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Review Article

Catalytic Biomass-to-Hydrogen Conversion: Emerging Technologies, Sustainability Challenges, and Prospects for Low-Carbon Energy Systems

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Abstract

The escalating global demand for renewable energy alternatives to conventional fossil fuels has positioned hydrogen as a pivotal energy vector for future energy systems. Hydrogen derived from biomass has garnered considerable attention in recent years, as it constitutes a renewable energy source while simultaneously contributing to the mitigation of greenhouse gas emissions associated with energy production. This paper will analyse the technological advances that have been made recently in producing hydrogen using biomass as a source. Recent studies have shown that the concept of using biomass and plastic for their co-pyrolysis is an area of synergistic research where the production of hydrogen can be increased by as much as 19.40 wt% by adding certain transition metal catalysts, namely nickel (Ni) and cobalt (Co), to increase hydrogen selectivity. The co-gasification process using plasma in combination with coal and biomass as fuel has been found to be a promising process to generate hydrogen gas at high efficiency levels. Production of hydrogen using biomass co-gasification technology in conjunction with plastic materials represents an additional viable pathway. Despite the many technological developments made in these hydrogen conversion methods, there are still difficulties like low volumetric productivity and high cost of production that hinder the scaling-up of their applications on an industrial scale. However, approaches that integrate thermochemical and plasma methods, along with improvements in bioreactor technology and catalysts, can serve as potential ways towards achieving high conversion efficiency and cost-effectiveness. This article ends with an assessment of the future prospects for hydrogen from biomass as an environmentally sustainable alternative source of hydrogen production compared to fossil fuels.

I. INTRODUCTION

Hydrogen enjoys an exceptionally favoured position among potential carriers of future energy sources, providing opportunities for developing a sustainable energy network without the drawbacks of burning fossil fuels. Due to its pivotal role in energy and transportation systems, experts often consider hydrogen as an essential foundation of the world's future energy structure [1]. A review of hydrogen production technologies encompasses current and prospective production methods, climate change policies, availability of raw materials, technological readiness, political considerations, and the economics of various production techniques. Recent advances in hydrogen generation technologies have improved their technological feasibility and expanded opportunities for future energy solutions. However, the technology ecosystem associated with hydrogen generation still requires stronger institutional and financial support to achieve commercial viability. The global transition toward a hydrogen economy necessitates the development of economically and environmentally sustainable hydrogen production pathways. In the coming years, hydrogen and fuel cell systems are expected to become key components of future energy systems [2].

Strategic elements supporting the hydrogen economy include hydrogen production, storage and distribution, fuel cell applications, fuelling infrastructure, regulations and standards, diversified feedstocks, and industrial integration. Hydrogen, as a green energy carrier, exhibits substantial potential owing to its capacity to supply energy across a diverse array of conversion technologies, including fuel cells and power generation systems. Currently, most global hydrogen production is achieved through thermochemical processes utilizing fossil fuels such as natural gas and coal, while other methods include water electrolysis and photolysis. Biomass represents one of the most promising sustainable feedstocks for hydrogen production and is among the world's largest primary energy resources. In many developing countries, biomass contributes significantly to total primary energy consumption. Thermochemical conversion routes, including pyrolysis, gasification, and combustion, constitute the primary pathways for hydrogen production from biomass, while biochemical processes such as hydrolysis and fermentation also contribute to hydrogen generation.

Despite their environmental impacts, fossil fuels remain the dominant source of global primary energy. Growing energy demand and concerns regarding environmental pollution have intensified the need for sustainable energy alternatives. Consequently, continued dependence on fossil fuels is both environmentally unsustainable and economically challenging. In 2016, global energy consumption reached 13,276.3 Mtoe, representing an increase of 1.0% compared to the previous year. During the same period, the global energy mix showed a gradual shift from coal toward alternative energy sources, while renewable electricity generation increased by 14.1%.

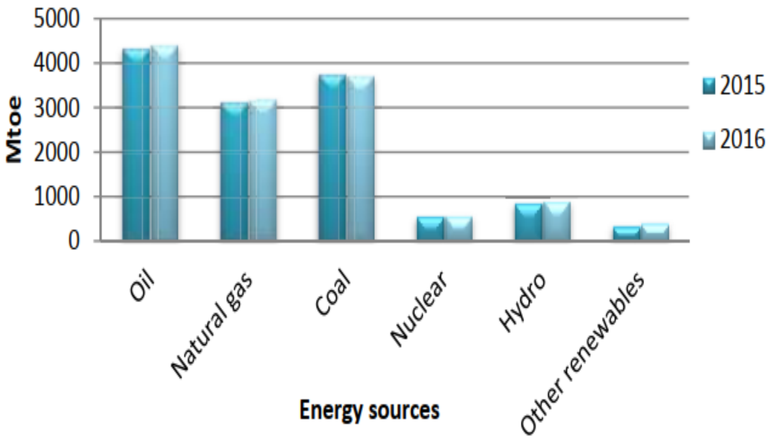

Fig.1 World Primary Energy Consumption Distribution Pattern (2015 vs. 2016)

Given its status as an environmentally friendly energy carrier, hydrogen is expected to play a central role in achieving sustainable, low-carbon energy systems. Its ability to reduce carbon emissions across difficult-to-abate sectors, including transportation, industry, and power generation, highlights its importance in the global energy transition. Amid growing concerns over climate change, the depletion of fossil fuel resources, and advancements in renewable energy technologies, hydrogen has gained increasing attention as a promising solution for reducing greenhouse gas emissions and supporting sustainable energy development.

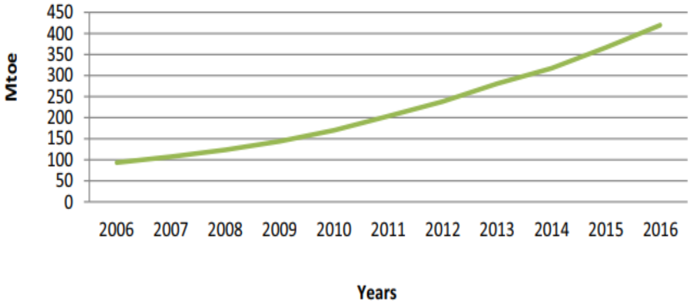

Fig.2 Trajectory of Global Renewable Energy Consumption (Excluding Nuclear And Hydropower), 2006–2016

Figure 2 shows the trend in global renewable energy consumption (excluding nuclear energy and hydropower) between 2006 and 2016. The results indicate a continuous shift toward alternative energy sources, highlighting the growing importance of biomass as a viable feedstock for future hydrogen production. Projections suggest that biomass could meet up to 50% of global energy demand in the coming century while contributing to significant reductions in greenhouse gas emissions. Biomass-based electricity generation has also expanded considerably, with more than 800 biomass power plants producing over 8,700 MW of electricity worldwide and more than 1,000 facilities operating in Europe alone [3].

Although hydrogen has emerged as a clean and efficient energy carrier, its current production remains largely dependent on fossil fuels, particularly natural gas through steam methane reforming (SMR), a process associated with substantial carbon dioxide emissions. Increasing environmental concerns and stricter regulations have intensified interest in low-carbon hydrogen production pathways. Among the available alternatives, biomass-based hydrogen production is considered one of the most technologically viable and commercially attractive options.

Hydrogen can be produced from biomass through thermochemical, biochemical, and electrochemical conversion processes. Thermochemical routes include pyrolysis, gasification, and combustion, while biochemical pathways involve fermentation and enzymatic hydrolysis. These processes generate hydrogen directly or produce synthesis gas (syngas), primarily composed of hydrogen, carbon monoxide, carbon dioxide, and methane [4]. Among these technologies, gasification and pyrolysis have attracted significant attention because of their high hydrogen production potential and compatibility with a wide range of biomass feedstocks.

Gasification is a thermochemical process in which biomass undergoes partial oxidation at temperatures of approximately 700–1000 °C using steam, oxygen, or air, producing a combustible gas mixture rich in hydrogen and carbon monoxide. The resulting syngas can subsequently be upgraded through water-gas shift reactions and purification processes to obtain high-purity hydrogen. Gasification offers feedstock flexibility but is associated with high energy requirements and syngas cleaning challenges.

Pyrolysis involves heating biomass under oxygen-limited conditions to produce bio-oil, biochar, and syngas [5]. Although less widely applied for hydrogen production than gasification, pyrolysis becomes particularly attractive when integrated with catalytic reforming or combined conversion processes. Its principal advantage is the relatively lower operating temperature, while additional upgrading is required to utilize the produced syngas effectively.

Recent research has increasingly focused on biomass torrefaction as a pretreatment method for enhancing biomass properties before hydrogen production. Torrefaction is typically carried out at temperatures between 200 and 300 °C in an inert atmosphere, resulting in a hydrophobic, energy-dense solid with improved grindability, reactivity, and storage characteristics. These improvements enhance the performance of subsequent gasification and pyrolysis processes [6].

Alongside thermochemical technologies, biological pathways based on microbial metabolism are being investigated as alternative routes for hydrogen production from biomass and organic wastes. The principal approaches include dark fermentation, photo-fermentation, and hybrid fermentation systems. While these methods operate under relatively mild conditions and offer environmental advantages, their hydrogen yields generally remain lower than those achieved through thermochemical conversion processes [7].

Despite substantial progress, biomass-based hydrogen production continues to face challenges related to low hydrogen yields and high production costs. Ongoing research focuses on catalyst development, microbial strain improvement, and integrated process design to enhance conversion efficiency and economic viability. Figure 3 illustrates the major thermochemical, electrochemical, and biological hydrogen production pathways, along with recent technological advancements aimed at improving hydrogen yield and process performance [8].

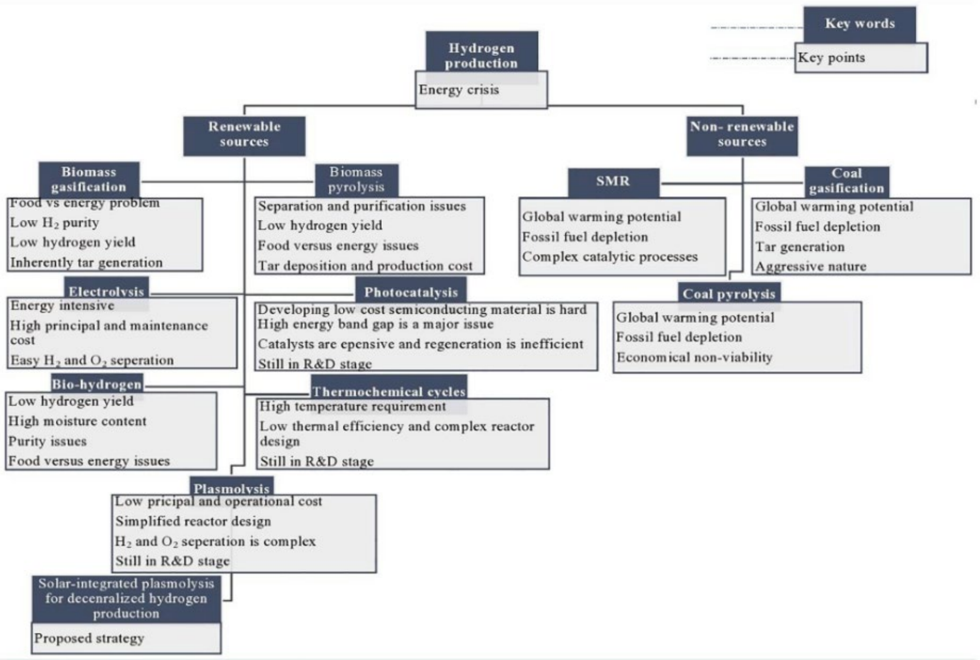

Fig.3 Schematic Overview of Principal Hydrogen Production Pathways Including Thermochemical, Electrochemical and Biological Routes

Despite these innovations in technology, the implementation of biomass for hydrogen production remains limited due to a range of interconnected issues, such as fluctuating raw materials, high levels of moisture reducing efficiency of the process, and additional facilities necessary for collecting and storing biomass. Additionally, cultivating biomass on a large scale in order to produce hydrogen poses certain questions regarding the competition with agriculture in terms of using available territories. Addressing these challenges is essential to render biomass-based hydrogen production economically viable and sufficiently scalable to contribute meaningfully to national hydrogen supply systems. According to one of the earliest investigations by Kirkpatrick, corona discharge yielded approximately 0.25 g of hydrogen per kWh. In contrast, subsequent studies employing a corona dielectric barrier discharge (Corona-DBD) hybrid reactor with water vapor as the feedstock reported a substantially higher hydrogen yield of 20 g per kWh [9].

II. PATHWAYS FOR HYDROGEN PRODUCTION

Hydrogen production can be achieved through a range of pathways, broadly classified into thermochemical, biological, and electrochemical routes. Different types of raw materials are used in these approaches, such as fossil fuels, biomass, and water. Each of the aforementioned pathways exhibits distinct advantages, limitations, and application domains, with their suitability varying across different regions worldwide.

A. Thermochemical Pathways

One of the most widely adopted approaches for hydrogen production is the thermochemical route, which employs high-temperature processes to decompose feedstocks into hydrogen and other by-products.

1. Steam-Methane Reforming (SMR): The most extensively employed method for hydrogen production is steam methane reforming (SMR), which accounts for over 80% of global hydrogen generation. This process is based on the reaction between methane (CH_4) and high-temperature steam (H_2O), typically carried out at temperatures between 700 and 1,000 °C, producing hydrogen along with carbon monoxide in the form of synthesis gas (syngas)**.** A subsequent step, known as the water–gas shift (WGS) reaction, involves the conversion of carbon monoxide through its reaction with steam, resulting in the production of hydrogen and carbon dioxide. Prior to steam methane reforming (SMR), natural gas and other hydrocarbon feedstocks are desulfurized to remove sulfur-containing compounds, typically through hydrodesulfurization or adsorption using activated carbon.

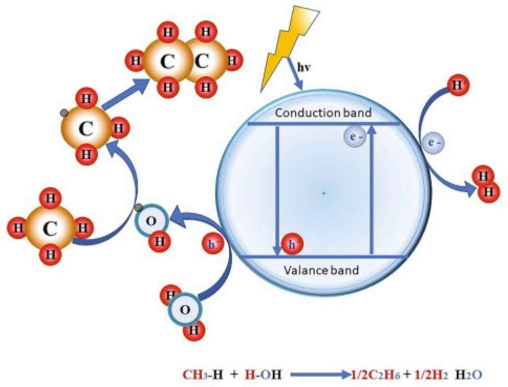

Fig.4 Photocatalytic Steam Methane Reforming (PSRM) Mechanism for Hydrogen Generation Via High-Temperature Semiconductor Activation

The water–gas shift (WGS) reaction is a key downstream step in steam methane reforming, in which carbon monoxide reacts with steam over iron- or copper-based catalysts to increase hydrogen production. The process is typically operated at temperatures of 700–1100 K and pressures of approximately 3.5 MPa to minimize coke formation on catalyst surfaces. Hydrogen is subsequently purified using pressure swing adsorption (PSA), which removes carbon dioxide and other impurities to produce high-purity hydrogen suitable for fuel cell applications. In addition, steam reforming of ethanol (SRE) has attracted considerable attention because it can theoretically produce up to six moles of hydrogen per mole of ethanol, as shown in the following reaction:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad (1)$$

The above reaction proceeds endothermically and therefore requires sustained heat input, typically at temperatures exceeding 500 degrees C, atmospheric pressure, and with excess steam relative to stoichiometric requirements. The efficiency of both ethanol reforming and SMR can be co-optimized through appropriate catalyst selection and reactor design. The principal decomposition and shift reactions governing the SMR pathway, together with their standard reaction enthalpies, are presented below [10]:

$$C_2H_5OH \rightarrow CO + CH_4 + H_2 \quad (\Delta H_{298}K = +49.0\ \text{kJ/mol}) \quad (2)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H_{298}K = +206.3\ \text{kJ/mol}) \quad (3)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (\Delta H_{298}K = +165.1\ \text{kJ/mol}) \quad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H_{298}K = -41.2\ \text{kJ/mol}) \quad (5)$$

Advantages: High efficiency and well-established technology.
Disadvantages: Significant CO_2 emissions and reliance on fossil fuels.

B. Coal Gasification Process

In coal gasification, coal is converted into synthesis gas (syngas) through partial oxidation with steam and oxygen at elevated temperatures and pressures. The resulting syngas primarily consists of hydrogen, carbon monoxide, and carbon dioxide, from which hydrogen is recovered through water–gas shift reactions and gas separation processes. Various catalysts have been investigated to enhance hydrogen production, including noble metals such as platinum (Pt) and rhodium (Rh), although nickel-based catalysts are generally preferred because of their lower cost and favorable catalytic performance. Hydrogen purities exceeding 90% have been achieved using advanced sorbent materials such as K-Li_4SiO_4 for CO_2 capture. A Ni-Co/CaO-$Ca_{12}Al_{14}O_{33}$ catalyst operating in sorption-enhanced steam reforming (SESR) mode produced a hydrogen concentration of 82.23% and a yield of 2.31 L/g at 650 °C. Similarly, lithium zirconate and MgO-modified Ni/CaO sorbent-catalysts have demonstrated excellent CO_2 adsorption performance, enabling hydrogen purities of up to 96–97% [11].

Global hydrogen production increased from negligible levels in 1975 to approximately 115 million tonnes annually by 2018. Currently, around 90% of hydrogen is produced from fossil-fuel-based thermochemical processes, generating approximately 830 million tonnes of CO_2 emissions each year [12]. Global hydrogen production is distributed among steam methane reforming (48%), oil fractions (30%), coal gasification (18%), and water electrolysis (4%). Steam reforming of ethanol (SRE) has attracted considerable attention because of its high theoretical hydrogen yield of up to six moles of H_2 per mole of ethanol [13].

However, challenges remain in process optimization and hydrogen purification. Despite these limitations, ethanol reforming represents a promising renewable alternative to conventional fossil-fuel-based hydrogen production. Water and methane can also be converted into hydrogen through photocatalytic steam methane reforming (PSMR), which employs semiconductor photocatalysts to simultaneously activate methane and split water molecules. Wide-bandgap semiconductor materials with strong redox properties are considered particularly promising for this application [16].

Steam methane reforming (SMR) remains the most mature and commercially established hydrogen production technology, accounting for approximately 80% of global hydrogen output. The process typically achieves efficiencies of 74–85% and benefits from decades of technological development that have reduced production costs. However, SMR requires high operating temperatures (700–1000 °C), complex catalytic systems, and predominantly fossil-based feedstocks. Furthermore, the process generates substantial carbon dioxide emissions, with life-cycle assessments reporting a global warming potential of approximately 9.46 kg CO_2 per kg of H_2 produced. Although carbon capture technologies can mitigate emissions, complete CO_2 removal is not feasible and significantly increases overall costs [17]. Consequently, despite its commercial maturity, SMR faces long-term sustainability challenges due to its dependence on non-renewable resources and associated greenhouse gas emissions.
Advantages: Can use low-grade coal; widely available feedstock.
Disadvantages: High CO_2 emissions and energy-intensive process.

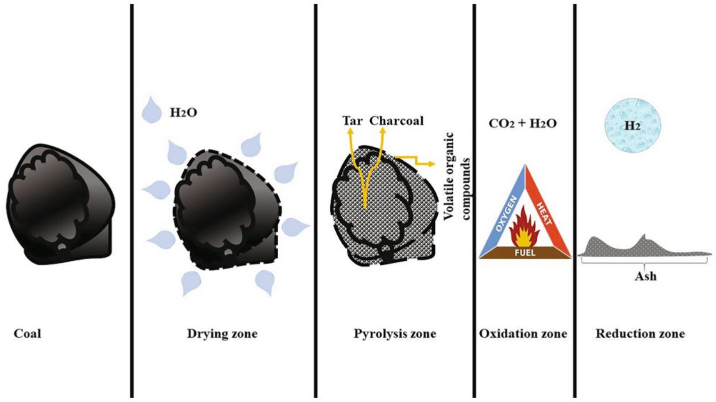

Fig.5 Coal Gasification Process Schematic Illustrating the Partial Oxidation Reactor and Downstream Syngas Cleaning Train

C. Biomass Gasification

Gasification is a well-established thermochemical process that converts solid carbonaceous feedstocks into hydrogen-rich synthesis gas (syngas) through partial oxidation using steam, oxygen, air, or their combinations. Biomass gasification is commonly conducted in entrained-flow, fixed-bed, and fluidized-bed reactors, with fluidized-bed systems being particularly attractive because of their superior heat and mass transfer characteristics, uniform temperature distribution, operational flexibility, and suitability for large-scale applications [18].

Coal and biomass are the most widely utilized feedstocks for gasification-based hydrogen production. In coal gasification, feedstocks react with steam and oxygen under elevated temperature and pressure conditions to produce syngas composed primarily of hydrogen, carbon monoxide, carbon dioxide, and steam, as illustrated in Figure 5 [19]. The resulting syngas is subsequently upgraded through the water–gas shift (WGS) reaction to increase hydrogen content, followed by purification and hydrogen recovery processes. Hydrogen production from coal gasification is summarized in Table I [20].

Despite its technical maturity, coal gasification is associated with significant environmental concerns, with lifecycle emissions estimated at approximately 29.33 kg CO_2 per kg of hydrogen produced, even at system efficiencies approaching 75%. Although carbon capture and storage (CCS) technologies can reduce emissions, their implementation is constrained by high capital and energy requirements. These limitations, combined with the finite nature of coal resources, have accelerated research into renewable hydrogen production pathways [21]. Supercritical water gasification (SCWG) has emerged as a promising approach for converting a wide range of biomass and waste feedstocks, including wheat straw, sewage sludge, chicken manure, and timothy grass, into hydrogen-rich gas streams. Typical operating temperatures range from 500–650 °C, while catalysts such as nickel-based nanocatalysts, activated carbon, KOH, and NaOH are frequently employed. Hydrogen yield is strongly influenced by feedstock composition, catalyst selection, and operating conditions, with chicken manure demonstrating some of the highest reported yields.

Similarly, superheated steam gasification has been successfully applied to lignocellulosic feedstocks such as rice husk, cotton stalk, sawdust, cornstalk, and wheat straw, often using CaO catalysts in dual fixed-bed reactors. At higher temperatures, complex waste streams including municipal solid waste and food waste can also be effectively converted into hydrogen-rich gas using cobalt-based catalysts. Overall, higher operating temperatures, active catalysts, and optimized reactor configurations generally enhance hydrogen production efficiency.

Biomass gasification has gained considerable attention as a flexible technology for producing hydrogen and other gaseous products, including CO, CO_2, CH_4, and light hydrocarbons (Figure 6). The process is typically conducted at temperatures between 700 and 1200 °C using steam, oxygen, air, or mixed gasifying agents. Steam gasification is particularly attractive because it promotes higher hydrogen concentrations and produces nitrogen-free syngas with improved calorific value. Catalyst selection plays a critical role in determining gas composition and hydrogen yield, with nickel-based catalysts being among the most widely adopted due to their high activity and economic advantages [22]. Biomass gasification has also been reported to be more cost-effective than coal gasification for equivalent energy production [23].

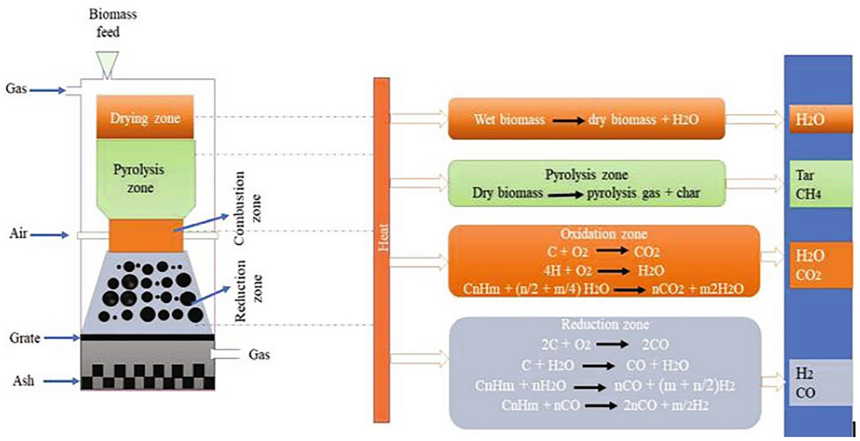

Fig.6 Biomass Gasification Process Flow for Hydrogen-Rich Syngas Generation, Including Catalytic Tar Reforming and Water-Gas Shift Stages

Techno-economic assessments reveal that the installed capital cost of a 1 MW biomass gasification plant is approximately 367 USD/kW, which is substantially lower than the estimated 720 USD/kW required for a coal gasification facility of comparable capacity, thereby highlighting the economic competitiveness of biomass as a feedstock for gasification-based energy systems [24].

Advantages: Renewable feedstock, lower carbon footprint compared to fossil fuels.

Disadvantages: Feedstock variability and high moisture content of biomass can affect efficiency.

D. Pyrolysis

Pyrolysis is a thermochemical conversion process in which biomass is heated under oxygen-free conditions, typically at temperatures between 400 and 600 °C, producing three main products: bio-oil, biochar, and syngas [25]. Depending on operating conditions, pyrolysis is generally classified as slow, fast, or flash pyrolysis. Hydrogen production is influenced by factors such as temperature, moisture content, vapor residence time, particle size, and catalyst selection. Higher temperatures and suitable catalysts generally promote greater hydrogen yields, while fast pyrolysis provides favorable conditions for the generation of hydrogen-rich gases.

Catalysts play a critical role in enhancing hydrogen production during biomass pyrolysis. Although noble metals such as rhodium (Rh) and ruthenium (Ru) exhibit excellent catalytic performance, their high cost limits commercial application. Consequently, nickel-based and zeolite-supported catalysts, particularly Ni/Al_2O_3 systems, have emerged as practical alternatives [26]. Experimental studies using a variety of biomass feedstocks and reactor configurations demonstrate that hydrogen yield is strongly dependent on feedstock characteristics, catalyst composition, and operating conditions. Nickel-containing catalysts consistently outperform many alternative catalytic systems owing to their superior reforming activity and cost-effectiveness. Metal oxide catalysts such as Cr_2O_3 and MnO have also been shown to enhance hydrogen production relative to non-catalytic operation. In addition to biomass pyrolysis, direct methane pyrolysis has attracted attention as a potential low-carbon hydrogen production pathway. This process converts natural gas into hydrogen and solid carbon without generating gaseous carbon oxides, thereby reducing the need for downstream gas-cleaning operations. Furthermore, methane pyrolysis requires less energy than steam methane reforming and may offer lower capital costs. However, its commercial viability depends largely on the development of value-added applications for the solid carbon by-product [27].

As concerns regarding fossil resource depletion continue to grow, increasing research attention is being directed toward biomass pyrolysis as a renewable and sustainable route for hydrogen production [28,29]. Reactor design is another important factor influencing hydrogen production during pyrolysis. Fluidized-bed reactors are particularly attractive because they provide excellent heat and mass transfer characteristics while minimizing tar formation and catalyst deactivation caused by coke deposition [30]. These advantages contribute to improved hydrogen yields and enhanced process stability. Despite significant progress, biomass pyrolysis for hydrogen production remains at an early stage of technological development. Major challenges include catalyst fouling caused by tar and char deposition, feedstock procurement and transportation costs, seasonal biomass availability, reactor material degradation under corrosive conditions, and hydrogen embrittlement issues. Although co-pyrolysis with hydrogen-rich materials such as plastics can reduce catalyst deactivation, further research is required to optimize process performance and enable large-scale commercialization [32].

Advantages: Suitable for various feedstocks, including waste plastics.

Disadvantages: Lower hydrogen yield compared to other methods.

E. Biological Pathways

The hydrogen production biologically involves a range of processes that involve the use of biological enzymes and processes within living organisms to produce hydrogen molecules through biochemical reactions. A key operational advantage of biological hydrogen production systems is that they operate under ambient temperature and pressure conditions, thereby diminishing the need for high thermal energy inputs typically required in thermochemical hydrogen production processes [33].

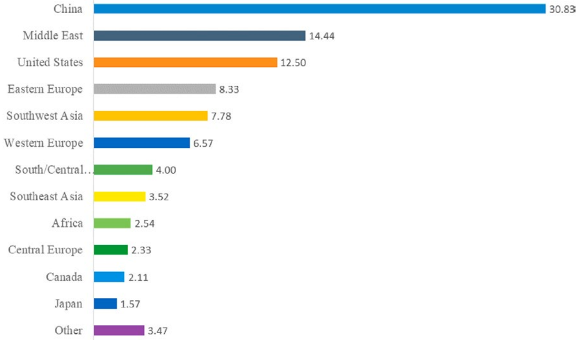

Fig.7 Geographic Distribution of Global Hydrogen Consumption by Sector and Region

1. Dark Fermentation Process: Hydrogen production via dark fermentation utilizes the metabolic activity of strictly anaerobic microorganisms to convert carbohydrate-rich organic substrates into hydrogen, carbon dioxide, and volatile fatty acids. The term *dark fermentation* refers to the absence of a light requirement, distinguishing it from photo-dependent biological hydrogen production processes. Hydrogen generation primarily occurs through the acetate and butyrate metabolic pathways. Research on dark fermentation has largely focused on bacteria of the *Clostridium* genus because of their high hydrogen production potential under anaerobic conditions. In addition to their productivity, *Clostridium* species exhibit rapid growth, spore-forming capability, and the ability to participate in mixed-culture fermentation systems, enabling the conversion of complex organic wastes into hydrogen-producing intermediates [34]. However, dark fermentation is associated with the accumulation of organic acids as metabolic byproducts, requiring subsequent treatment. Furthermore, the process is inherently self-limiting, as elevated hydrogen partial pressure suppresses hydrogen evolution and redirects carbon metabolism toward alternative pathways, as illustrated in Figure 8.

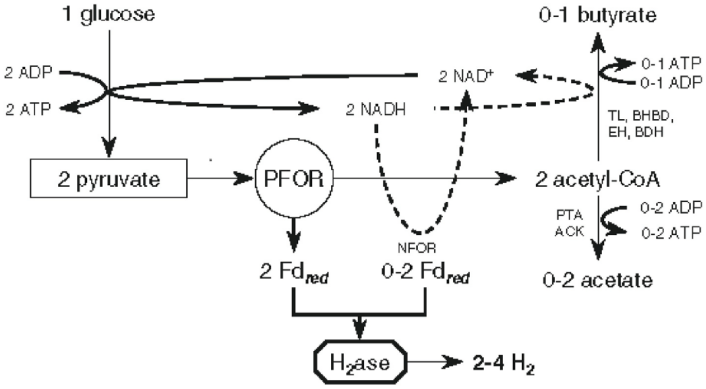

Fig.8 Metabolic Map of Dark Fermentative Hydrogen Production Pathways, Illustrating Competing Routes Via Acetate and Butyrate Intermediates

A variety of pure and mixed microbial cultures have been investigated for fermentative hydrogen production from carbohydrate-rich substrates. Hydrogen productivity is commonly expressed as the amount of hydrogen generated per unit of substrate consumed. Studies using anaerobic digestion sludge as a substrate, together with microbial strains such as *Clostridium bifermentans* and *Pseudomonas* sp., have demonstrated the feasibility of converting organic wastes into hydrogen. In addition to *Clostridium* species, *Enterobacter aerogenes* and other enteric bacteria have attracted attention for biological hydrogen production. Unlike *Clostridium*, enteric bacteria produce hydrogen primarily through formate cleavage, a pathway that is less susceptible to inhibition by elevated hydrogen partial pressures [35]. Furthermore, their facultative anaerobic nature enables rapid growth under aerobic conditions and hydrogen production under anaerobic conditions, offering operational flexibility for industrial bioreactor systems [36]. Maintaining a stable and active microbial population is essential for efficient hydrogen production. Contaminating microorganisms can adversely affect process performance by competing with hydrogen-producing species and altering metabolic pathways [37]. Consequently, appropriate feedstock pretreatment and sterilization strategies are important considerations in process design. Hyperthermophilic microorganisms such as *Thermotoga neapolitana* have also been investigated because of their ability to produce hydrogen efficiently at elevated temperatures while reducing contamination risks [38].

Advantages: Low energy requirement and sustainable feedstocks.
Disadvantages: Low hydrogen yield and the need for post-treatment to remove impurities.

F. Photo-fermentation

Certain photosynthetic bacteria can utilize light energy to convert low-molecular-weight organic acids into molecular hydrogen. This process, known as photo-fermentation, employs light as the primary energy source for hydrogen production, distinguishing it from conventional fermentation processes. One of the principal advantages of photo-fermentation is its ability to harness renewable solar energy, thereby reducing dependence on organic substrates for energy generation [39].

$$16ATP + 16H_2O + N_2 + 10H^+ + 8e^- \xrightarrow{[hv]} 16ADP + 16pi + 2NH_4^+ + H_2 \quad (8)$$

Among the most extensively studied photo-fermentative microorganisms are photosynthetic bacteria of the genera *Rhodobacter* and *Rhodospirillum*, particularly *Rhodobacter sphaeroides*. A promising strategy for improving overall hydrogen production is the integration of dark fermentation and photo-fermentation, in which volatile fatty acid (VFA)-rich effluent from the first stage is directly utilized as a substrate in the second stage, enabling more complete utilization of the original feedstock [40]. In photo-fermentation, purple non-sulfur (PNS) bacteria use photosynthetically generated energy to drive nitrogenase-mediated hydrogen production. Volatile fatty acids produced during dark fermentation, including acetate, propionate, butyrate, and lactate, serve as important substrates for this process, as illustrated in Equations (9)–(12). Photo-fermentation is theoretically capable of achieving higher hydrogen yields than dark fermentation. In addition, PNS microorganisms can utilize a broad light spectrum (400–900 nm) and metabolize a wide variety of organic waste substrates, making them attractive candidates for sustainable hydrogen production [41].

$$\text{Acetate: } CH_3COOH + 2H_2O + \text{'light energy'} \rightarrow 4H_2 + 2CO_2 \quad (9)$$

$$\text{Propionate: } C_3H_6O_2 + 4H_2O + \text{'light energy'} \rightarrow 7H_2 + 3CO_2 \quad (10)$$

$$\text{Butyrate: } C_4H_8O_2 + 6H_2O + \text{'light energy'} \rightarrow 10H_2 + 4CO_2 \quad (11)$$

$$\text{Lactate: } C_3H_6O_3 + 3H_2O + \text{'light energy'} \rightarrow 6H_2 + 3CO_2 \quad (12)$$

Numerous studies have investigated hydrogen production through photosynthetic microorganisms, particularly cyanobacteria and purple non-sulfur (PNS) bacteria. Species belonging to the genus *Rhodobacter* are considered promising candidates for hydrogen generation via anoxygenic photosynthesis and photo-fermentation [42]. Both cyanobacteria and algal microorganisms can utilize light across a broad wavelength range, including the photosynthetically active region (400–700 nm). However, large-scale photo-fermentation remains challenging because efficient light delivery is difficult to maintain in dense microbial cultures, where self-shading reduces the illuminated volume of the photobioreactor. Consequently, reactor designs with high surface-area-to-volume ratios are required to improve light penetration and distribution.

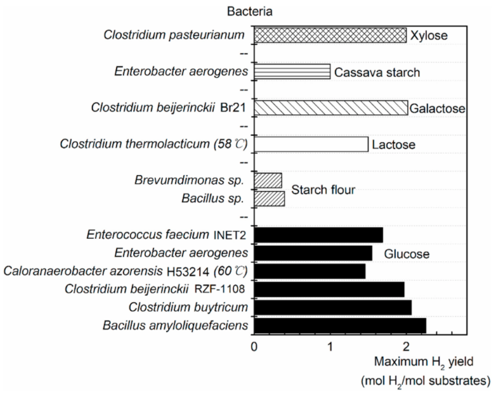

Fig.9 Representative Hydrogen Production Rates for Single Bacterial Strains in Dark Fermentation at 34–37°C

One approach to overcoming light-distribution limitations in photo-fermentation is the use of fiber-optic arrays, which guide and distribute incident light more effectively within the photobioreactor. In addition to improving light delivery, fiber-optic systems can regulate the light spectrum available to microorganisms by filtering unusable wavelengths, thereby reducing excess heat generation [43]. LED-illuminated photobioreactors have also been proposed as an effective alternative for large-scale photo-fermentation. Their advantages include uniform light distribution, reduced shading effects, compact design, and lower installation and operating costs compared with conventional illumination systems. However, the overall efficiency of photo-fermentative hydrogen production remains limited. Under optimal conditions, purple non-sulfur (PNS) bacteria exhibit a maximum light quantum efficiency of approximately 10%, and additional energy losses occur during subsequent electricity generation in proton-exchange membrane (PEM) fuel cells and LED-based illumination cycles [44].
Advantages: Renewable and sustainable process.
Disadvantages: Light-dependent, slow reaction rates, and low efficiency.

G. Hybrid Fermentation

Hybrid fermentation combines dark fermentation and photo-fermentation in a sequential process, where the organic acids generated during dark fermentation are utilized as substrates in the subsequent photo-fermentation stage. This integration improves carbon utilization, reduces residual by-products, and significantly enhances overall hydrogen yield, making it one of the most promising biological hydrogen production strategies [45]. However, hybrid systems remain subject to many of the operational challenges associated with photo-fermentation, particularly efficient light delivery and reactor design. Experimental studies have demonstrated the benefits of this integrated approach. For example, Chen *et al.* reported that coupling dark fermentation with photo-fermentation increased hydrogen yield from 3.80 to 10.02 mol H_2 per mol sucrose while achieving a chemical oxygen demand (COD) removal efficiency of 72% [46]. The improvement was attributed to the utilization of organic acids generated during dark fermentation as substrates for photo-fermentative microorganisms. Similarly, Chookaew *et al.* investigated a two-stage process employing *Klebsiella sp. TR17* and *Rhodopseudomonas palustris TN1* for hydrogen production from crude glycerol. Additional studies have shown that photo-fermentation can effectively utilize residual compounds remaining after dark fermentation, further enhancing hydrogen recovery while contributing to wastewater treatment and waste management applications [47].

H. Electrochemical Pathways

Electrochemical hydrogen production involves water splitting driven by an applied electric current through the electrolysis process. In this reaction, hydrogen is generated at the cathode, while oxygen is produced at the anode, with no additional chemical by-products formed. The key to the eco-friendly nature of this technique lies in the type of electricity used since renewable electricity leads to zero emissions during the lifetime of the product.

1. Water Electrolysis: Water electrolysis produces hydrogen by passing direct current through water using two electrodes separated by a membrane or diaphragm, splitting water into hydrogen and oxygen. When powered by renewable energy sources, electrolysis is considered one of the most sustainable hydrogen production pathways. Since water splitting is a thermodynamically non-spontaneous process, continuous external energy input is required to sustain operation [48]. Commercial electrolysis technologies include alkaline water electrolysis (AWE), proton exchange membrane (PEM) electrolysis, solid oxide electrolysis cells (SOECs), and other high-temperature electrolysis systems. These technologies differ in electrolyte type, operating temperature, efficiency, and cost. While alkaline and PEM electrolyzers typically operate near 373 K, SOEC systems require temperatures of approximately 800–1273 K [48,49].

High-temperature electrolysis offers important thermodynamic advantages because a greater proportion of the required energy can be supplied as heat rather than electricity, and the theoretical cell voltage decreases with increasing temperature. However, these systems require expensive ceramic materials and currently remain more costly than conventional steam methane reforming (SMR) technologies [49,50]. Nevertheless, SOEC systems benefit from the ability to utilize relatively inexpensive ceramic electrode materials without the need for precious metal catalysts. Although electrolysis currently accounts for only about 4% of global hydrogen production [51], it is attracting increasing attention due to its potential for low-carbon hydrogen generation. Alternative approaches, such as methanol-assisted electrolysis, have also been investigated because they can reduce electrical energy requirements; however, carbon dioxide is produced during the process, diminishing some of its environmental benefits [52]. The net decomposition reaction for hydrogen and oxygen conversion (water splitting) can be written as:

$$\mathrm{H2O} + \text{Electrical Energy} \rightarrow \mathrm{H2} + \tfrac{1}{2}\,\mathrm{O2} \tag{13}$$

The environmental performance of electrolysis depends strongly on the source of electricity. When powered by fossil-fuel-dominated grids, the carbon footprint of electrolytic hydrogen increases substantially. Conversely, coupling electrolysis with renewable electricity enables the production of green hydrogen with minimal greenhouse gas emissions [53]. Among commercial technologies, alkaline water electrolysis remains the most mature and economically competitive option because of its proven reliability and relatively low capital cost [54]. However, continued technological improvements, economies of scale, and declining renewable energy costs are accelerating the deployment of PEM and SOEC systems worldwide. According to the IEA, global electrolyzer capacity expanded significantly during the last decade, driven largely by supportive policies and the growing demand for green hydrogen [55].

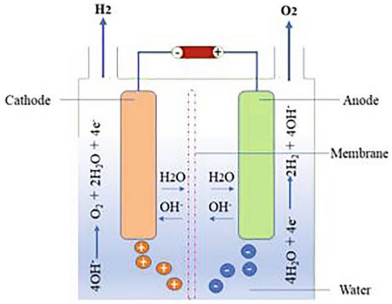

Fig.10 Alkaline Water Electrolysis Cell Schematic: Electrode Reactions, Ionic Transport, And Gas Evolution at Anode and Cathode

The availability of a portfolio of electrolysis projects having a capacity in the range of several hundred megawatts was becoming increasingly common and anticipated to become operational around the early 2020s. Capital cost estimates for 10 MW commercial electrolyzer units range from 0.7 to 1.4

EUR/W for alkali water electrolysis, while those for proton exchange membrane (PEM) electrolysis range from 0.8 to 2.2 EUR/W. The Idaho National Laboratory (INL) has established an experimental facility capable of testing up to 25 kW of high-temperature electrolysis (HTE) [56].
Advantages: Zero emissions when renewable energy is used, high-purity hydrogen.
Disadvantages: High energy consumption and operational costs.

2. Polymer Electrolyte Membrane (PEM) Electrolysis: In proton exchange membrane (PEM) electrolysis, a proton-conducting polymer membrane, typically Nafion, serves as both the electrolyte and gas-separation barrier, enabling compact system designs with high proton conductivity and efficient separation of hydrogen and oxygen. PEM electrolyzers generally operate at temperatures of 50–80 °C and offer higher current densities, faster response times, and greater operational flexibility than conventional alkaline electrolyzers. Table 4 summarizes the principal techno-economic parameters of PEM-based hydrogen production systems [57]. Economic analyses indicate that centralized PEM electrolysis facilities are generally more cost-effective than distributed systems due to lower capital and electricity costs resulting from economies of scale. Although energy consumption remains similar across both configurations, larger facilities benefit from reduced unit production costs and improved economic performance.

3. Alkaline Electrolysis: Among electrolytic hydrogen production technologies, alkaline water electrolysis (AWE) remains the most mature and widely commercialized. It utilizes an aqueous alkaline electrolyte, typically potassium hydroxide (KOH) or sodium hydroxide (NaOH), with the anode and cathode compartments separated by a porous diaphragm. Although alkaline electrolyzers are generally more cost-competitive than proton exchange membrane (PEM) systems, they operate at lower current densities and exhibit less operational flexibility [58]. The growing deployment of electrolyzers powered by renewable energy sources highlights the increasing integration of hydrogen production with wind and solar power systems. Numerous demonstration and commercial projects worldwide have successfully utilized renewable electricity for hydrogen generation, supporting applications in transportation, energy storage, and fueling infrastructure [59,60]. In the longer term, nuclear energy may also play an important role in large-scale hydrogen production by providing either high-temperature heat for thermochemical processes or low-carbon electricity for electrolysis. The integration of nuclear power with hydrogen production systems has been identified as a technically viable pathway for future low-carbon hydrogen generation [61].

4. Plasmolysis and Advanced Techniques: Emerging plasma-based and microwave-assisted technologies represent the next generation of advanced water-splitting and hydrocarbon-reforming processes for hydrogen production, offering the prospect of higher energy efficiencies and more flexible operation than conventional thermochemical routes [62].

I. Other Emerging Pathways

Several innovative hydrogen production methods are under research to enhance efficiency and sustainability:

1. Photocatalysis: Photocatalytic water splitting is a solar-driven process in which semiconductor catalysts absorb photons and utilize the resulting energy to drive the thermodynamically non-spontaneous decomposition of water into hydrogen and oxygen. By using sunlight as the primary energy source and water as the feedstock, this technology offers a promising route for sustainable hydrogen production with minimal environmental impact. In addition to hydrogen generation, photocatalysis has been widely investigated for applications such as selective organic synthesis, carbon dioxide reduction, pollutant degradation, and microbial disinfection [63]. Owing to its potential for renewable and large-scale hydrogen production, photocatalytic water splitting has attracted significant research interest over recent decades. The overall water-splitting reaction and the principal mechanisms governing photocatalytic hydrogen evolution over semiconductor materials are illustrated in the following figure [64].

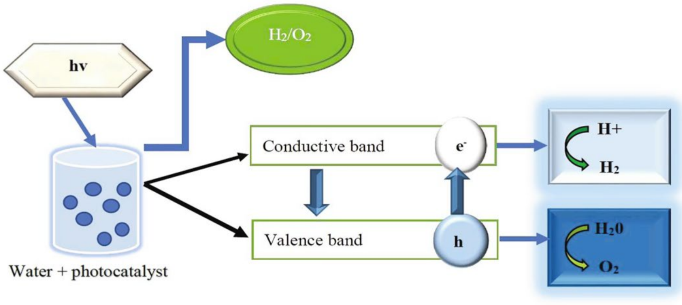

Fig.11 Photocatalytic Water Splitting Mechanism: Light Absorption, Electron-Hole Pair Generation, Charge Migration, and H_2/O_2 Evolution

Photocatalytic hydrogen production proceeds through three fundamental steps: (1) absorption of photons by a semiconductor catalyst, generating electron–hole pairs; (2) migration and separation of the photogenerated charge carriers toward the catalyst surface; and (3) surface redox reactions, where conduction-band electrons reduce protons to hydrogen while valence-band holes oxidize water to oxygen. A major limitation of photocatalytic systems is the rapid recombination of electron–hole pairs, particularly in wide-bandgap semiconductors such as TiO_2, which significantly reduces hydrogen production efficiency. To mitigate this issue, various approaches have been developed, including heterojunction engineering, incorporation of co-catalysts, and the use of electron-transfer mediators to enhance charge separation and suppress recombination. Noble metals such as platinum exhibit excellent catalytic activity for hydrogen evolution; however, their high cost has motivated the exploration of more abundant alternatives, including nickel-based materials. Among semiconductor photocatalysts, TiO_2 remains one of the most extensively studied materials, while visible-light-responsive semiconductors such as CdS have attracted considerable attention due to their narrower bandgaps and improved utilization of the solar spectrum [65,66].

Water is the most commonly employed feedstock in photocatalytic hydrogen production studies conducted under ultraviolet, visible, or simulated solar irradiation. Experimental investigations have demonstrated that catalyst composition, light wavelength, co-catalyst selection, and catalyst architecture strongly influence hydrogen evolution performance. Advanced composite photocatalysts incorporating sulfide semiconductors, graphene-based materials, and metal co-catalysts have consistently shown superior activity owing to enhanced charge separation and reduced recombination losses. Overall, photocatalytic water splitting represents a promising route for sustainable hydrogen generation, although further improvements in catalyst stability, solar-to-hydrogen conversion efficiency, and large-scale implementation are required for commercial deployment. Beyond photocatalytic water splitting, several thermochemical and nuclear-assisted hydrogen production pathways have also been investigated, including the Sulfur–Iodine (S–I), Copper–Chlorine (Cu–Cl), Magnesium–Chlorine (Mg–Cl), and Hybrid Sulfur (HyS) cycles. These technologies utilize high-temperature heat derived from nuclear or solar energy sources to enhance hydrogen production efficiency and reduce overall production costs. Their performance is strongly influenced by reactor design, operating temperature, and system integration, making them promising candidates for future large-scale low-carbon hydrogen production systems.

2. Thermochemical Cycles: Thermochemical water-splitting cycles utilize high-temperature heat, typically supplied by advanced nuclear reactors or concentrated solar energy systems, to drive a sequence of chemical reactions that collectively decompose water into hydrogen and oxygen without net consumption of chemical reagents. Depending on the specific cycle, operating temperatures generally range from 500 to 2,000 °C. Since all intermediate compounds are continuously recycled, water serves as the only feedstock, while hydrogen and oxygen are the sole products, making these processes attractive low-carbon pathways for hydrogen generation. More than 200 thermochemical cycles have been proposed, including two-step metal oxide cycles, multi-step cycles, and hybrid thermochemical–electrochemical systems, with increasing numbers of reaction steps generally allowing lower peak operating temperatures and improved materials compatibility [67]. Among the most extensively studied thermochemical cycles are the sulfur–iodine (S–I), hybrid sulfur (HyS), copper–chlorine (Cu–Cl), and magnesium–chlorine (Mg–Cl) systems. Hybrid thermochemical–electrochemical cycles, particularly the HyS and Cu–Cl processes, have received considerable attention due to their reduced temperature requirements and potential for integration with nuclear and renewable heat sources [68]. Lower-temperature cycles such as Cu–Cl and Mg–Cl can utilize industrial waste heat and medium-temperature nuclear reactors, whereas sulfur-based cycles are more suitable for coupling with high-temperature nuclear and concentrated solar systems. Although these technologies have not yet achieved the commercial maturity of steam methane reforming or alkaline electrolysis, they offer significant potential for sustainable large-scale hydrogen production, with reported cycle efficiencies approaching 52% under optimized conditions. Continuous hydrogen production has also been demonstrated at pilot scale, highlighting the growing technological maturity of thermochemical water-splitting systems [69].

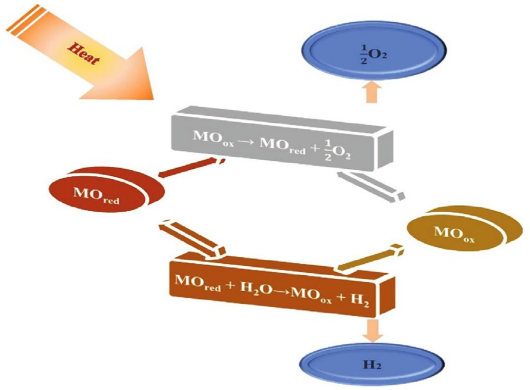

Fig.12 Two-Step Metal Oxide Thermochemical Cycle for Water Splitting: High-Temperature Reduction and Low-Temperature Oxidation Phases

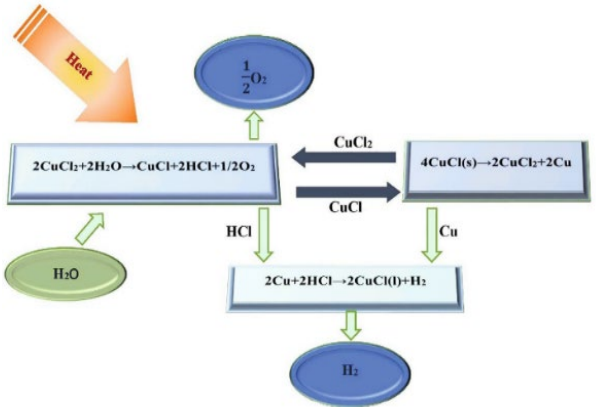

Fig.13 Three-step Copper-Chloride (Cu-Cl) Thermochemical Cycle Configuration

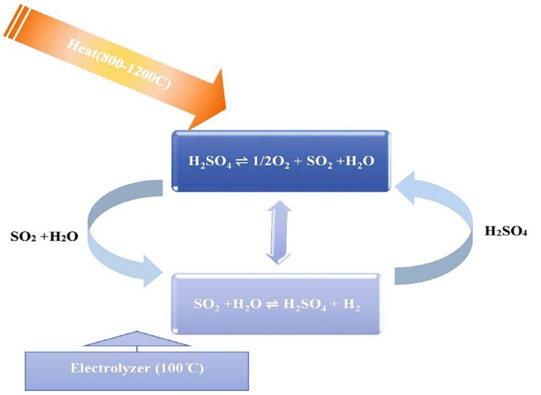

Fig.14 Four-Step Cu-Cl Cycle with Electrochemical Step Integration

3. Plasmolysis: Plasma-assisted hydrogen production utilizes non-equilibrium plasma environments to generate highly reactive species capable of promoting water splitting and hydrocarbon reforming reactions under relatively mild operating conditions. In these systems, electrical discharges produce energetic electrons, radicals, and ions that enhance reaction kinetics and facilitate hydrogen generation from feedstocks such as water vapor, methanol, ethanol, hydrocarbons, and other hydrogen-rich compounds [69,70].
Recent developments have focused on plasma-assisted catalytic (PACT) reactors, which combine plasma activation with catalytic materials to improve hydrogen yield, selectivity, and energy efficiency. Common reactor configurations employ catalytically active metals such as nickel, ruthenium, palladium, rhodium, or gold integrated within dielectric barrier discharge (DBD) or corona-discharge systems. Among these technologies, DBD reactors have attracted particular attention due to their stable operation at higher power levels and suitability for large-scale plasma-chemical processing [71].

Advances in reactor miniaturization and microplasma technologies have further expanded the potential of plasma-assisted hydrogen production. Microreactor systems offer enhanced control over reaction conditions, improved mass and heat transfer characteristics, reduced energy losses, and the possibility of decentralized hydrogen generation. Such systems may facilitate on-site hydrogen production for transportation, fuel cells, and distributed energy applications, thereby reducing challenges associated with hydrogen storage and distribution. Despite these advantages, further improvements in energy efficiency, reactor scalability, and process economics are required before plasma-based hydrogen production can achieve widespread commercial deployment [71].

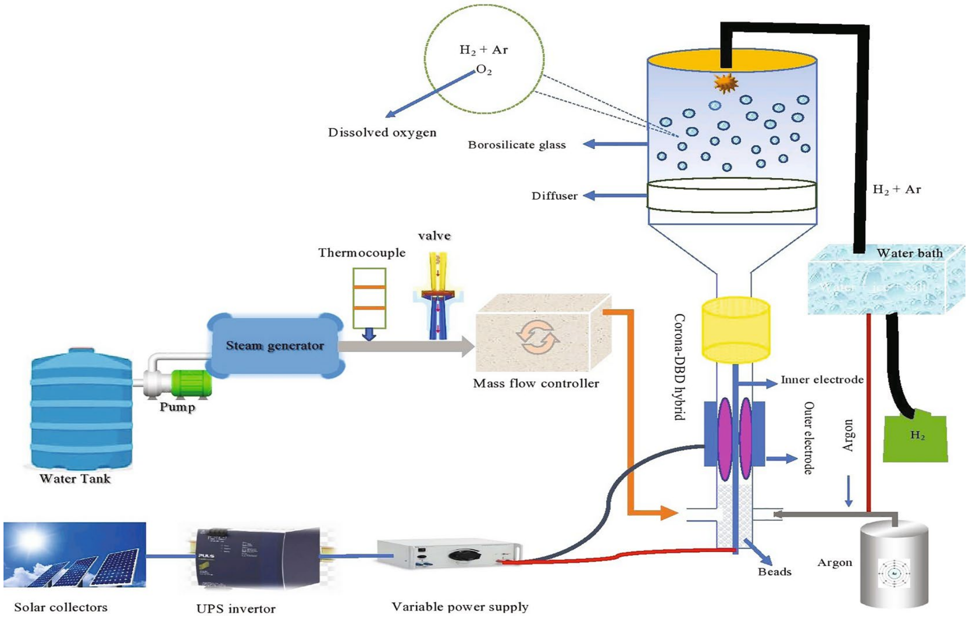

Fig.15 Proposed Plasmolysis System for Water Vapor Splitting: Plasma Reactor, Condenser Trap, Gas Separation, and Argon Recycle Loop

Hydrogen storage is another important issue for plasmolysis technology commercialization. Hydrogen can be stored and transported using a variety of solid and liquid media, including porous storage materials, liquid ammonia-based carriers, intermetallic hydrides, high-entropy alloy hydrides, complex metal hydrides, and liquid organic hydrogen carriers. The scientific community widely regards liquid hydrogen as the most suitable medium for large-scale storage and transportation due to its high energy density considerations. Moreover, the significant reduction in electricity auction prices for renewable energy in regions with strong wind and solar resources has greatly improved the economic viability of green hydrogen production via electrolysis and plasmolysis [70]. In remote regions with limited electricity infrastructure but strong renewable energy potential, hydrogen production via electrolysis or plasma-based technologies, followed by storage in liquid form, represents a commercially viable alternative [72].

III. COMPARISON OF PATHWAYS

TABLE II COMPARISON OF PATHWAYS

Production Pathway	Primary Feedstock	System Efficiency	Emission Profile	Production Cost	Technology Readiness
Steam Methane Reforming Process (SMR)	Natural gas (fossil)	High (74–85%)	High CO_2 (~9.5 kg/kg H_2)	Low (~2.9 $/kg)	Fully commercialized
Coal Gasification Process	Coal (fossil)	Medium (40–58%)	Very high CO_2	Medium	Commercialized
Biomass Gasification Process	Agricultural/woody biomass	Medium-High (45–60%)	Near-neutral CO_2	Medium-High	Pilot to commercial
Biomass Pyrolysis	Organic feedstock/plastic waste	Moderate (30–50%)	Low to moderate CO_2	Medium	Pilot scale
Dark Fermentation Process	Organic waste/biomass	Low (10–20%)	Low CO_2 emissions	High	Research/Pilot
Photo-fermentation	Organic acids, light	Very low (1–5%)	Negligible CO_2	Very High	Laboratory scale
Water Electrolysis Process (PEM)	Water + electricity	High (60–75%)	Zero (if renewable)	High (~5–8 $/kg)	Growing/commercial
Photocatalysis	Water + solar energy	Very low (<5%)	Zero emissions	Very High	Early research
Thermochemical Cycles	Water + nuclear/solar	Medium (33–52%)	Zero (closed-loop)	High	Demonstration
Plasmolysis	Water/hydrocarbons + plasma	Low-Medium (20–40%)	Variable	High	Research stage

IV. CONCLUSION

Biomass-derived hydrogen represents a promising and sustainable pathway for supporting the global transition toward a low-carbon energy future. As concerns over fossil fuel depletion and greenhouse gas emissions continue to intensify, biomass offers a renewable and widely available feedstock for hydrogen production through diverse conversion routes, including gasification, pyrolysis, steam reforming, and fermentation. Unlike conventional fossil fuel–based technologies such as steam methane reforming and coal gasification, biomass-based processes have the potential to significantly reduce net carbon emissions while simultaneously enabling the valorization of agricultural, forestry, municipal, and industrial waste resources. Despite substantial technological progress, several challenges continue to limit the large-scale commercialization of biomass-derived hydrogen, including feedstock variability, process efficiency, catalyst deactivation, and economic competitiveness. Addressing these limitations will require continued advancements in catalyst development, reactor design, process integration, and supply-chain management. Furthermore, coupling biomass conversion technologies with renewable energy sources and carbon management strategies could further enhance their environmental and economic performance. Overall, biomass-derived hydrogen has considerable potential to contribute to future sustainable energy systems. Continued research, technological innovation, and supportive policy frameworks will be essential for accelerating its deployment and establishing biomass as a key renewable resource in the emerging hydrogen economy.

Declaration of Conflicting Interests

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Use of Artificial Intelligence (AI)-Assisted Technology for Manuscript Preparation

The authors confirm that no AI-assisted technologies were used in the preparation or writing of the manuscript, and no images were altered using AI.

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