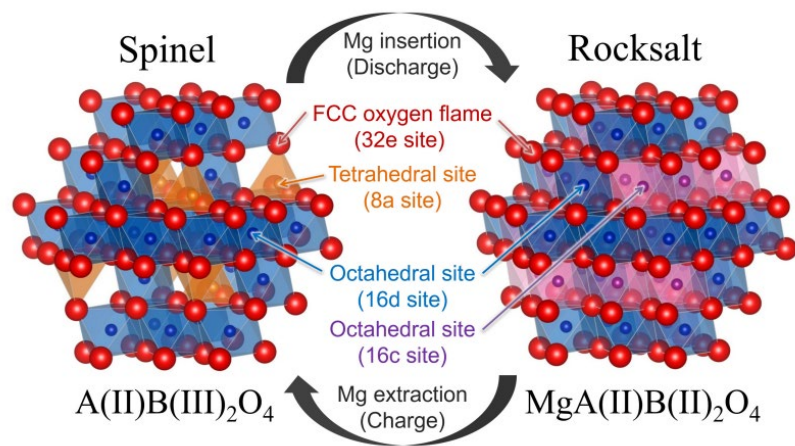


Figure 5. Structure diagram of spinel [41].

For CaFe_2O_4 oxygen carriers, Hu et al. [42] synthesized two types of oxygen carriers, which were CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$, by adjusting the Ca:Fe ratio. The results showed that $\text{Ca}_2\text{Fe}_2\text{O}_5$ oxygen carriers formed at a Ca:Fe ratio of 1:1 had a higher hydrogen production rate, attributed to their redox performance. However, after three cycles, Si from the biomass disrupted the Fe-Ca metal structure, forming CaSiO_3 and Fe_2O_3 , leading to a decrease in hydrogen production during the chemical cycle. Liu, Luo et al. [43] studied the solid-solid reaction of CaFe_2O_4 with biomass tar and the gas-solid reaction between steam and oxygen carriers. They found that the main components of the solid-solid reaction were CO and CO_2 , with CO transforming into CO_2 as the reaction temperature increased. However, hydrogen production mainly originated from the gas-solid reaction.

For the NiFe_2O_4 spinel, Huang et al. [44] investigated the redox ability of NiFe_2O_4 in the process of chemical-looping steam reforming. The results showed that the

synergistic effect between Fe and Ni exhibited a strong hydrogen-production ability after reduction in a reducing atmosphere. However, thermodynamic constraints caused the reduced-state oxygen carriers to only partially restore lattice oxygen in a steam atmosphere to a ternary mixture phase of Ni, Fe_3O_4 , and $\text{Ni}_{(1-x)}\text{Fe}_{(2+x)}\text{O}_4$. To improve the stability of NiFe_2O_4 , Gao et al. [45] doped Ce into NiFe_2O_4 oxygen carriers to enhance hydrogen production efficiency and reaction stability. The results showed that when the addition of Ce was 6%, NiFe_2O_4 oxygen carriers had the highest hydrogen production rate, which was attributed to the fact that doping with Ce improved the oxygen release capability and the stability of oxygen carriers.

3. Other hydrogen production methods

3.1. Water electrolysis for hydrogen production

The basic principle of hydrogen production using electrolytic water is that, under the action of direct current, water molecules are separated into hydrogen and oxygen through an electrochemical process, which are precipitated at the cathode and anode poles, respectively. Depending on the differences in technology and structural principles, water electrolysis methods can be divided into alkaline water (ALK) electrolysis, proton-exchange membrane (PEM) pure water electrolysis, anion-exchange membrane (AEM) hydro-electrolysis, solid oxide electrolyzer cell (SOEC) hydrolysis, and other methods. For the first three reaction temperatures of about 70–90 °C, SOEC needs to react at a high temperature of 700–800 °C.

ALK and PEM electrolytic hydrogen productions have been commercialized, while AEM and SOEC electrolytic hydrogen productions are still in the laboratory investigation stage. The technical routes of the above-mentioned four electrolytic-water hydrogen productions are shown in **Figure 6**.

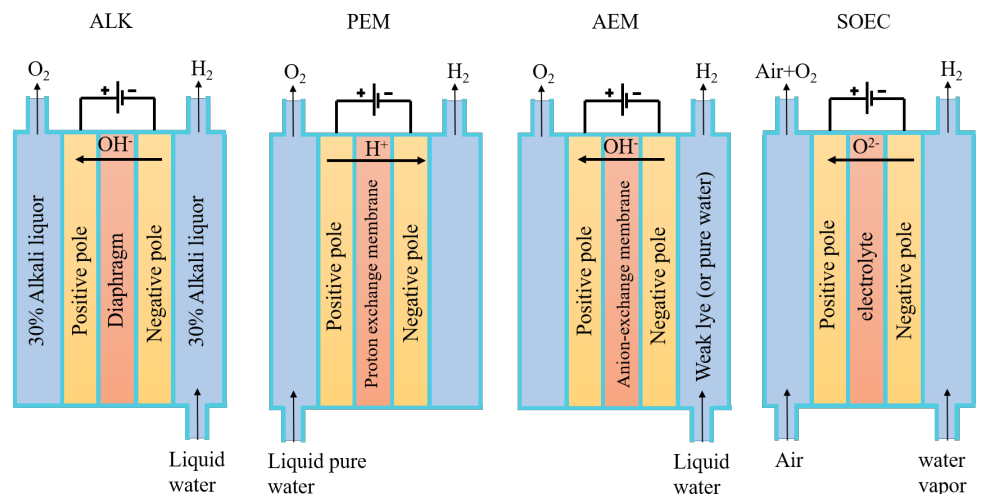


Figure 6. Four principles of hydrogen production via electrolytic water.

3.1.1. Alkaline water (ALK) electrolysis

Alkaline water electrolysis is one of the most widely used methods to produce hydrogen via electrolysis. The principle of ALK electrolysis is to produce hydrogen

by electrolyzing water molecules in an alkaline solution, and this conversion predominantly encompasses two electrode reactions:

Negative pole:



Positive pole:



The alkaline water electrolysis method has high potential and can precipitate high concentrations of alkali metal cations. Therefore, in the production of high-concentration and high-purity products, the alkaline water electrolysis method has significant advantages. In addition, the alkaline water electrolysis method is suitable for the treatment of a variety of complex raw materials, such as organic matter, inorganic matter, and biomass.

Precious metal ruthenium (Ru) demonstrates impressive results as an electrocatalyst for hydrogen evolution reaction (HER). However, its high cost is one of the main obstacles to widespread application. So, studies have been conducted to reduce its cost. For instance, Wang et al. [46] incorporated titanium dioxide (TiO₂) into Ru and observed its influence on hydrogen evolution reaction. Their study revealed that the synergistic interaction between TiO₂ and Ru substantially accelerated the hydrolysis of intermediate hydrogen and the subsequent production of H₂ via an electrochemical hydrogen evolution reaction.

Similarly, Guo et al. [47] enhanced the electrocatalytic performance of Ru significantly via hybridization with cobalt oxide (CoO). The catalytic effect of this Ru/CoO hybrid was revealed to be similar to those of the most advanced platinum/carbon (Pt/C) catalysts. This enhancement was attributed to strong interactions between Ru nanoparticles and the support, ensuring the long-term stability of the prepared Ru/CoO hybrid catalyst. Apart from these precious metals, non-precious metals, such as nickel (Ni) and cobalt (Co), have also been explored.

The positional surface self-reconstruction of the electrocatalyst plays a crucial role in the efficient catalytic hydrogen reaction and the oxidation reaction of organic compounds. Li et al. [48] developed a metal pre-electric catalyst with a Ni@O-rich Ni layer (Ni@O-Ni) and a core@shell structure. The results showed that the structure had a unique adaptive capacity to reconstruct the dependent power level, thereby generating the actual active position of the catalytic reaction. Reconstructed Ni@Ni/NiO_x demonstrated excellent HER activity during cathode activation.

Li et al. [49] successfully developed Co₉S₈-Ni₃S₂ hetero-interfacial nanotubes (Co₉S₈-Ni₃S₂ HNTs/Ni) using a two-step hydrothermal method. It was found that the catalytic performance was significantly superior to that of monophase Co₉S₈ nanotubes and Ni₃S₂ nanosheets on Ni foam. This was probably due to the formation of a defect-rich heterogeneous interface between Co₉S₈ nanotubes and Ni₃S₂ nanosheets, as well as a significant change in binding energies of Co 2p and Ni 2p energy levels between Co₉S₈ and Ni₃S₂, resulting in a synergistic action to enhance catalytic activities of HER and oxygen evolution reaction (OER).

However, ALK electrolytic cell faces the problems of low H₂ purity, high ohmic loss, and slow kinetics in a high-PH electrolyte. The modification of electrocatalysts with transition metal can alleviate these problems to some extent.

3.1.2. Proton-exchange membrane (PEM) pure water electrolysis

PEM pure water electrolysis is electrolysis in an acidic solution. Its electrolytic efficiency is relatively high but it will produce a lot of by-products, such as chlorine gas. The acid electrolysis rule is mainly applicable to the production of high-purity and high-concentration products. In some cases, the acid electrolysis method can even obtain close to the theoretical maximum current density. Acidic electrolysis has a high reaction rate and easily controlled ionic mobility, which maximizes current efficiency [50]. Fukazawa et al. [51] developed an electrocatalytic asymmetric hydrogenation reaction using a PEM reactor. The results showed that current efficiency was good under mild conditions.

3.1.3. Anion-exchange membrane (AEM) hydro-electrolysis

The main structure of an AEM electrolytic cell consists of an anion-exchange membrane and two transition-metal catalytic electrodes [52]. Generally, distilled water or a low-concentration alkaline solution is used as the electrolyte. The role of the anion-exchange membrane in the AEM electrolytic water system is to conduct OH^- from the cathode to the anode, while preventing the direct transfer of gas and electrons between the electrodes [53]. AEM electrolysis technology combines the advantages of ALK water electrolysis and PEM hydro-electrolysis, allowing for the use of non-precious metal catalysts, such as Ni, Co, and Fe, in an alkaline medium. Additionally, it does not require a concentrated alkaline liquid as its electrolyte, thus avoiding pollution from the product gas [54–56].

However, due to the cost of anionic membranes, this method has not been applied on a large-power scale in China [57]. Jiang et al. [58] synthesized poly(biphenyl alkylene) (PBPA) AEM for water electrolysis in an efficient and durable anion-exchange membrane. The findings demonstrated that the polymer composition and the choice of electrolyte significantly influenced the performance and durability of PBPA-based anion-exchange membrane water electrolysis (AEMWE) systems, highlighting the potential of PBPA-based AEM electrolysis systems for achieving industrial-scale hydrogen production.

3.1.4. High-temperature solid oxide electrolyzer cell (SOEC) hydrolysis

A solid oxide electrolyzer cell (SOEC) usually consists of four layers, which are the hydrogen electrode, the electrolyte, the oxygen electrode, and the intermediate layer between the oxygen electrode and the electrolyte. The water supplied on the cathode side is reduced to H_2 and O^{2-} . O^{2-} passes through the electrolyte and eventually forms O_2 through oxidation on the anode side. Operating at 700–800 °C, an SOEC can significantly reduce the power required to split water into hydrogen, thus reducing the cost of hydrogen production [59].

Although the current research on SOEC hydrolysis has made great progress, there are still a number of limitations. Due to the high temperature and humidity of the working environment, there are extremely high requirements for materials and equipment. Compared with ALK, PEMs, and AEMs, SOECs have a shorter service life and higher operating and maintenance costs. Due to the influence of the above factors, the hydrogen production technology of SOECs is still in the laboratory research stage [60].

Compared with traditional fossil fuels for hydrogen production, the advantage of various hydrogen electrolysis water technologies is that the environmental impact is small. They basically do not produce pollutants but can maintain high hydrogen production efficiency. But the main challenges are hydrogen purity and the production cost. As Liu et al. [61] noted in their research, the cost of H₂ produced via PEMWE is three times higher than that of steam-methane reforming. Although the cost of PEMWE hydrogen production is expected to be reduced from \$4–\$8 kg⁻¹ to \$2.5–\$4 kg⁻¹ by 2030, it is still not able to compete with hydrogen production using fossil fuels.

The comparative advantages and disadvantages of various hydrogen production technologies and their emergence time are listed in **Table 1** [62].

Table 1. Comparison of advantages and disadvantages of hydrogen production from different electrolytic water.

Electrolysis technique	ALK	PEM	AEM	SOEC
Electrode/catalyst	Nickel, cobalt, manganese	Platinum, iridium, titanium, gold	Nickel, cobalt, iron	Perovskite and other ceramic metals
Hydrogen purity	≥99.8%	≥99.99%	≥99.99%	≥99.99%
Electrolysis efficiency	60%–75%	70%–90%	60%–75%	85%–100%
Emergence time	In the 1950s	In the 1950s	In the 1960s	In the 1970s
Advantages	Mature technology	Safe and pollution-free, high flexibility, mature technology	Good adaptability, safe and pollution-free	Safe and pollution-free, high efficiency
Disadvantages	Long response time, high cost	Membrane core technology needs to be improved, high cost	Exchange membrane technology needs to be broken through	High working temperature, Immature technology

For hydrogen production via the electrolysis of water, current problems mainly include high energy consumption and high costs. In order to improve the efficiency of electrolysis and reduce energy consumption and costs, future research directions may include the development of new technologies for hydrogen production via the electrolysis of water and the optimization of reaction mechanisms and electrode materials.

3.2. Plasma hydrogen production

Plasma is an ensemble that, under conditions of extreme temperature or potent magnetic fields, ionizes to form electrons, negative ions, positive ions, atoms, and free radicals. The term “plasma” was first proposed by Tonks and Langmuir [63] in 1929. Leveraging its intrinsic properties, plasma has been employed in recent times for the conversion of biomass-tar-specific hydrocarbons, such as benzene and toluene, into hydrogen. A study conducted by Liu et al. [64], prepared LaNiO₃ catalysts at varying temperatures for plasma-enhanced steam-reforming of toluene. Their results revealed that the catalyst produced at 600 °C offered the highest selectivity towards CO and the least towards CH₄. Conversely, the catalyst synthesized at 800 °C displayed superior resistance against carbon accumulation. These outcomes diverged from traditional thermal catalysis results, potentially due to the electric fields engendered by plasma.

Chung et al. [65] proposed a method for producing hydrogen from liquid benzene using plasma. The method used perovskite as a catalyst, and liquid plasma was released from liquid reactants to crack liquid benzene to produce hydrogen. The only

gaseous product of this reaction was H₂, and no CO₂ was generated, making the method a green hydrogen-production technology.

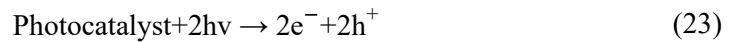
However, the challenges faced by plasma hydrogen production are the difficulty of plasma production and control and the high technical complexity.

Therefore, future research directions may include in-depth studies on plasma generation, plasma control mechanisms, optimization of reaction conditions and equipment to help reduce complexity and the cost of technology, and improvement of the efficiency of hydrogen production.

3.3. Photocatalytic hydrogen production

In essence, photocatalysis refers to the phenomenon wherein semiconductor materials absorb light energy, leading to the excitation of electrons (e⁻) from the valence band onto the conduction band, concurrently leaving behind holes (h⁺) within the valence band. Given the significant reduction and oxidation capacities of photo-excited electrons and holes, respectively, they can initiate respective redox interactions with species adsorbed onto the catalyst's surface. Presently, harnessing solar energy for the direct photocatalytic decomposition of water into hydrogen is seen as a clean, sustainable method, boasting extensive prospects for the future.

Semiconductor:



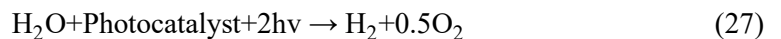
In the solution:



Redox reaction:



Overall reaction:



Recently, there is a significant interest in photocatalytic materials in the field. Alharthi et al. [66] reported their investigation of a Zn₃V₂O₈/rGO composite for photocatalytic hydrogen generation. Their findings demonstrated that the Zn₃V₂O₈/rGO composite displayed superior cyclic stability, and they attributed the augmented photocatalytic activity of the composite to the collaborative interplay amongst its constituents.

Zhang et al. [67] used a simple photoradiation-assisted thermal excitation method. The results showed that with P25 as the model compound, water decomposition in the photocatalytic hydrogen production significantly improved.

He et al. [68] selected Ni-doped Zn_{0.2}Cd_{0.8}S quantum dots mixed with TiO₂ microspheres to form a step-scheme heterojunction through a DFT simulation. Their findings showed that Ni-mixed structures regulated high-activity S sites and enhanced the production of H₂, and the output of hydrogen significantly improved.

Li et al. [69] induced a linkage effect in bandgap-broken heterojunction V₂O₅/amorphous carbon nanoparticles/GdCrO₃, which facilitated the migration and separation of the carrying fluid at the interfaces of the gap. The results showed that it produces about seven times more hydrogen than the normal V₂O₅/GdCrO₃ catalyst.

Li et al. [70] conducted a DFT-calculations-supported characterization experiment by locating the broken-gap heterojunction at the interface or surface. The results showed that the broken-gap heterojunction rich in defects had higher carrier separation and light collection ability and good surface reaction. The results also proved that it can be used as an integrated heterojunction photocatalyst for solar energy conversion.

For photocatalyst hydrogen production, the problems are mainly low photo-transformation efficiency and low hydrogen purity. Future directions of research may include higher-cost synthetic photocatalysts to improve photo-calibration efficiencies and hydrogen purity.

4. Comparison of hydrogen production technologies

To summarize the above-mentioned hydrogen production methods, **Table 2** is drawn up, which contains the advantages and disadvantages of the various hydrogen production methods and their development time [71–76].

Table 2. Comparison of advantages and disadvantages of hydrogen production methods.

Hydrogen production process	Emergence time	Advantage	Disadvantages
Biomass gasification	In the 2006s	Reliable quality and efficiency	High temperature (500–800 °C), effects of by-products
Biomass tar reforming	In the 2000s	High hydrogen conversion efficiency	High cost, lack of new skills
Chemical-looping hydrogen generation	In the 1983s	No expensive and energy-intensive gas separation processes	Performance of oxygen carriers affected by number of cycles and temperature
Water electrolysis for hydrogen production	In the 1950s	H ₂ is produced twice the amount of O ₂ (by-product), high hydrogen purity	High cost, insufficient facilities to conduct process
Plasma hydrogen production	In the 2000s	Plasma reactors can be turned off at any time with no repercussions	High cost, operational risk
Photocatalytic hydrogen generation	In the 1972s	Clean and sustainable reaction process	High cost of photocatalysts, low efficiency of large-size photocatalysts

5. Summary and prospects

Given the myriad issues stemming from the exploitation of fossil fuels, the search for viable energy substitutes or enhanced methodologies is pressing. While hydrogen energy represents an ideal candidate, it is predominantly sourced from fossil fuels currently. Recent advancements in various hydrogen production technologies, such as renewable energy, chemical reactions, water electrolysis, photocatalysis, and plasma technology, along with the diversification of energy sources, have laid the foundation for potential clean energy production in the future. The obstacles and future research prospects are as follows:

- 1) The limited large-scale application of renewable energy can be attributed to its inherent intermittency and instability. How to store and transport the generated hydrogen is also one of the problems that needs to be solved. Because hydrogen is flammable and explosive, hydrogen storage and transportation are difficult and

hence more safe and reliable storage and transportation technologies need to be developed.

- 2) For techniques such as chemical looping, electrocatalysis, photocatalysis, and plasma, hurdles related to materials and production costs remain to be surmounted. The focus of future research should be on reducing energy consumption, increasing hydrogen production efficiency, reducing equipment costs, and improving the optical stability and quantum efficiency of photocatalysts. Strengthening the integration and optimization of multiple hydrogen technologies to improve overall efficiency and reduce energy use should focus on development strategies for diversification, integration, high efficiency, and environmental protection to meet growing market demands and environmental challenges.
- 3) The development and application of these technologies also need further in-depth research and practical verification. Only through in-depth theoretical research and experimental verification can we better understand the performance and mechanism of various hydrogen production technologies and provide strong support for their future application and development.

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