

Overview and prospects of low-emissions hydrogen (H_2) energy systems: Roadmap for a sustainable H_2 economy

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ABSTRACT

Hydrogen (H_2) has a big role to play in energy transition to achieve net-zero carbon emissions by 2050. For H_2 to compete with other fuels in the energy market, more research is required to mitigate key issues like greenhouse gas (GHG) emissions, safety, and end-use costs. For these reasons, a software-supported technical overview of H_2 production, storage, transportation, and utilisation is introduced. Drawbacks and mitigation approaches for H_2 technologies were highlighted. The recommended areas include solar thermal or renewable-powered plasma systems for feedstock preheating and oxy-hydrogen combustion to meet operating temperatures and heat duties due to losses; integration of electrolysis of H_2O into hydrocarbon reforming methods to replace air separation unit (ASU); use of renewable power sources for electrical units and the introduction of thermoelectric units to maximise the overall efficiency. Furthermore, a battery system for small-scale energy storage; new synthetic hydrides with lower absorption and desorption energy; controlled parameters and steam addition to the combustor/cylinder and combustors with fitted heat exchangers to reduce emissions and improve the overall efficiency are also required. This work also provided detailed information on any of these systems implementations based on location factors and established a roadmap for H_2 production and utilisation. The proposed H_2 production technologies are hybrid pyrolysis-electrolysis and integrated AD-MEC and DR systems using renewable, bioelectrochemical and low-carbon energy systems. Production and utilisation of synthetic natural gas (NG) using renewable-powered electrolysis of H_2O , oxy-hydrogen and direct air capture (DAC) is another proposed H_2 energy system for a sustainable H_2 economy. By providing these factors and information, researchers can work towards pilot development and further efficiency enhancement.

1. Introduction

The continuous combustion of fossil fuels for energy and the rapid growth of world populations have increased greenhouse gas (GHG) emissions. In addition, the growing energy demand and war in Europe and the Middle East have increased end-use costs resulting in inflation in importing countries (Chen et al., 2023). While more weather extreme is likely year-by-year because of continuous global climate change caused by continuous GHG emissions. If the trend of increasing energy demand is to continue, a renewable and low-carbon source of energy is required to limit fossil fuels' combustion and keep the temperature increase below 1.5 °C in line with the Paris climate agreement (IPCC, 2015). Furthermore, simple and reliable transport and storage of renewable and low-carbon energy systems is required because of their intermittencies. Over the years, battery energy storage has been introduced to reduce fossil fuel combustion by storing the produced renewable energy for

later use. However, self-discharge and environmental issues are the main disadvantages of battery energy storage. As of 2019, global battery sales was \$120 billion with an annual increase by 7 % and pose more health and environmental issues (Dehghani-Sanij et al., 2019). Nowadays, the global energy system is moving towards renewable and sustainable energy systems. Considering the carbon footprints, limitations and availability of fossil fuels and batteries, shifting towards a H_2 economy has received so much attention recently. H_2 is regarded as an energy carrier due to its low natural occurrence and a sustainable fuel of the future. H_2 can be burnt to produce heat in combustion engines or reactor furnaces and ovens. H_2 can also be combined with air or O_2 to release electrons in fuel cell (FC) systems. Currently, the demand for H_2 fuel is growing and expected to reach 18 % of the world's energy demand by 2050 at a sales price of \$1.80/kg (Kannah et al., 2021). The H_2 economy has the potential to create 30 million new jobs and reduce carbon emissions by 6Gt per year. H_2 fuel cell (FC) application is

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expected to grow to reach 25 % in powertrains and 10 % in buildings by 2050 (Uyar and Beşikci, 2017; Mostafaeipour et al., 2016; Acar and Dincer, 2029).

H_2 is a flammable, odourless and non-toxic substance with an atomic weight of 1.008. Due to its low density, it is considered the simplest and lightest element in the universe. Molecular H_2 was first discovered by Paracelsus between 1493 and 1541. The well-known H_2 was discovered by Henry Cavendish in 1766 (Jacobson, 2002). Nowadays, H_2 is mostly produced from fossil fuel technologies where CO_2 is released into the environment or captured. Fossil fuel routes for H_2 production emit between 8.8 – 13.7 kg CO_2 for every 1 kg H_2 and the introduction of carbon capture and storage (CCS) increases the cost (Bareiß et al., 2019). Renewable sources of H_2 production such as electrolysis of H_2O are considered carbon negative if it is operated by electricity from renewable energy sources such as solar or wind. However, as recently reported by the Hydrogen Council, green H_2 costs \$5.62/kg H_2 which is still above \$2.16/kg H_2 for the obtained H_2 from the hydrocarbon reforming processes with CCS unit (Omid et al., 2024; Argyris et al., 2023). Recently, the use of solar thermal and oxy-hydrogen to preheat feedstocks in hydrocarbon reforming methods was investigated and the result revealed that 4 kg CO_2 by-product for every 1 kg H_2 is feasible (Onwuezezie et al., 2024). Although, Guo et al (Guo et al., 2024). studies on the prospect of green H_2 from H_2O electrolysis suggested the use of low-cost electrocatalysts in PEM electrolyser, stability improvement of alkaline electrolyser cells and long service life for solid oxide electrolysis cell (SOEC) to reduce the cost of green H_2 . Nevertheless, recent investigation on green H_2 system maintained that the integration of renewable sources of H_2 production into utility power systems such as wind farms to use excess electricity for H_2 production can lower the cost of green H_2 . Other options to reduce capital expenditures (CAPEX) by 33 % include scaling up green H_2 production capacity from 1 to 20 MW (Niblett et al., 2024). Nowadays, more efforts are being made to increase the share of biohydrogen. For instance, Salamony et al. investigated an integrated microbial fuel cell (MFC) and microbial electrolysis cell (MEC) of feather hydrolysate and reported current and power densities of 9.26 W/m² and 11.5 A/m², in addition to 7.5 mmol/day.L of biohydrogen (Salamony et al., 2024). The researched work also reported a MEC current of 10 mA - 60 mA, which can be utilised to operate other units. Most recently, integrated anaerobic digestion (AD) and dry reforming (DR) to use the recovered heat for AD feed pretreatment and AD biogas as DR feedstock was investigated. The finding shows lower volatile fatty acids (VFAs) formation and absence of carbon emissions from thermal units by adopting solar thermal and oxy-hydrogen systems for heat production (Onwuezezie and Darabkhani, 2024a).

Long-distance transport of pure H_2 or blended H_2 with natural gas (NG) using an existing NG pipeline offers the most promising route to prevent major investment in new infrastructure. Nonetheless, current NG pipelines were constructed with steel materials, which means that hydrogen embrittlement and hydrogen-induced crack (HIC) are inevitable (Wu et al., 2022). To prevent the interaction of H_2 and other alloying metals, steel pipelines for H_2 transport may undergo heat and surface pretreatments, including shot peening, electroplating and cathodic protection (CP) (Zhu et al., 2024). In addition, Zhang et al (Zhang et al., 2024a). proposed a controlled flowrate and leak detection monitoring to mitigate hydrogen embrittlement.

At present, H_2 can be stored in compressed, liquid, cryogenic and solid forms to increase the storage volume and density, as 1 kg of H_2 occupies 11 m³ and 0.09 kg/m³ under ambient and atmospheric conditions. Not long ago, a review of H_2 production and utilisation by Ishaq et al (Ishaq et al., 2020). suggested an NH_3 -based H_2 storage method and H_2 recovery from NH_3 at the point of use. In addition, several researchers have proposed the improvement of the volumetric and gravimetric density of H_2 storage and the use of H_2 in internal combustion engines (ICEs) and micro gas turbine (MGT) engines (Abdalla et al., 2018; Rasul et al., 2022).

H_2 can be utilised in a fuel cell (FC) to generate electricity and in heat engines to generate both heat and power in utility applications and thrust in propulsion systems. In FC systems, H_2 react with air or O_2 to produce electricity, heat and H_2O as by-products. Lower emissions of nitrogen oxides (NO_x) and higher efficiency are achieved in the oxy-hydrogen reaction/combustion in contrast to air-hydrogen reaction/combustion. Due to H_2 low density (0.0813 g/l at 25 °C and 1 bar), high energy density (120 MJ/kg) and flammability limit in air (4–75 %), high NO_x formation at higher reaction temperatures, thermal combustor wall stress, pre-ignition, short reactant residence time and low volumetric efficiency are some of the drawbacks in contrast to the competing engines (Verhelst, 2001; Abdel-Aal et al., 2005; Jo and Crowl, 2010; Gao et al., 2022; Babayev et al., 2021; Møller et al., 2017). For example, a H_2 ICE operated with a supercharged unit achieved a maximum thermal efficiency of 50 % and thermal brake efficiency of 37 % (Verhelst et al., 2009). Overall, safety and end-use costs of H_2 are some of the barriers for fossil fuels' substitution. H_2 production, transportation, storage and utilisation methods are represented in Fig. 1a and 1b.

For H_2 to compete with other fuels in the energy market, hybrid fossil fuel and renewable sources of H_2 production systems utilising renewable and low-carbon energy sources for operations are required for cost reduction. In addition, the use of H_2 fuel in domestic applications may consider synthetic NG through CO_2 reduction and hydrogenation to mitigate safety issues and reuse the existing infrastructure. For these reasons, this article has provided a detailed and comprehensive overview of the current H_2 systems covering production, transportation, storage and utilisation using Aspen Plus Software for some schematic diagrams. This work also covers an estimation of carbon emissions of H_2 energy systems at a given feed rate for individual units, progress of low-carbon and efficiency of H_2 energy systems, comparisons and suitable locations for implementation. This is important to broaden readers' understanding of the various H_2 energy systems. Integrated CH_4 pyrolysis and electrolysis of H_2O and hybrid anaerobic digestion (AD) and a microbial electrolysis cell (MEC) coupled with biogas reforming methods were developed as sustainable H_2 production technologies. Both proposed sustainable H_2 production systems utilised solar thermal or renewable powered-plasma systems and an oxy-hydrogen furnace, solar PV, wind turbine and microbial fuel cell (MFC) units for heat and electricity production to achieve carbon neutrality. The sustainable use of H_2 in heat engines applied electrolysis of H_2O , oxy-hydrogen and direct air capture (DAC) systems to produce synthetic NG for the reuse of existing NG infrastructures. This paper is structured as follows:

1. Section one (the introduction) provides a brief description of the importance of H_2 technologies, recent progress and challenges to establish the novelty of this work and schematic diagrams of H_2 energy systems.
2. The overview of H_2 production methods (fossil fuels and renewable sources) and its roadmap is provided in section two.
3. Section three covers the overview of H_2 transportation routes.
4. H_2 storage systems are given in section four.
5. Section five illustrates H_2 utilisation technologies and roadmap.
6. The final section covers the conclusion that summarised the findings of this study.

Supplementary such as comparisons of current H_2 production, storage methods and pilot studies on H_2 energy technologies are in the appendix.

2. Overview of H_2 production processes

At present, hydrocarbon reforming (steam methane, plasma, auto-thermal, partial oxidation, dry and sorption enhanced-chemical looping (SE-CL)), hydrocarbon pyrolysis and solid fuel gasification are fossil fuel methods of producing H_2 . H_2O splitting (electrolysis, thermolysis and photolysis), thermochemical (biomass pyrolysis and gasification), and

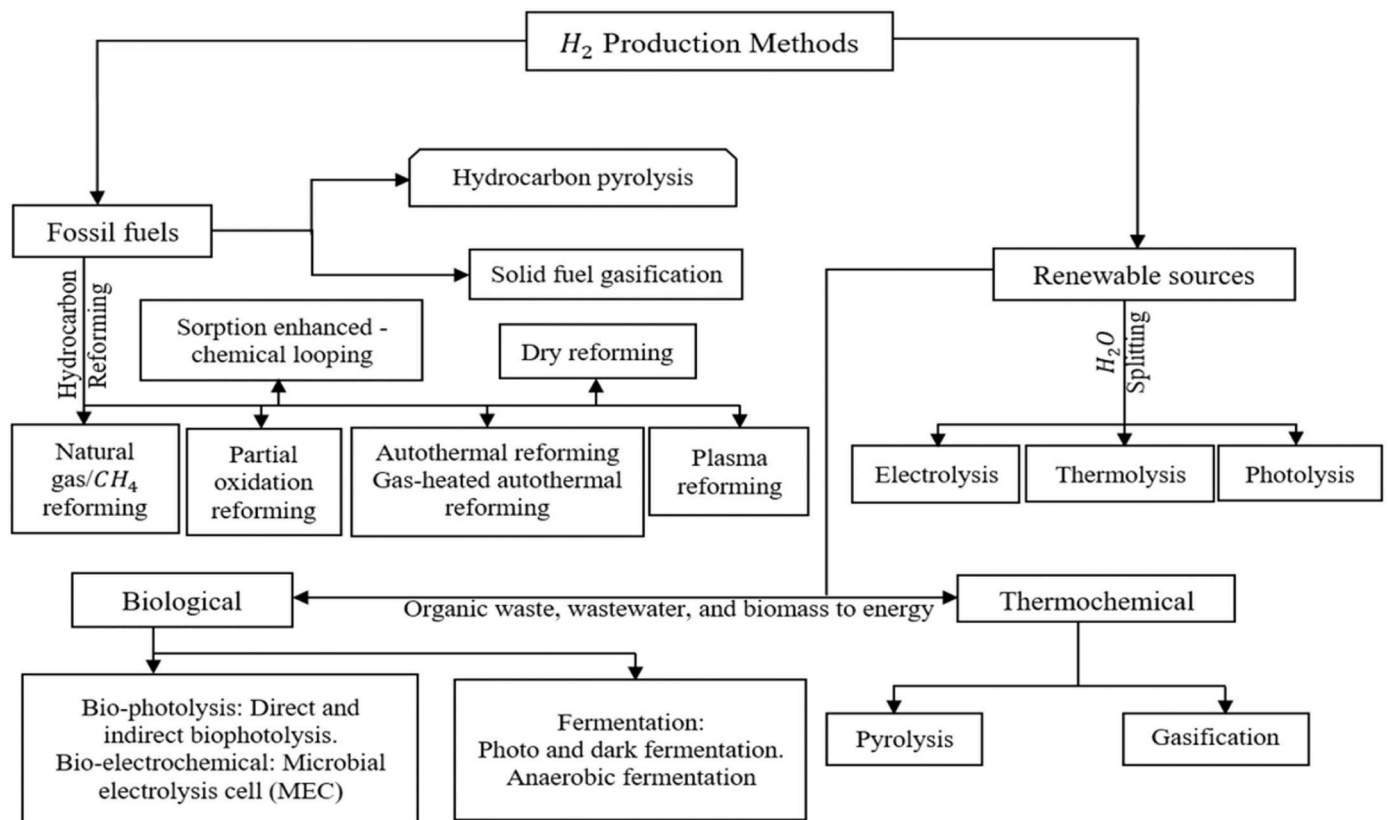


Fig. 1a. H₂ production methods from fossil fuels and renewable sources.

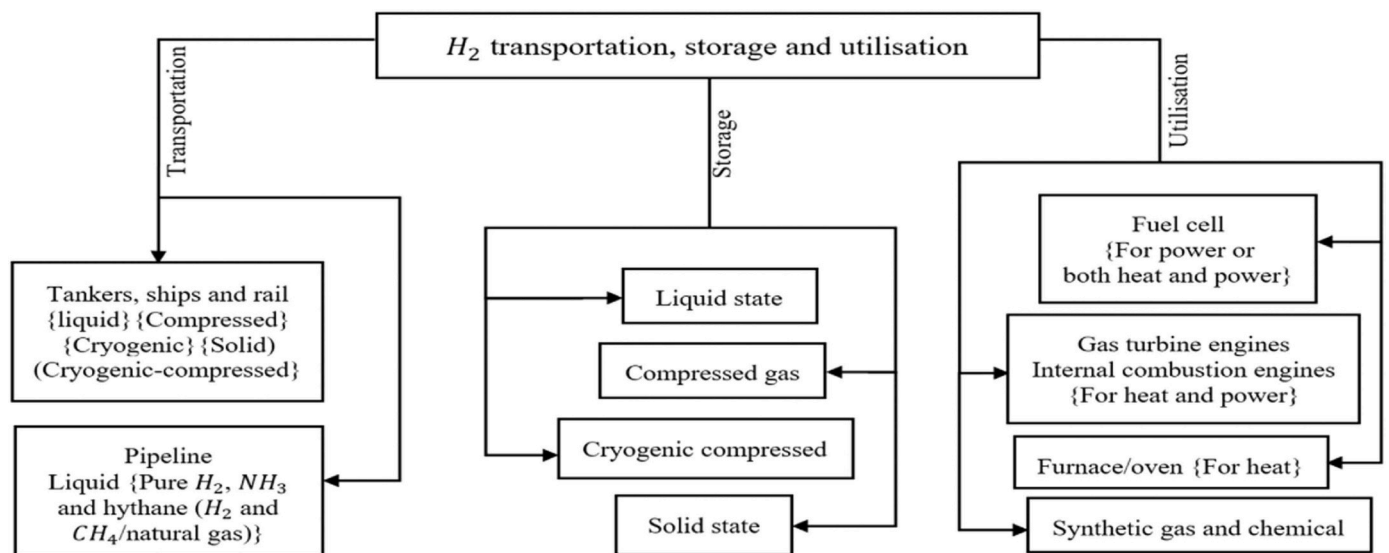


Fig. 1b. H₂ transportation, storage and utilisation routes.

biological (bio-photolysis, bio-electrochemical and fermentation) processes are renewable sources of H₂ production.

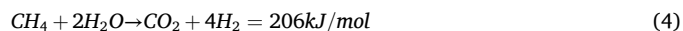
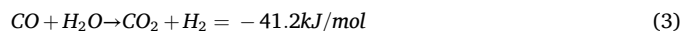
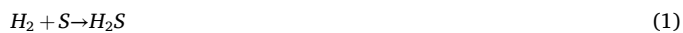
2.1. Hydrocarbon reforming and pyrolysis, and solid fuel gasification processes of H₂ production

2.1.1. Steam methane reforming (SMR) method

SMR is one of the most advanced and cheapest H₂ production methods with an efficiency of 74–85 % and accounts for 48 % of global H₂ production (Onwuezezie et al., 2023a). This method requires heat

for sulphur removal, steam production and the endothermic reaction of H₂O_{gas} with CH₄ in the reformer or reactor. The main by-products of SMR reformer are carbon monoxide (CO) and H₂ and require the presence of catalysts such as promoted nickel (Ni)-based or bi/polymetallic catalyst at a reaction temperature of 700–900 °C and pressure up to 3270kPa (Kim et al., 2018). Although, Fe-based catalysts for SMR reformers were suggested to reduce the operation cost in contrast to Ni-based catalysts (Li et al., 2023). Other SMR reformer catalysts for include Ni/SiO₂/Al₂O₃ at 3.5 S/C ratio and Ru/La–Al₂O₃, Ru/Al₂O₃@Al, Ru/Nb₂O₅ and Ru/MgO at ≥ 3 S/C ratio (Zhang et al.,

2021). As desulphurisation and steam reaction with CH_4 are the first and second steps, the third step is the introduction of steam in water gas shift (WGS) units to convert CO to CO_2 and increase the H_2 concentration. The desulphurisation stage reduces the chances of early catalysts' deactivation. In this stage, natural gas (NG) or CH_4 is preheated to $350\text{ }^\circ\text{C}$ prior to desulphurisation column where H_2 or other elements react with approximately 5 % of sulphur content in the CH_4 gas to form H_2S . WGS units are made up of a high-temperature shift (HTS) and a low-temperature shift (LTS) with heat exchangers for proper control of reactants' temperatures (Gillis and O'Sullivan, 2003). The operating temperatures of HTS and LTS are $350\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$ respectively, and both use different catalysts such as promoted Ni/Al_2O_3 catalyst with palladium- ruthenium (Pd-Ru) to increase the conversion efficiency of H_2 and CO_2 Iulianelli et al. (2016). In the final stage, H_2 from WGS units is separated from CO_2 in the separation column (pressure swing adsorption (PSA)) (Onwuemezie et al., 2023a). NG or CH_4 is the simplest alkane and abundant, making it the preferred feedstock for hydrocarbon reforming processes in contrast to other light hydrocarbons (C_2H_6 , C_3H_8 , C_4H_{10} and C_5H_{10}). At a daily production capacity of $379,387\text{ kg}_{H_2}$, feedstock cost accounts for 61 %, 29 % for investment and 10 % for operation and maintenance (Steinberg and Cheng, 1989). Eqs. 1 – 4 describe the chemical reaction of SMR. A program-based schematic diagram of the SMR process is shown in Fig. 2a.



With 33.8 kg/hr_{H_2O} and $15.75\text{ kg/hr}_{CH_4}$ mass flowrates, 7.54 kg/hr_{H_2} , $41.15\text{ kg/hr}_{CO_2}$ and 0.18 kg/hr_{H_2O} were produced. At $\$0.13/\text{kWh}_{NG}$ and $\$0.37/\text{kWh}_e$ for thermal and electrical units, 17.3 kg_{CO_2} from the SMR reformer furnace, 7.3 kg_{CO_2} from CH_4 preheater and steam vaporiser and $< 0.3\text{ kg}_{CO_2}$ from the pressure increaser was emitted. The energy input and emission from the separator unit were excluded. However, ASU uses $0.31 - 0.63\text{ kWh/kg}_{N_2\text{gas}}$ which is equivalent to $1.17 - 2.37\text{ kWh/kg}_{O_2\text{gas}}$ and PSA for H_2 recovery from other by-products requires $2.4\text{ kWh/kg}_{H_2\text{gas}}$. The efficiency of hydrocarbon processes can be calculated using Eq. 5.

$$\text{Efficiency}(\eta) = \frac{H_2LHV * \text{mass flowrate}}{\text{heat input } (Q_H)} \tag{5}$$

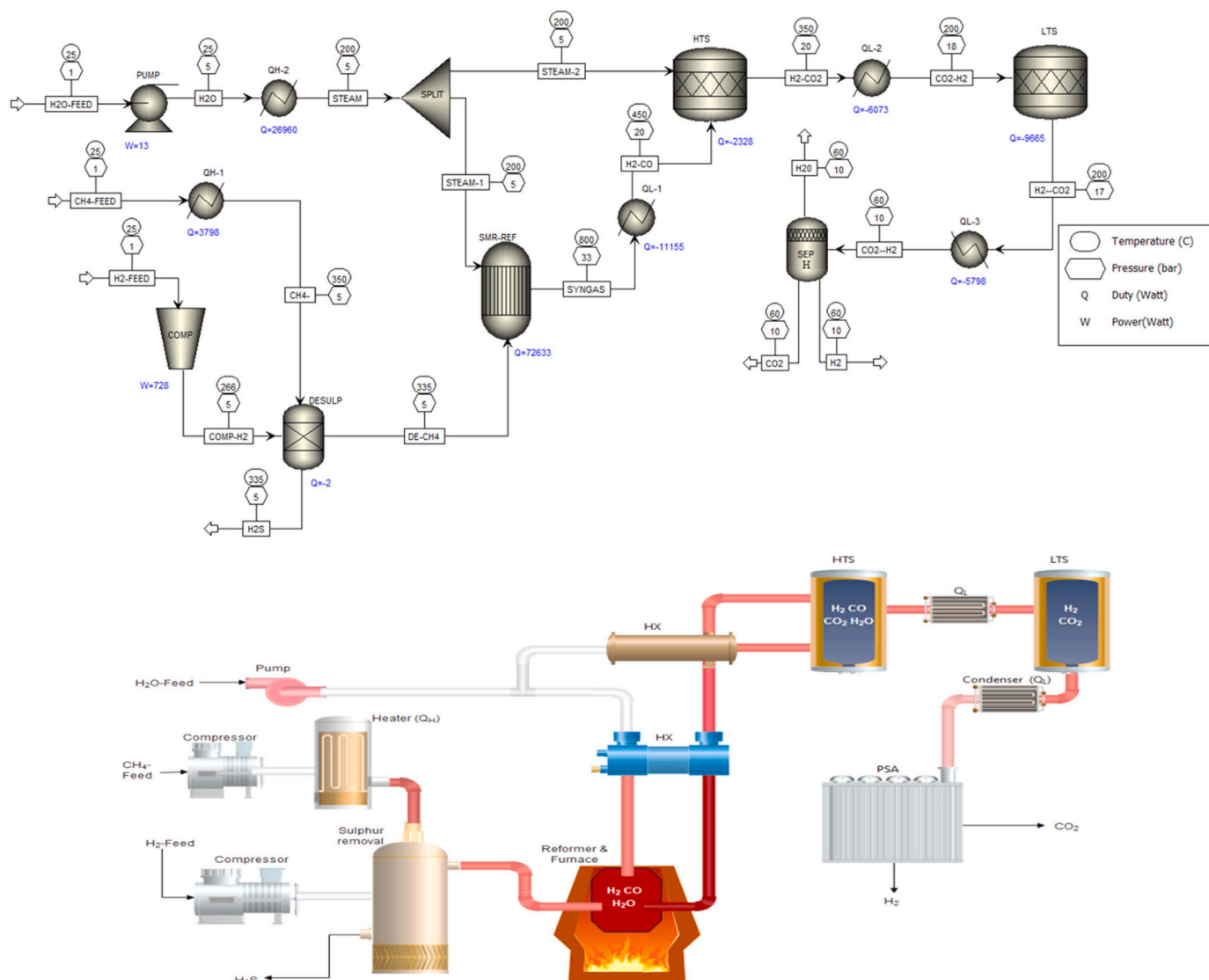
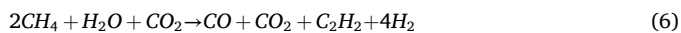


Fig. 2a. Schematic diagrams of SMR process of H_2 production.

2.1.2. Plasma dry reforming method (PDRM)

PDRM of H_2 production is a combination of SMR and dry reforming (DR) processes that allow the recycling of a CO_2 by-product. Although, it differs from single SMR and DR by using electricity instead of heat for the endothermic reaction, with/without catalysts in the reformer and the CO_2 conversion in the reformer favours acetylene (C_2H_2) formation. This process is considered more environmentally friendly than SMR because of the usage of electricity from renewable sources to decompose CH_4 feedstock before the addition of steam into the reformer to produce H_2 and CO . However, the ecotoxicity impact of using electricity from renewable energy sources like wind is another issue with PDRM (King et al., 2021). In addition, by using electricity from fossil fuel power plants such as coal plants to operate a microwave plasma reformer (MPR), the carbon footprint is higher than other competing hydrocarbon reforming processes. Hybrid microwave discharge plasma (HMDP) reforming has been investigated in previous studies and the results showed that it is energy intensive and cannot substitute SMR despite the usage of electrical energy as heat is cheaper than electricity (Onwuemezie et al., 2023a). A similar result was reported by Czyilkowski et al (Czyilkowski et al., 2016). during the investigation of HMDP as a replacement for SMR. Eq. 6 describes the chemical reaction of plasma reforming. While Fig. 2b displays a software-aided schematic diagram of the PDRM. The same operating parameters as the SMR were used except for CO_2 recycling and a higher H_2O mass flowrate and nearly the same H_2 by-product was obtained. However, higher CO_2 and H_2O , lower C_2H_2 by-products and higher input energy which decreases the overall efficiency were recorded. By using electricity from renewable sources to operate the plasma microwave reformer, $17.4kg_{CO_2}$ can be avoided. However, $> 17.3kg_{CO_2}$ from the same unit (plasma microwave reformer) can be emitted if the reformer's electricity comes from fossil fuels powerplants without CCS units.

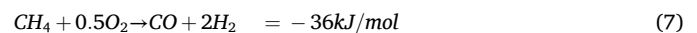


2.1.3. Partial oxidation reforming (POR)

The POR process of producing H_2 and other by-products such as CO_2 is considered exothermic and has an efficiency of 60 – 75 % (Holladay et al., 2009). However, this process is not exothermic because it requires a large amount of thermal energy for the reaction of CH_4 or another hydrocarbon with O_2 in the reformer to produce H_2 and CO . Unlike the SMR method, using hydrocarbon feedstocks like CH_4 , the reformer or

combustor requires less energy (heat) to achieve partial combustion in catalytic reforming processes. Nonetheless, the H_2 concentration in the POR reformer is lower than that of other reforming methods except for the ATR. When a catalyst is involved in the reaction, POR becomes catalytic partial oxidation reforming (CPOR). In the absence of catalysts, higher reaction temperatures up to $1350^\circ C$ may be needed for higher H_2 and CO formations (Holladay et al., 2009). The reaction temperature of the CPOR reformer is about $\geq 800^\circ C$. By using metal catalysts such as Ni/CeO_2 and noble metal catalysts (lanthanum (La), Ru, iridium (Ir), rhodium (Rh), Pd, and platinum (Pt)) in the reformer, high syngas conversion efficiency can be achieved (Osman, 2020). In addition, $\leq 99\%$ yield of the reformer syngas (CO) can be achieved using bimetallic catalysts such as $ZrO_2-Al_2O_3$ with either Ni or Co support at a reaction temperature of $800^\circ C$ (Boscherini et al., 2023). Other reformer or reactor catalysts for POR are doped $Ni/\gamma-Al_2O_3$ with Fe support, bimetallic $Ru-Ni/CeO_2$, $Ru-CeO_2$, $Ni-CeO_2$, $0.5\%Pt-0.5\%Pd/CeO$ and $0.5\%Pt-0.5\%Ru/CeO$ (Fazlikeshteli et al., 2024; Khaleel et al., 2023).

In terms of feedstock flexibility, the POR method is superior to other hydrocarbon reforming processes. Similar to SMR, better conversion efficiency can be achieved by using CH_4 or NG as one of the reforming feedstocks instead of other hydrocarbons. WGS units, syngas separation and purification processes are entirely the same as the SMR process. Investment and operating costs for the POR (54.5 % and 19.5 %) are higher compared to the SMR system because of the involvement of ASU. Although, the feedstock cost for POR which represents 26 % is much lower than that of the SMR method (Steinberg and Cheng, 1989). Eq. 7 illustrate POR chemical reaction pathways. The schematics of a POR process is depicted in Fig. 3a. In the schematics of POR, air is compressed and cooled to a cryogenic temperature in the ASU to release O_2 feed to the reformer where it reacts with steam to produce syngas for the WGS units. The downstream units are entirely the same as the SMR process.



With $16.9 kg/hr_{H_2O}$, $129.7kg/hr_{air}$ and the same CH_4 mass flowrate as the SMR method, $5.6kg/hr_{H_2}$, $41.15kg/hr_{CO_2}$, $15kg/hr_{O_2}$ and $0.1 kg/hr_{H_2O}$ were produced from the POR process. At $\$0.13/kWh_{NG}$ and $\$0.37kWh_e$ for thermal and electrical units, $2.1kg_{CO_2}$ from the combustor furnace, $4.1kg_{CO_2}$ from CH_4 preheated and steam vaporiser furnaces, $5.1kg_{CO_2}$ from the air compressor and $13.6kg_{CO_2}$ from the O_2 cryogenic unit was emitted. Excess O_2 by-product reduces the energy efficiency of

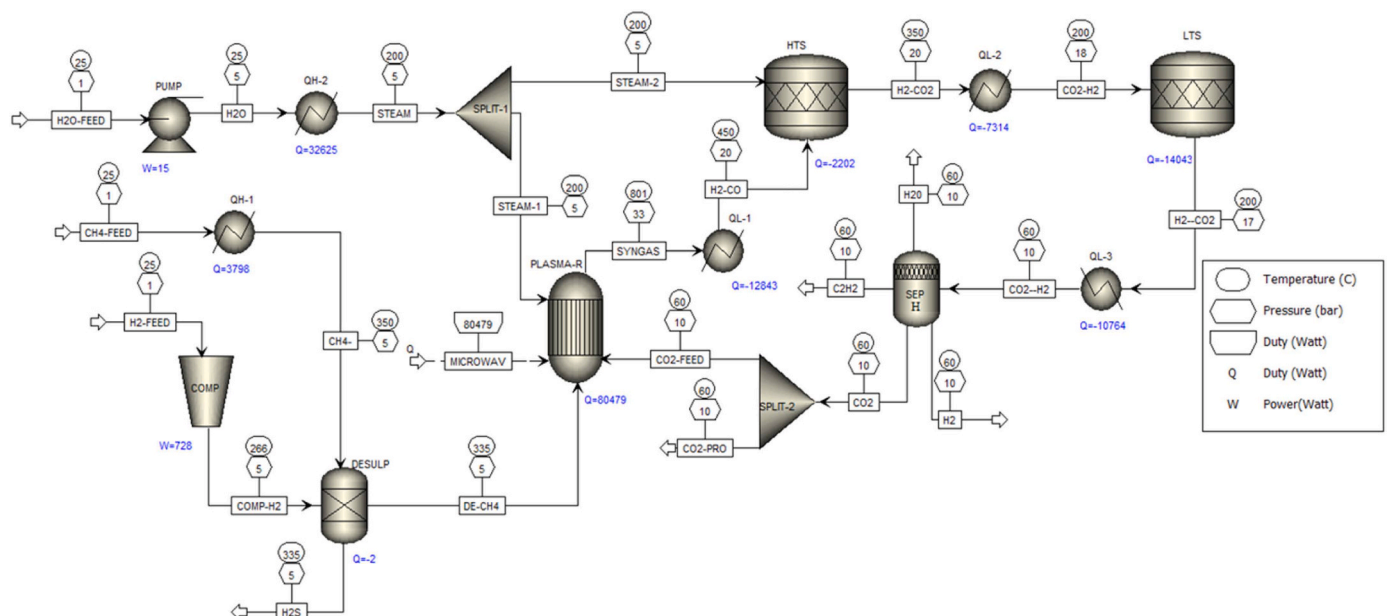


Fig. 2b. A schematic diagram of PDRM of H_2 production.

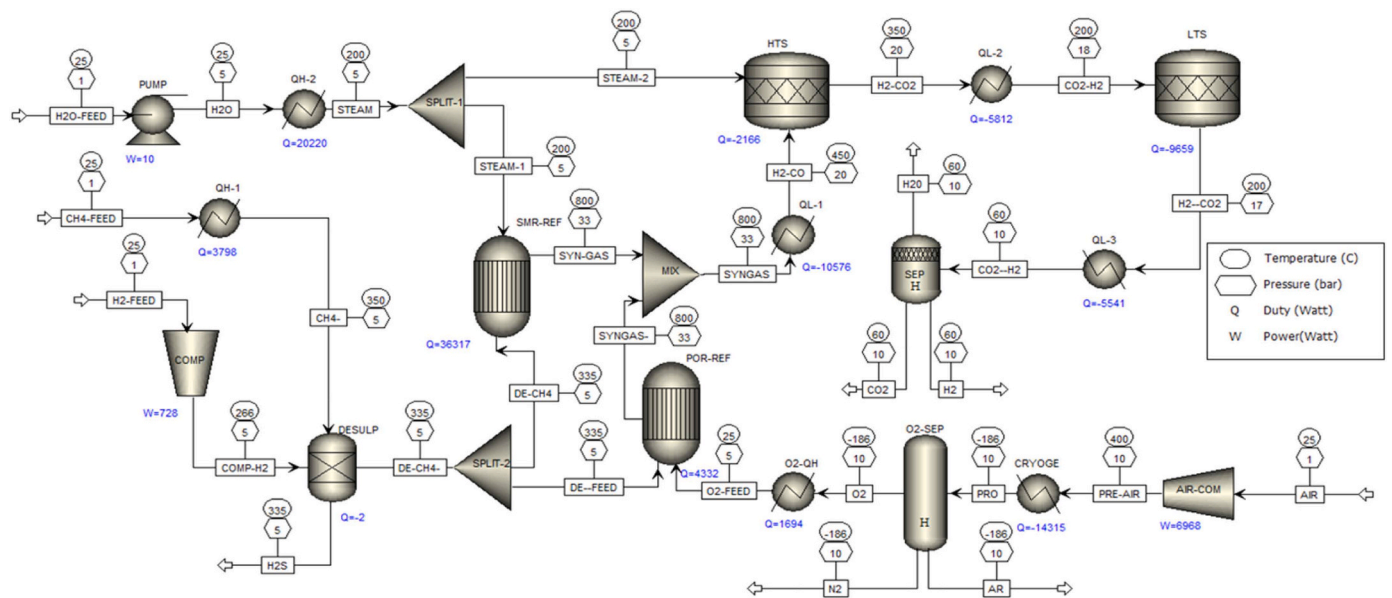


Fig. 3c. A schematic diagram of GH-ATR process of H₂ production.

8.66 kg/hr_{H₂O} were produced from the ATR method. At \$0.13/kWh_{NG} and \$0.37kWh_e for thermal and electrical units, 1.9kg_{CO₂} from the ATR reformer furnace, 5.7kg_{CO₂} from CH₄ preheated and steam vaporiser furnaces, 2.5kg_{CO₂} from an air pressure unit and 6.7kg_{CO₂} from the refrigerant unit was emitted. Unlike the conventional ATR, GH-ATR operating with the same feeds' mass flowrate, emits 9.6kg_{CO₂} from reformer and combustor furnaces and produced 6.6kg/hr_{H₂}, 41.15kg/hr_{CO₂} and 0.1kg/hr_{H₂O}. At a plant size of 300 MW capacity, H₂ sales price of POR, ATR and GH-ATR ranges from £ 2.36 to £ 2.56/kg. However, in a larger plant of approximately 1000 MW capacity, the sales price of H₂ from any of the hydrocarbon reforming methods is between \$2.16 and \$2.40/kg (Argyris et al., 2023).

2.1.5. Dry reforming (DR) method

The DR route for producing H₂ and recycling half of CO₂ by-product involves the endothermic reaction of hydrocarbons such as CH₄ with CO₂ to produce H₂ and CO₂. The DR method is similar to other hydrocarbon reforming methods, except for the absence of O₂ and steam in the

reformer. Nonetheless, sulphur removal, WGS and syngas separation units are entirely the same as the other hydrocarbon reforming technologies (Onwuemezie et al., 2024). However, plasma assistance DR has an energy efficiency of 66 % and DR can be integrated into any reforming method, either as dual-reforming or triple-reforming to feed CO₂ by-product from the PSA unit to the reformer (Cleiren et al., 2017). The DR method requires the use of catalysts to reduce energy input to the reformer and increase the energy efficiency of the process. Among other catalysts, nickel upgraded slag oxides (Ni-UGSO), Ni-based catalysts with CeO₂-ZrO₂-SiO₂ supports, Ni/Al₂O₃ catalysts with CeO₂-ZrO₂ supports, NiO-Mg/Ce-ZrO₂/Al₂O₃ and Ni/Al₂O₃ catalyst with noble metal support exhibit good resistance to H₂S deposition on catalysts and higher feed conversion rate in both dual and triple DR methods (Dega et al., 2019; Deng et al., 2021; Aboosadi et al., 2022). The purchase price of obtained H₂ from DR or plasma reforming methods would be < 30 higher than other reforming methods because of the involvement of CO₂ feedstock. A schematic diagram of the DR method is depicted in Fig. 4a. Eq. 8 shows the DR chemical reaction for

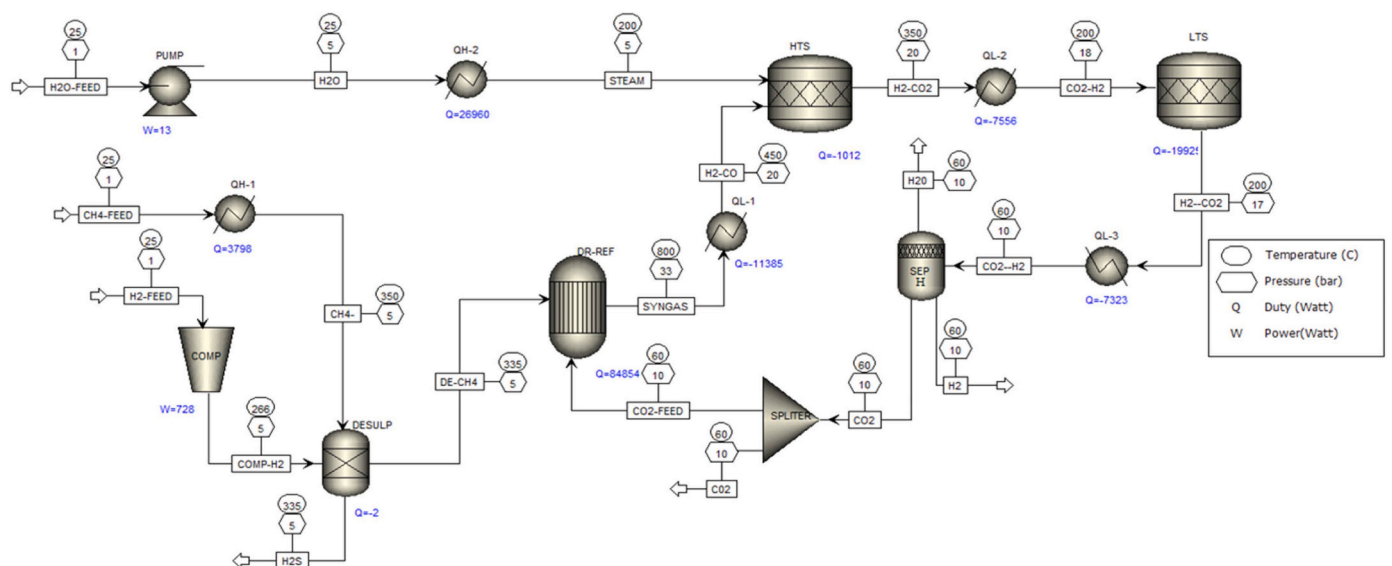


Fig. 4a. A schematic diagram of DR process of H₂ production.

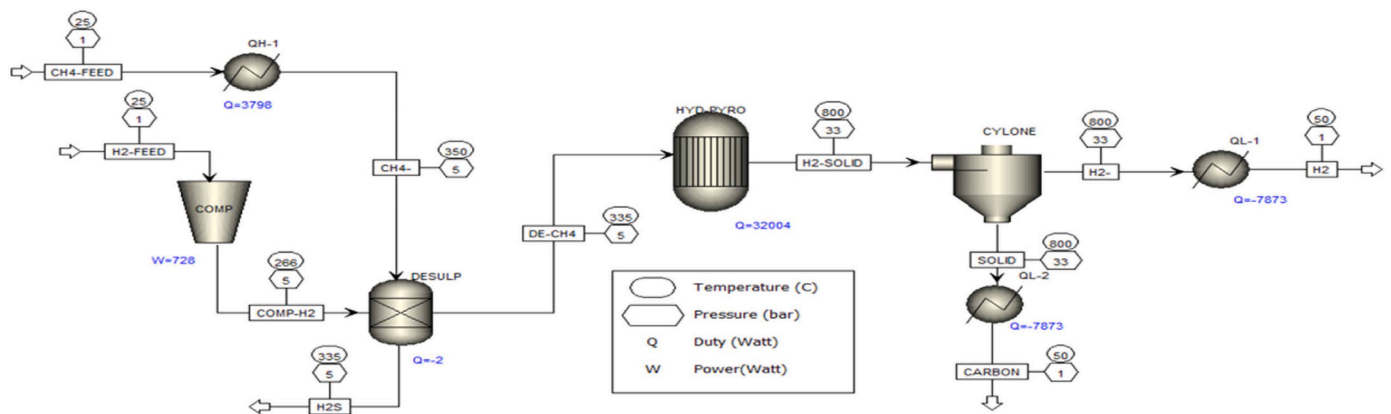


Fig. 5a. A schematic diagram of CH₄ pyrolysis process of H₂ production.

making plants excludes H₂ recovery from other syngas by burning the mixture of CO, CH₄ and H₂ syngas in thermal units like blast furnace (BF) or basic oxygen furnace (BOF) (Onwuemezie and Darabkhani, 2024b). A software-aided schematic diagram of the SFG process is shown in Fig. 5b. In the depicted diagram of the SFG method using coal as the decomposer feed, coal is decomposed into gas and solid residues before the removal of solid residues like carbon or ash in the cyclone. Sulphur was removed by the absorption process before H₂ and CO recovery in the first separator. The downstream units (WGS and separation) are entirely the same as the hydrocarbon reforming methods. The proximate and ultimate analyses of the utilised Shenmu coal (SM) were taken from Song, et al (Song et al., 2022). work. The efficiency of coal gasification with and without CCS is between 43 % and 60 % and the H₂ sales price ranges from \$0.9 - \$2.11/kg (Sánchez-Bastardo et al., 2021; Li et al., 2022).

With 15.75kg/hr_{coal} and 0.5kg/hr_{H₂O} mass flowrates, 0.4kg/hr_{H₂}, 1.65kg/hr_{CH₄}, 10.5kg/hr_{carbon} and 1.23kg/hr_{CO₂} were produced from the coal gasification method (CGM). CO₂ emission from thermal and electrical units was < 3 kg/hr. The prospect of H₂ production by CGM should consider thermal energy recovery and the integration of renewable energy-powered low-temperature electrolysis of H₂O to increase the H₂ production rate. To prevent carbon emissions from the CGM, it is also recommended to use renewable power systems for electrical units and oxy-hydrogen combustion in the decomposer furnace.

2.1.9. Advances and prospects of hydrocarbon reforming and pyrolysis methods (HRPMs) for low-carbon H₂ production

Since 0.356kg_{CO₂} for 1kWh and 0.24kg_{CO₂} for 1kWh are released in natural gas energy plants, reducing carbon footprints represents a pathway to achieve sustainable H₂ production by HRPMs. More recently, concentrating solar power (CSP) and oxy-hydrogen units for heat production, solar PV and wind turbine systems for electricity generation and heat recovery systems such as thermoelectric converters and heat exchangers to operate other downstream units were demonstrated. Only 20 % of by-product CO₂ was produced and captured by these approaches, resulting in an efficiency improvement of > 10 % (Onwuemezie et al., 2024). In addition, H₂ production by plasma reforming of H₂O at a lower power input (0.8 kW) and temperature (150 °C) was investigated to substitute the electrolysis of H₂O. The studied work achieved an energy efficiency of 10.31 %. In another study, CH₄ or H₂O was replaced with banana as the reformer feedstock using a pseudo-stem. The investigated work reported a H₂ selectivity of 98.8 % and a yield of 70.7 % (Oner and Dincer, 2023; Saad et al., 2024). Advances in HRMs that rely on O₂ as one of the feedstocks, low-carbon thermal units and renewable energy systems to achieve carbon neutrality were demonstrated in recent studies by substituting O₂ from ASU with that of the electrolyser system. The application of this approach by producing the electrolyser feed (distilled H₂O or steam) with the recovered heat and feeding the electrolyser O₂ to the reformer/reactor resulted in energy savings of 0.25 kW/H₂ - 0.75 kW/H₂ (Onwuemezie et al. (2024). Furthermore, molten hydrides, supported, non-supported, doped heteroatom metal and alloy catalysts, as well as

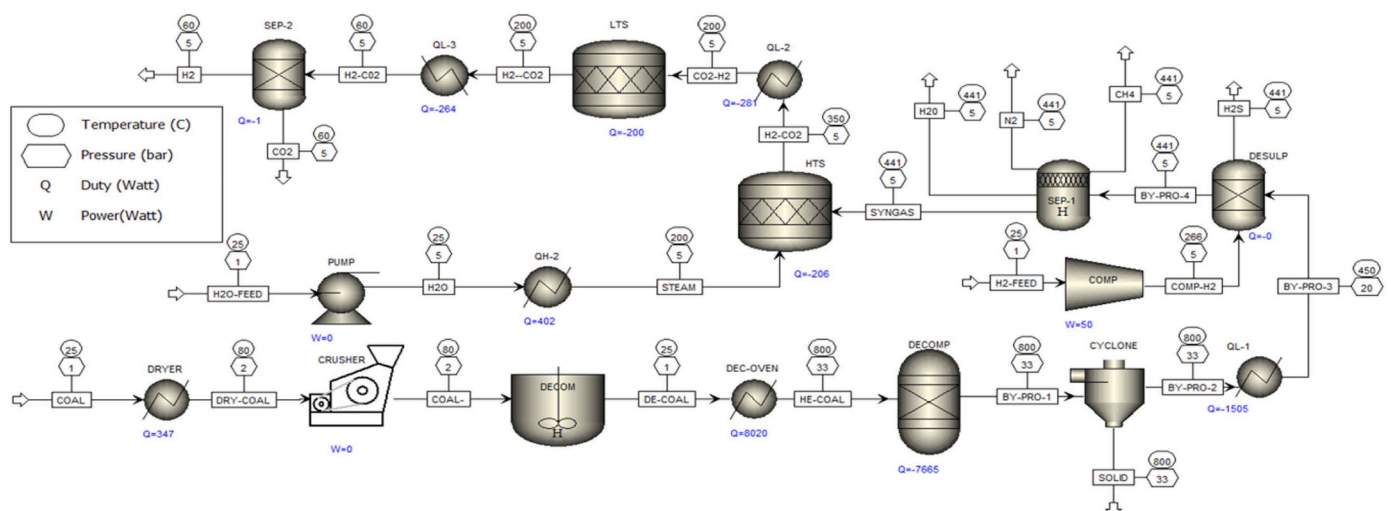


Fig. 5b. A schematic diagram of solid fuel (coal) steam gasification process of H₂ production.

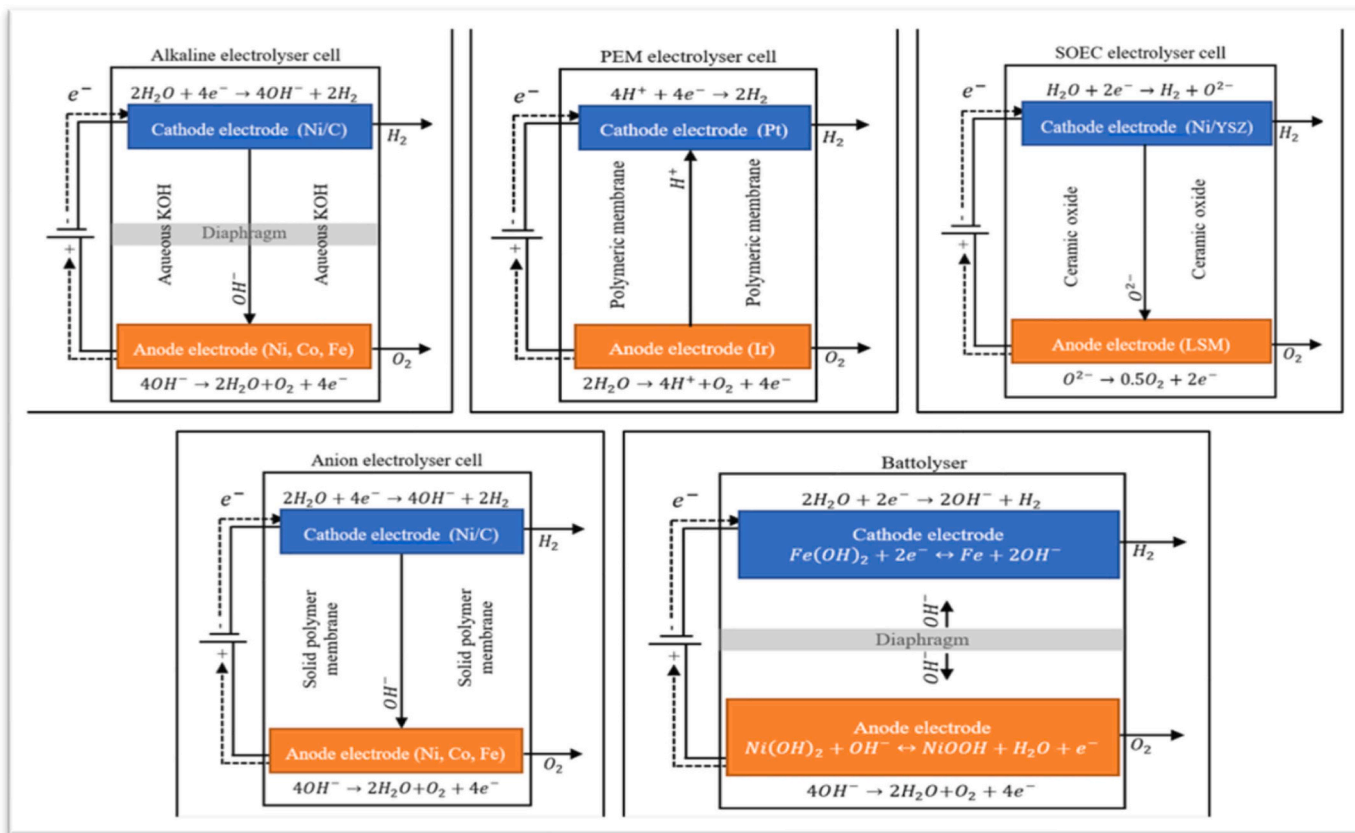


Fig. 7a. Different types of commercially available and emerging electrolyser systems for green H₂ production.

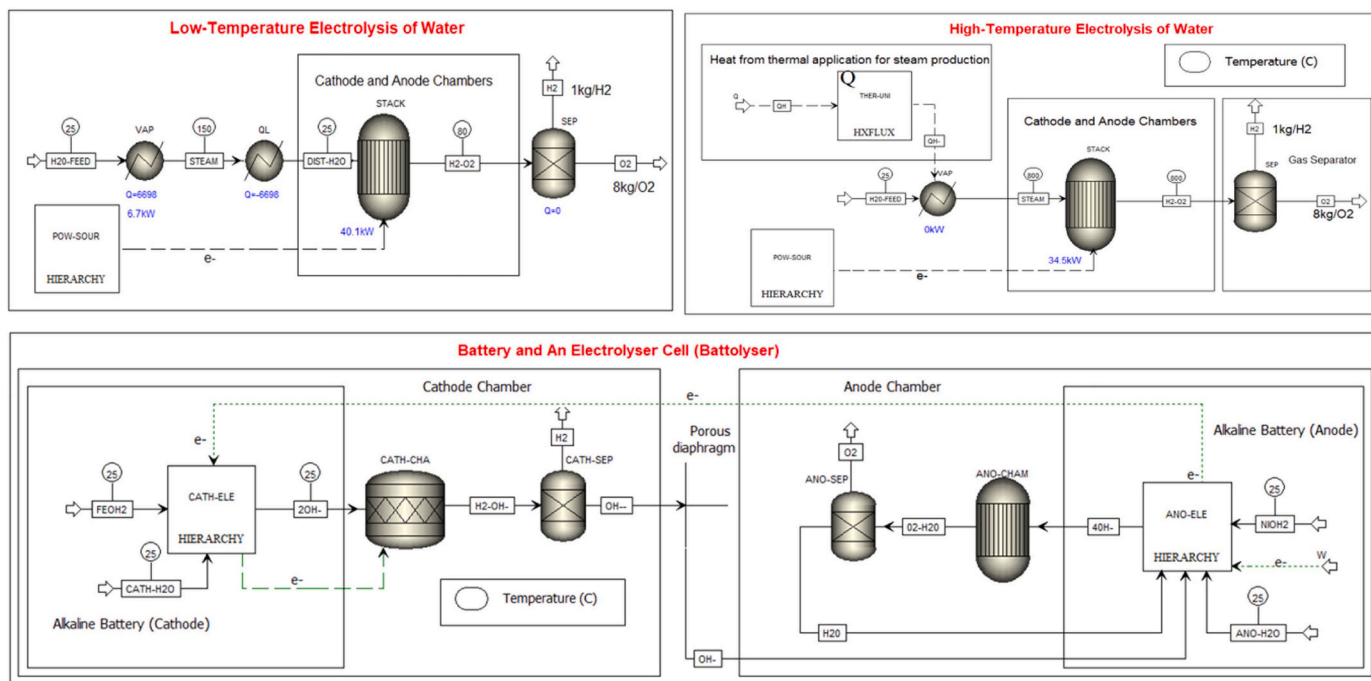
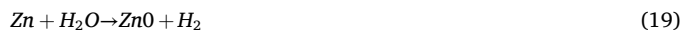
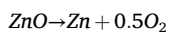


Fig. 7b. Schematic diagrams of H₂O electrolysis systems for combined electricity storage and H₂ production.

electrolyser stack. The chemical reactions of H₂O thermolysis through ZnO and H₂SO₄ redox reactions are represented in Eqs. 18 – 22.



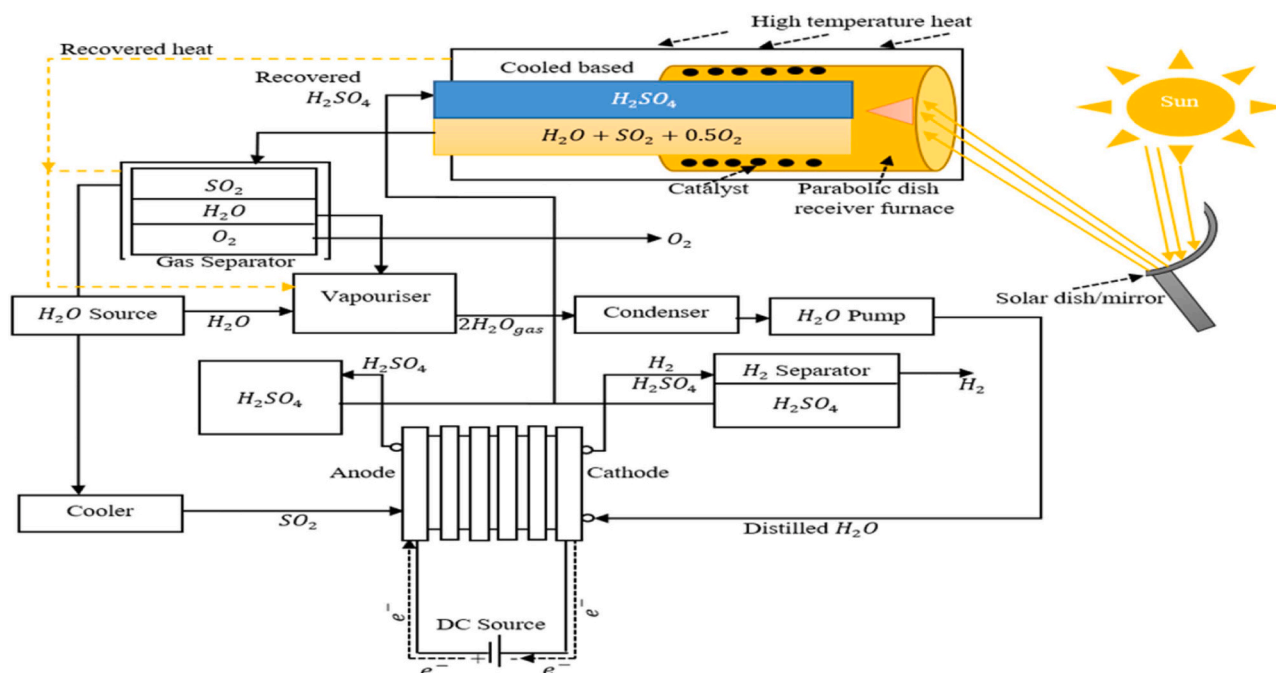


Fig. 8a. A schematic diagrams of thermolysis method of H_2 production.

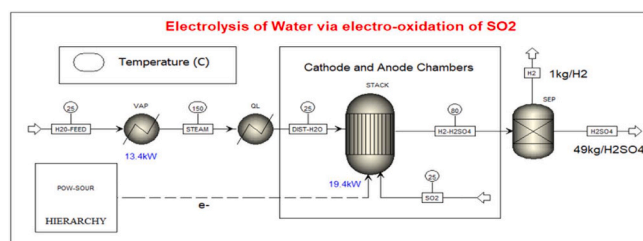


Fig. 8b. A schematic diagram of H_2 production via the electro-oxidation of SO_2 .



With 18kg/hr_{H_2O} mass flowrate, 1kg/hr_{H_2} and $49\text{kg/hr}_{H_2SO_4}$ were produced from the sulphur depolarised electrocatalyst process of H_2 production. Integrating this thermolysis-electrolysis unit into thermal applications to decompose H_2SO_4 with recovered heat and deployment of renewable energy sources would achieve carbon negative and higher efficiency. Unlike other electrolysis processes, the electro-oxidation of the SO_2 electrolysis system, including the vapouriser unit requires 32.8 kW to produce 1 kg of H_2 .

2.2.4. Photolysis (photoelectrolysis of H_2O)

Photolysis uses p-type and n-type photon-harvesting semiconductors greater than the bandgap to generate the required DC for substrate (H_2O) dissociation into H_2 and O_2 (Acar et al. (2016). In this system, the properties of photolysis materials include high stability to pH change, resistance to corrosion in aqueous solution, good narrow bandgap and absorption spectrum, voltage above the theoretical value (1.23 V) within the bandgap and good photocatalytic efficiency (Wang et al., 2012). Furthermore, this green H_2 production pathway as displayed in Fig. 8c requires additional electrons from another source to increase the H_2 production rate. The efficiency of the photolysis method is 30% and the sales price of the obtained H_2 is $\$3.12/\text{kg}$ (Frowijn and Sark, 2021; Jia et al., 2016). Corrosion, instability and low H_2O dissociation

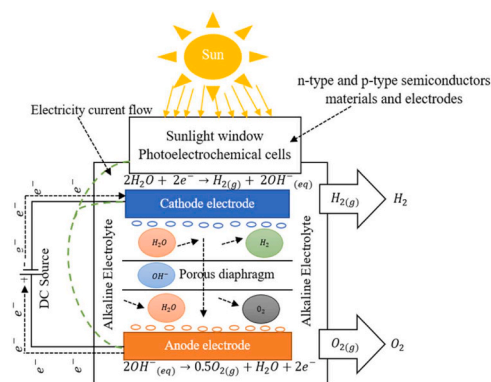


Fig. 8c. A schematic diagram of photoelectrochemical method of H_2 production.

efficiency are some of the drawbacks of H_2O photolysis.

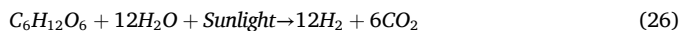
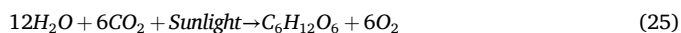
2.2.5. Biophotolysis (artificial photosynthesis (APS))

The biophotolysis process of H_2 production bio-mimics natural occurring photosynthesis (PS), using sunlight, H_2O , CO_2 and microorganisms that absorb radiation between 400 and 700 nm for cells' growth to produce H_2 reach gas. APS methods which involves direct and indirect H_2O splitting is part of the biological process of H_2 production and uses light-driven cyanobacteria and blue-green algae to produce H_2 . In biophotolysis, H_2O and photon (sunlight) are reagents of photosynthesis (PS) for the conversion of light to chemical energy by organisms through chlorophyll. The creation of chemical energy requires light and dark reactions in the chloroplast. In these reactions, generated ATP and reduced ferredoxin (Fd) or NADPH coenzyme molecules as energy carriers (electrons), receive O_2 stream from the oxidised H_2O or atmospheric CO_2 through fixation by oxygenase (O_2ase) enzyme to produce energy rich-carbohydrate (CH_2O) stores. The production of CH_2O takes place in light and dark reactions. The light reaction (PS I) involves coenzyme molecules generated by photon energy and H_2O oxidation. In dark reaction (PS II), energy from the generated ATP and reduced NADPH molecules initiate a chemical pathway for H_2O and atmospheric

CO_2 reduction to form a 3-carbon product (glyceraldehyde-3-phosphate (G3P)) that generates C-C covalent bonds of CH_2O and O_2 as by-products (Dogutan and Nocera, 2019). In direct biophotolysis (DBP), microorganisms absorb 680 nm solar radiation to activate Fd reduction via PS II and PS I reactions to release e^- , H^+ and O_2 . A wavelength of 680 nm is required to reduce Fd. The reduced Fd donate electrons to the hydrogenase (H_2 ase) enzyme to generate ATP and convert nicotinamide adenine dinucleotide phosphate ($NADP^+$) to NADPH which produces H_2 (Ipatá and Pesi (2015). O_2 -sensitive and crossover to H_2 ase chamber are some of the disadvantages of DBP (Nirmala et al., 2023). The chemical reaction of DBP is represented in Eqs. 23 and 24.



Efforts to inhibit O_2 in H_2 ase enzymes and mixture with H_2 led to the discovery of indirect biophotolysis (IBP). This biological route for H_2 production uses separate chambers for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) to mitigate the O_2 sensitivity issue in the DBP method. In the two-stage IBP process, O_2 and CH_2O are produced with the aid of photon/light energy. In the second stage, the produced CH_2O absorbs light and is converted to H_2 and CO_2 with minimal O_2 by-product under anaerobic conditions. As this H_2 production pathway occurs in an anaerobic environment after the conversion of sugar to CO_2 and organic acid, a nitrogenase (N_2 ase) enzyme is induced to fix N_2 , which is responsible for NH_3 production (Chandrasekhar et al., 2015). The sales price of H_2 from APS methods ranges from \$1.42 - \$3.10 kg (Goria et al., 2024; Frowijn and Sark, 2021). However, Nirmala et al. reported a purchase price of \$7.24/kg H_2 for DBP and \$7.44/kg H_2 for IBP (Nirmala et al., 2023). The chemical reactions of IBP are described in Eqs. 25 and 26.

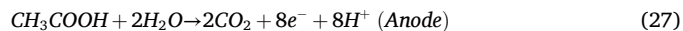


APS pathways have been suggested for CCS in high-carbon-emitting industries. Nonetheless, the high cost of bionic leaf catalysts and poor efficiency (<2 %) because of low H_2 yield, impurity, high O_2 production, light dependency and O_2 sensitivity limits economic feasibility and commercialisation. APS Schematic diagrams are given in Fig. 9a.

2.2.6. Bio-electrochemical

Bioelectrochemical method utilises a microbial electrolysis cell (MEC) and substrates such as organic waste, acidified H_2O , wastewater and salt solution to produce H_2 . The MEC requires a cell voltage between 0.2 V and 0.8 V to initiate exoelectrogenic microorganisms' activities responsible for H_2 production. In dual-chambers MEC with wastewater feed, H_2 is produced in the cathode chamber and both CH_4 and CO_2 are

by-products of mixed-culture MEC systems. High H_2 selectivity can be achieved using food processing wastewater and electron transfer microorganisms (electrogenera) like *Shewanella* spp and *Geobacter* spp at a neutral pH value (Osman et al., 2020). H_2 purchase price of MEC operating with domestic or winery wastewater feed is approximately \$6/kg H_2 and the efficiency is within 41 - 75 %. The microbial fuel cell (MFC) has higher chemical oxygen demand (COD) removal rate in contrast to MEC because of O_2 leakage. For the conversion of winery wastewater to energy, MFC is more efficient than MEC. However, MEC outperforms MFC in terms of wastewater to energy (Cusick et al., 2010; Jia et al., 2012; Kundu et al., 2013). The anode, cathode and overall chemical reactions of the dual MEC are described in Eqs. 27 - 29. Schematic diagrams of dual and single MEC systems are shown in Fig. 9b.



2.2.7. Fermentation

Photo and dark fermentation are well-known biological processes of H_2 production. Glucose, starch, cellulose and organic acid containing matters are the primary choice of fermentation substrates. Although, H_2 yield from the glucose substrate, which is more expensive than other feedstocks, is much higher (Sivaramakrishnan et al., 2021). The yield of the biohydrogen by-product depend on reactor or digester configuration, total solid (TS) and volatile solid (VS) contents, pH values, fermenter operating temperatures, hydraulic retention time (HRT) and organic loading rate (OLR).

Photo fermentation (PF) uses light-absorbing organic acids like butyrate, acetate, succinate and malate in CO_2 environment to donate electrons to purple non-sulphur (PNS) photosynthetic bacterium and generate ATP from the reduced Fd in electron backflow. In the absence of environmental CO_2 through H_2 ase catalytic chemical reactions, oxidation of carbon substrates to release CO_2 and H^+ occurs. Whereas the citric acid cycle (CAC) conveys electrons to the PNS photosynthetic bacterium. The choice of substrates to use depends on the light intensity, the carbon source and the level of anaerobiosis (tricarboxylic acid cycle (TCA)) (Park et al., 2018; Akhlaghi and Najafpour-Darzi, 2020). In a PF reactor as displayed in the below diagram (left), solar irradiance from the visible light between 400 and 1000 nm is captured by butyrate or other organic acid with bacteria and CH_2O -rich organic waste or VFA from the DF. An air and O_2 free bioreactor operating under mesophilic-thermophilic conditions to produce ATP and electrons required in the Fd reduction process is commonly used in the PF process to produce H_2 . Biohydrogen is produced when reduced Fd from the high-energy electron drives the proton reduction in the bioreactor. The

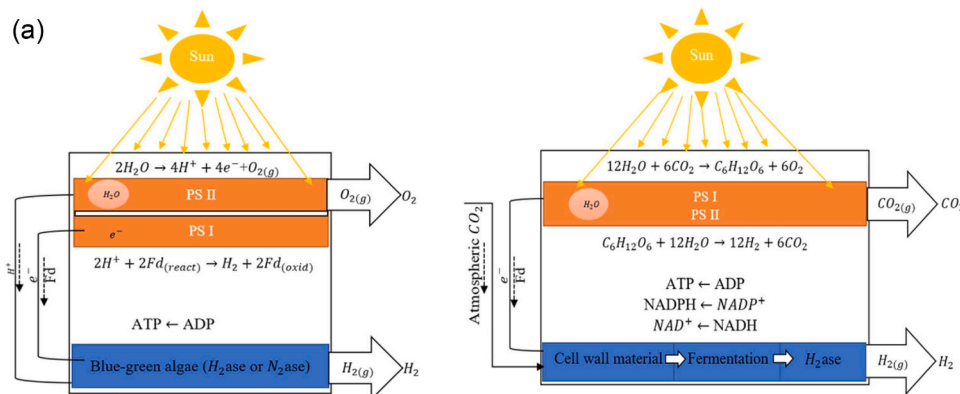


Fig. 9a. Schematic diagrams of DBP (left) and IBP (right) biological method of H_2 production.

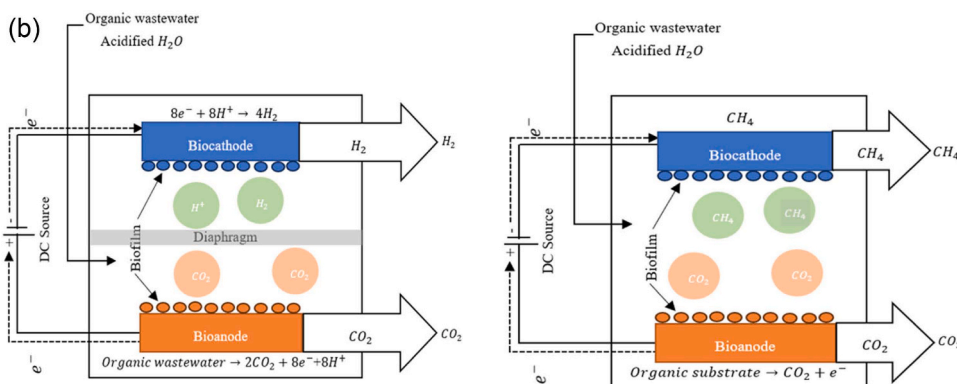
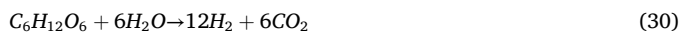


Fig. 9b. Schematic diagrams of dual MEC (left) and mixed-culture MEC (right) biological method of H₂ production.

average efficiency of PF is 25 % and H₂ produced from PF costs \$3.5/kg (Lee, 2021; Hosseinzadeh et al., 2022). The PF overall chemical reactions are described in Eqs. 30 and 31.



Dark fermentation (DF) uses complex methods and biochemical reactions to convert organic matter into H₂ in the absence of light, H₂O and O₂. In the DF method, carbohydrates from hydrolysed substrates are stored in the form of acetic acid, propionic acid, butyric acid, malic acid

or ethanol and converted into pyruvic acid by glycolysis. Acetyl coenzyme (Acetyl-CoA) and CO₂ are formed by the oxidative decarboxylation of pyruvate by the pyruvate ferredoxin oxidoreductase (PFOR) decomposition pathway. The hydrogenase microbes in the DF fermenter consume some of the acidic by-products of PFOR to release H₂ under mesophilic-thermophilic conditions. *Scenedesmus obliquus* and *algae Chlamydomonas reinhardtii* species are commonly used in the DF of biological method of H₂ production (Giang et al., 2019; Khetkorn et al., 2017; Gorla et al., 2024). The average efficiency of DF and hybrid DF-PF is 34 % and 70 % respectively and the sales price of the obtained H₂ from the DF costs \$2.3/kg (Lee, 2021; Hosseinzadeh et al., 2022).

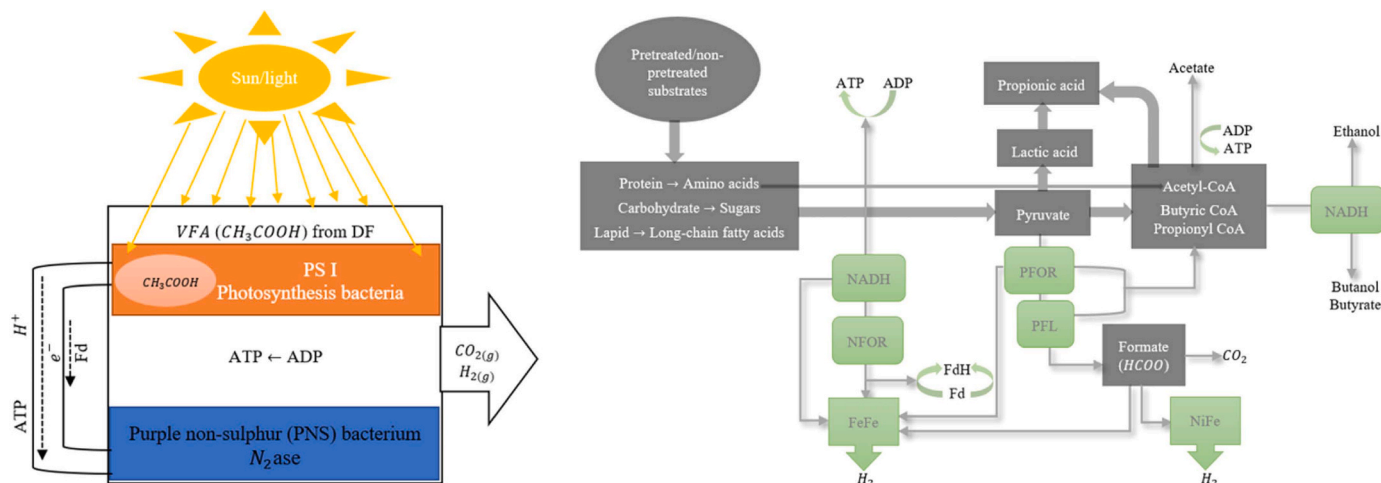
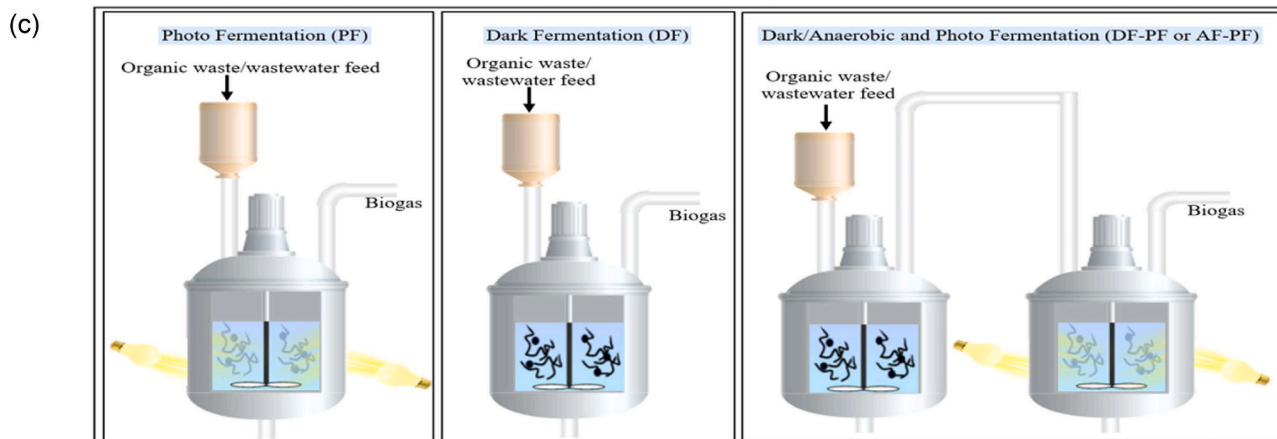
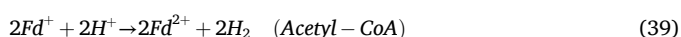
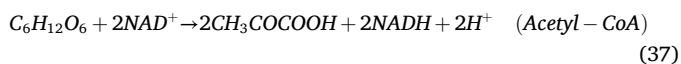
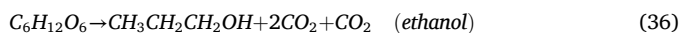
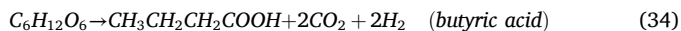
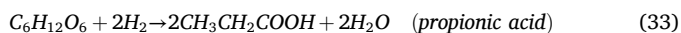
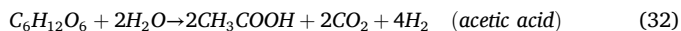


Fig. 9c. Schematic diagrams of PF (left) and DF (right) biological method of H₂ production.

Although, *Nirmala et al.* reported a purchase price of \$7.61/kg_{H₂} for fermentation methods of H₂ production (*Nirmala et al., 2023*). PF, DF and DF-PF bioreactors, PF (left) and DF (right) processes of biohydrogen production are displayed in Fig. 9c. The chemical reactions of DF are shown in Eqs. 32 - 39.



Anaerobic fermentation (AF) is similar to the AD method except for the methanogenesis reaction stage and involves hydrolysis, acidogenesis and acetogenesis reaction pathways to convert organic waste into energy. Acidogenesis is the rate-limiting step and products such as amino acids are formed in this stage. In the acetogenesis stage, the acetogen enzyme consumes acidogenesis product to release H₂ and other by-products. High volatile fatty acid (VFA) production, syngas impurities and low H₂ concentration are some of the challenges of fermentation methods of biohydrogen production (*Onwumezie and Darabkhani, 2024a*).

2.2.8. Advances and prospects of renewable H₂ production methods

Nowadays, more research is being undertaken to enhance the rate of COD (chemical oxygen demand) removal in the integrated MFC-MEC system as the nature of electrocatalytic materials such as anode materials, microbes like genetically modified microorganisms and the mediator increases the performance of biofilms (*Kannah et al., 2021*). Applying any of these approaches can increase the EET (extracellular electron transfer) efficiency. For example, *Liu et al.* studied a shared anode and cathode cell configuration to maximise the EET efficiency in an integrated MFC-MEC that enabled the released electrons from MFC to power MEC for biohydrogen production (*Liu et al., 2024*). The investigated work reported a power density of 120.9 mW/m² which is 2.3 higher than that of a control-operated MFC-MEC at a fixed resistance (Ref-MFC-MEC). Other recently investigated work includes feeding AF by-products into MFC to generate electricity for the electrolysis of H₂O stack (*Onwumezie and Darabkhani, 2024c*). In addition to the recent advances in renewable H₂ production technologies, the prospect of H₂ recovery by H₂O electrolysis should work towards the target parameters reported in Table 1; integration of high-temperature H₂O electrolysis into thermal units where the recovered waste heat can be utilised for steam production. H₂SO₄ redox reaction and aqueous solution of SO₂ in thermolysis-electrolysis may require the introduction of a solar thermal unit for the decomposition of H₂SO₄ and the use of a suitable composite membrane to prevent sulphur poisoning and improve proton conductivity and stability. For instance, the use of suitable polybenzimidazole membrane composites can lower the chances of sulphur poisoning (membrane deactivation), formation and crossover to the cathode chamber. Photolysis systems may require suitable composite photonic energy catalysts and polymer membranes to improve stack and photon absorber stabilities, resistance to corrosion and H₂O dissociation efficiency.

Infrared and red light absorber materials such as silicon (Si) with a wavelength > 680 nm and a self-heating-repairing catalyst (bionic leaf

can improve biophotolysis efficiency by ≥ 20 %. The use of a bionic leaf catalyst that exhibits good stability in a neutral pH environment and charge separation; introduction of green algae and heterocystous cyanobacteria to enable heterocyst formation and oxygenic PS to protect N₂ase and promote O₂ sensitivity; use of O₂ tolerance H₂ase microorganisms like algae that conduct PS and the transition from H₂ase to N₂ase microorganisms such as cyanobacteria are also suggested (*Chandrasekhar et al., 2015*).

A mixed culture MEC that promotes higher biogas production and the application of reforming methods for the conversion of biogas to biohydrogen can minimise the high cost and stack electricity consumption of the H₂ membrane separator. It was evident that the internal resistance in the dual-chamber MEC system is relatively higher than that of the mixed culture MEC-producing biogas (CH₄ and CO₂) (*Onwumezie and Darabkhani, 2024a*). Integrated MEC-AD, slow pyrolysis to obtain biochar for AD reactor and reforming methods for the conversion of both wastewater and organic wastes into biogas with high total solid content can be a promising route for biohydrogen production. In this approach, liquid oil and char from low-temperature pyrolysis of biomass can promote biogas concentration in the methanogenic stage. The integration of combined DF-PF or AF-PF into the thermolysis of organic VFAs seems promising. In this suggested hybrid system, the DF/AF by-products will feed PF and VFAs from PF will feed the thermolysis unit to recover CH₄, CO₂, C₂H₄, C₃H₆, alcohol fuels and ketene. While the incorporation of MFC to the hybrid DF/AF-PF should utilise a battery system to store electricity for the digester/fermenter operation.

2.2.9. Summary and comparisons of H₂ technologies and proposed roadmap for a sustainable H₂ production systems

Table 2 summarises the H₂ production systems, proposed thermal and electrical sources of energy, possible integration units and areas of applications. Renewable energy sources for electrical units of the H₂ systems include solar, wind, geothermal and others. The proposed combined H₂ production technologies using advanced waste heat conversion to electrical energy, renewable and low-carbon energy systems are shown in Fig. 10a.

Fig. 10b presents the proposed integrated pyrolysis and electrolysis systems for H₂ production. In the presented hybrid H₂ production technology, both solar thermal and oxy-hydrogen furnace were utilised to preheat the pyrolyser feedstock and compensate for heat losses. The waste heat recovered from cooling the pyrolyser syngas was used to produce steam for both high-temperature electrolysis of H₂O and steam Rankine cycle. The obtained thermal energy from cooling H₂ and O₂ from the high-temperature electrolyser stack was also utilised for distillation and preheat the organic Rankine cycle (ORC) working fluid (cyclopentane (C₅H₁₀)). In addition to the produced electricity by the Rankine cycle units, solar PV or wind turbine systems generated more electricity for the electrical units. Part of the produced H₂ and O₂ were consumed in the oxy-hydrogen furnace to exclude the carbon footprint.

In addition, a hybrid AD-MEC and DR for biohydrogen production is given in Fig. 10c. The displayed integrated H₂ production system utilised exhaust heat of an oxy-hydrogen furnace for thermal pretreatment of AD feedstock in the hydrolysis stage. The methanogenic stage was also improved by adding biochar from the low-temperature pyrolyser unit. For biohydrogen production, DR was incorporated for the conversion of AD-MEC biogas into biohydrogen and bio-CO₂. The absorption process was used to capture the bio-CO₂ from the DR unit. In locations with limited sunshine or wind, the proposed system introduced an option of using the released electrons from the MFC to operate the electricity units such as MEC stack or AD reactors. Both proposed H₂ production technologies achieved carbon neutrality and higher efficiency. Thus, they represent a perfect roadmap for sustainable H₂ production systems. Table 3 which depicts the comparison of different H₂ production methods can be found in the appendix.

Table 2
Summary of H_2 production processes, thermal energy source, compactable technologies and suitable areas of application.

Technology	Thermal energy sources	Possible technology for integration	Suitable locations.
Hydrocarbon reforming and pyrolysis (HRP).	Solar thermal (CSP) systems and oxy-hydrogen combustion. Electricity from wind or solar during low demand for the plasma reforming process without CO_2 feed.	Electrolysis of H_2O . Thermolysis via oxidation of SO_2 . Steam, organic or gas cycles with heat recovery units. Thermoelectric converters for heat flux conversion to electricity.	Areas with higher solar radiation and long sunny days. Areas with more wind such as the UK for plasma reforming and CH_4 pyrolysis methods.
Solid fuel gasification. Biomass pyrolysis and gasification.	The same as HRP. Oxy-hydrogen combustion. Renewable powered-plasma furnace. Solar thermal for gasification with slurry feed.	Low-temperature H_2O electrolysis. The same as HRP.	Cement, iron and steel plants. Any location with more feedstock. Areas with higher solar radiation for the gasification unit.
Electrolysis of H_2O . Photolysis.	Solar thermal for high-temperature electrolysis systems. Waste heat for high-temperature electrolysis systems.	Any of the fossil fuel methods but more suitable for technologies that require O_2 feed.	Thermal industries for waste heat conversion to usable energy. Location with more freshwater.
Thermolysis Biological (Bio-photolysis) Bio-electrochemical(MEC).	The same as HRP. The same as HRP for substrate pretreatment.	Low-temperature alkaline H_2O electrolysis. MFC, DF, AF and AD. Aerobic digestion.	The same as HRP. Locations with higher solar radiation. Wastewater and organic waste treatment plants. Fertiliser and synthetic fuel production plants.
Fermentation		MFC, AF and AD. Thermolysis of VFAs coupled with catalytic CH_4 pyrolysis.	Organic waste and wastewater treatment plants.

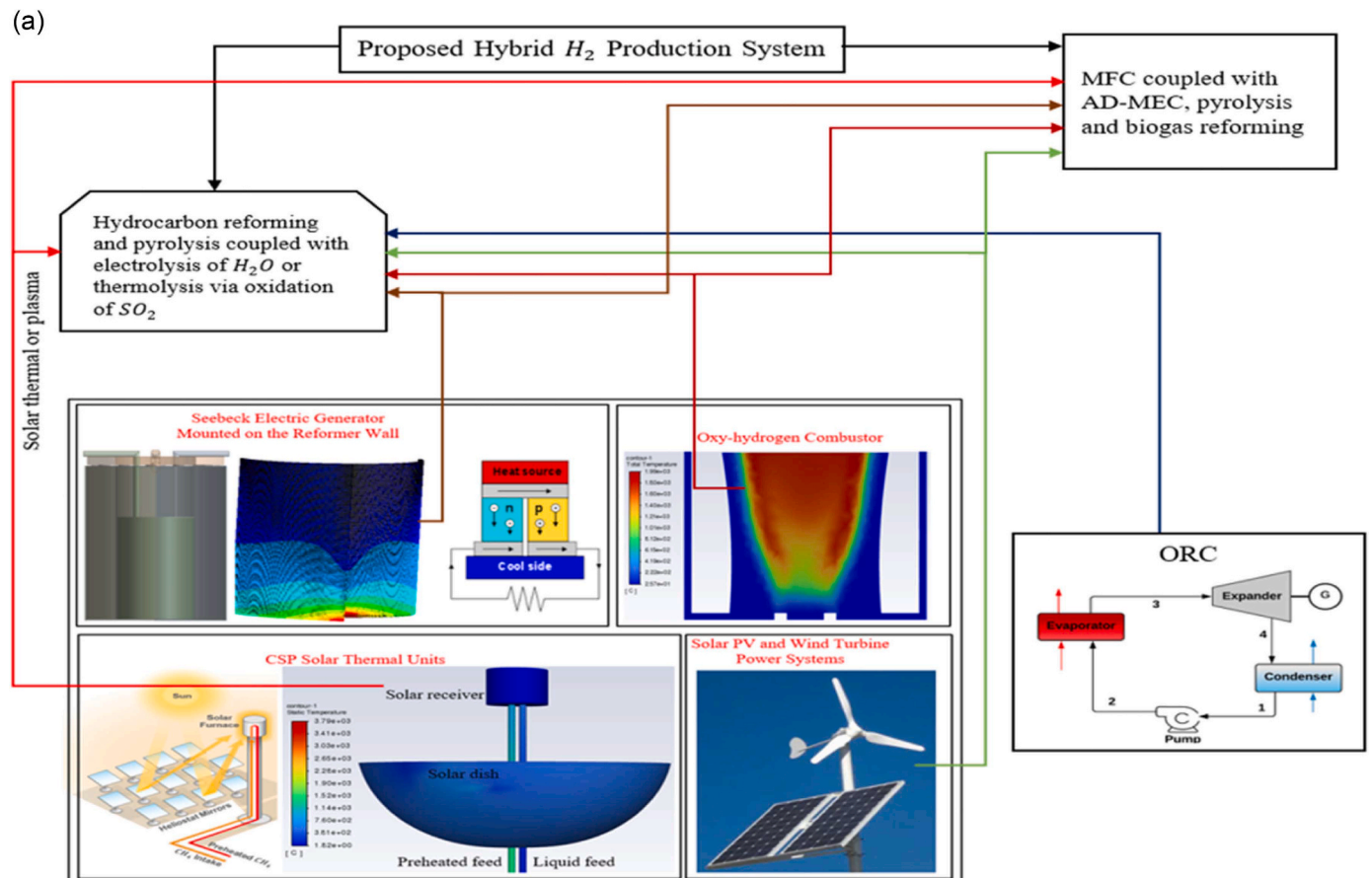


Fig. 10a. Renewable and low-carbon energy systems for integrated H_2 production technologies (Onwuemezie et al., 2024; Onwuemezie and Darabkhani, 2024a, 2024d).

3. Overview of H_2 Transportation Routes

Stored H_2 in liquid, gas and solid forms can be transported by pipeline, ships, rail and tankers. H_2 pipeline transport is the same as natural gas (NG) pipeline transport except for higher infrastructure and

maintenance costs, embrittlement, higher flow velocity (250 - 270 %) and lower pressure loss (5.8 times) (Thawani et al., 2023). Similar to NG, H_2 pipeline transport may require recompression in every 200 km to compensate for pressure losses (S, 2021). A computational model of NG pipeline transport at 800 kg/s flowrate, intake pressure of 300 bar and

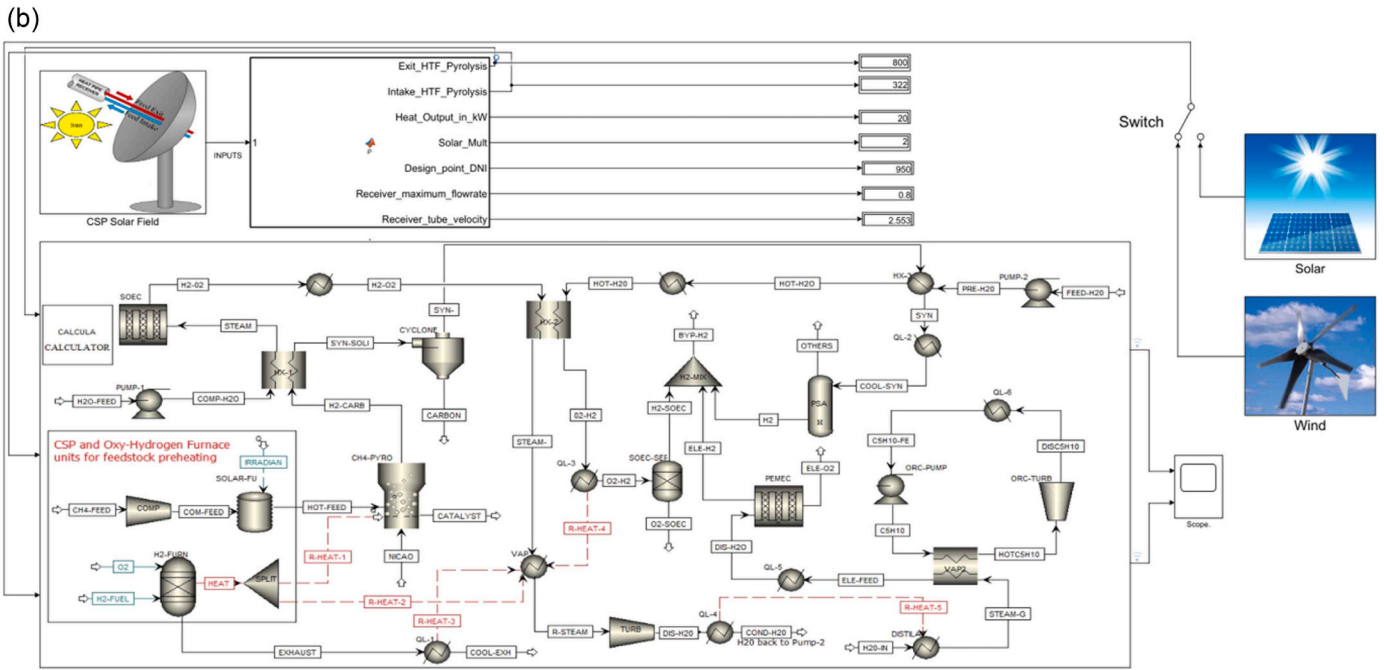


Fig. 10b. Proposed H₂ production system through renewable powered hybrid pyrolysis and electrolysis technologies.

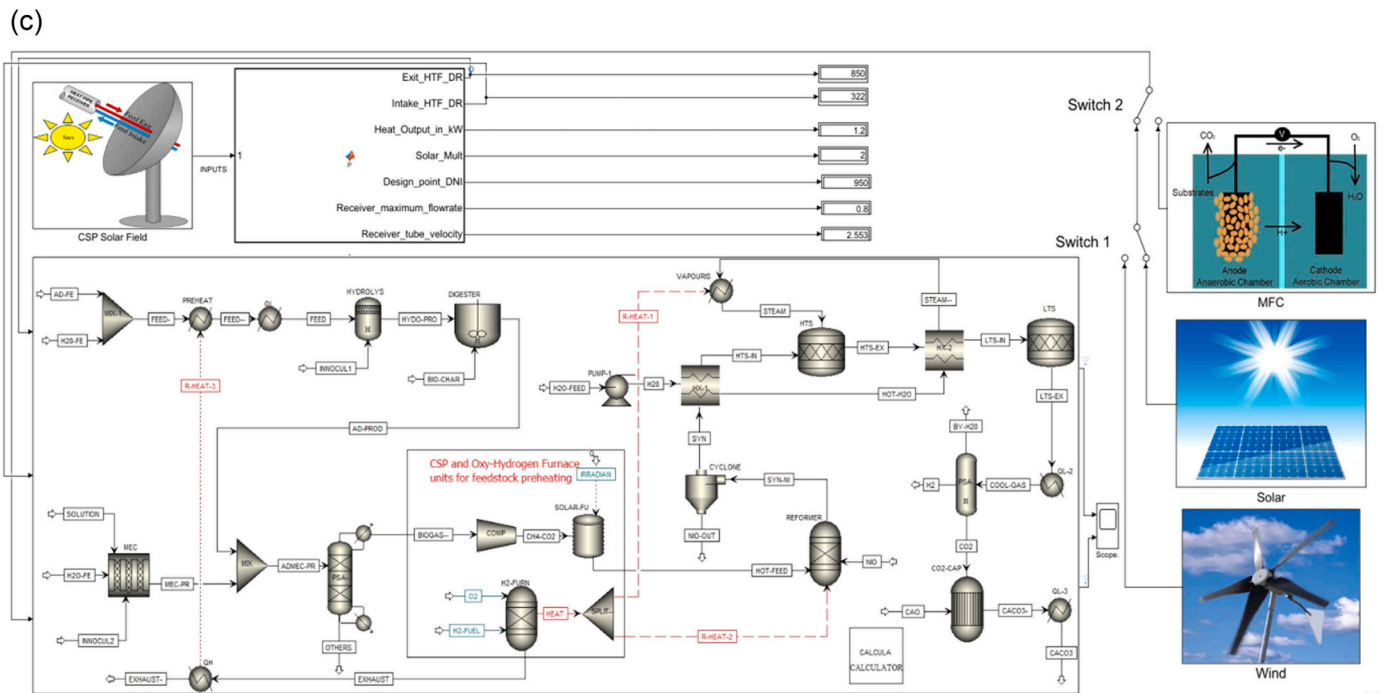


Fig. 10c. Proposed H₂ production technology via renewable and MFC powered integrated AD-MEC and DR systems.

4801 km distance may not necessarily require recompression (Prasad et al., 2023). Other forms of H₂ pipeline transport include mixture or blending with NG/CH₄ (hythane) and reacting with other elements to form NH₃ and light hydrocarbons. H₂ blend to form any of these gases, liquid fuels or elements for ease of storage or transportation may require H₂ production facilities for recovery, which may increase the purchase price. Fig. 11 shows pipeline, tanker, ship and rail modes of H₂ transportation.

3.1. Advances and outlooks of H₂ transport

Since hydrogen embrittlement is one of the drawbacks of H₂ transport by pipeline, researchers have proposed the use of alloy materials with high entropies and special microstructures. This can be achieved by using nitriding, carburising and shot peening treatments in addition to ceramic or metallic coatings to enhance the microstructures and surface properties needed to resist hydrogen embrittlement. Other materials suggested for H₂ pipeline construction include composites and polymers, while advanced purification of H₂ to remove other elements such



Fig. 11. Schematic diagrams of H₂ transportation modes.

as H₂O or O₂ has also been proposed to mitigate embrittlement (Mohammadi et al., 2022; Laadel et al., 2022). In addition, proper handling to mitigate leakage and the use of carbon fibre-reinforced polymers (CFRPs) for better insulation and weight reduction and pressure relief systems should be considered for compressed and liquid H₂ transport (Muhammed et al., 2023). Furthermore, local H₂ pipeline delivery to reduce maintenance costs and safety concerns is encouraged.

4. Overview of H₂ storage methods

H₂ can be stored in liquid, compressed, cryogenic and solid states. Compressed H₂ storage, which increases storage capacity up to 35 kg/m³ due to its low density requires lightweight composite storage units and a storage pressure up to 800 bar. Liquid H₂ storage at a standard boiling point -252.87 °C to maximise storage capacity (70 kg/m³) twice that of compressed H₂ at 800 bar, operates at atmospheric pressure conditions (Faye et al., 2022). Solid state H₂ storage under atmospheric

pressure conditions can increase storage capacity up to 150 kg/m³ and use metal alloy composites and hydrides (metal, non-metal and complex) absorbents. Alloy solid state storage includes Mg-Mg₂Ni, Mg-Mg₂Cu, Mg₂Fe and Mg₂Cu. Some of these hydrides for H₂ storage by absorption form KAlH₄, LiBH₄ and SiO₂, H₃NB₃, LiAlH₄, Ca(BH₄)₂ and others. Currently, H₃NB₃ and LiBH₄ have the highest solid state H₂ storage capacity (18 - 10 wt%) (Tarhan and Çil, 2021a). The liquefied H₂ storage at -252.87 °C requires 7.34 kW/kg_{H₂}, 6 kW/kg_{H₂} for compression at 600 - 800 bar, 2 kW/kg_{H₂} for hydride LiBH₂ and 4.3 kW/kg_{H₂} for MgH₂. For the liquefied and hydride H₂ storage, a similar amount of energy for hydrogenation may be required for dehydrogenation. An increase in H₂ storage capacity decreases the energy input per 1kg_{H₂} and H₂ storage by NH₃ production using N₂ from the ASU unit in hydrocarbon reforming methods is energy intensive during dehydrogenation. Fig. 12 displays compression, liquid and solid means of H₂ storage.

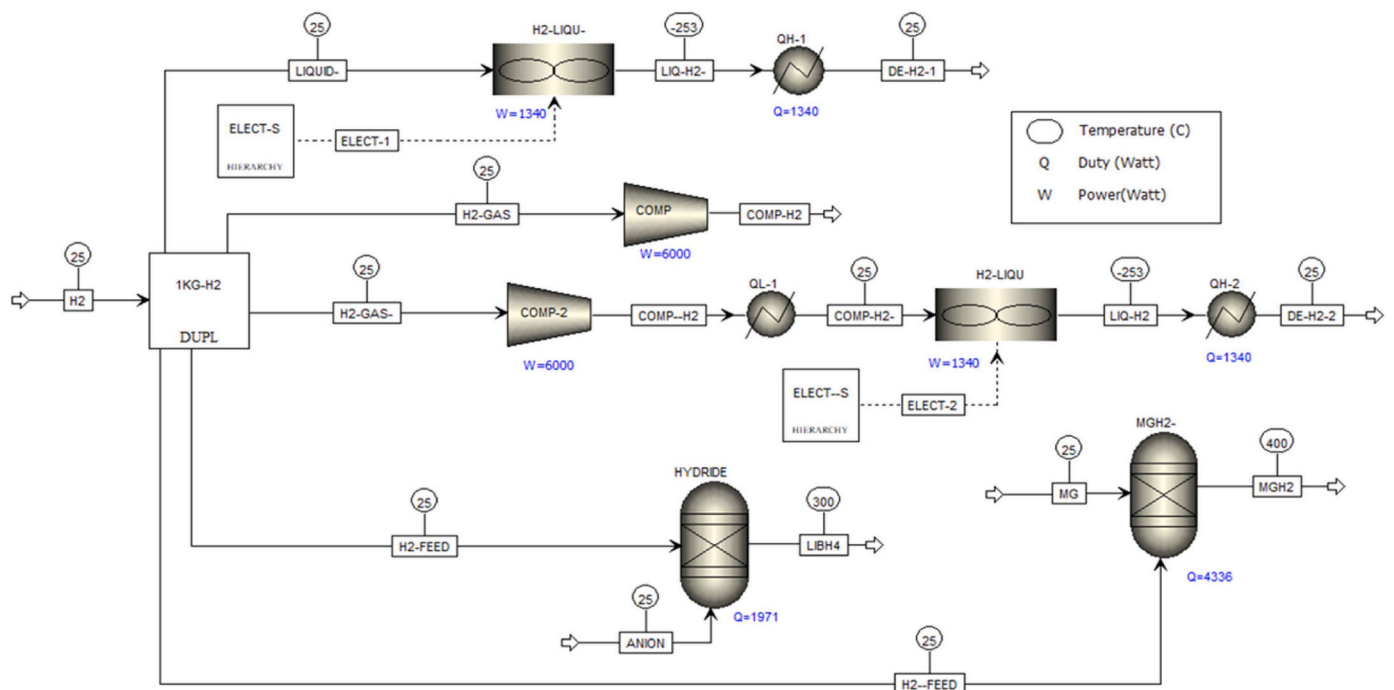


Fig. 12. Schematic diagrams of H₂ storage methods.

4.1. Advances and outlooks of H₂ storage

Solid-state H₂ storage through metal-organic frameworks (MOFs) adsorbents looks promising against other storage methods such as the compression route. However, an uptake increase by ≥ 5 g/L is needed for applications that require > 30 cycles per year to be cost-competitive as thermal, solvent and waste based manufacturing routes cost between 10 \$/kg and 70 \$/kg (Peng et al., 2024). Recently, Zhou et al. conducted a review of Mg/MgH₂ solid state H₂ storage using MOFs and carbon-based porous material as catalysts' supports to minimise sintering issues. The reviewed work suggested advances in economical catalysts with high catalysts' recovery rates, improved stability, fast H₂ uptake and Mg/MgH₂ release to promote the practical application (Zhou et al., 2024). In addition, the prospect of H₂ storage by hydrides should look towards improving the kinetics and thermodynamic performance such as reducing the energy consumption of hydrogenation (absorption) and dehydrogenation (desorption). Consideration should be given to salt cavern storage in locations (Netherlands, China, the USA and others) where salt mountains can be found since it is impossible to use a single H₂ storage material as a medium for real-life applications in solid-state storage routes. Table 6 which summarises the H₂ storage in solid state is given in the appendix.

5. Overview of H₂ Utilisation

Similar to the three main types of H₂O electrolysis, H₂ FC includes proton exchange membrane fuel cell (PEMFC), Alkaline fuel cell (AFC), solid oxide fuel cell (SOFC) and anion exchange membrane fuel cell (AEMFC) and works in reverse of electrolysis to produce electricity. H₂ fuel cells outperform batteries in terms of recharge time, service life and range. However, the lower efficiency (52 %) of FC compared to batteries (~90 %) limits the full transition from battery to FC in some applications like automobiles (Thomas, 2009).

H₂ heat engines are classified into H₂ internal combustion engines (H₂ICEs), H₂-fuelled gas turbine engines (H₂ GTEs) and H₂-based ovens/furnaces. In each of these heat engines, H₂ fuel is burnt with air or O₂ oxidants in the combustor or cylinder to produce energy in the form of heat. The produced energy is converted to electricity with the use of turbines and electric generators and can also be transferred to elements/molecules such as H₂O for tap-water/central heating systems. Fig. 13 depicts the H₂ utilisation in FC and heat engines.

In the FC unit of the displayed diagram, H₂ react with air or O₂ to generate electricity. The compressed ambient air combusts with H₂ fuel in the combustor to release high-pressure-temperature gas to drive the turbine connected to the compressor, while the exit gas from the turbine enters the nozzle and leaves as thrust. On the other hand, the turbine outlet gas drives another low-pressure turbine connected to the utility generator to generate electricity. The recuperator preheats the com-

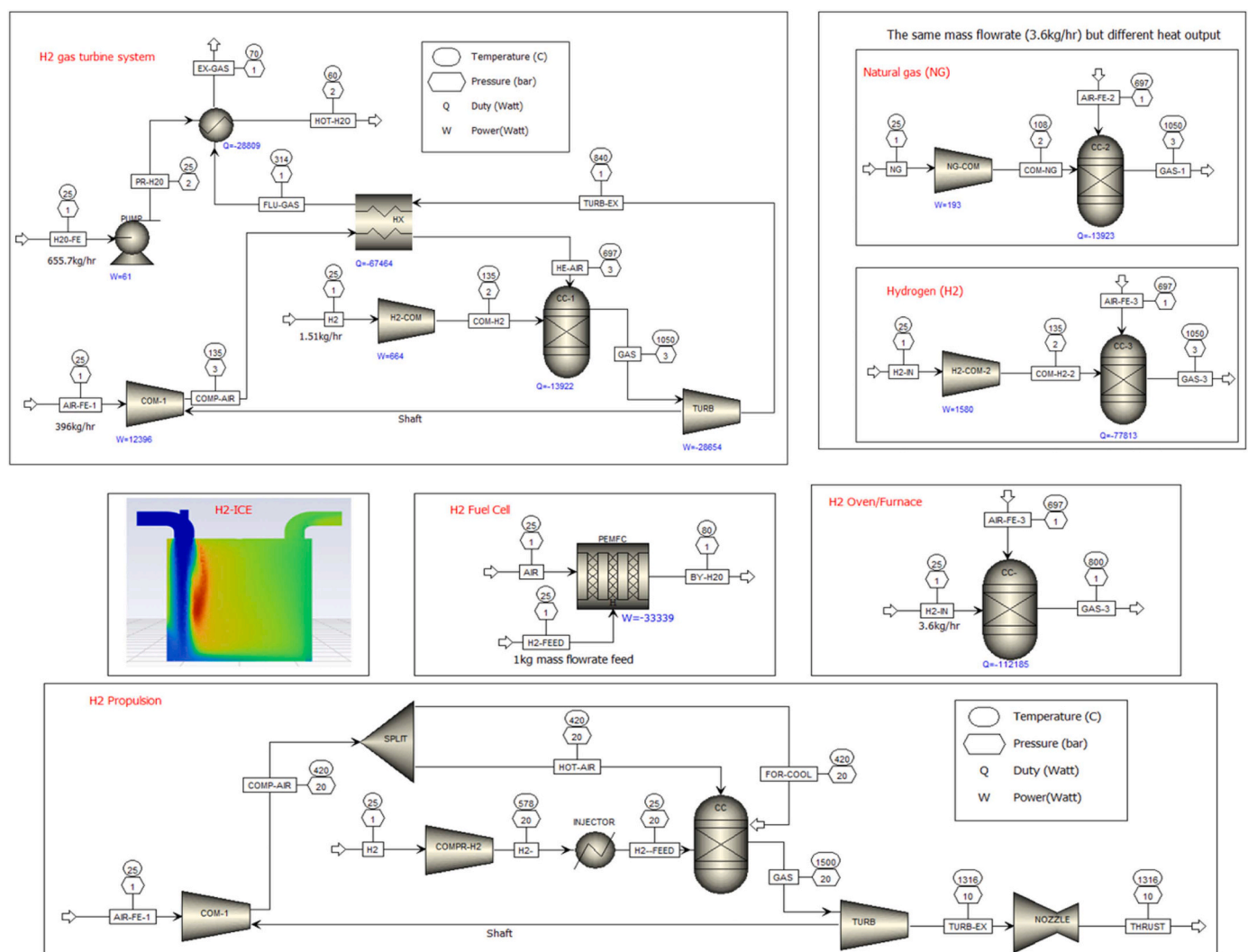
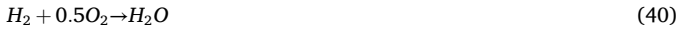


Fig. 13. Schematic diagrams of H₂ utilisation in fuel cell (FC) and heat engines.

pressed air to the combustor. H_2 ICE is a stroke cycle engine, and the 4-stroke cycle engine involves an air intake through an air manifold, air compression, combustion for piston movement and exhaust. The mechanical work from the combustion stroke drives the crankshaft or utility generation. In addition, H_2 can be used to produce chemicals such as fertilisers or synthetic fuels/gas (NH_3 , C_2H_6O/C_2H_5OH , CH_3OH and biodiesel). The overall reaction of H_2 and air or O_2 in FC and heat engines are described in Eqs. 40 and 41.



With 396kg/hr_{air} feed, a 1:2.42 NG to H_2 ratio was required to achieve the same combustor heat output. Although, the NG compressor uses less electricity in contrast to the H_2 pressure increaser. A H_2 low-temperature fuel cell on the other hand, produced 33 kW for 1kg/hr_{H_2} feed. The produced electricity from 1kg/hr_{H_2} in the H_2 fuel cell decreases as the stack temperature increases. This shows that PEMFC is more power efficient than SOFC. In addition, the combined heat and power (CHP) system based on a gas turbine system is preferable in applications where more heat is needed. However, a H_2 fuel cell system is the right choice for applications that require more electricity. The efficiency of a H_2 -fuelled gas turbine system can be estimated using Eq. 42.

$$n = \left[\frac{\dot{m}_a (h_{steam} - h_{water})}{\dot{m}_f (H_2 LHV)} \right] * 100 + \left[\frac{W_{net}}{Q_H} \right] * 100 \tag{42}$$

Where: \dot{m}_a = Steam flowrate; h_{steam} = Steam enthalpy; h_{water} = Feed H_2O enthalpy; \dot{m}_f = H_2 mass flowrate to the gas compressor; LHV = Low heating value; W_{net} = Turbine work – (compressors + pump works); Q_H = Boiler heat.

5.1. Advances, outlooks and proposed roadmap for H_2 utilisation in heat engines and for synthetic fuel production

H_2 production using excess electricity (between 3–5 %) from wind farms and hydropower plants and its utilisation in grid balancing via fuel cell application was investigated, with findings showing that both approaches are economically feasible. The studied work utilised power plants with a capacity of 1 – 30 MW and between 16,000 MWh/day and 9340 MWh/day were recovered with a profit of \$27.13 - 617.92/kg for the wind farm and \$162.87 - 342.42/kg for the hydropower plant (Souza et al., 2024). Most recently, efforts were made to substitute fossil fuel gas turbine systems with pure H_2 systems. For instance, Banihabib et al.

reported NOx formation of 22 ppm during an investigation on pure H_2 utilisation in a gas turbine system using a H_2 fuel train and controller approaches (Banihabib et al., 2024). In addition, H_2 utilisation should look towards the addition of steam to reduce thermal wall stress and NOx formation in the combustor/cylinder, heat recovery using thermophotovoltaic systems and the introduction of a combustor with a fitted heat exchanger for distillation. Furthermore, the transition from a single-piston H_2 heat engine to an opposed-piston engine (OPE) and the integration of H_2O electrolysis to generate H_2 fuel to reduce end-use costs should be considered.

Given that the reuse of existing facilities or infrastructures for H_2 transportation and storage faces many challenges as mentioned above, Fig. 14 presents the synthetic natural gas (NG) production via the H_2 pathway and its utilisation in a combined heat and power (CHP) system. The presented hybrid system for H_2 production and utilisation to produce synthetic NG includes a gas turbine cogeneration system, solar-wind powered low-temperature H_2O electrolysis and oxy-hydrogen aided direct air capture (DAC) units. In this integrated system, H_2 and O_2 were produced from the electrolyser cell, and part of the produced H_2 is synthesised with CO_2 from the DAC unit and fed to the gas turbine system to produce heat and power. CO_2 present in the exhaust gases of the gas turbine system was captured by DAC and was released from the $CaCO_3$ with the aid of an oxy-hydrogen furnace where the remaining produced H_2 was burnt. The efficiency of the proposed H_2 utilisation system was 96 % (20 % for power and 76 % for heat), 80 % for PEMEC and between 40 % and 55 % for combined PEMEC and oxy-hydrogen furnace. This proposed carbon-free system means that building new infrastructures for H_2 transport and utilisation in small or medium sized utility systems can be avoided and represent a sustainable pathway to reduce reliance on the grid.

5.2. Challenges, policy and collaborations for scalability and applicability enhancement of the proposed H_2 systems

One of the challenges of the proposed H_2 production and utilisation systems is the cost (installation) as each hybrid system has different subunits. For example, a PEMEC electrolyser costs \$1400/kW as written in Table 1 and requires < \$200/kW to achieve < \$2kg $_{H_2}$. Therefore, research and development (R&D) funding from different collaborative platforms is required to mitigate costs and other issues that may arise in these proposed H_2 systems. In addition, the involvement of policy-makers to subsidise the cost of each unit of the hybrid systems such as electrolyser stacks is highly encouraged. For example, a plan to support

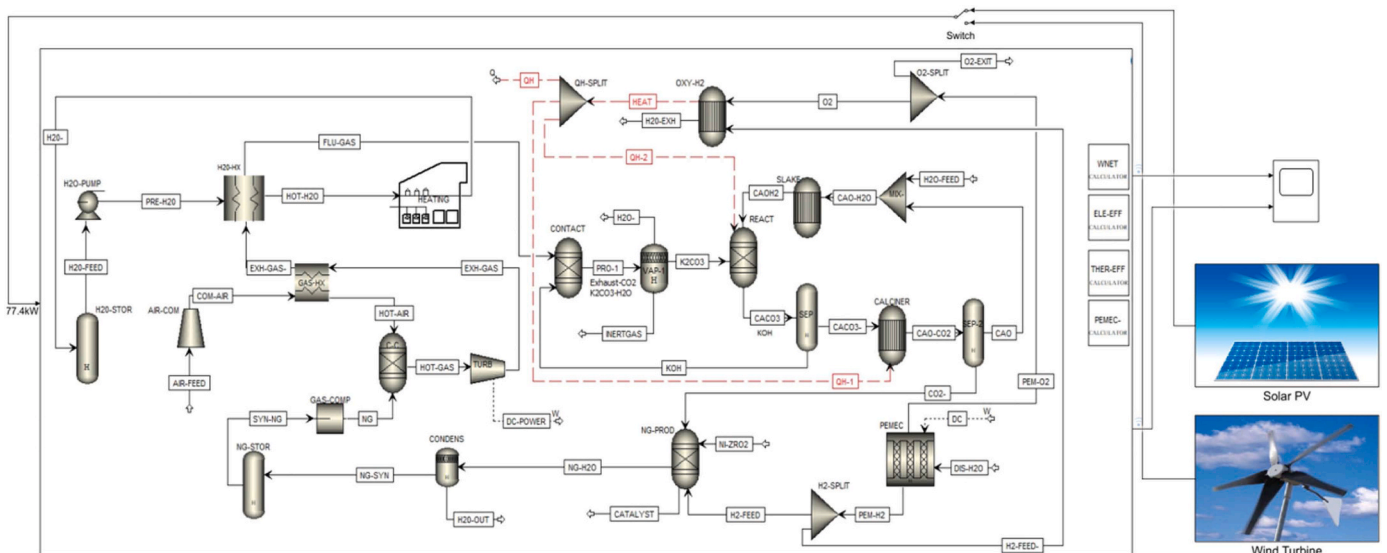


Fig. 14. Proposed H_2 utilisation for synthetic NG production for small and medium scale applications.

and subsidise electrolyser manufacturers in India was announced back in September 2021 with the aim to increase the share of a green H_2 production system and promote the integration to other units for efficiency improvement (Jeje et al., 2024). Another approach to promote the proposed H_2 energy systems involve a scheme to financially support the end-users when these proposed technologies are readily available as a similar approach was demonstrated by the UK government for heat pumps. For example, in the UK, buyers of electric heat pumps received £ 5000 for air source and £ 6000 for ground source as of 2024. A streamline by policymakers to encourage the transfer of research findings to industries for practical applications can also facilitate technological breakthroughs in H_2 energy systems. On the other hand, a scheme to promote collaboration between researchers and industries in H_2 energy systems can enhance the scalability and applicability of emerging technologies such as those proposed.

Conclusion

H_2 technologies (production, storage, transportation and utilisation) were developed and discussed to gain a comprehensive understanding of their performance, advances and areas for improvement. The study proposed the use of solar thermal units such as CSP technologies or renewable powered-plasma systems during low electricity demand to preheat the reformer feedstocks rather than burning fossil fuel in reformer furnaces. In addition, the use of oxy-hydrogen furnaces to compensate for heat losses was highlighted. Renewable power sources such as solar, wind, MFC and others were recommended to generate electricity for the electrical units. Waste heat recovery through heat exchangers (HXs) and thermoelectric converter systems was proposed for matured H_2 production technologies to improve their energy efficiency. Hydrocarbon reforming methods of H_2 production, coupled with the electrolysis of H_2O to feed O_2 by-product to the reformer was also

suggested to exclude the use of an ASU. The proposed H_2 production systems were hybrid pyrolysis and electrolysis and integrated MFC, AD-MEC and DR using renewable and low-carbon energy sources to achieve carbon neutrality. One of the proposed H_2 production technologies also included Rankine cycles for the conversion of medium and low temperature waste heat to electricity. To alleviate the storage and transportation issues associated with H_2 fuel, a hybrid green H_2 production and utilisation with the aid of DAC to capture CO_2 for hydrogenation to synthetic NG was proposed and developed. This study also indicated that applications of the proposed H_2 energy systems will enable the reuse of existing networks and infrastructures. The highlighted areas for future research include the direct combustion of pure H_2 in gas turbine engines with steam addition to reduce NO_x formation and wall thermal stress and H_2 utilisation in opposed piston engines for electricity generation.

CRedit authorship contribution statement

Linus Onwuemezie: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

Appendix

Table 3
Comparison of current and proposed H_2 production systems (Onwuemezie et al., 2023b).

H_2 production methods	Advantages	Disadvantages	Cost (\$)	Efficiency (%)
Hydrocarbon reforming, pyrolysis and gasification	Low cost of H_2 and good working efficiencies.	Reliance on fossil fuels for thermal and electrical energy production. Carbon emissions from combustion without CCS units	1.91 - 2.9	35 - 85
Electrolysis of H_2O	Carbon neutral when renewable power systems generate the stack electricity. Good working efficiency and abundant feedstock (H_2O).	High cost of green H_2 and requires more energy in contrast to fossil fuel H_2 production systems.	5.10 - 10.3	68 - 100 (high-temperature electrolysis cell)
Photocatalyst	Low cost of H_2 and abundant feedstock.	Impurities and poor conversion efficiency.	9	0.06
Fermentation (photo and dark)	Low cost of H_2 and minimal energy requirement.	Impurities, high VFA production and poor conversion efficiency.	2.57 - 2.83	0.1 - 10.14
Propose hybrid pyrolysis and electrolysis system	Reduced CH_4 feedstock. Carbon negative. High efficiency.	Higher installation cost and coke deposition on pyrolyser catalysts.	< 3	70 - 87
Proposed integrated MFC-AD-MEC	Higher syngas yield. Carbon neutral. Waste to energy and abundant feedstocks.	VFAs production. Higher installation cost because of MEC and MFC stacks.	< 5	50 - 80

Table 4
Comparison of H_2 storage methods (Zhou et al., 2024; Usman, 2022).

H_2 storage route	H_2 content (wt%)	Volumetric density (g/L)	Volumetric energy density (MJ/L)	Operation	Safety	Technical level	Cost
Gaseous state. 1 - 700 bar	5.7 - 100	0.0814 - 40.8	0.01 - 4.9	Easy	Poor	Matured	Lower
Liquid state. 1 bar - 253 °C	14 - 100	51 - 70.8	6.12 - 8.5	Difficult	Poor	Maturing	High
Solid state (metal hydrides)	1.89 - 7.9	20 - 114	2.4 - 13.7	Easy	Safe	More matured	Low

Table 5
Advantages and drawbacks of H_2 storage methods (Tarhan and Çil, 2021b).

H_2 storage route	Advantages	Drawbacks
Gaseous state. 1 - 700 bar	Matured on small scales. Fast filling and discharge.	Losses (15%). Safety issues due to leakage. Required low temperature or high pressure for storage.
Liquid state. 1 bar - 253 °C	Low storage pressure. High energy density. Safer than compressed form because of lower storage pressure.	Higher losses (30%). Required cooling system to reduce boil-off within days.
Solid state (metal hydrides)	Large storage in a small volume.	High weights of the utilised materials for H_2 storage (absorption).

Table 6
Advantages and drawbacks of MOFs/hydrides materials for H_2 storage (Klopčič et al., 2023).

MOFs/hydrides materials for H_2 storage	Advantages	Drawbacks
MgH_2	Low cost; abundant; high storage weight (7.6 wt%); good stability under thermal conditions and reuse.	Poor hydrogenation, cycle stability and kinetics; O_2 sensitivity and high dehydrogenation temperature (300 °C).
$TiFe$	Low cost; abundant; good cycling stability under low temperature (30 - 70 °C) conditions and reuse.	Low storage weight; higher activation temperature (400 °C); high storage pressure (10 - 20 bar); low H_2 recovery rate and sensitivity to gas impurities.
$TiMn_2$	Low cost; abundant; good kinetics and stability under ambient temperature and mild activation conditions.	Sensitive to gas impurities; high storage pressure with hysteresis effects and limited bonding strength because of high oxidation caused by oxygen-affine.
$LaNi_5$	Resistance to impurities and high cycling stability under ambient temperature and atmospheric pressure; high hydrogenation and volumetric ability.	High cost due to limited availability; low storage weight (1.4 wt%) and flammability.
$NaAlH_4$	Low cost; abundant and moderate operating temperature.	Sluggish hydrogenation, kinetics and reversibility; pose significant physical hazards when ignited (pyrophoric).
$LiBH_4$	High storage capacity and lightweight.	High cost and dehydrogenation temperature (>300 °C); flammable; sluggish kinetics.

Pilot studies on H_2 energy technologies

A short while ago, H_2 energy systems including production using solar-powered electrolysis of H_2O , storage with metal hydride and batteries and utilisation in a fuel cell for electricity generation in a market administration building were investigated. The finding shows that > 50 % CO_2 reduction can be achieved when implemented in buildings (Segawa et al., 2022). Another pilot-scale experimental study utilised locally generated H_2 in urban buildings because of the challenges of deploying renewable energy systems in non-rural buildings. The experimental work involved off-site metal hydride storage of $100 Nm^3_{H_2}$ at a pressure of < 1 MPaG and the result indicates that green H_2 utilisation in metropolitan buildings requires $300 Nm^3_{H_2}$ to achieve carbon negative (Segawa et al., 2024). The pilot-scale study on biohydrogen production from hybrid DF-PF reveals that $9.37 t_{CO_2}$ can be emitted for every $1 t_{H_2}$ using 171,530 MJ of energy for fermenters and purification units (Zhang et al., 2024b). Carbon reduction on residential buildings in Spain, Portugal, Southwest France and Novales Spain by generating H_2 with surplus electricity and utilising it for load balancing during high demand has recently been demonstrated on a pilot scale. The outcome shows that with the aid of a tracking device and remote operation of the solar-powered electrolysis of H_2O system, $2260 kg_{CO_2}$ reduction, 15200 kWh energy saving and €1170 energy bill avoidance on social housing could be feasible within 2 years (Maestre et al., 2024). All proposed hybrid systems suggested the use of solar thermal and PV or wind-powered plasma during periods of low energy demand to be both environmentally and economically beneficial.

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