Green Hydrogen Technologies: A Review of Alternate Innovative Pathways Beyond Water Splitting

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***Abstract*—This review critically examines emerging hydrogen production technologies that have the potential to overcome the limitations of conventional hydrogen production routes, with particular emphasis on brine electrolysis, methane pyrolysis, direct air electrolysis, wastewater electrolysis through the Integrated Forward Osmosis–Alkaline Water Electrolysis (FO–AWE) system, and photoelectrochemical water splitting. The reviewed technologies are comparatively evaluated with conventional hydrogen production pathways based on feedstock requirements, process characteristics, technology maturity, advantages, limitations, and techno-economic performance. Particular emphasis is placed on comparing the gross and net Levelized Cost of Hydrogen (LCOH) by accounting for revenues generated from valuable co-products, including chlorine, sodium hydroxide, oxygen, treated wastewater, and solid carbon. Overall, these alternative hydrogen production technologies demonstrate significant potential to complement or replace conventional hydrogen production in specific applications by improving resource utilization, reducing carbon emissions, and enhancing economic viability, thereby supporting the transition towards a sustainable and diversified hydrogen economy.**

***Index Terms*—Green hydrogen, brine electrolysis, biogas pyrolysis, turquoise hydrogen, electrochemical systems, thermochemical processes, air moisture hydrogen production, decentralized energy systems, renewable energy, low-carbon hydrogen.**

I. INTRODUCTION

Climate change and global warming caused by excessive greenhouse gas emissions from fossil fuel consumption have become major environmental challenges worldwide [1], [2]. Increasing carbon dioxide emissions, rising global temperatures, extreme weather events, and depletion of conventional energy resources have accelerated the global transition toward clean and sustainable energy systems [1], [3]. Meanwhile, rapid growth has been observed in renewable energy capacities compared with conventional fossil-fuel-based power generation systems [4]. However, the global energy mix continues to be dominated by fossil fuels, which account for nearly 80% of total energy consumption [1]. In this context, the development of low-carbon-emission fuels in addition to renewable energy systems has become essential for achieving global climate goals, energy security, and sustainable industrial growth [2], [5].

In comparison with conventional fuels such as petrol, diesel, coal, and even relatively cleaner fuel options like Liquefied Petroleum Gas (LPG) and natural gas, hydrogen is considered a significantly cleaner and more versatile energy carrier capable of supporting deep decarbonization across multiple sectors, including power generation, transportation, and industrial applications [5], [6].

Owing to its high gravimetric energy density and its ability to produce only water as a by-product during combustion or electrochemical utilization, hydrogen is regarded as a key component of future sustainable energy systems [5].

However, the environmental impact of hydrogen depends strongly on the production pathway adopted. At present, the majority of hydrogen is produced through fossil-fuel-based processes such as Steam Methane Reforming (SMR) and Autothermal Reforming (ATR), commonly referred to as grey hydrogen production, which results in significant carbon dioxide emissions [1], [6]. This has led to increasing interest in green hydrogen, typically defined as hydrogen produced through water electrolysis powered by renewable energy sources [3], [5]. Despite its environmental advantages, large-scale electrolysis faces several challenges, including high

capital cost, significant electricity demand, and freshwater requirements [5], [7].

In response to these limitations, research and development efforts have expanded toward alternative hydrogen production pathways beyond conventional water splitting. These include electrochemical routes such as brine electrolysis, thermochemical pathways such as methane pyrolysis, and emerging atmospheric moisture- and air-based hydrogen generation systems [6], [7]. In addition, innovative hydrogen production technologies utilizing wastewater, seawater brine, and atmospheric moisture are being explored for their potential to produce hydrogen with reduced environmental impact and improved resource utilization [6].

In this context, the present review aims to systematically explore and analyse these alternative and innovative hydrogen production technologies, highlighting their operating principles, advantages, limitations, techno-economic feasibility, and potential to overcome the limitations of conventional hydrogen production pathways while supporting a diversified and sustainable hydrogen economy.

II. OBJECTIVES OF THE PAPER

The main objectives of this review are:

- To present an overview of conventional hydrogen production methods and their limitations.
- To explore and systematically review alternative hydrogen production technologies beyond water splitting.
- To analyze the working principles and key reactions involved in selected emerging technologies such as brine electrolysis and biogas pyrolysis.
- To evaluate the technical, environmental, and economic advantages and limitations of each pathway.
- To compare different hydrogen production routes based on scalability, resource requirement, and sustainability.
- To identify promising technologies suitable for decentralized and large-scale applications.
- To highlight research gaps and future development needs for commercialization of alternative hydrogen production systems

III. REQUIREMENT OF HYDROGEN

A. Definition and Characteristics

Hydrogen is a chemical element represented by the symbol H and atomic number 1. It is the simplest and lightest element in the periodic table, consisting of one proton and one electron in its most common isotope. Under standard conditions, hydrogen exists as a diatomic gas (H_2) and is widely distributed in nature, primarily in combined forms such as water, hydrocarbons, and organic matter. Due to its high energy content per unit mass, hydrogen is considered a potential clean energy carrier for future sustainable energy systems [1], [5].

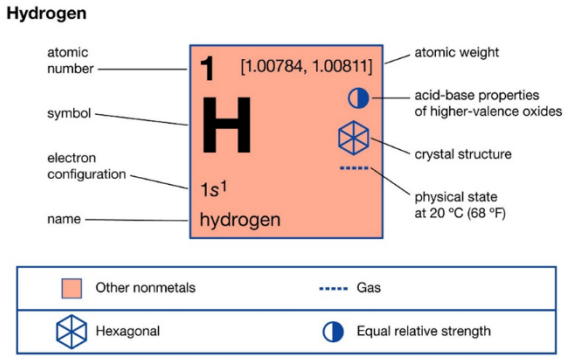

Fig. I. Hydrogen element properties [8]

B. Characteristics of Hydrogen

Hydrogen exhibits several unique physical and chemical characteristics, including:

- Lightest element: It has the lowest atomic mass among all elements [9].
- Colourless, odourless, and tasteless gas: It is not detectable by human senses under normal conditions [9].
- Highly flammable: Hydrogen burns easily in the presence of oxygen, producing water as the only product [10].
- High energy content: It has a high gravimetric energy density compared to fossil fuels [10].
- Diatomic nature: It naturally exists as H_2 under normal atmospheric conditions [9].
- Wide reactivity: It readily reacts with oxygen, halogens, and various metals under suitable conditions [10].
- Non-toxic combustion product: Its combustion produces water, making it environmentally clean at the point of use [10].

- Low density: It requires compression or liquefaction for efficient storage and transport [11].
- Diffusive nature: It has very small molecular size and high diffusivity, enabling easy leakage through materials [11]

C. Potential Applications of Hydrogen

Hydrogen is a versatile energy carrier with wide-ranging applications across multiple sectors due to its high energy density and clean combustion characteristics. Its role is expected to expand significantly in future sustainable energy systems [9]–[11]:

- Power generation:

Hydrogen can be utilized in gas turbines and fuel cells for electricity generation. It is particularly suitable for grid balancing, renewable energy storage, and backup power systems [10], [11].

- Transportation sector:

Hydrogen is used in fuel cell electric vehicles (FCEVs), including buses, trucks, trains, and potentially aviation and shipping, enabling near-zero tailpipe emissions [10].

- Industrial applications:

It is extensively used in petroleum refining, ammonia production via the Haber–Bosch process, methanol synthesis, and steel production through direct reduced iron (DRI) processes [10], [11].

- Energy storage:

Hydrogen serves as a long-duration energy storage medium, enabling the storage of excess renewable energy from solar and wind systems for later use [11].

- Residential and commercial use:

It can be blended with natural gas for heating applications and utilized in fuel cells for decentralized energy supply [11].

- Chemical industry:

Hydrogen acts as a key feedstock in the production of fertilizers, chemicals, and synthetic fuels [10].

- Aerospace applications:

Due to its high specific energy, liquid hydrogen is used as rocket propellant in space exploration missions [10].

- Emerging applications:

These include hydrogen-based microgrids, green steel production, and integration with carbon capture and utilization (CCU) systems [11].

IV. CONVENTIONAL HYDROGEN PRODUCTION TECHNOLOGIES

A. Steam Methane Reforming Process

Steam Methane Reforming (SMR) is an industrial thermochemical process for hydrogen production in which methane (CH_4), typically derived from natural gas, reacts with steam (H_2O) at high temperatures in the range of 973–1273 K (700–1000 °C) under elevated pressure conditions, generally 10–30 atm, in the presence of a nickel-based catalyst to produce hydrogen (H_2) and carbon monoxide (CO) [12].

The carbon monoxide further undergoes the water–gas shift reaction to generate additional hydrogen and carbon dioxide (CO_2) [13].

As per Market Trends, SMR remains the most widely deployed commercial hydrogen production pathway; however, its integration with carbon capture, utilization, and storage (CCUS) is increasingly investigated to reduce lifecycle emissions and enable low-carbon ("blue") hydrogen production [13], [14]. Recent studies highlight that SMR coupled with CCUS can achieve substantial CO_2 mitigation, though economic and efficiency trade-offs remain key challenges for large-scale deployment [14].

$$2CH_4 + 2H_2O \rightleftharpoons 2CO + 3H_2;\ \Delta H +206\ kJ/mol \quad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2;\ \Delta H -41\ kJ/mol \quad (2)$$

[Water-gas shift reaction (exothermic)]

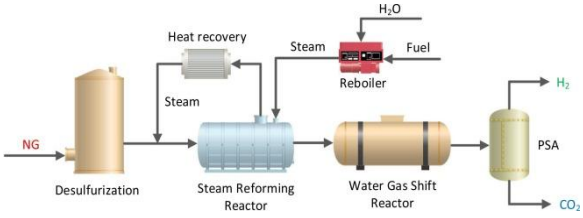

Fig. II Process flow diagram of a standard industrial Steam Methane Reforming (SMR) plant layout, featuring raw material desulfurization, primary steam reforming, water-gas shift conversion, and pressure swing adsorption (PSA) purification stages [15].

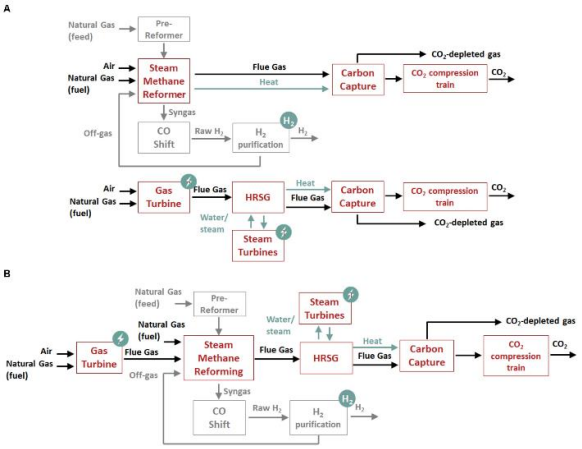

Fig. III. Process flow diagrams comparing decarbonized configurations for hydrogen and power production:

(A) Base layout featuring decoupled standalone Steam Methane Reforming (SMR) and gas turbine blocks with individual post-combustion carbon capture;
(B) Thermodynamically integrated layout utilizing gas turbine exhaust flue gas as the primary combustion oxidant in the SMR furnace, coupled with a Heat Recovery Steam Generator (HRSG) [16].

Fig. II shows the conventional steam methane reforming (SMR) process integrated with carbon capture and hydrogen purification units. The process includes key stages such as desulfurization of natural gas, steam reforming to produce synthesis gas (syngas), water–gas shift reaction to increase hydrogen yield, and pressure swing adsorption (PSA) for hydrogen purification. The diagram also indicates the separation and capture of carbon dioxide (CO_2), which can be further compressed for storage or utilization.

Fig. III presents a detailed process flow diagram of blue hydrogen production using steam methane reforming combined with carbon capture and storage (CCUS). It illustrates the movement of major process streams, including natural gas, steam, syngas, hydrogen, and carbon dioxide, across different unit operations. The figure highlights the integration of hydrogen production with CO_2 capture and storage systems, enabling reduced greenhouse gas emissions while producing hydrogen at scale.

This is currently the dominant hydrogen production technology in India, supplying nearly 95% of the hydrogen demand for petroleum refining, ammonia, methanol, and other chemical industries. Conventional SMR produces grey hydrogen with a gross LCOH of ₹120–200/kg H_2, primarily influenced by natural gas prices, plant capacity utilization, and steam generation costs. The installed CAPEX of a conventional SMR plant is approximately ₹6–10 crore/MW (H_2 equivalent), while natural gas accounts for nearly 60–75% of the total hydrogen production cost. However, the process emits approximately 9–12 kg CO_2 per kg H_2, making it carbon intensive despite its economic competitiveness.

The integration of Carbon Capture, Utilization and Storage (CCUS) converts grey hydrogen into blue hydrogen by capturing 90–95% of the CO_2 generated during the reforming process. The addition of CO_2 capture, compression, transportation, and storage infrastructure increases the total plant CAPEX to approximately ₹8–13 crore/MW (H_2 equivalent), resulting in a gross LCOH of ₹170–270/kg H_2. Although the utilization of captured CO_2 in the manufacture of urea, methanol, beverages, or enhanced oil recovery can provide limited economic benefits, the market for CO_2 utilization in India remains relatively small. Consequently, the net LCOH of SMR-CCUS generally remains within ₹160–250/kg H_2, depending on the degree of CO_2 utilization and carbon pricing. Owing to its lower carbon footprint and compatibility with existing natural gas infrastructure, SMR-CCUS is widely regarded as a transitional technology for large-scale low-carbon hydrogen production until renewable electricity and electrolyser costs decline further.

Table I Summary of Steam Methane Reforming (SMR)

Parameter	SMR (Grey Hydrogen)	SMR + CCUS (Blue Hydrogen)
Feedstock/ Input	3.5–4.5 kg Natural Gas + 4–6 kg Steam	3.5–4.5 kg Natural Gas + 4–6 kg Steam
Hydrogen Yield	~1 kg H_2	~1 kg H_2
Co-products	None	Captured CO_2 (for utilization or geological storage)
Plant CAPEX	₹6–10 crore/MW	₹8–13 crore/MW (including CCUS)
Natural Gas Cost Contribution	60–75% of LCOH	55–65% of LCOH
Additional CCUS Cost	–	₹30–60/kg H_2

Gross LCOH	₹120–200/kg H_2	₹170–270/kg H_2
Net LCOH	₹120–200/kg H_2	₹160–250/kg H_2*
CO_2 Emissions	9–12 kg CO_2/kg H_2	3–5 kg CO_2/kg H_2 (60–70% (commercial); >90% possible with additional flue gas capture)
Technology Status	Commercial (TRL 9)	Commercial (TRL 9)
Hydrogen Type	Grey Hydrogen	Blue Hydrogen
Major Cost Drivers	Natural gas price, steam generation, catalyst replacement, plant utilization, financing cost	Natural gas price, CO_2 capture efficiency, compression, transport and storage costs, plant utilization, financing cost

**The net LCOH for SMR-CCUS assumes partial economic credit from CO_2 utilization. If the captured CO_2 is permanently stored without commercial utilization, the net LCOH is generally close to the gross LCOH. In India, where CO_2 utilization opportunities are currently limited, most techno-economic studies use the gross LCOH as the representative production cost.*

B. Autothermal Reforming Process

Autothermal Reforming (ATR) is a catalytic process used for hydrogen production in which hydrocarbons such as natural gas are converted into hydrogen-rich synthesis gas (syngas) through a combination of partial oxidation and steam reforming reactions within a single reactor [17]. In this process, oxygen and steam are introduced together, and the heat required for the endothermic steam reforming reactions is generated internally through the exothermic partial oxidation of methane, making the system thermally self-sustaining [17]. Compared to conventional steam methane reforming (SMR), ATR is more suitable for integration with carbon capture and storage (CCUS) because it produces a relatively concentrated stream, which simplifies downstream separation and improves capture efficiency [17], [18]. Therefore, ATR is widely recognized as a promising pathway for large-scale blue hydrogen production with reduced carbon emissions [17].

The major reactions occurring in the ATR reactor are:
Partial Oxidation Reaction (Exothermic):

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (3)$$

Steam Reforming Reaction (Endothermic):

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (4)$$

Water-Gas Shift Reaction (Exothermic):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (5)$$

The overall process results in the production of a hydrogen-rich syngas stream containing hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and residual steam. Following reforming, the syngas is typically processed through water-gas shift reactors and gas purification units such as Pressure Swing Adsorption (PSA) to obtain high-purity hydrogen suitable for industrial applications [17], [18].

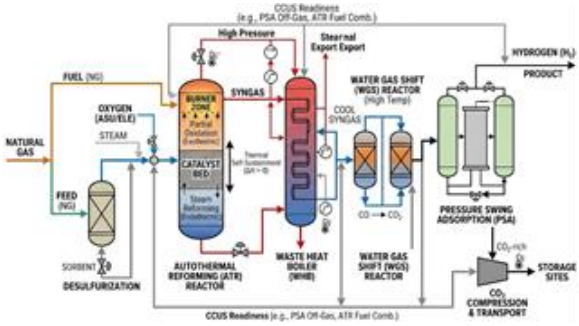

Fig. IV. Process flow diagram of an advanced industrial blue hydrogen plant layout using an Autothermal Reforming (ATR) reactor.

The system features feedstock desulfurization, oxygen-fired partial oxidation integrated with internal steam reforming, high-temperature water-gas shift (WGS) conversion, and a centralized carbon capture, utilization, and storage (CCUS) train handling both pressure swing adsorption (PSA) off-gas and synthesis gas compression loops.

ATR without carbon capture can produce hydrogen at a gross LCOH of approximately ₹140–220/kg H_2, it is seldom adopted commercially due to its significant CO_2 emissions, comparable to those of SMR. The installed CAPEX of an ATR plant is typically ₹7–11 crore/MW (H_2 equivalent), including the Air Separation Unit, while natural gas remains the dominant operating cost, contributing approximately 55–70% of the total hydrogen production cost.

The integration of Carbon Capture, Utilization and Storage (CCUS) has made ATR the preferred

technology for large-scale blue hydrogen production because the process produces a concentrated CO_2 stream that enables 90–98% carbon capture with lower energy penalties than SMR-CCUS. Incorporating CO_2 capture, compression, transportation, and storage increases the total plant CAPEX to approximately ₹10–15 crore/MW (H_2 equivalent), resulting in a gross LCOH of ₹180–260/kg H_2.

The net LCOH can decrease slightly to ₹170–240/kg H_2 where captured CO_2 is commercially utilized; however, in India, the limited demand for CO_2 utilization means that most projects consider the gross LCOH as the representative production cost. Due to its high carbon capture efficiency, lower emissions (0.5–2 kg CO_2/kg H_2), and compatibility with large industrial facilities, ATR-CCUS is increasingly regarded as one of the most promising transitional technologies for low-carbon hydrogen production.

TABLE II SUMMARY OF AUTOTHERMAL REFORMING (ATR)

Parameter	ATR	ATR + CCUS
Feedstock/Input	3.0–4.0 kg Natural Gas + 1.5–3.0 kg Steam + 0.8–1.0 kg O_2 per kg H_2	Same as ATR
Hydrogen Yield	~1 kg H_2	~1 kg H_2
Co-products	None	Captured CO_2 (for utilization or geological storage)
Plant CAPEX	₹7–11 crore/MW (including ASU)	₹10–15 crore/MW (including ASU and CCUS)
Natural Gas Cost Contribution	55–70% of LCOH	50–60% of LCOH
Additional CCUS Cost	–	₹25–50/kg H_2
Gross LCOH	₹140–220/kg H_2	₹180–260/kg H_2
Net LCOH	₹140–220/kg H_2	₹170–240/kg H_2*
CO_2 Emissions	8–10 kg CO_2/kg H_2	0.5–2 kg CO_2/kg H_2 (90–98% capture)

Parameter	ATR	ATR + CCUS
Technology Status	Commercial (limited deployment)	Commercial (TRL 9)
Hydrogen Type	Grey Hydrogen	Blue Hydrogen
Major Cost Drivers	Natural gas price, oxygen production (ASU), steam generation, plant utilization, financing cost	Natural gas price, ASU power consumption, CO_2 capture efficiency, compression, transport and storage costs, plant utilization, financing cost

C. Water Electrolysis. Process (Green Hydrogen)

Water electrolysis is the fundamental electrochemical process behind green hydrogen production. It passes a direct electric current (DC) through water to break its chemical bonds, splitting the molecules into high-purity hydrogen (H_2) and oxygen (O_2) gases. When this electricity is supplied exclusively by renewable resources like solar or wind power, the process is completely carbon-free. [19], [20].

The net thermodynamic breakdown of water is represented by the following chemical equation:

$$2H_2O\,(l) \rightarrow 2H_2\,(g) + O_2\,(g) \qquad (6)$$

Instead of using liquid thermal systems, industrial green hydrogen installations deploy the process across four main electrolyzer architectures [21]–[24]:

- Alkaline Water Electrolysis (AWE):

The most mature commercial technology, utilizing a liquid potassium hydroxide (KOH) electrolyte and non-precious catalysts [21], [22].

- Proton Exchange Membrane (PEM) Electrolysis:

A highly flexible, compact system using a solid acidic polymer membrane, ideal for pairing with variable solar and wind grids [21], [22].

- Solid Oxide Electrolysis Cells (SOEC):

A high-temperature system (600–850°C) that uses steam instead of liquid water, achieving high electrical efficiency by utilizing industrial waste heat [23].

- Anion Exchange Membrane (AEM) Electrolysis:

An emerging technology designed to combine the low material costs of Alkaline systems with the high dynamic responsiveness of PEM [24].

By mass, water consists of roughly 11.2% hydrogen and 88.8% oxygen. Therefore, under ideal theoretical conditions [25], [26]:

- To produce 1 kg of green hydrogen, you require a minimum of 8.93 kg (Ltrs) i.e 9 Ltrs of pure water.
- This reaction simultaneously yields 7.93 kg of high-purity oxygen as a byproduct.

In real-world industrial plants, the actual water consumption is higher due to system inefficiencies, water purification losses (reverse osmosis rejects), and moisture removal during the gas drying phases [27], [28]:

- Standard industrial electrolyzers consume between 10 to 12 Litres of demineralized water per 1 kg of hydrogen produced [27].
- If starting from raw water (like tap or seawater) before on-site purification, a facility typically needs to intake 20 to 30 Litres of raw water per kg of hydrogen to account for the purification system's wastewater stream. [27], [28].

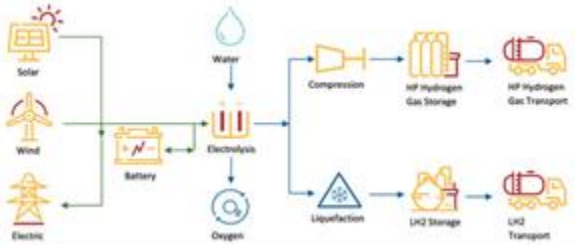

Fig. V. Process flow diagram of an integrated renewable-to-hydrogen energy framework.

The pathway models green hydrogen production driven by variable solar and wind power blocks paired with a battery energy storage system (BESS) for grid-balancing and localized power buffering. The separation process yields molecular oxygen as a valuable secondary byproduct, while the downstream product delivery branches into twin logistical pathways: a gaseous route featuring mechanical compression for High-Pressure (HP) gas transport, and a cryogenic route using a liquefaction train for liquid hydrogen () storage and long-distance bulk distribution [31].

It is currently the most mature technology for "Green" or Low Carbon Hydrogen with a levelized cost of hydrogen (LCOH) ranging from ₹320–450/kg H_2, depending on renewable electricity tariffs, electrolyser capital installed cost of alkaline electrolysers in India is approximately ₹5–6 crore/MW, whereas PEM electrolysers cost ₹8–9 crore/MW.

In addition, the development of captive renewable energy infrastructure requires significant capital investment, with utility-scale solar photovoltaic plants costing approximately ₹3.5–4.5 crore/MW, onshore wind projects ₹6–7 crore/MW, and solar–wind hybrid projects ₹5–6.5 crore/MW. Consequently, a green hydrogen facility with a 1 MW electrolyser and dedicated renewable power generally requires a total capital investment of ₹9–15 crore/MW, depending on the selected electrolyser technology and renewable energy configuration.

Renewable electricity contributes nearly 50–70% of the total hydrogen production cost, making it the single largest component of the LCOH. When powered by low-cost solar or hybrid renewable energy at ₹2.0–2.5/kWh, the electricity cost decreases to approximately ₹100–125/kg H_2, enabling the overall LCOH to fall to ₹200–300/kg H_2, particularly for large-scale projects operating at high-capacity utilization. Continued reductions in electrolyser CAPEX through domestic manufacturing under the National Green Hydrogen Mission are expected to further reduce production costs.

TABLE III SUMMARY OF WATER ELECTROLYSIS

Parameter	Value
Technology	Water Electrolysis (Alkaline/PEM)
Feedstock/Input	9–12 L demineralized water + 50–55 kWh renewable electricity per kg H_2
Hydrogen Yield	~1 kg H_2
Co-products	~8 kg O_2
Electrolyser CAPEX	Alkaline: ₹5–6 crore/MW; PEM: ₹8–9 crore/MW
Renewable Energy Plant CAPEX	Solar PV: ₹3.5–4.5 crore/MW; Wind: ₹6–7 crore/MW; Solar–Wind Hybrid: ₹5–6.5 crore/MW

Parameter	Value
Total Integrated CAPEX	₹9–15 crore/MW (Electrolyser + Captive RE + Balance of Plant)
Electricity Cost Contribution	₹100–138/kg H_2 (assuming ₹2.0–2.5/kWh renewable electricity)
Gross LCOH	₹320–450/kg H_2 (current commercial projects)
Net LCOH	₹300–430/kg H_2 (after oxygen utilization/credit, where applicable)
Technology Status	Commercial (TRL 9)
Hydrogen Type	Green Hydrogen
Major Cost Drivers	Renewable electricity tariff, electrolyser CAPEX, renewable energy plant CAPEX, capacity factor, financing cost, water treatment, and O&M

D. Limitation and Requirement of Alternative Hydrogen Production Technologies

The technical, environmental, and economic limitations associated with conventional fossil-fuel-based hydrogen production and water electrolysis have accelerated the need for alternative hydrogen generation technologies. Although Steam Methane Reforming (SMR) and Autothermal Reforming (ATR) remain commercially dominant, their dependence on fossil fuels and associated greenhouse gas emissions continue to hinder the transition toward a truly carbon-neutral hydrogen economy [5], [12], [17], [18]. Even with Carbon Capture, Utilization, and Storage (CCUS), challenges such as methane leakage, incomplete carbon capture efficiency, and additional energy penalties reduce the overall sustainability of these processes [14], [16], [18].

Similarly, green hydrogen production through water electrolysis faces several barriers related to high electricity consumption, dependence on intermittent renewable energy sources, requirement of expensive noble metal catalysts, and the need for large quantity of ultrapure water [20]– [25]. Large-scale deployment of electrolyzers may therefore become economically and resource intensive, particularly in water-scarce regions [25], [27], [28].

In this context, alternative hydrogen production pathways are gaining increasing research and industrial interest. Technologies such as brine electrolysis, methane pyrolysis, wastewater-assisted electrolysis, and air/moisture-based hydrogen generation offer the possibility of reducing freshwater dependence, utilizing waste-derived feedstocks, lowering carbon emissions, and enabling decentralized hydrogen production systems [5], [20], [30]. These technologies can complement conventional electrolysis while improving resource utilization and energy security [3], [5].

Furthermore, alternative pathways may support circular economy approaches by converting agricultural residues, municipal waste, saline water, and atmospheric moisture into valuable hydrogen fuel [3], [4], [5]. Their development is particularly important for developing countries with abundant biomass resources, saline water availability, and growing renewable energy capacities [1], [3], [4]. Therefore, continued research, pilot-scale demonstrations, catalyst development, and policy support are essential for advancing these innovative hydrogen production technologies toward commercial deployment and long-term sustainability [1], [3], [20].

V. ALTERNATIVE HYDROGEN PRODUCTION TECHNOLOGIES

Alternative hydrogen production technologies refer to innovative hydrogen generation pathways developed to overcome the environmental, economic, and resource limitations associated with conventional fossil-fuel-based hydrogen production and water electrolysis systems. These technologies aim to reduce greenhouse gas emissions, improve energy efficiency, minimize freshwater consumption, and utilize renewable or waste-derived feedstocks for sustainable hydrogen generation [1], [3], [5], [20].

These technologies include electrochemical processes such as brine electrolysis, wastewater electrolysis through the Integrated Forward Osmosis–Alkaline Water Electrolysis (FO–AWE) system, and atmospheric moisture-based hydrogen production, as well as thermochemical pathways such as methane pyrolysis. Many of these approaches utilize alternative feedstocks, including seawater brine, wastewater, atmospheric moisture, and natural gas, thereby reducing dependence on freshwater resources while

enabling decentralized hydrogen production and facilitating renewable energy integration [3], [4], [5], [30].

Alternative hydrogen production technologies are gaining increasing attention due to their potential to address the limitations of conventional hydrogen production routes by improving resource utilization, reducing greenhouse gas emissions, lowering freshwater consumption, and generating commercially valuable co-products [1], [3], [20], [25]. These technologies are particularly promising for regions experiencing freshwater scarcity, possessing abundant saline water resources, or seeking to maximize the utilization of renewable energy. Furthermore, they can complement existing renewable energy infrastructure by converting intermittent solar and wind energy into storable hydrogen fuel while improving overall process economics through the recovery of value-added by-products such as chlorine, sodium hydroxide, oxygen, treated wastewater, and solid carbon [1], [3], [20], [30]. Continued advancements in catalyst development, reactor design, process optimization, renewable energy integration, and supportive policy frameworks are essential for improving the commercial viability and large-scale deployment of these emerging hydrogen production pathways [1], [3], [20].

Technologies to be discussed in this paper are:

1. Brine Electrolysis
2. Atmospheric Moisture/Air-Based Electrolysis
3. Wastewater Electrolysis
4. Photoelectrochemical Water Splitting
5. Methane Pyrolysis

A. Brine Electrolysis (Chlor- Alkali Process)

Brine electrolysis, also known as the chlor-alkali process, is an electrochemical hydrogen production technology in which aqueous sodium chloride (NaCl) solution is electrolyzed to produce sodium hydroxide (NaOH), chlorine gas (Cl_2), and hydrogen gas (H_2). The primary objective of this process is the industrial production of caustic soda (NaOH), while hydrogen is generated as a valuable by-product [32], [33]. During electrolysis, chlorine gas is evolved at the anode and hydrogen gas at the cathode according to the following reaction [32]:

$$2H_2O + 2NaCl \rightarrow 2NaOH + H_2 + Cl_2 \quad (7)$$

In this process, a brine solution consisting of approximately 58 kg sodium chloride (NaCl) dissolved in 18 kg water (H_2O) is supplied to a caustic soda electrolyzer [33].

The electrolyzer consumes nearly 80 units (kWh) of electrical energy for the production of 1 kg of hydrogen (H_2) [33], [34].

Along with 1 kg of hydrogen, the process simultaneously generates nearly 35 kg of chlorine (Cl_2) and 40 kg of caustic soda (NaOH).

A brine electrolyser, also referred to as a sodium chloride (NaCl) electrolyser or chlor-alkali electrolytic cell, is an electrochemical system used for the electrolysis of aqueous sodium chloride solution to produce chlorine gas, hydrogen gas, and sodium hydroxide. The electrolytic cell consists of an anode (positive electrode) and a cathode (negative electrode) separated by a diaphragm or ion-exchange membrane to prevent the mixing of chlorine and hydrogen gases during operation [32], [35].

During electrolysis, chloride ions are oxidized at the anode to produce chlorine gas, while water molecules are reduced at the cathode to generate hydrogen gas and hydroxide ions. The remaining sodium ions in the electrolyte combine with hydroxide ions to form sodium hydroxide solution [32], [35].

The overall electrochemical reaction is represented as:

$2H_2O + 2NaCl \rightarrow 2NaOH + H_2(g) + Cl_2(g)$ *(8)*

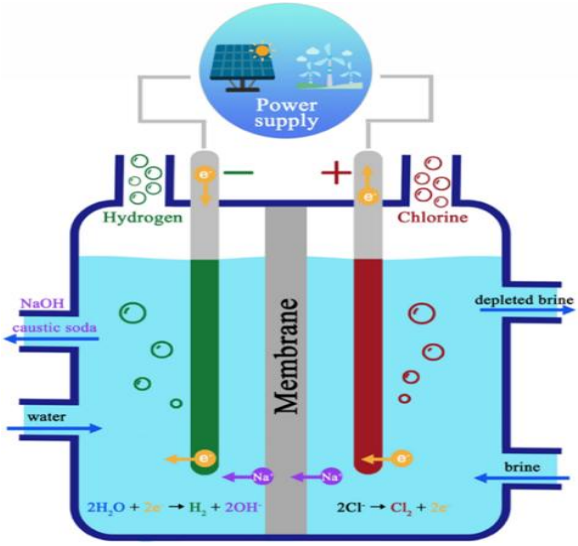

Fig. VI. Schematic representation of membrane-based brine electrolysis (chlor-alkali process) showing hydrogen evolution at the cathode and chlorine evolution at the anode [38].

The anode is generally fabricated using inert and corrosion-resistant materials such as graphite or platinum-coated titanium to withstand the highly oxidative chlorine environment [35]. The cathode is commonly manufactured from metallic materials such as iron or nickel (Ni). In advanced systems, oxygen-depolarized cathodes are employed to improve energy efficiency. These cathodes are typically composed of fine silver particles combined with hydrophobic polymers such as polytetrafluoroethylene (PTFE), which facilitate oxygen utilization as a depolarizer during electrochemical reactions [36].

The electrode reactions occurring within the electrolytic cell are as follows:

At the anode:

$2Cl^- \rightarrow Cl_2 + 2e^-$ (9)

At the cathode:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (10)

In conventional chlor-alkali industries, the hydrogen produced is often reacted with chlorine to manufacture hydrochloric acid (HCl). [33], [37]. In cases where chlorine is utilized for other industrial applications, the hydrogen may be further used for ammonia (NH_3) synthesis through the Haber–Bosch process [29], [30], [37].

A significant advantage of brine electrolysis is the simultaneous production of three commercially valuable products—hydrogen (H_2), chlorine (Cl_2), and sodium hydroxide (NaOH)—from a single electrochemical process [32], [33]. Unlike conventional water electrolysis, which primarily generates hydrogen and oxygen, brine electrolysis produces co-products that have well-established industrial markets.

Chlorine is extensively used in water treatment, disinfectants, polyvinyl chloride (PVC) manufacturing, pharmaceuticals, and chemical synthesis, while sodium hydroxide is widely utilized in pulp and paper production, alumina refining, textile processing, soap manufacturing, and numerous chemical industries [33], [37].

The generation of these valuable co-products can improve process economics and resource utilization, provided sufficient market demand exists for chlorine and caustic soda.

The current gross LCOH is estimated to range from ₹300–500/kg H_2, depending primarily on renewable electricity tariffs, electrolyser capital cost, brine pretreatment, and corrosion-resistant system components. Brine electrolysers typically require 85–90 kWh of electricity per kilogram of hydrogen, which is considerably higher than conventional water electrolysis, making electricity the dominant cost component and contributing approximately 55–70% of the total production cost.

The installed CAPEX of brine electrolysers is approximately ₹5.5–7 crore/MW, while dedicated renewable energy infrastructure requires an additional investment of ₹6–9 crore/MW, depending on whether solar photovoltaic, wind, or hybrid renewable energy systems are employed. Since continuous operation is essential for maintaining high electrolyser utilization, projects powered exclusively by renewable energy generally require either Battery Energy Storage Systems (BESS) costing approximately ₹4–6 crore/MWh or grid-assisted renewable integration to compensate for the intermittency of solar and wind resources. Consequently, the total integrated project CAPEX, including the electrolyser, renewable energy plant, BESS or grid interconnection, and balance of plant, typically ranges between ₹12–20 crore/MW. When low-cost renewable electricity is available at ₹2.0–2.5/kWh, the electricity cost contribution is approximately ₹170–225/kg H_2. Furthermore, revenues generated from the co-production of approximately 35.5 kg of chlorine and 40 kg of sodium hydroxide per kilogram of hydrogen can reduce the net LCOH to approximately ₹150–300/kg H_2, depending on product prices, market demand, and the cost allocation methodology. Therefore, integrated chlor-alkali and green hydrogen facilities represent one of the most economically attractive hydrogen production pathways for India's coastal industrial clusters, particularly where renewable energy resources and markets for chlorine and caustic soda already exist.

Although brine electrolysis offers an industrially mature route for hydrogen generation, it is presently not considered a major large-scale green hydrogen production pathway because the overall process economics depend heavily on the utilization, market demand, or safe management of the substantial

quantities of co-produced chlorine and sodium hydroxide [32], [33], [37].

TABLE IV SUMMARY OF BRINE ELECTROLYSIS

Parameter	Value
Technology	Brine Electrolysis
Feedstock/Input	Saturated brine (NaCl solution) + 85–90 kWh renewable electricity per kg H_2
Hydrogen Yield	~1 kg H_2
Co-products	~35.5 kg Cl_2 + ~40 kg NaOH + ~8 kg O_2
Electrolyser CAPEX	₹5.5–7 crore/MW
Renewable Energy Plant CAPEX	Solar PV: ₹6–8 crore/MW*; Wind: ₹6–7 crore/MW; Solar–Wind Hybrid: ₹7–9 crore/MW
Battery Energy Storage System (BESS)	₹4–6 crore/MWh (if dedicated renewable operation and continuous hydrogen production are required)
Alternative Power Supply	Grid-connected or RE–Grid hybrid configuration to improve electrolyser utilization and reduce BESS requirement
Total Integrated CAPEX	₹12–20 crore/MW (Electrolyser + Renewable Energy Plant + BESS/Grid Interconnection + Balance of Plant)
Electricity Cost Contribution	₹170–225/kg H_2 (assuming 85–90 kWh/kg H_2 and renewable electricity tariff of ₹2.0–2.5/kWh)
Gross LCOH	₹300–500/kg H_2
Net LCOH	₹150–300/kg H_2 (after co-product credits for Cl_2 and NaOH)
Technology Status	Pilot to Early Commercial (TRL 6–8)
Hydrogen Type	Green Hydrogen
Major Cost Drivers	Renewable electricity tariff, high specific energy consumption, electrolyser CAPEX, renewable energy plant CAPEX, BESS or grid integration, brine pretreatment, corrosion-resistant materials, membrane durability, O&M, and market value of chlorine and sodium hydroxide.

**Note: A higher renewable energy plant capacity may be required than for conventional water electrolysis because of the higher specific electricity consumption (~88 kWh/kg H_2). In practice, hybrid solar–wind systems or grid-assisted operation are often preferred to maintain a high electrolyser capacity factor while minimizing battery storage requirements.*

B. Atmospheric Moisture/Air-Based Electrolysis

Hydrogen production from atmospheric air has recently emerged as an innovative electrochemical approach for sustainable hydrogen generation, particularly in regions facing freshwater scarcity. Researchers at the University of Melbourne developed a Direct Air Electrolysis (DAE) module capable of producing hydrogen by directly utilizing moisture present in ambient air [39]. Unlike conventional water electrolysis systems that require purified liquid water, the DAE system captures atmospheric humidity and converts it into hydrogen and oxygen using renewable electrical energy.

The DAE module consists of a central water-harvesting unit positioned between two platinum mesh electrodes coupled with gas collectors and connected to an external power supply. The water-harvesting layer is composed of porous materials such as melamine sponge and sintered glass foam impregnated with a deliquescent electrolyte solution. The electrolyte primarily contains potassium acetate (CH_3COOK), potassium hydroxide (KOH), and sulfuric acid (H_2SO_4), which collectively act as hygroscopic substances capable of absorbing moisture directly from the atmosphere through exposed surfaces [39].

Once atmospheric moisture is absorbed, the captured water diffuses toward the electrode surfaces, where electrochemical water splitting occurs. Hydrogen evolution takes place at the cathode, while oxygen evolution occurs at the anode. The electrochemical reactions occurring in the DAE module are represented below:

Reaction at Cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (10)$$

Reaction at Anode:

$$4OH^- \rightarrow O2 + 2H2O + 4e^- \qquad (11)$$

Overall Reaction:

$2H2O \rightarrow 2H2 + O2$ (12)

This technology demonstrates significant potential for decentralized hydrogen production in arid and remote regions where freshwater availability is limited. Furthermore, integration with renewable energy sources such as solar and wind power can enable carbon-neutral hydrogen generation. However, the technology is still at an early research stage and faces challenges related to large-scale moisture harvesting efficiency, material durability, system stability, and commercial scalability [39].

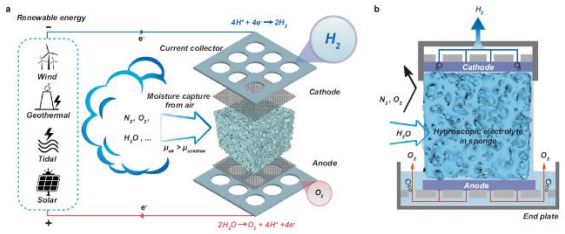

Fig. VII (a) Conceptual schematic of the Direct Air Electrolysis (DAE) system showing atmospheric moisture capture using a hygroscopic electrolyte integrated with renewable energy sources for hydrogen production, and (b) cross-sectional configuration of the DAE module illustrating the sponge-based hygroscopic electrolyte positioned between the cathode and anode for electrochemical splitting of absorbed water into hydrogen and oxygen [39].

This technology is particularly attractive for arid and water-stressed regions of India, such as Rajasthan, Gujarat, and Ladakh, where water availability poses a major constraint for conventional electrolysis. However, due to the additional energy required for atmospheric moisture capture, water adsorption–desorption, and electrochemical conversion, the process typically consumes 70–90 kWh of electricity per kilogram of hydrogen, resulting in higher production costs than conventional water electrolysis. The installed CAPEX of direct air electrolysers is currently estimated at ₹8–12 crore/MW, reflecting the early-stage nature of the technology and the need for specialized moisture harvesting materials and integrated electrochemical systems. In addition, dedicated renewable energy infrastructure requires approximately ₹6–9 crore/MW, while continuous operation under standalone renewable power generally necessitates Battery Energy Storage Systems (BESS) costing ₹4–6 crore/MWh, or alternatively, grid-assisted renewable integration to improve electrolyser utilization and reduce storage requirements.

Consequently, the total integrated project CAPEX, including the electrolyser, renewable energy plant, BESS or grid interconnection, and balance of plant, is estimated to range between ₹15–25 crore/MW. The current gross LCOH is estimated at ₹500–900/kg H_2, with renewable electricity contributing nearly 60–75% of the total production cost. Since oxygen is the only significant co-product and often has limited commercial value, the net LCOH remains close to the gross LCOH, typically in the range of ₹480–880/kg H_2.

Although the technology is presently at the laboratory to pilot stage (TRL 3–5), continued advancements in moisture-harvesting materials, electrolyser efficiency, and renewable energy integration are expected to substantially reduce production costs, making Direct Air Electrolysis a promising long-term solution for decentralized hydrogen production in water-scarce regions.

TABLE V. SUMMARY OF DIRECT AIR ELECTROLYSIS (DAE)

Parameter	Value
Technology	Direct Air Electrolysis (DAE)
Feedstock/Input	Atmospheric moisture + 70–90 kWh renewable electricity per kg H_2
Hydrogen Yield	~1 kg H_2
Co-products	~8 kg O_2
Electrolyser CAPEX	₹8–12 crore/MW
Renewable Energy Plant CAPEX	Solar PV: ₹6–8 crore/MW; Wind: ₹6–7 crore/MW; Solar–Wind Hybrid: ₹7–9 crore/MW
Battery Energy Storage System (BESS)	₹4–6 crore/MWh (for standalone renewable operation)
Alternative Power Supply	Grid-connected or Renewable Energy–Grid hybrid configuration
Total Integrated CAPEX	₹15–25 crore/MW (Electrolyser + Renewable Energy Plant + BESS/Grid

Parameter	Value
	Interconnection + Balance of Plant)
Electricity Cost Contribution	₹140–225/kg H_2 (assuming 70–90 kWh/kg H_2 and renewable electricity tariff of ₹2.0–2.5/kWh)
Gross LCOH	₹500–900/kg H_2
Net LCOH	₹480–880/kg H_2 (after oxygen utilization/credit, where applicable)
Technology Status	Laboratory to Pilot Scale (TRL 3–5)
Hydrogen Type	Green Hydrogen
Major Cost Drivers	Renewable electricity tariff, atmospheric moisture harvesting efficiency, electrolyser CAPEX, renewable energy plant CAPEX, BESS or grid integration, ambient humidity, balance of plant, operation & maintenance, and financing cost.

C. Wastewater Electrolysis (Integrated Forward Osmosis-Alkaline Water Electrolysis System)

The Integrated Forward Osmosis–Alkaline Water Electrolysis (FOWSAWE) system is an advanced wastewater-to-hydrogen technology developed for simultaneous municipal wastewater treatment and green hydrogen production [40]. The system integrates forward osmosis (FO) membrane separation with alkaline water electrolysis (AWE) to overcome freshwater limitations associated with conventional electrolysis-based hydrogen production.

In the FOWSAWE system, municipal wastewater effluent acts as the feed solution in the forward osmosis module. Clean water is extracted across a thin-film composite forward osmosis (TFC-FO) membrane into a concentrated potassium hydroxide (KOH) draw solution. The diluted KOH solution is subsequently supplied to the alkaline water electrolysis unit for hydrogen production. The extracted water replenishes the electrolyte consumed during electrolysis, thereby enabling continuous hydrogen generation.

The alkaline water electrolyzer consists of bipolar nickel-alloy electrodes separated by polymer diaphragms. Hydrogen is generated at the cathode, while oxygen evolution occurs at the anode according to the following electrochemical reactions:

Reaction at Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (13)$$

Reaction at Anode:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (14)$$

Overall Reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (15)$$

The study demonstrated that the FOWSAWE system achieved one of the highest hydrogen production rates reported for alternative water-resource electrolysis systems, reaching approximately 448 Nm^3 day^{-1} m^{-2} of TFC-FO membrane area with hydrogen purity exceeding 99% [40]. The system also exhibited a low specific energy consumption (SEC) of nearly 4.43 kWh. $N.m.^{-3}$, which further decreased to 3.96 $kWh.N.m^{-3}$ through utilization of waste heat generated during alkaline water electrolysis operations [40]. Additionally, the integrated system maintained stable operation for more than 168 hours using real municipal wastewater effluent under varying wastewater compositions.

The FOWSAWE system offers several advantages, including reduced freshwater dependency, simultaneous wastewater treatment and water reuse, improved water recovery, and enhanced sustainability for decentralized hydrogen production. Furthermore, the integration of FO and AWE technologies can potentially reduce the capital cost of water treatment compared with conventional reverse osmosis-based systems.

However, several technical challenges still limit large-scale implementation of the technology. Membrane fouling, concentration polarization, reverse salt flux, electrolyte contamination, and long-term membrane degradation can adversely affect operational stability and hydrogen production efficiency [40]. In addition, the requirement for advanced FO membranes, controlled electrolyte management, and integrated process optimization increases system complexity and operational cost. Consequently, further research is

required to improve membrane durability, reduce energy consumption, optimize wastewater compatibility, and enhance long-term techno-economic feasibility before commercial-scale deployment can be realized.

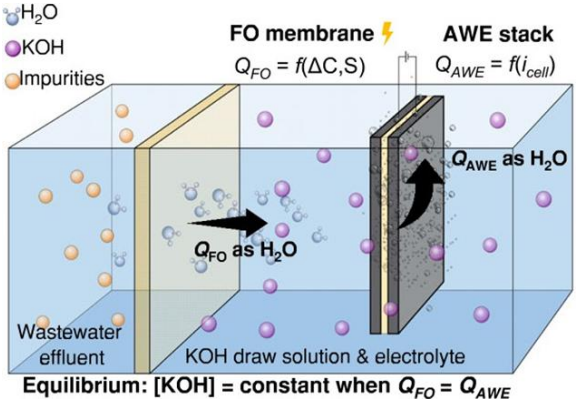

Fig. VIII Schematic representation of the Integrated Forward Osmosis–Alkaline Water Electrolysis (FOWSAWE) system for hydrogen production from municipal wastewater.

The figure illustrates water transport from wastewater effluent through the forward osmosis (FO) membrane into the potassium hydroxide (KOH) draw solution, followed by water consumption in the alkaline water electrolysis (AWE) stack for hydrogen production. The system maintains electrolyte equilibrium when the forward osmosis water flux (Q_{FO}) equals the water consumption rate in the electrolyzer (Q_{AWE}) [40].

The process utilizes municipal or industrial wastewater as the primary feedstock with potassium hydroxide (KOH) as the electrolyte, making it particularly suitable for water-stressed regions and industrial clusters in India. Recent pilot-scale studies have reported a hydrogen production rate of approximately 448 $Nm^3\ day^{-1}\ m^{-2}$ membrane area, with a specific electricity consumption of 4.5–5.4 kWh/Nm^3 H_2.

The installed CAPEX of the alkaline electrolyser is estimated at ₹5–7 crore/MW, while the forward osmosis unit contributes an additional ₹1–2 crore/MW. Furthermore, the deployment of captive renewable energy infrastructure requires an investment of approximately ₹3.5–6.5 crore/MW, and projects relying solely on renewable power generally require Battery Energy Storage Systems (BESS) costing ₹4–6 crore/MWh or renewable energy–grid hybrid integration to ensure continuous plant operation and higher electrolyser utilization.

Consequently, the total integrated project CAPEX, including the electrolyser, FO unit, renewable energy plant, BESS or grid interconnection, and balance of plant, typically ranges between ₹11–18 crore/MW. The current gross LCOH is estimated to be ₹220–380/kg H_2, while the net LCOH can decrease to approximately ₹190–340/kg H_2 owing to reduced freshwater consumption, savings in wastewater treatment costs, and the potential utilization of oxygen as a co-product. Although the technology is currently at the pilot stage (TRL 5–7), continued improvements in membrane durability, fouling resistance, renewable energy integration, and system optimization are expected to enhance its commercial viability for decentralized green hydrogen production in India.

TABLE VI. SUMMARY OF FOWSAWE (WASTEWATER ELECTROLYSIS)

Parameter	Value
Technology	Integrated Forward Osmosis–Alkaline Water Electrolysis (FO–AWE)
Feedstock/Input	Municipal wastewater + KOH electrolyte + 4.5–5.4 kWh renewable electricity/Nm^3 H_2
Hydrogen Yield	~448 $Nm^3\ day^{-1}\ m^{-2}$ membrane area
Co-products	Treated wastewater + Oxygen (O_2)
Electrolyser CAPEX	₹5–7 crore/MW
Forward Osmosis (FO) Unit CAPEX	₹1–2 crore/MW equivalent
Renewable Energy Plant CAPEX	Solar PV: ₹3.5–4.5 crore/MW; Wind: ₹6–7 crore/MW; Solar–Wind Hybrid: ₹5–6.5 crore/MW
Battery Energy Storage System (BESS)	₹4–6 crore/MWh (for standalone renewable operation)
Alternative Power Supply	Grid-connected or Renewable Energy–Grid hybrid configuration
Total Integrated CAPEX	₹11–18 crore/MW (Electrolyser + FO Unit + Renewable Energy Plant + BESS/Grid Integration + Balance of Plant)
Gross LCOH	₹220–380/kg H_2
Net LCOH	₹190–340/kg H_2 (after wastewater treatment savings and oxygen utilization, where applicable)

Parameter	Value
Technology Status	Pilot (TRL 5–7)
Hydrogen Type	Green Hydrogen
Major Cost Drivers	Renewable electricity tariff, FO membrane cost and replacement, wastewater pretreatment, electrolyser CAPEX, renewable energy plant CAPEX, BESS/grid integration, membrane fouling, O&M, and financing cost.

D. Photoelectrochemical Water Splitting

Photoelectrochemical (PEC) water splitting is an emerging hydrogen production technology that directly converts solar energy into chemical energy in the form of hydrogen. Unlike conventional water electrolysis, which requires an external electricity source, PEC systems utilize semiconductor photoelectrodes to absorb sunlight and generate electron–hole pairs that drive water-splitting reactions. This technology combines the principles of photovoltaics and electrolysis into a single integrated system, thereby offering the potential for efficient and sustainable solar hydrogen production [41], [42].

A typical photoelectrochemical (PEC) cell consists of a semiconductor photoanode, a cathode, an electrolyte, and an external circuit. The photoanode is commonly fabricated from semiconductor materials such as titanium dioxide (TiO_2), hematite (α-Fe_2O_3), tungsten trioxide (WO_3), bismuth vanadate ($BiVO_4$), or tantalum nitride (Ta_3N_5), which absorb solar radiation and generate electron–hole pairs. The cathode is generally composed of catalytic materials such as platinum (Pt), nickel (Ni), molybdenum sulfide (MoS_2), or nickel–molybdenum alloys that facilitate the hydrogen evolution reaction (HER). Upon illumination, photogenerated holes migrate to the photoanode surface and oxidize water to produce oxygen, while electrons are transported through the external circuit to the cathode, where hydrogen gas is generated [41]–[43].

The electrochemical reactions occurring in a PEC cell are as follows [41]:

At the Photoanode (Oxidation):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (16)$$

At the Cathode (Reduction):

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (17)$$

Overall Reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (18)$$

Common semiconductor materials investigated for PEC water splitting include titanium dioxide (TiO_2), hematite (α-Fe_2O_3), tungsten trioxide (WO_3), bismuth vanadate ($BiVO_4$), and silicon-based photoelectrodes [42], [43]. These materials are selected based on their bandgap energy, chemical stability, charge transport properties, and ability to absorb visible light.

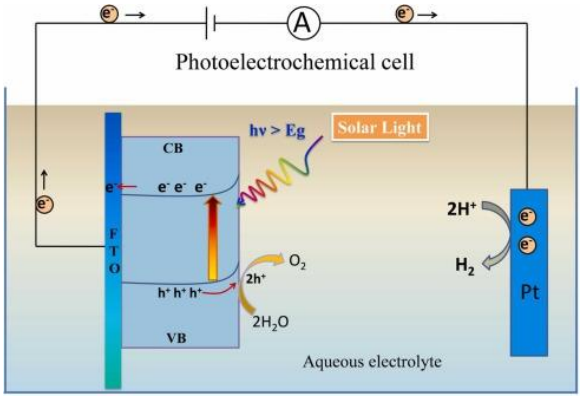

Fig. IX. Schematic of a photoelectrochemical (PEC) cell setup for water splitting [46], illustrating the transport of photogenerated electrons (e^-) from the FTO-supported semiconductor photoanode to a platinum (Pt) counter electrode under solar illumination ($h\nu > E_g$).

Current laboratory-scale photoelectrochemical systems typically achieve hydrogen production rates ranging from 0.1 to 1.5 $Nm^3\ m^{-2}\ day^{-1}$, which corresponds to approximately 0.009–0.135 kg $H_2\ m^{-2}\ day^{-1}$, depending on the semiconductor material, solar irradiance, and cell configuration. Advanced tandem PEC devices have demonstrated solar-to-hydrogen (STH) efficiencies exceeding 19%, highlighting their potential for future large-scale renewable hydrogen production [45].

The installed CAPEX of PEC systems is presently estimated at ₹10–18 crore/MW (equivalent hydrogen production capacity) due to the high cost of semiconductor photoelectrodes, catalyst coatings, and reactor assemblies. Since the technology primarily utilizes solar radiation, dedicated renewable electricity generation is not essential; however, auxiliary equipment such as water circulation, monitoring, control systems, and hydrogen compression may require limited electrical power, which can be supplied

either through small photovoltaic systems or grid connectivity. Consequently, the total integrated project CAPEX, including PEC modules, balance of plant, auxiliary electrical systems, and hydrogen handling infrastructure, is estimated at ₹12–20 crore/MW. The current gross LCOH is estimated to range between ₹420–850/kg H_2, while the net LCOH remains approximately ₹400–820/kg H_2, as oxygen is the only significant co-product and generally contributes limited economic value. Although PEC water splitting is presently at the research to pilot stage (TRL 3–5), continued advancements in photoelectrode stability, solar-to-hydrogen efficiency, catalyst development, and large-scale manufacturing are expected to significantly reduce hydrogen production costs, making PEC technology a promising long-term pathway for sustainable hydrogen production in India. The major advantages of PEC water splitting include direct utilization of solar energy, elimination of separate photovoltaic and electrolyzer units, reduced greenhouse gas emissions, and the potential for decentralized hydrogen production. However, the technology faces several challenges, including low solar-to-hydrogen conversion efficiency, photoelectrode corrosion, charge carrier recombination losses, and high material costs [41]–[45].

Consequently, significant research efforts are focused on developing efficient semiconductor materials, protective coatings, and catalyst systems to improve device performance and long-term stability.

Although still at the research and pilot scale, photoelectrochemical water splitting represents a promising pathway for future large-scale renewable hydrogen production and may contribute significantly to the development of a sustainable hydrogen economy [41]– [45].

TABLE VII. SUMMARY OF PHOTOELECTROCHEMICAL (PEC) WATER SPLITTING

Parameter	Value
Technology	Photoelectrochemical (PEC) Water Splitting
Feedstock/Input	Water + Solar Radiation
Hydrogen Yield	0.009–0.135 kg H_2 m^{-2} day^{-1}
Co-products	Oxygen (O_2)
PEC Reactor CAPEX	₹10–18 crore/MW (equivalent hydrogen production capacity)
Auxiliary Solar PV/Grid Power	Small Solar PV system or Grid Supply (for pumps, controls, monitoring and hydrogen compression)
Battery Energy Storage System (Optional)	₹4–6 crore/MWh (if off-grid operation is adopted)
Total Integrated CAPEX	₹12–20 crore/MW (PEC Modules + Auxiliary Systems + Hydrogen Handling + Balance of Plant)
Gross LCOH	₹420–850/kg H_2
Net LCOH	₹400–820/kg H_2 (after oxygen utilization, where applicable)
Technology Status	Research to Pilot (TRL 3–5)
Hydrogen Type	Green Hydrogen
Major Cost Drivers	Photoelectrode material cost, solar-to-hydrogen conversion efficiency, catalyst durability, reactor lifetime, auxiliary power requirement, hydrogen collection and compression, balance of plant, and financing cost.

E. Methane Pyrolysis

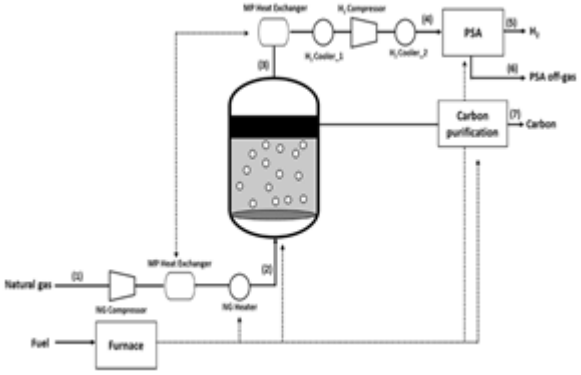

Fig. X. Process flow diagram of methane pyrolysis for hydrogen production [51].

Methane pyrolysis is an emerging thermochemical pathway for hydrogen production that involves the thermal decomposition of methane in the absence of oxygen. Unlike conventional hydrogen production routes such as steam methane reforming (SMR) and autothermal reforming (ATR), methane pyrolysis does not directly generate carbon dioxide during hydrogen production. Instead, the carbon present in methane is recovered as solid carbon, making the process a low-carbon hydrogen production technology. Hydrogen

produced through this route is commonly classified as turquoise hydrogen because of its significantly lower greenhouse gas emissions compared with conventional fossil-fuel-based hydrogen production methods [47], [48].

Methane used in the process is generally obtained from natural gas, which typically contains 85–98% methane, with the remaining composition consisting of ethane, propane, nitrogen, carbon dioxide, and other trace gases depending on the gas source [48], [49]. During methane pyrolysis, natural gas is introduced into a high-temperature oxygen-free reactor operating typically between 800 and 1200 °C, where methane molecules undergo thermal cracking according to the following reaction [47], [48]:

$$CH_4 \rightarrow C + 2H_2 \quad (19)$$

The reaction produces hydrogen gas and high-purity solid carbon as the principal products. The solid carbon can be utilized in the manufacture of carbon black, graphite, activated carbon, battery electrode materials, advanced composites, pigments, rubber products, and construction materials, thereby generating an additional revenue stream that can significantly improve the overall economics of hydrogen production. Since carbon remains in the solid phase rather than being released as carbon dioxide, methane pyrolysis offers substantial environmental benefits and contributes to greenhouse gas emission reduction [47], [48].

From a stoichiometric perspective, 16 g of methane produces 4 g of hydrogen, indicating that approximately 4 kg of methane is theoretically required to produce 1 kg of hydrogen [47]. Considering practical operating conditions, including incomplete methane conversion, reactor heat losses, hydrogen purification, carbon separation, and auxiliary energy requirements, the actual methane consumption generally ranges from 4.2 to 5.0 kg of natural gas per kilogram of hydrogen produced [48], [50].

The methane pyrolysis process typically consists of five major stages. Initially, natural gas undergoes pretreatment to remove impurities such as sulfur compounds, moisture, and higher hydrocarbons that may deactivate catalysts or affect reactor performance. The purified methane is subsequently introduced into a high-temperature pyrolysis reactor, where thermal decomposition produces hydrogen and solid carbon. The generated hydrogen is then separated, purified, compressed, and stored for downstream applications, while the solid carbon is continuously collected for industrial utilization or commercial sale [48], [49].

The installed CAPEX of methane pyrolysis plants is estimated at ₹7–10 crore/MW (H_2 equivalent). When renewable electricity or renewable thermal energy is employed, additional investments of approximately ₹3.5–6.5 crore/MW are required for captive renewable energy infrastructure, while Battery Energy Storage Systems (BESS) costing ₹4–6 crore/MWh or renewable energy–grid hybrid integration may be necessary to ensure continuous reactor operation. Consequently, the total integrated project CAPEX generally ranges between ₹10–17 crore/MW, including the methane pyrolysis reactor, renewable energy system, BESS or grid interconnection, hydrogen purification, carbon collection, and balance of plant. The current gross LCOH of methane pyrolysis is estimated to range from ₹160–260/kg H_2, primarily depending on natural gas prices, reactor technology, energy source, and plant capacity. A major economic advantage of methane pyrolysis is the production of approximately 3 kg of solid carbon per kilogram of hydrogen, which can be marketed as carbon black, graphite, activated carbon, battery materials, or advanced carbon nanomaterials. Depending on carbon purity and market value, the sale of solid carbon can generate significant revenue, reducing the net LCOH to approximately ₹80–180/kg H_2. Consequently, methane pyrolysis is increasingly recognized as one of the most economically attractive low-carbon hydrogen production technologies, particularly where markets for high-value carbon products and low-cost natural gas are available. Future advancements in reactor design, catalyst development, renewable energy integration, and carbon valorization are expected to further improve process efficiency and commercial competitiveness. Methane pyrolysis offers several advantages, including near-zero direct carbon dioxide emissions, lower lifecycle greenhouse gas emissions than conventional steam methane reforming, high hydrogen purity, and the production of valuable solid carbon co-products. Unlike SMR with carbon capture and storage (CCUS), methane pyrolysis avoids the need for carbon dioxide capture, transportation, and long-term geological storage, thereby reducing process complexity and eliminating risks associated with CO_2 leakage [47], [48].

TABLE VIII. SUMMARY OF METHANE PYROLYSIS

Parameter	Value
Technology	Methane Pyrolysis
Feedstock/Input	Natural Gas (CH_4) + 10–15 kWh energy/kg H_2 (electricity or thermal energy)
Hydrogen Yield	~1 kg H_2
Co-products	~3 kg Solid Carbon
Reactor CAPEX	₹7–10 crore/MW (H_2 equivalent)
Renewable Energy Plant CAPEX	Solar PV: ₹3.5–4.5 crore/MW; Wind: ₹6–7 crore/MW; Solar–Wind Hybrid: ₹5–6.5 crore/MW (when renewable energy is used)
Battery Energy Storage System (BESS)	₹4–6 crore/MWh (for renewable-powered operation)
Alternative Energy Supply	Grid-connected or Renewable Energy–Grid hybrid configuration
Total Integrated CAPEX	₹10–17 crore/MW (Reactor + Renewable Energy + BESS/Grid Integration + Hydrogen Purification + Carbon Collection + Balance of Plant)
Natural Gas Consumption	~4.2–5.0 kg CH_4/kg H_2
Gross LCOH	₹160–260/kg H_2
Net LCOH	₹80–180/kg H_2 (after credit from solid carbon sales)
Technology Status	Demonstration to Early Commercial (TRL 6–8)
Hydrogen Type	Turquoise Hydrogen
Major Cost Drivers	Natural gas price, reactor temperature, energy source, reactor CAPEX, renewable energy cost (if used), carbon purity, carbon selling price, hydrogen purification, O&M, and financing cost.

VI. COMPARISON OF ALL THE ALTERNATIVE TECHNOLOGIES WITH CONVENTIONAL

The alternative hydrogen production technologies reviewed in this paper, namely Brine Electrolysis, Direct Air Electrolysis (DAE), Integrated Forward Osmosis–Alkaline Water Electrolysis (FO–AWE), Photoelectrochemical (PEC) Water Splitting, and Methane Pyrolysis, have been developed to address the technical, economic, and environmental limitations associated with conventional hydrogen production technologies such as Steam Methane Reforming (SMR), Autothermal Reforming (ATR), and Water Electrolysis. These emerging technologies employ unconventional feedstocks, improve resource utilization, reduce greenhouse gas emissions, and, in several cases, generate valuable co-products that can enhance the overall process economics.

Although each alternative technology offers distinct advantages, no single pathway can universally replace the existing commercial hydrogen production technologies. Their suitability depends on factors such as feedstock availability, energy requirements, technology maturity, infrastructure, environmental performance, and economic feasibility. Therefore, a systematic comparison is necessary to evaluate their potential for complementing or replacing conventional hydrogen production pathways under different deployment scenarios.

TABLE IX COMPARISON OF FEEDSTOCK REQUIREMENT, HYDROGEN YIELD AND CO-PRODUCTS OF DISCUSSED HYDROGEN PRODUCTION TECHNOLOGIES

Technology	Feedstock Requirement	Hydrogen Yield	Co-products / Additional Outputs
Steam Methane Reforming (SMR)	~4–4.5 kg natural gas + 9–12 kg steam	~1 kg H_2	~9–10 kg CO_2
SMR with CCUS	~4–4.5 kg natural gas + 9–12 kg steam	~1 kg H_2	Captured CO_2 (60–70% capture efficiency)

Technology	Feedstock Requirement	Hydrogen Yield	Co-products / Additional Outputs
Autothermal Reforming (ATR)	~3.8–4.2 kg natural gas + oxygen + steam	~1 kg H_2	~8–9 kg CO_2
ATR with CCUS	~3.8–4.2 kg natural gas + oxygen + steam	~1 kg H_2	Captured CO_2 (≈90% capture efficiency)
Water Electrolysis	9–12 L demineralized water + 50–55 kWh electricity	~1 kg H_2	~8 kg O_2
Brine Electrolysis	60–70 kg NaCl (brine) + 18–25 L water + 85–90 kWh electricity	~1 kg H_2	~35.5 kg Cl_2 + ~40 kg NaOH + ~8 kg O_2
Direct Air Electrolysis (DAE)	Atmospheric moisture + 70–90 kWh electricity	~1 kg H_2	~8 kg O_2
FO–AWE (Wastewater Electrolysis)	Municipal wastewater + KOH electrolyte + 50–60 kWh electricity	~448 $Nm^3\ day^{-1}\ m^{-2}$ membrane area	Treated wastewater + O_2
Photoelectrochemical (PEC) Water Splitting	Water + solar radiation	0.009–0.135 kg $H_2\ m^{-2}\ day^{-1}$	O_2
Methane Pyrolysis	~4.2–5.0 kg CH_4 + thermal energy (800–1200 °C)	~1 kg H_2	~3 kg solid carbon

TABLE X COMPARISON OF ADVANTAGES AND LIMITATIONS OF CONVENTIONAL AND ALTERNATIVE HYDROGEN PRODUCTION TECHNOLOGIES

Technology	Major Advantages	Major Limitations
Steam Methane Reforming (SMR)	Lowest production cost, commercial maturity, established infrastructure	High CO_2 emissions, fossil fuel dependence
SMR with CCUS	Reduced carbon emissions, utilizes existing SMR infrastructure	Additional CAPEX and OPEX, carbon capture limited to ~60–70%, storage requirement
Autothermal Reforming (ATR)	Higher hydrogen productivity, compact process, suitable for large-scale production	Oxygen production requirement, CO_2 emissions
ATR with CCUS	High hydrogen purity, better carbon capture (~90%), suitable for blue hydrogen	High capital investment, oxygen plant requirement
Water Electrolysis	Carbon-free hydrogen with renewable energy, mature technology, high purity hydrogen	High electricity consumption, freshwater requirement, high renewable energy CAPEX
Brine Electrolysis	Eliminates freshwater dependency, produces Cl_2 and NaOH, lower net LCOH	High electricity demand, corrosion, chlorine handling, membrane degradation
Direct Air Electrolysis (DAE)	Utilizes atmospheric moisture, suitable for arid regions, no freshwater requirement	Low TRL, humidity dependent, high capital cost and energy consumption
FO–AWE (Wastewater Electrolysis)	Utilizes wastewater, simultaneous water treatment and hydrogen production, lower freshwater demand	Membrane fouling, pretreatment requirement, pilot-stage technology
Photoelectrochemical (PEC) Water Splitting	Direct solar-to-hydrogen conversion, no external electricity requirement, zero direct emissions	Low solar-to-hydrogen efficiency, expensive photoelectrodes, poor durability
Methane Pyrolysis	Near-zero direct CO_2 emissions, valuable solid carbon, low net LCOH, utilizes existing natural gas infrastructure	High-temperature operation, carbon separation and reactor fouling, limited commercial deployment

TABLE XI COMPARATIVE TECHNO-ECONOMIC PERFORMANCE OF CONVENTIONAL AND ALTERNATIVE HYDROGEN PRODUCTION TECHNOLOGIES

Technology	Gross LCOH (₹/kg H_2)	Net LCOH (₹/kg H_2)	Major Revenue / Cost Reduction Source
Steam Methane Reforming (SMR)	120–200	120–200	No significant co-products
SMR with CCUS	170–270	160–250	Carbon credits / limited CO_2 utilization
Autothermal Reforming (ATR)	140–220	140–220	No significant co-products
ATR with CCUS	180–260	170–240	Carbon credits / CO_2 utilization
Water Electrolysis	320–450	300–430	Oxygen (~8 kg O_2 per kg H_2)
Brine Electrolysis	300–500	150–300	Chlorine (~35.5 kg), NaOH (~40 kg) and Oxygen
Direct Air Electrolysis (DAE)	500–900	480–880	Oxygen
FO–AWE (Wastewater Electrolysis)	220–380	190–340	Treated wastewater, oxygen and reduced freshwater consumption
Photoelectrochemical (PEC) Water Splitting	420–850	400–820	Oxygen
Methane Pyrolysis	160–260	80–180	Solid carbon (~3 kg per kg H_2)

TABLE XII COMPARISON OF TECHNOLOGY READINESS AND POTENTIAL APPLICATIONS OF CONVENTIONAL AND ALTERNATIVE HYDROGEN PRODUCTION TECHNOLOGIES

Technology	Technology Readiness Level (TRL)	Potential Applications	Commercial Readiness
Steam Methane Reforming (SMR)	9	Refineries, ammonia plants, methanol production, fertilizer industry	Fully Commercial
SMR with CCUS	8–9	Blue hydrogen hubs, refineries, fertilizer and petrochemical industries	Commercial
Autothermal Reforming (ATR)	9	Large-scale hydrogen production, ammonia and methanol plants	Fully Commercial
ATR with CCUS	8–9	Blue hydrogen production, integrated industrial clusters	Commercial
Water Electrolysis	9	Renewable energy parks, green ammonia, mobility, industrial hydrogen	Fully Commercial
Brine Electrolysis	6–8	Coastal hydrogen production, chlor-alkali industries, integrated chemical complexes	Pilot–Early Commercial
Direct Air Electrolysis (DAE)	3–5	Water-scarce regions, remote renewable energy systems, desert applications	Research–Pilot
FO–AWE (Wastewater Electrolysis)	5–7	Municipal wastewater treatment plants, industrial wastewater facilities, decentralized hydrogen production	Pilot
Photoelectrochemical (PEC) Water Splitting	3–5	Distributed solar hydrogen production, off-grid applications	Research
Methane Pyrolysis	6–8	Natural gas processing, refineries, fertilizer plants, carbon material industries	Demonstration–Early Commercial

TABLE XIII NEAR-TERM AND LONG-TERM DEPLOYMENT POTENTIAL OF ALTERNATIVE HYDROGEN PRODUCTION TECHNOLOGIES

Alternative Technology	Near-term Deployment Potential (0–10 years)	Long-term Deployment Potential (>10 years)
Brine Electrolysis	High	Very High
Direct Air Electrolysis (DAE)	Low	High
FO–AWE (Wastewater Electrolysis)	Moderate	High
Photoelectrochemical (PEC) Water Splitting	Low	Very High
Methane Pyrolysis	High	Very High

Tables IX–XIII collectively compare the conventional and alternative hydrogen production technologies from technical, operational, economic, commercial, and deployment perspectives. The comparison indicates that conventional technologies, namely Steam Methane Reforming (SMR), Autothermal Reforming (ATR), and Water Electrolysis, remain the dominant hydrogen production routes owing to their high technology readiness levels (TRL 9), established industrial infrastructure, and large-scale commercial deployment. However, SMR and ATR emit approximately 8–10 kg CO_2 per kilogram of hydrogen, whereas renewable water electrolysis requires approximately 9–12 L of demineralized water and 50–55 kWh of electricity for producing 1 kg of hydrogen, making freshwater availability and electricity cost the major constraints for large-scale deployment.

As shown in Table IX, the alternative hydrogen production technologies significantly diversify the feedstock base by utilizing seawater brine, municipal wastewater, atmospheric moisture, solar energy, and methane. Brine electrolysis requires approximately 60–70 kg of NaCl, 18–25 L of water, and 85–90 kWh of electricity to produce 1 kg of hydrogen, while simultaneously generating approximately 35.5 kg of chlorine, 40 kg of sodium hydroxide, and 8 kg of oxygen. These commercially valuable co-products substantially improve the economic viability of the process. Similarly, methane pyrolysis consumes approximately 4.2–5 kg of methane to produce 1 kg of hydrogen together with approximately 3 kg of solid carbon, thereby avoiding direct carbon dioxide emissions unlike SMR and ATR. FO–AWE utilizes municipal wastewater instead of freshwater and has demonstrated hydrogen production rates of approximately 448 $Nm^3\ day^{-1}\ m^{-2}$ membrane area, while Direct Air Electrolysis (DAE) utilizes atmospheric moisture and requires approximately 70–90 kWh of electricity per kilogram of hydrogen. In comparison, Photoelectrochemical (PEC) Water Splitting directly converts solar energy into hydrogen, although the reported hydrogen production rate remains relatively low at 0.009–0.135 kg $H_2\ m^{-2}\ day^{-1}$. The operational comparison presented in Table X further demonstrates that each alternative technology addresses specific limitations associated with conventional hydrogen production. Brine electrolysis and FO–AWE eliminate the dependence on high-purity freshwater by utilizing saline water and municipal wastewater, respectively, whereas DAE completely removes the requirement for liquid water by extracting atmospheric moisture. Similarly, methane pyrolysis virtually eliminates direct carbon dioxide emissions through thermal decomposition of methane into hydrogen and solid carbon, while PEC Water Splitting eliminates external electricity consumption by directly utilizing solar radiation. Despite these advantages, the alternative technologies continue to face challenges related to higher electricity consumption (70–90 kWh kg^{-1} H_2 for brine electrolysis and DAE), membrane degradation, catalyst durability, reactor fouling, corrosion, and lower technology readiness compared with conventional hydrogen production technologies.

The techno-economic assessment presented in Table XI indicates that conventional hydrogen production technologies continue to exhibit the lowest gross hydrogen production costs. SMR and ATR achieve gross LCOH values of approximately ₹120–200 kg^{-1} and ₹140–220 kg^{-1}, respectively, whereas renewable water electrolysis exhibits considerably higher gross LCOH values of approximately ₹320–450 kg^{-1}, primarily due to renewable electricity costs. However, when revenues generated through commercially valuable co-products are incorporated into the economic analysis, several alternative technologies

become significantly more competitive. Brine electrolysis exhibits one of the largest reductions in hydrogen production cost, with the net LCOH decreasing from approximately ₹300–500 kg^{-1} to ₹150–300 kg^{-1}, mainly due to revenues generated from chlorine and sodium hydroxide. Similarly, methane pyrolysis achieves one of the lowest projected nets LCOH values of approximately ₹80–180 kg^{-1}, compared with a gross LCOH of ₹160–260 kg^{-1}, owing to the commercial value of solid carbon. FO–AWE also demonstrates favourable economics, with the net LCOH reducing from approximately ₹220–380 kg^{-1} to ₹190–340 kg^{-1} through wastewater treatment savings and oxygen utilization. In contrast, water electrolysis, DAE, and PEC Water Splitting derive relatively limited economic benefits from oxygen production alone, resulting in comparatively smaller reductions in net LCOH.

The technology readiness assessment summarized in Table XII indicates that conventional technologies have already attained TRL 9, while SMR and ATR integrated with CCUS have reached TRL 8–9. Among the alternative technologies, Brine Electrolysis and Methane Pyrolysis demonstrate comparatively higher technology readiness levels (TRL 6–8) and have progressed to pilot, demonstration, or early commercial deployment. FO–AWE has achieved TRL 5–7, whereas DAE and PEC Water Splitting remain at relatively early development stages (TRL 3–5) and continue to require substantial improvements in efficiency, durability, and large-scale validation before commercialization.

The deployment outlook presented in Table XIII further indicates that Brine Electrolysis and Methane Pyrolysis possess the highest near-term commercialization potential owing to their relatively advanced technology readiness, favourable economics, and compatibility with existing industrial infrastructure. FO–AWE also demonstrates promising prospects for decentralized hydrogen production integrated with municipal wastewater treatment facilities. Conversely, DAE and PEC Water Splitting are expected to play a more significant role over the long term as continued advancements in catalyst development, membrane technology, photoelectrode efficiency, and renewable energy integration improve their overall techno-economic performance.

Overall, the comparative assessment demonstrates that alternative hydrogen production technologies should currently be considered complementary rather than direct replacements for conventional hydrogen production pathways. Among the technologies reviewed, Brine Electrolysis emerges as the most promising alternative to conventional water electrolysis because it eliminates freshwater dependency while reducing the net hydrogen production cost by approximately 40–50% through revenues generated from chlorine and sodium hydroxide. Similarly, Methane Pyrolysis represents the strongest alternative to conventional natural gas reforming by reducing net LCOH by approximately 30–50% while simultaneously eliminating direct carbon dioxide emissions through solid carbon production. FO–AWE offers significant opportunities for decentralized hydrogen production in urban and industrial regions, whereas Direct Air Electrolysis and Photoelectrochemical Water Splitting remain long-term technologies with considerable future potential once technological maturity and economic competitiveness improve.

VII. CONCLUSION

Hydrogen is expected to play a pivotal role in achieving global decarbonization and facilitating the transition towards a sustainable energy economy. Although conventional hydrogen production technologies, namely Steam Methane Reforming (SMR), Autothermal Reforming (ATR), and Water Electrolysis, continue to dominate industrial hydrogen production due to their commercial maturity and established infrastructure, they remain constrained by significant challenges, including greenhouse gas emissions, dependence on fossil fuels or freshwater resources, high electricity consumption, and increasing production costs. These limitations have accelerated research into alternative hydrogen production technologies capable of improving environmental sustainability, resource utilization, and economic viability.

This review comprehensively evaluated five emerging alternative hydrogen production technologies, namely Brine Electrolysis, Direct Air Electrolysis (DAE), Integrated Forward Osmosis–Alkaline Water Electrolysis (FO–AWE), Photoelectrochemical (PEC) Water Splitting, and Methane Pyrolysis, and compared them with conventional hydrogen production pathways. The comparative assessment demonstrated

that each alternative technology addresses specific limitations associated with conventional processes through the utilization of unconventional feedstocks, renewable energy integration, carbon-free hydrogen production, or the generation of commercially valuable co-products. Among the technologies reviewed, Brine Electrolysis and Methane Pyrolysis exhibited the greatest potential for near-term commercialization due to their relatively higher technology readiness levels (TRL 6–8), favourable techno-economic performance, and significant reductions in net Levelized Cost of Hydrogen (LCOH). Brine Electrolysis reduced the net LCOH from approximately ₹300–500 kg^{-1} to ₹150–300 kg^{-1} through revenues generated from chlorine and sodium hydroxide, whereas Methane Pyrolysis achieved a net LCOH of approximately ₹80–180 kg^{-1} through the commercialization of solid carbon. FO–AWE demonstrated considerable promise for decentralized hydrogen production integrated with wastewater treatment, while DAE and PEC Water Splitting represent long-term technologies with substantial potential for deployment in water-scarce and renewable energy-rich regions as technological maturity improves.

The review further highlights that the future competitiveness of hydrogen production technologies will depend not only on hydrogen production efficiency but also on effective feedstock utilization, renewable energy integration, co-product valorisation, lifecycle carbon emissions, and technology readiness. In particular, the comparison between gross and net LCOH illustrates that the commercialization of valuable by-products can significantly enhance the economic viability of emerging hydrogen production pathways. Consequently, future technology selection should consider regional resource availability, infrastructure, market demand for co-products, and application-specific requirements rather than relying solely on hydrogen production costs.

Overall, no single hydrogen production technology can presently satisfy all technical, economic, and environmental requirements. Instead, a diversified portfolio comprising both conventional and alternative hydrogen production pathways is likely to be required to support the growing global demand for low-carbon hydrogen. In the Indian context, Brine Electrolysis offers considerable opportunities for coastal chemical and chlor-alkali industries, FO–AWE is well suited for integration with municipal and industrial wastewater treatment facilities, and Methane Pyrolysis presents a viable low-carbon alternative for natural gas-based industrial sectors. Continued advancements in catalyst development, membrane technology, photoelectrode materials, reactor design, carbon management, and renewable energy integration will be essential to improve process efficiency, reduce production costs, and accelerate commercialization. The successful deployment of these technologies will play a crucial role in achieving India's National Green Hydrogen Mission and establishing a resilient, sustainable, and economically competitive hydrogen economy.

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