Hydrogen-Based Combined Heat and Power Systems: A Review of Technologies and Challenges

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Abstract

This article comprehensively reviews hydrogen-based Combined Heat and Power (CHP) systems as an ideal energy system for reducing environmental pollution and carbon emissions. Hydrogen has a heating value three times that of gasoline, and its lifecycle carbon footprint is reduced by 50% compared to traditional fuels. The advantages and characteristics of hydrogen are examined, and the technical features of functional equipment, such as internal combustion engines, gas turbines, and fuel cells, are explored for hydrogen-based CHP systems. Notably, fuel cells can achieve efficiencies of up to 90%. Furthermore, with 96% of global hydrogen production relying on traditional fossil fuels, this review summarizes traditional and emerging hydrogen production, storage, and transport methods suitable for these systems. Additionally, key challenges, including cost reduction, infrastructure development, and integration with renewable energy sources, are discussed to address the large-scale implementation of hydrogen-based CHP systems. This review aims to lay a foundation for improved hydrogen energy utilization, inspire researchers to design more efficient and environmentally-friendly CHP systems and offer suggestions for future development.

Keywords: CHP systems, Internal Combustion Engines, Gas turbines, Fuel cells, Hydrogen production, Hydrogen storage

Nomenclature

Abbreviations

AEM	Anion Exchange Membrane
AEMFCs	Anion Exchange Membrane Fuel Cells
AFCs	Alkaline Fuel Cells
CCHP	Combined Cooling, Heating and Power
CCS	Carbon Capture and Storage
CHP	Combined Heat and Power
CI	Compression-Ignition
COV_{imep}	Covariance of Indicated Mean Effective Pressure
DDF	Diesel Dual Fuel
DMFCs	Direct Methanol Fuel Cells
EGR	Exhaust Gas Recirculation
FCs	Fuel Cells
GTs	Gas Turbines
GTCC	Gas Turbine Combined Cycle
H-SOFCs	Proton-Conducting Solid Oxide Fuel Cells
HT-PEMFCs	High-Temperature Proton Exchange Membrane Fuel Cells
ICEs	Internal Combustion Engines
LOHC	Liquid Organic Hydrogen Carrier
LT-PEMFCs	Low-Temperature Proton Exchange Membrane Fuel Cells
MCFCs	Molten Carbonate Fuel Cells
MT	Microturbine
O-SOFCs	Oxygen-Conducting Solid Oxide Fuel Cells
PAFCs	Phosphoric Acid Fuel Cells
PEMFCs	Proton Exchange Membrane Fuel Cells
PSA	Pressure Swing Adsorption
PV	Photovoltaic
SI	Spark-Ignition
SOFCs	Solid Oxide Fuel Cells
WP	Wind Power

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1 Introduction

As the global energy demand continues to grow and environmental pollution issues become increasingly severe, traditional energy utilization methods are no longer sufficient to satisfy the sustainable development demands of society and the economy. Therefore, seeking an efficient, clean, reliable, and economical approach to energy utilization is becoming increasingly important. Combined Heat and Power (CHP) systems, which simultaneously produce electricity and heat, have become a research hotspot in contemporary energy due to their high energy efficiency and low carbon emissions. However, most CHP systems still rely on fossil fuels such as oil and natural gas, leading to severe environmental pollution and greenhouse gas emissions. According to the 2021 Energy Statistics Yearbook, natural gas can serve as a transition fuel due to its lower carbon emissions than coal and oil, but it is not the ultimate energy solution.

To further increase energy efficiency and reduce carbon emissions, hydrogen has emerged as one of the most attractive energy carriers because of its zero-carbon characteristic and high energy density. Numerous countries, including Germany [1], Japan [2], America [3], China [4], and others, have proposed strategies for hydrogen energy technology development. Meanwhile, an increasing number of investigations have been conducted on hydrogen production [5], storage [6], and utilization [7]. As part of its application, the integration of hydrogen energy into CHP systems offers the potential for even higher efficiencies, reduced emissions, and improved reliability, making them an attractive option for various applications such as residential, commercial, and industrial energy supply. Consequently, the hydrogen-based CHP system has been deemed a promising technology to replace fossil fuel CHP systems, offering reduced emissions and improved energy efficiency.

Despite the numerous advantages of hydrogen-based CHP systems, their widespread adoption faces several challenges, including system design and optimization[8, 9] and integration with onsite hydrogen production [10, 11]. Consequently, extensive research has been conducted in recent years to address these challenges and explore novel approaches for enhancing the performance and viability of hydrogen-based CHP systems[12-14]. To date, many researchers have reviewed CHP systems [15-18] and hydrogen-related equipment (including engines [19, 20], turbines [21, 22], and fuel cells [23-25]). Existing reviews mostly focus on CHP prime movers [26], CHP systems combined with renewable energy sources such as solar or biomass energy [27, 28], hydrogen applications in power generation and transportation sectors [29], or specific technologies within CHP systems [30, 31]. However, literature is lacking on the hydrogen-based CHP system integrated with hydrogen production and storage.

This paper aims to fill this gap by comprehensively understanding various aspects of hydrogen-based CHP systems. A thorough review of the current research on hydrogen-based CHP systems is presented, emphasizing the advantages and system design characteristics compared to traditional fossil fuel (such as oil and natural gas) CHP systems. The review explores the potential for integrating renewable energy sources into hydrogen production to enhance the sustainability of hydrogen-based CHP systems. By examining various aspects, such as hydrogen production technologies, hydrogen storage methods, and different types of energy equipment for CHP systems, an in-depth understanding of hydrogen-based CHP systems is offered. Meanwhile, the main challenges and opportunities in the field are highlighted, and potential future research directions are outlined to promote the further development of hydrogen-based CHP systems. Additionally, the role of spatial planning and infrastructure design in optimizing these systems' overall performance and cost-effectiveness is discussed. By providing a comprehensive review of hydrogen-based CHP systems, valuable insights are contributed for researchers, policymakers, and industry practitioners working in this field.

The rest of the paper is organized as follows: 1. The main energy sources and configuration of hydrogen-based CHP systems (Section 2), 2. The source and storage of hydrogen for CHP systems (Section 3), 3. The research gaps and challenges in the existing literature (Section 4), and 4. Some concluding remarks (Section 5).

2 Hydrogen CHP systems and main energy sources

According to the energy supply methods, hydrogen CHP systems can be classified into two categories: heat engine-based hydrogen CHP systems (engines and turbines) and electrochemistry-based hydrogen CHP systems (fuel cells).

2.1 Hydrogen internal combustion engines

Internal Combustion Engines (ICEs) convert chemical energy into mechanical energy by burning fuel inside the machine. They are prevalent in power generation, transportation, industry, and agriculture. However, the exhaust gas generated by combustion results in significant energy waste. To address this issue, ICE-CHP systems can recycle low-grade waste heat and improve energy efficiency by utilizing waste heat for power generation and providing heating in buildings or producing domestic hot water [32]. Figure 1 depicts the diagram of an ICE-CHP system, where the engine burns hydrogen or hydrogen-blended fuel for electricity generation and is cooled by an ICE cooler. The waste heat boiler generates low-pressure steam at 100-120 °C or hot water through waste heat recovery. Implementing ICE-CHP systems can significantly increase energy efficiency, reduce waste heat, and produce both electricity and heat for various applications.

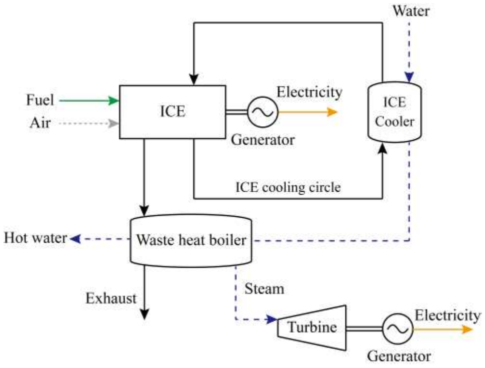


Fig. 1. Typical layout of an ICE-based CHP system [33, 34].

According to the fuel type, ICE-CHP systems can be classified into two types: mono-fuel ICE-CHP systems and blended fuel ICE-CHP systems, which are detailed in the following parts.

2.1.1 Mono-fuel ICE-CHP systems

Gasoline and diesel are the primary fuels for internal combustion engines, with gasoline-powered spark-ignition engines offering lightweight, compact designs and low noise emissions. In contrast, diesel-powered compression-ignition engines provide greater power, high thermal efficiency, and better economic performance. However, gasoline and diesel combustion contribute to significant CO_2 emissions and increased environmental pollution [35]. Table 1 compares the properties of several common fuels.

Table 1

The properties of several common fuels [36-39].

Properties	Unit	Fuel type				
		Gasoline	Diesel	Natural gas	Biodiesel	Hydrogen
Lower heating value	MJ/kg	44.5	43.4	50	39-43	120
Density	kg/m3	0.72-0.78	0.84-0.88	0.72	0.86-0.9	0.09
Boiling point	°C	27-225	180-370 /350-410	-161.5	325-350	-253
Stoichiometric AFR	kg(a)/kg(f)	14.6	14.5	17.12	12.5-14.5	34.3
Stoichiometric CO_2 emissions	mass%	71.9	86	54.9	-	0
Flame speed	m/s	0.37-0.43	0.4-0.8	0.38	0.05-0.37	1.85
Minimum ignition energy	mJ	0.2	0.24	0.31	-	0.02
Cetane number	-	-	52	-	49-56	-

Latent heat of vaporization	kJ/kg	305	270	509	<230	-

Natural gas is abundant, low in price and carbon content, which can be used as fuel for micro-CHP systems based on SI engine [39]. However, low combustion temperature and long ignition delay periods will reduce the overall efficiency and cannot solve the problem of CO_2 emissions [40]. Biodiesel is a kind of renewable biofuel and can reduce the emission of particles, hydrocarbon and CO. besides, the emission of CO_2 can be ignored [41]. However, compared with natural gas, the cost of biodiesel is higher with the same power output [42].

Hydrogen has a higher calorific value than gasoline and diesel, providing almost three times more energy than diesel with the same mass. It also has low CO_2 emissions and a minimum ignition energy of only 0.02 mJ, with the efficiency of hydrogen CHP and Combined Cooling, Heating, and Power (CCHP) is equivalent to that of diesel [43]. However, using pure hydrogen fuel in ICEs remains challenging due to its fast combustion speed and high-temperature combustion, which can lead to abnormal combustion, poor thermal efficiency of internal combustion engines, and high nitrogen oxide emissions [44]. Table 2 summarizes some research and conclusions on hydrogen-fueled ICEs.

Table 2

Research of hydrogen-fueled ICEs.

Author	Engine type	Fuel	Conclusions
Smirnov et al.[45]	SI engine	H_2	The dependence of ignition delay time on pressure for hydrogen-oxygen mixtures is non-monotonous, with three characteristic regions. Simulations of hydrogen premixed and non-premixed combustion showed a transition process from deflagration to detonation.
Szwaja et al.[46]	SI engine	H_2	Fast and unstable combustion initiated by spark discharge can cause light knock, which is harmful to the engine. Unburnt hydrogen auto-ignition at the end of combustion can cause a heavy knock, which can damage the engine in a shorter time.
Hamada et al. [47]	SI engine	H_2	Regarding spark ignition timing, it can prevent abnormal combustion in the case of a richer mixture and early injection start.
Lee et al. [48]	CI engine	H_2	A hydrogen-fueled CI engine is feasible, but it requires a high hydrogen-air pre-mixture compression ratio for the cold start (at least around 32), which decreases to 26 with an increased equivalence ratio under firing conditions.
Yadav et al. [49]	CI engine	H_2	A hydrogen-enriched engine has maximum efficiency with around 70% of full load. At 70% of full load, the optimal injection timing of the hydrogen-fueled engine was found to be at 20°CA BTDC with a flow rate of 120g/h.
Sun et al. [50]	CI engine	H_2	Evaluation of ICEs cycle change by the COV_{imep} parameter found that it decreases as the fuel-air ratio increases, and quickly decreases as the throttle position increases when the throttle position is less than 20%.

* COV_{imep}, a parameter indicating the degree of variation in the combustion cycle of an engine.

2.1.2 Blended fuel ICEs

Diesel Dual Fuel (DDF) combustion can address the problem of abnormal combustion and emissions to some degree. The peak power of hydrogen-diesel engines is improved by 14% compared to mono-diesel engines [51], and the thermal efficiencies are comparable [52]. Blended fuel can also reduce carbon and NO_x emissions of CHP systems. As the hydrogen content increases, the CHP power-to-heat ratio increases, and higher power efficiency can be achieved [53]. However, increasing hydrogen content will cause incomplete combustion [40] and abnormal combustion when the hydrogen content exceeds 50% under high load conditions [54]. Table 3 compares the emissions of several hydrogen-blended fuels in ICEs according to relevant literature.

Table 3

The emissions of several hydrogen-blended fuels.

Author	Engine type	Fuel (H_2 content)	Brake thermal efficiency	HC	CO	CO_2	NO_x	Comparison object
Dahake et al. [55]	CRDI engine	H_2/diesel (-)	↑	↓	↓	↓	↑	Diesel
	CRDI+EGR	H_2/diesel (-)	↑	↓	↓	↓	↓	Diesel
			↓	↑	↑	↑	↓	No EGR H_2/diesel
Kanth et al. [56, 57]	CI engine	H_2-enriched Karanja biodiesel (10%, 20%)	↓	↓	↓	↑	↑	Diesel
		H_2-enriched rice biodiesel (10%, 20%)	↓	↓	↓	↑	↑	Diesel
			↓	↓	↑	↓	↓	H_2-enriched Karanja biodiesel
Bhasker et al. [58]	lean burn SI engine	H_2/natural gas (5%, 10%)	↑	↓	-	-	↓	Natural gas
Tian et al. [59]	lean burn SI engine	H_2/alcohols (10%)	↑	↓	↓	↓	↑	Alcohols
Dimitrova et al. [60]	HCCI engine	H_2/H_2O_2 (H_2O_2 10%)	↑	-	-	-	↓	H_2
Cong et al. [61]	SI engine	H_2/Dimethyl ether (Dimethyl ether 1.4%-3%)	↑	↑	↑	-	↓	H_2

*EGR, exhaust gas recirculation.

The Wobbe Index (I_W) is used as an indicator to analyze the compatibility of electrical appliances with different types of fuels. For any given orifice, all gas mixtures with the same I_W will transfer the same amount of heat [62]. The I_W of pure hydrogen is 48 MJ/Nm^3, which is within the safe range acceptable for most burners. But it should be noted that most combustion units that use natural gas cannot use hydrogen directly. This is because the combustion rate of hydrogen is increased compared to natural gas. Therefore, controlling the flame becomes challenging. Therefore, special burners need to be installed in existing combustion plants to use hydrogen as a direct fuel.

2.2 Hydrogen gas turbines

2.2.1 CHP systems of gas turbine

Gas Turbines (GTs) are widely used in various electricity plants to produce electricity. High-grade heat energy is used to generate steam or directly used in industry. Low-grade heat energy is used to produce hot water or local heating. In GTs, fuel is injected into the combustion chamber and blended with the air from the compressor to trigger combustion. The kinetic energy and part of the thermal energy are converted into mechanical energy by using the combustion gas exhaust velocity. The residual thermal energy can be used to heat the compressed air entering the combustion chamber through the heat exchanger and can also be used for heating or domestic hot water in CHP systems. Compared with ICEs, GTs have fewer emissions and pollution, and the emitted heat is easy to be collected, which is suitable for high requirements of heat sources and emissions. In addition, the temperature of GTs' exhaust gas is high, which is about 540°C. Then the high-temperature exhaust gas can be used as the heat source of the boiler to generate steam for electricity generation in the steam turbines, which is called the Gas Turbine Combined Cycle (GTCC) [63]. In GTCC systems, the thermal efficiency of the steam turbine is 25-34 %, the gas turbine is 32-42 %, and the thermal efficiency of GTCC is 49-62 % [64]. Figure 2 is the schematic of GTCC systems.

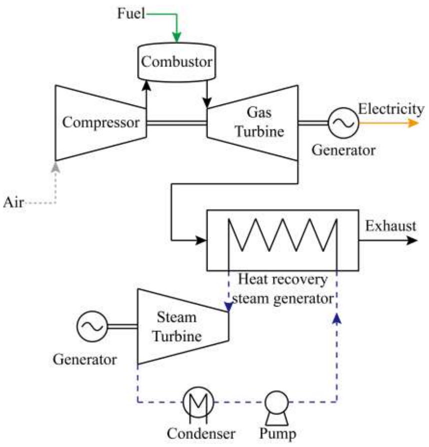


Fig. 2. Typical layout of a GTCC system [64].

2.2.2 Hydrogen fuel gas turbines

Pure hydrogen or hydrogen-blended fuel can be used as an alternative fuel for GTs to achieve carbon reduction. Due to the limitation of the thermodynamic cycle, it is insignificant to reduce carbon emissions by increasing thermal efficiency. Pure hydrogen or blended fuel with hydrogen can be used as a substitute fuel for GTs to achieve carbon reduction. The most common proportion of mixed fuel is 30 vol.-% hydrogen, and higher mixing ratios, about 77 vol.-% and 100 vol.-% hydrogen are also used in small scale [65]. The research of Cappelletti et al.[66] proved the operability of pure hydrogen as GT fuel and found that it can reduce NO_x emissions (the best arrangement can limit the NO_x emissions to 17 ppm), but may also cause safety issues. Figure 3 compares the gas consumption and thermal efficiency of the systems under different inlet pressures in a GT with a net power of 50 MW.

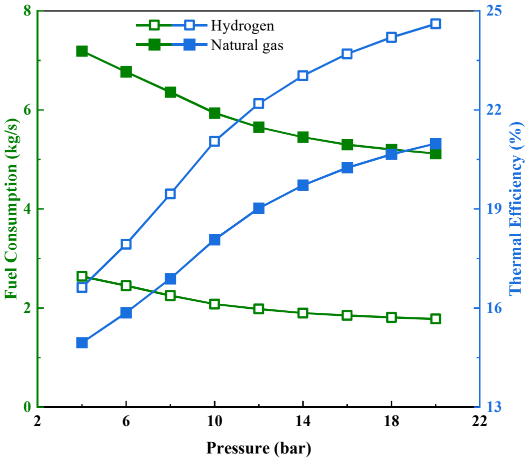


Fig. 3. Hydrogen and natural gas consumption, and system thermal efficiency at varying inlet pressures in a 50 MW GT [67].

Microturbines (MTs) are small GTs suitable for distributed energy resources with high flexibility. The electrical efficiency of MT is 22%-28%, and the total efficiency is 63%-70% [17]. The generated power is small (about 25-300kW), and it has the characteristics of fast installation and easy maintenance. MTs are also affected by outdoor environmental conditions[68]. Compared with the 15 °C ISO conditions, the electrical efficiency of MT-CHP systems decreases by 0.51%, the thermal efficiency increases by 0.7%, and the thermal-to-electricity power ratio increases by 1.3% when the ambient temperature increases by 1 °C [69]. Besides, extremely high ambient temperature conditions such as heat waves and droughts can increase the power load, reduce the efficiency of gas turbines, and affect the operation of the grids [70]. They can be integrated into the smart grid as CHP units [71], or combined with fuel cells or thermal cycle units to form combined cycle systems.

2.3 Hydrogen fuel cells

Fuel cells (FCs) are more compatible with distributed generation systems' ideal requirements compared to many other devices [72]. The fundamental structure of a fuel cell includes a cathode, anode, and electrolyte. Fuel cells are connected in series to form a stack structure, achieving the desired voltage. During electricity generation, fuel cells also produce heat, which can be used for heating, domestic hot water supply, or stored in energy storage mediums. The five common hydrogen fuel cells used in FC-CHP systems are Alkaline Fuel Cells (AFCs), Proton Exchange Membrane Fuel Cells (PEMFCs), Solid Oxide Fuel Cells (SOFCs), Phosphoric Acid Fuel Cells (PAFCs), and Molten Carbonate Fuel Cells (MCFCs). However, considering the similarity of system structure, operating temperature, and principle, the following only describes in detail the application of AFCs, PEMFCs, and SOFCs to CHP systems. Table 4 compare the chemical reactions and characteristics in various hydrogen fuel cells. Fuel cells produce no greenhouse gases or harmful pollutants during operation, giving them a significant advantage over traditional CHP systems. By combining electrical and thermal efficiencies, FC-CHP systems can achieve a total efficiency of nearly 90%, higher than traditional CHP systems [73].

Table 4

Chemical Reactions and characteristics of fuel cells [74-80].

FC type	AFC	SOFC	PEMFC	PAFC	MCFC
Anode reaction	$H_2+2OH^- \rightarrow 2H_2O+2e^-$	$H_2+O^{2-}\rightarrow H_2O+2e^-$ $H_2\rightarrow 2H^++2e^-$	$H_2\rightarrow 2H^++2e^-$	$H_2\rightarrow 2H^++2e^-$	$H_2+CO_3^{2-} \rightarrow H_2O+CO_2+2e^-$
Ion	OH^-	O^{2-}, H^+	H^+	H^+	CO_3^{2-}
Cathode reaction	$\frac{1}{2}O_2+H_2O+2e^- \rightarrow 2OH^-$	$\frac{1}{2}O_2+2e^-\rightarrow O^{2-}$ $\frac{1}{2}O_2+2H^++2e^- \rightarrow H_2O$	$\frac{1}{2}O_2+2H^++2e^- \rightarrow H_2O$	$\frac{1}{2}O_2+2H^++2e^- \rightarrow H_2O$	$\frac{1}{2}O_2+CO_2+2e^- \rightarrow CO_3^{2-}$
Temperature (°C)	60-220	600-1000 (O^{2-}) 400-800 (H^+)	60-85 (LT) 130-220 (HT)	160-220	600-700
Pressure (MPa)	0.5	0.3	1-2	0.1	0.2
Electrolyte	35wt%-85wt% KOH	Ceramics, e.g., YSZ	Polymer membrane	Phosphoric acid	Carbonates, e.g., Na_2CO_3, Li_2CO_3
Anode catalyst	Ni, Pt/C	Ni, Zr	Pt/C	Pt/C	Ni (Cr, Al)
Cathode catalyst	Ag, Pt/C	$LaMnO_4$	Pt/C	Pt/C	NiO
Electrical efficiency	45-60%	50-60%	40-60%	40-45%	45-55%
CHP efficiency	68-76%	79-87%	60-80%	85-90%	85%
Available fuel	Pure hydrogen	Natural gas, Hydrogen, CO, HC	Hydrogen	Natural gas, Hydrogen, LPG	Nature gas, Hydrogen, LPG
Oxidant	O_2	Air	Air	Air	Air
Sensitive impurity	S, CO_2	S	S, CO, NH_3	S	S
Electrolyte storage matrix	Asbestos	-	-	SiC	$LiAlO_2$
Lifetime (h)	8k	80k	80k	60k	20k
Stack output power (kW)	1-100	5-3000	1-100	150-400	300-1000
Start time	1-10min	>30min	1-5s	1-10min	>30min
CO tolerance	<10ppm	<10%	<10ppm (LT) <1% (HT)	<1%	<10%
CO_2 tolerance	<100ppm	<10% (O^{2-}) <5% (H^+)	<15%	<15%	<15%
NH_3 tolerance	-	<0.5%	<0.1ppm	<4%	-

*LT, low-temperature. HT, high-temperature.

FC-CHP systems consist of one or more fuel cell stacks for energy production and several subsystems, including the fuel process system, reactant delivery system, thermal management system, and control system. The fuel process system is mainly for fuel preprocessing to convert fuel into an acceptably purity supply of hydrogen. The fuel process system primarily preprocesses fuel into an acceptably pure hydrogen supply. The reactant delivery system transport's reaction gas, water, and steam through a compressor or pump, which are also the primary noise sources in CHP systems (40-55 dB for FC-CHP systems and 95-99 dB for ICE-CHP systems). Thermal management systems recover, utilize, and store the heat produced by fuel cell stacks using liquid, vapor, or air. The control system regulates power stability and ensures system safety, acting as the system's brain [81]. FC-CHP systems have higher efficiency and lower CO_2 emissions than traditional CHP systems. More importantly, FC-CHP systems provide a wide range of operation temperatures and power supply, making them suitable for widespread use in industrial or residential buildings in the future.

2.3.1 Alkaline fuel cell CHP systems

AFCs, the earliest fuel cells to be used, and are currently the most mature fuel cell technology with advantages such as low cell-component costs, high startup speeds, and low operating temperatures [82]. They have been used in aerospace projects and can be applied to micro-CHP systems in buildings.

In AFCs, a KOH aqueous solution serves as the electrolyte and reacts with CO_2 to form K_2CO_3, necessitating CO_2 removal from the air before entering the cathode. The schematic of an AFC-CHP system is shown in Figure 4. The reaction is generally exothermic, causing the electrolyte temperature to rise and some of the water to be discharged from the fuel cell stacks. The electrolyte and airflow from the cathode enter the electrolyte tank, where the water in the electrolyte evaporates and is exhausted by the airflow. The electrolyte then transfers heat through a heat exchanger and returns to the fuel cell stack. The primary purpose of the electrolyte cycle is to maintain the electrolyte concentration and recover the reaction heat [77].

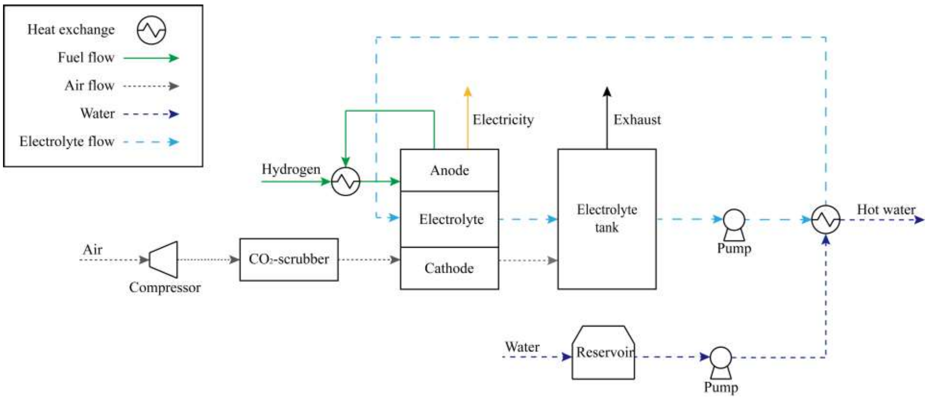


Fig. 4. Typical layout of an AFC-based CHP systems [77].

AFCs require highly pure hydrogen and may suffer from electrolyte leakage. However, with the gradual replacement of traditional liquid electrolytes by solid Anion Exchange Membranes (AEMs), Anion Exchange Membrane Fuel Cells (AEMFCs) are gaining increasing attention. AEMFCs and AFCs share a similar reaction principle, with the main difference being the electrolytes used; AFCs employ a KON aqueous solution, while AEMFCs use anion exchange membranes. The water consumed in the cathode is mostly generated by the anode, which is transmitted by back diffusion through AEM, and the water in the cathode can also be moved to the anode by electro-osmotic drag. AEMFCs operate at standard temperatures of 40-80 °C and can reach up to 120 °C under high-temperature operation [83].

Compared to traditional AFCs, AEMFCs exhibit better CO_2 tolerance, prevent electrolyte leakage and offer superior anion conductivity [84]. Increasing the operating temperature of AEMFCs will impact their performance. Research by Yassin et al. [83] explored the effect of operating temperature on AEMFC performance, revealing a significant improvement as the temperature increased from 45°C to 120°C. Under certain conditions, the stability of AEMFCs also improves with higher temperatures. And the simulated curve is basically consistent with the curve measured by Douglin et al. [85]. Compared with acid fuel cells, i.e., PAFCs and PEMFCs, the high pH of AFCs and AEMFCs provides better corrosion resistance and lower component costs, offering substantial commercial potential [84]. However, challenges remain before AEMFCs can achieve optimal performance, such as AEM thickness and membrane stability above 80°C.

As AEMFCs continue to develop, they may eventually replace PEMFCs.

Currently, AEMFCs are still in the experimental research stage and have yet to be commercialized. However, AFCs have some demonstration projects applied to CHP systems. In Lower Saxony, northern Germany, AFC Energy and Air Products collaborated on the world's first large-scale demonstration of a 500 kW alkaline fuel cell system (POWER-UP) [86]. Canada's Alkaline Fuel Cell Power Corp launched a micro fuel cell commercial CHP system (PWWR Flow) in 2022 for use in multi-residential and commercial applications [87].

2.3.2 Proton exchange membrane fuel cell CHP systems

PEMFCs, similar to AFCs, exhibit low operating temperatures and rapid start-up times, making them suitable for small and medium-sized CHP systems. These fuel cells also demand high fuel purity, but they demonstrate better CO_2 tolerance and employ a solid electrolyte membrane. PEMFCs can be classified into Low-Temperature Proton Exchange Membrane Fuel Cells (LT-PEMFCs) and High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFCs) based on their operating temperatures.

LT-PEMFCs utilize a water-based acidic polymer membrane as an electrolyte and operate at lower temperatures (60-85°C), capable of achieving a cold start at approximately -30°C [88]. Figure 5(a) illustrates an LT-PEMFC-CHP system, where the hydrogen source is steam-reformed natural gas. In contrast to AEMFCs, water produced in PEMFCs' cathodes evaporates on the catalyst layer, diffuses through the gas-diffusion and microporous layers, and finally condenses on colder surfaces. The reaction gas typically expels the condensed water to prevent a reduction in mass transfer velocity within the cathode diffusion layer. Additionally, 80-90% of the heat in PEMFCs is generated in the cathode catalyst layer, which can be removed by various cooling technologies or repurposed using heat recovery technology [89]. In the anode, the primary focus is on pre-processing gaseous fuel. CO present in steam-reformed hydrogen can poison the Pt catalyst, affecting fuel cell power and lifespan [90]. Consequently, it is crucial to reduce the CO content in reformed hydrogen-rich syngas to below 10 ppm using Pressure Swing Adsorption (PSA) or catalyst oxidation in a CO-scrubber [91]. LT-PEMFCs' polymer membrane requires high humidity, necessitating the maintenance of a water-saturated state for optimal performance. Thus, the hydrogen and air humidity must be increased via a humidifier.

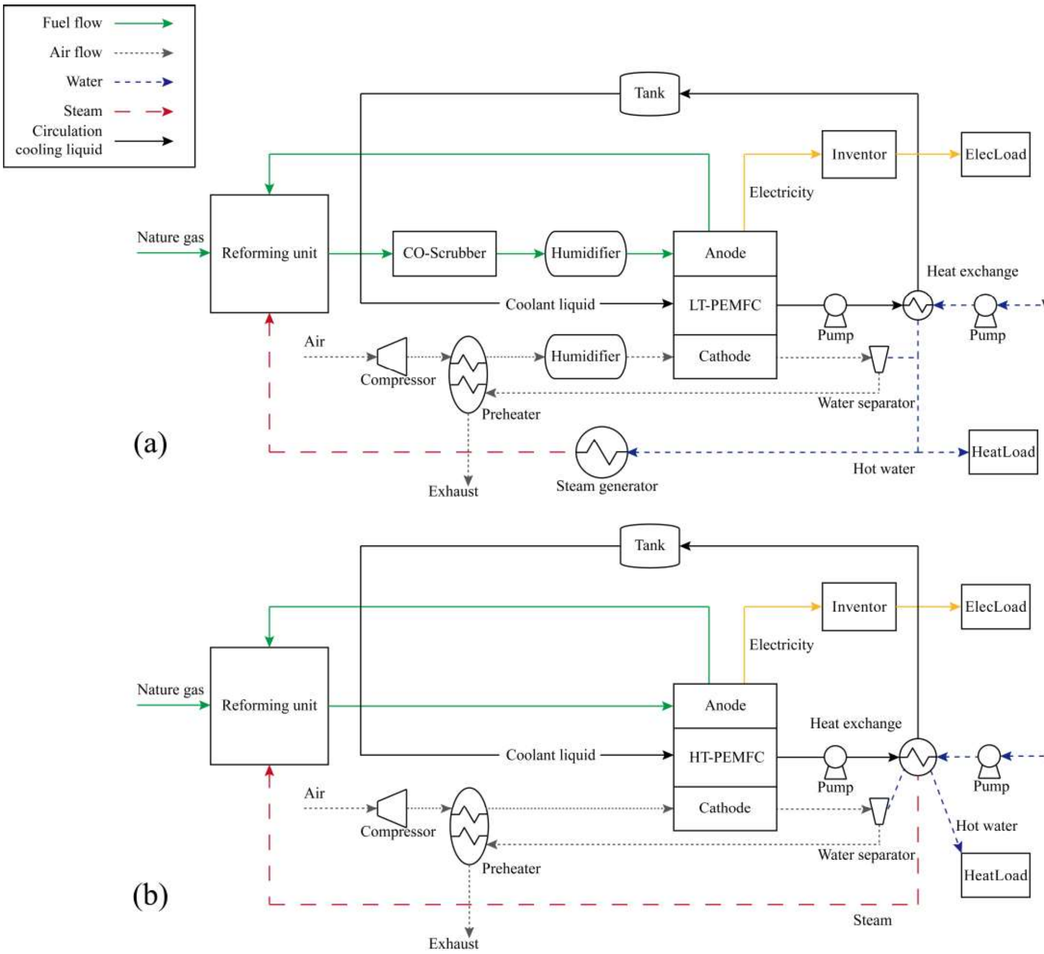


Fig. 5. (a) Typical layout of a LT-PEMFC-based CHP system. (b) Typical layout of a HT-PEMFC-based CHP system.

Compared to LT-PEMFCs, HT-PEMFCs operate at elevated temperatures and exhibit higher CO tolerance due to reduced CO adsorption on the Pt catalyst [92]. Furthermore, HT-PEMFCs employ a modified polymer membrane (transitioning from water-based to inorganic acid), enhancing membrane strength and thermal stability at high temperatures (130-220°C), reducing humidity dependence, and improving transmission capacity. As a result, HT-PEMFC-CHP systems have a more simple fuel pre-processing structure [93], as shown in Figure 5(b). However, HT-PEMFCs cannot achieve cold starts like LT-PEMFCs. Simultaneously, HT-PEMFC systems generate a significant amount of low-grade energy, making them suitable for CCHP systems based on adsorption refrigeration [94].

2.3.3 Solid oxide fuel cell CHP systems

In contrast to AFCs and PEMFCs, SOFCs have lower hydrogen purity requirements and exhibit greater CO tolerance in reforming gas. These fuel cells can utilize natural gas as fuel, without the need for noble metal catalysts, which consequently reduces costs to a certain extent. Typically, SOFCs are employed in large-scale CHP systems (100 kW - 1 MW), the necessitating rapid temperature rises from 20°C to 800°C during start-up. The excessive temperature gradient resulting from this rapid heating process can lead to SOFC damage, making cooling and thermal management key research areas [95]. The high operating temperature also results in longer start-up times for SOFCs compared to PEMFCs, but it simultaneously provides the required heat for fuel autothermal reforming. Researchers are also investigating compact SOFC stacks for small-scale SOFC-CHP systems (<5 kW) to achieve faster and more stable start-ups and operations [96].

SOFCs can be categorized into Oxygen-Conducting Solid Oxide Fuel Cells (O-SOFCs) and Proton-Conducting Solid Oxide Fuel Cells (H-SOFCs), depending on the electrolytes conducting ions (chemical reactions are shown in Table 4) [97]. Among fuel cells, SOFCs exhibit the highest operating temperatures. O-SOFCs, characterized by oxygen ion conduction, typically function at temperatures exceeding 600°C, whereas H-SOFCs, with hydrogen ion conduction, generally operate within a 400-800°C range [98]. Under normal conditions, SOFCs demonstrate an electricity generation efficiency of 50-60%, which can increase to 60-70% when integrated with GTs. The GT type also impacts system efficiency. Figure 6 illustrates a SOFC-GT-CHP system based on autothermal reforming of natural gas. The reforming element can either be incorporated into the SOFC anode or situated externally (related contents detailed in section 3.1). As the majority of water produced in the system is present as steam at the O-SOFC anode, certain O-SOFC systems utilize internal autothermal reforming within the anode. In contrast, H-SOFCs generate water at the cathode, resulting in inadequate steam to promote the water-gas shift reaction, making natural gas electrochemical autothermal reforming inappropriate for these systems [99].

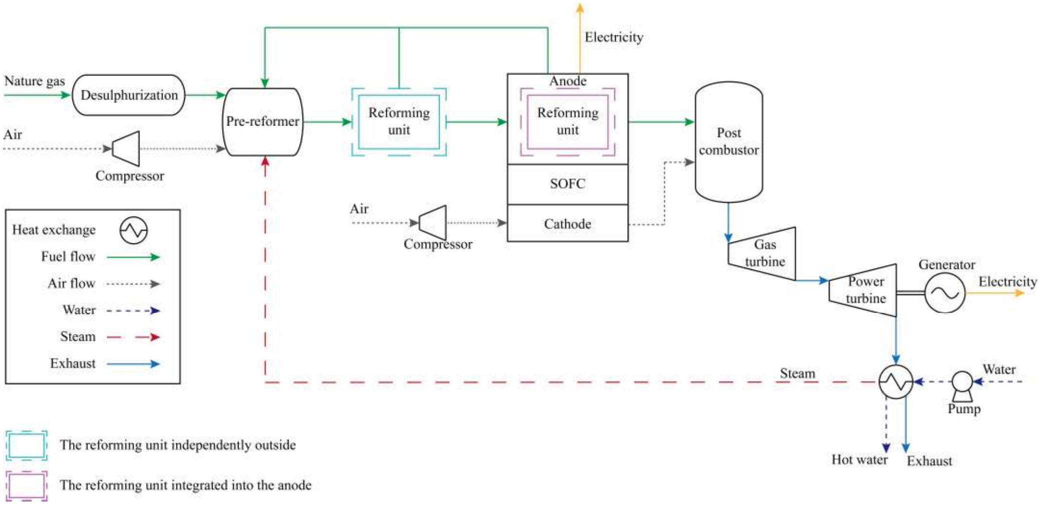


Fig. 6. Layout of a SOFC-GT-based CHP system with reforming unit.

In addition to being combined with GTs, SOFCs can also be integrated with other thermodynamic devices to drive thermodynamic cycles that recover waste heat while generating electricity, such as the organic Rankine cycle [100], Rankine cycle [101], absorption power cycle [102], Stirling cycle [103] and others. As shown in Figure 7, the steam generator's heat is derived from SOFC exhaust. This mode enhances system efficiency, reduces fuel consumption, and decreases costs. Moreover, SOFCs can be applied to CCHP systems [104].

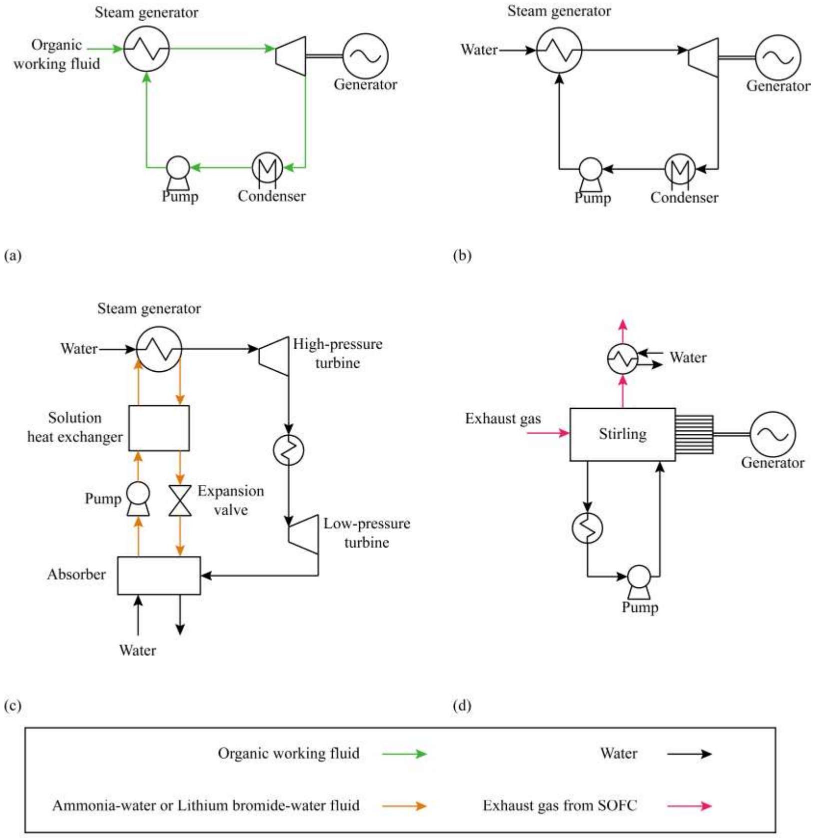


Fig. 7. Typical layout of four thermodynamic cycles (a. organic Rankine cycle, b. Rankine cycle, c. absorption power cycle, d. Stirling cycle).

However, Elmer et al.[105] emphasized that despite fuel cells being considered key technologies for realizing future low-carbon infrastructures, numerous challenges remain. These include high fuel cell costs, difficulty in hydrogen fuel supply, and the impact of auxiliary equipment. Additionally, fuel cell degradation and failure reduce cell lifespan; however, most current methods for proving durability through long-term operation tests are not feasible. New technology is needed to predict fuel cell lifetimes within relatively short test durations to expedite technology development cycles [96]. Thus, fuel cells still hold significant potential for further development.

2.4 Hydrogen CHP systems application projects

Nowadays, CHP systems are being vigorously developed and distributed around the world. For instance, in the United States, as of December 2020, over 4,700 CHP facilities have been installed across the country, with an installed capacity exceeding 81 gigawatts, representing 8% of the nation's total electricity capacity. Approximately 78% of these systems are utilized for commercial purposes, while 16% are designated for industrial use [106]. The United Kingdom has also strongly promoted CHP applications; in 2020, there were 2,659 CHP sites in the UK, with an installed capacity of around 11 GW [107].

Most existing CHP systems rely on fossil fuels as energy sources, while hydrogen-based CHP systems are mainly limited to laboratory or pilot demonstrations. Table 5 shows the project of hydrogen CHP in the near term. Japan leads the world in the development and deployment of fuel cell micro-CHP. Since the introduction of ENE-FARM in 2009, nearly 400,000 domestic FC-micro-CHP systems have been installed in Japan, generating electricity and heat through the chemical reaction between hydrogen extracted from natural gas and atmospheric oxygen. By 2030, Japan aims to have ENE-FARM systems installed in 10% of households [108]. Duke Energy operates a CHP system that supplies steam and 2.8 MW of power to Clemson University, while also providing 15 MW of power to the public electricity grid. The system can operate in island mode during grid interruptions [109]. The UK's first 100% hydrogen CHP system, installed by 2G Energy at Kirkwall Airport, collaborates with the airport's existing heating systems to satisfy the thermal and electricity needs of major airport buildings [110]. APEX's hydrogen plant in Germany, which includes a CHP unit, has a 2 MW electrolytic hydrogen production capacity, a 100 kW power output from fuel cells, and 1 MWh battery storage, making it Europe's largest grid-connected hydrogen plant [111].

Table 5
Project of hydrogen CHP.

Project	Country and Year	Type of CHP	CHP equipment	Generating capacity	Thermal capacity	Market Sector
ENE-Farm	JPN, since 2009	Fuel Cell	Panasonic PEMFC (700W), Aisin SOFC (700W), Kyocera SOFC (400W)	700W	-	Residential
Clemson University Duke Energy	South Carolina, US, in 2020	Combined Cycle Gas Turbine	Siemens SGT-400 combustion turbine, Howden TWIN steam turbine, heat recovery steam generator	17.8 MW	125, 000 lb/hr steam	Institutions
Kirkwall Airport CHP Unit	Orkney, UK, in April 2021	Engine	2G Energy's agenitor 406	170kW	183kW	Municipal
APEX Energy hydrogen power plant	Rostock-Laage, GER, in 2020	Engine	2G Energy's agenitor 404c	115kW	129kW	Industrials

3 Hydrogen management for CHP systems

3.1 Hydrogen production for CHP systems

Hydrogen can be produced from hydrogen-containing raw materials such as fossil fuels, water and biomass [112]. At present, the most economical approach is constructing a hydrogen production station near a continuous operation hydrogen CHP system to save on storage and transportation costs [113].

3.1.1 Fossil fuels for CHP hydrogen production

Presently, hydrogen in CHP systems mainly comes from methane reforming, as depicted in Figure 8. Large hydrogen plants, often located in suburban areas, entail extra costs and energy consumption for transportation. However, connecting small reforming hydrogen production plants directly to CHP systems can considerably decrease transportation expenses.

Traditional high-pressure steam methane reformers are illustrated in Figure 9(a). Methane reforming requires 700-850°C and proceeds to high- and low-temperature water-gas shift units for CO and H_2O to CO_2 and H_2 conversion. The gas is then purified to separate oxycarbide and hydrogen-rich gas, which undergoes PSA to hydrogen purification for compression and storage. Despite rapid steam reforming reactions, substantial energy requirements increase costs and lower conversion rates [114].

Autothermal reforming, depicted in Figure 9(b), uses oxygen and steam in the reformer without external heat input. Most heat for reactions comes from internal oxidation, while oxygen provision influences hydrogen production and temperature gradients. The hydrogen produced still contains CO, requiring the same purification as traditional steam reforming [115]. External equipment increases system costs, and oxygen production for autothermal reforming is expensive due to low-temperature processes. [92]. Safety concerns arise from explosive CH4/O2 mixtures, and carbon deposition affects cell's performance. However, integrating autothermal reforming into O-SOFC anodes mitigates these issues and uses anode-generated heat to balance electrode temperature distribution [116].

Figure 9(c) demonstrates the electrochemical autothermal reforming of methane, primarily using heat generated by the O-SOFC anode to produce syngas (CO and H_2). Nanofibrous Ni/CeO_2-Al_2O_3 coatings on anode surfaces or porous frames enable methane pre-reforming and resolve current collection issues [116]. Methane undergoes direct CO_2 or indirect O^{2-} reforming on the catalyst layer, with syngas oxidation by O^{2-}. Then, oxidation-generated steam and CO_2 react with methane in the catalyst bed, producing syngas. This method effectively utilizes the heat generated by the anode to mitigate temperature distribution imbalances within the electrode.

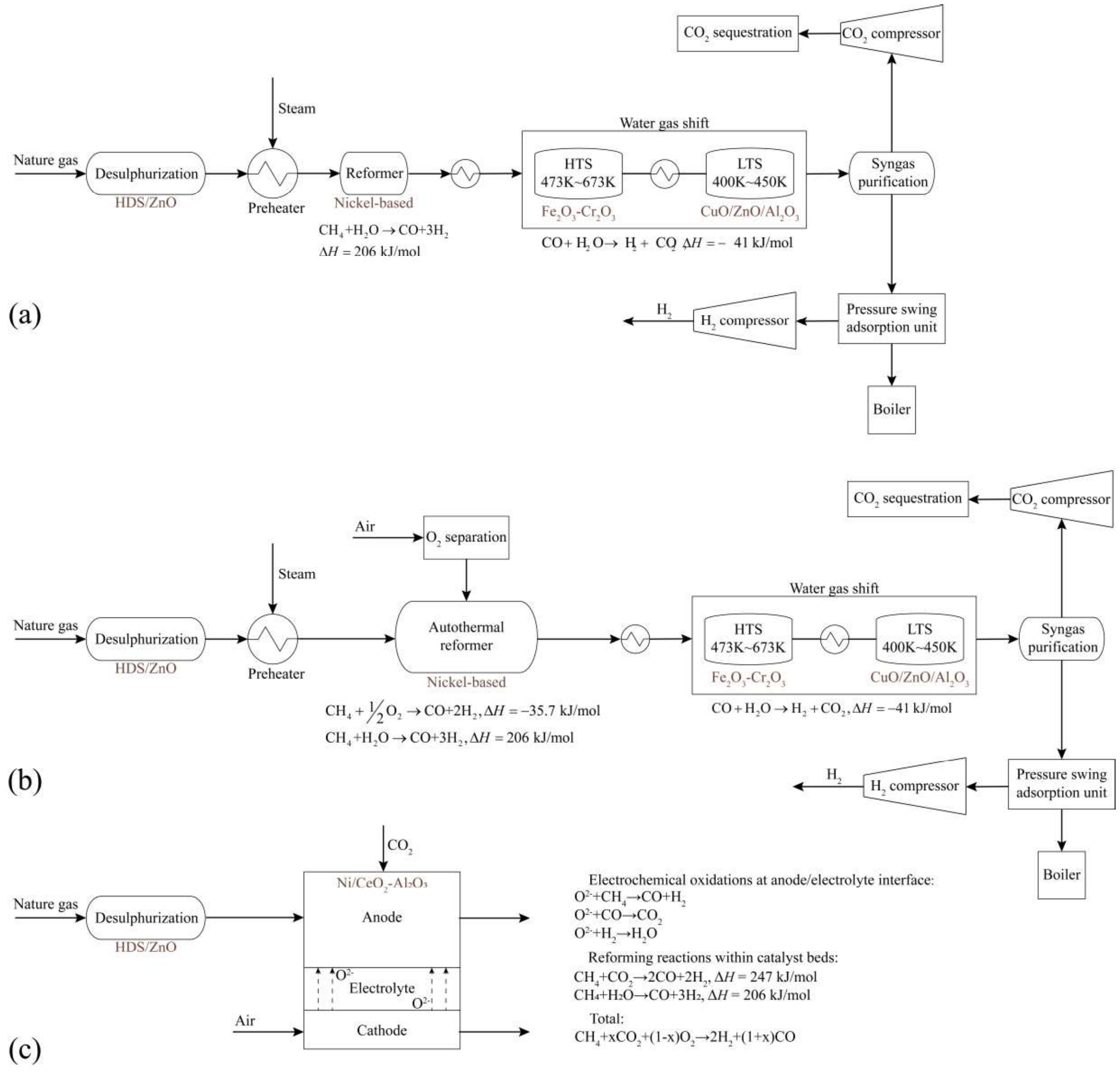


Fig. 8. Three fossil fuel reforming methods for hydrogen production. (a) Steam reforming with CCS. (b) Autothermal reforming with CCS. (c) electrochemical autothermal reforming[114, 117, 118].

Besides methane, methanol, an alternative hydrogen production source, offers low reforming temperatures (200-300°C) and high H/C ratios [119]. Researchers currently focus on methanol reforming and adsorption for vehicle hydrogen production [120]. Methanol can also fuel Direct Methanol Fuel Cells (DMFCs), with High-temperature DMFCs with above 100°C suitable for CHP systems, but research is limited. Table 6 shows several commercial hydrogen production equipment that can be combined with the hydrogen CHP systems.

Fossil fuel hydrogen production generates oxycarbide. Carbon Capture and Storage (CCS) offers a promising solution for continued fossil fuel use, significantly reducing carbon emissions during hydrogen production. Without CCS, hydrogen costs from steam and autothermal reforming are similar; with CCS, autothermal reforming is cheaper [117]. However, CCS technology remains expensive and immature for practical application [121], and carbon sequestration techniques, like CO_2 injection into deep geological layers, face landform constraints [122], hindering widespread adoption.

Table 6

Commercial hydrogen production equipment

Equipment	Manufacturer	Hydrogen capacity (Nm^3/h)	Hydrogen pressure (bar)	Raw material	Methods
HYDROPRIME [123]	Linde Engineering	330-32000	13.8	Methane	Steam reforming
Hydroform C [124]	Mahler AGS	200-10000	10-30	Methane	Steam reforming
Hydroform M [125]	Mahler AGS	200-5000	10-30	Methanol	Steam reforming
SynCOR [126]	TOPSOE	-	-	Methane	Autothermal reforming
Topsoe's SOEC [127]	TOPSOE	32000	2	Water	SOEC electrolysis
HySTAT [128]	Cummins	10-100	10	Water	Alkaline Electrolyzers
HyLYZER [128]	Cummins	200-4000	30	Water	PEM Electrolyzers

3.1.2 Hydrolysis for CHP hydrogen production

Water, a rich hydrogen source, can produce hydrogen through electrolysis, generating only hydrogen and oxygen. Seawater is also suitable for hydrogen production [129]. Power-to-Gas systems convert off-peak or excess renewable energy into electricity for water electrolysis, suitable for hydrogen production in CHP systems. However, water electrolysis is energy-intensive, and using fossil-fuel-generated electricity is unsustainable. Renewable energy-based electrolysis is more feasible and environmentally friendly, but large electricity consumption and low production efficiency limit its rapid adoption. Additionally, Catalysts can improve water decomposition efficiency [130], and photoelectrochemical methods can reduce energy consumption [131].

Figure 9(a) compares four water electrolysis methods. Alkaline and PEM electrolysis is commercialized, while Solid Oxide and AEM electrolysis remain in research. Efficiency depends on operating temperature and heat source efficiency [132]. Compare with Table 4, it can be seen that the electrolytic cell is a fuel cell with reverse operation.

Photocatalytic hydrogen production directly converts solar energy into chemical energy, offering better flexibility and cost than PV hydrogen production. However, low efficiency hinders large-scale application, and suitable catalysts remain a research focus [133]. These catalysts have a high demand for visible light, and their excitation is limited by the wavelength of visible light [134]. Despite a Japanese research team's breakthrough in large-scale photocatalytic hydrogen production [135], commercial application is still far off.

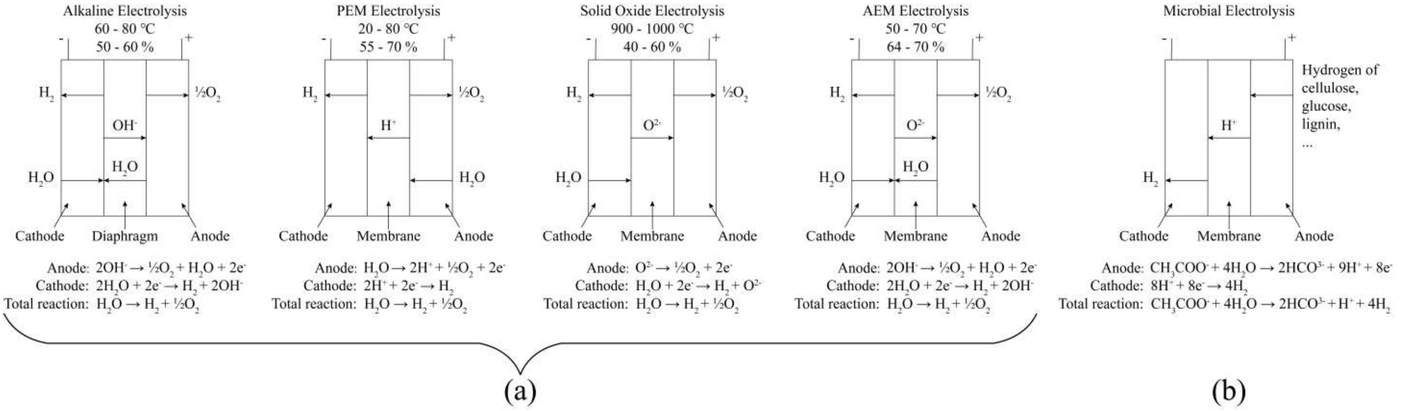


Fig. 9. Reaction principles, temperatures, and efficiencies of five electrolysis methods for hydrogen production. (a) Water electrolysis methods. (b) Microbial electrolysis method. [136-138].

Thermochemical cycles can also decompose water using thermal energy from geothermal, concentrated solar, or nuclear reaction waste heat [139](shown in Table 7). Although thermal energy is cheaper than electric energy and environmentally friendly, this method is inefficient. Metal oxide thermochemical cycles require extremely high temperatures (1350°C-1600°C) [140], leading to significant heat loss. Currently, the efficiency and cost of thermochemical cycles for hydrogen production are higher than those of electricity generation, and long-term operation remains a challenge. However, researchers still believe this technology holds significant potential for development.

Table 7

Comparison of thermochemical cycle hydrogen production methods [139, 141].

Criteria	SnO/SnO_2	IS cycle	UT-3 cycle	Cu-Cl cycle	Mg-Cl cycle	Westinghouse cycle
Thermal efficiency	42%	47-60%	35-50%	40-45%	12.7-45%	45%
Maximum process temperature (°C)	1600/600	850	750	550	450	870
Numbers of reactions	2	3	4	4	3-4	2
Separation process	Solid/gas, gas/gas	Gas/gas, liquid/liquid	Solid/liquid, solid/gas	Gas/liquid	Solid/gas	Gas/liquid

3.1.3 Biomass for CHP hydrogen production

Biomass hydrogen production holds great potential for sustainable development due to its low-cost materials and environmental benefits. Currently, biomass-based hydrogen primarily comes from algae [142], lignocellulose [143], or sludge with various microorganisms [144]. With sunlight and water, photosynthetic bacteria can break down water into H_2 and O_2, while in the absence of sunlight and oxygen, anaerobic bacteria ferment biomass into H_2, CO_2, and volatile fatty acids [145]. Table 8 compares four biomass hydrogen production methods, and Figure 9(b) illustrates the microbial electrolysis cell schematic. During the reaction, the electrochemical potential generated by anodic oxidation is insufficient for the cathodic hydrogen evolution reaction, necessitating additional voltage (0.2V-1.0V) [138].

Table 8

Four Methods for Hydrogen Production from Biomass [132].

Type	Feedstock	Energy	Efficiency	Reaction
Photolysis	Water	Solar	0.50%	$2H_2O \xrightarrow{\text{solar}} 2H_2+O_2$
Photo fermentation	Biomass	Solar	0.10%	$CH_3COOH+2H_2O \xrightarrow{\text{solar}} 4H_2+2CO_2$
Dark fermentation	Biomass	Biochemical	60-80%	$C_6H_{12}O_6+2H_2O\rightarrow 2CH_3COOH+2CO_2+4H_2$
Microbial electrolysis cell	Biomass	Electric	78%	$CH_3COO^-+4H_2O\rightarrow 2HCO^{3-}+H^++4H_2$

3.2 Hydrogen storage for CHP systems

Hydrogen storage technologies are crucial for hydrogen-centric CHP systems in grids and serve as bridges between hydrogen CHP plants and electricity grids [146]. To compensate for load deficiencies caused by renewable energy fluctuations, off-grid regenerative power systems require alternative energy sources [147]. These systems can store converted hydrogen during normal load periods and transmit it to CHP systems for electricity and heat generation during peak load periods, enhancing scheduling flexibility and addressing the intermittency of renewable energy resources [148]. Furthermore, due to high hydrogen consumption in PEMFC systems (approximately 0.8 Nm^3 of hydrogen per kW), safe, economical, and effective hydrogen storage methods are essential for smooth CHP system operation. Generally, three types of hydrogen storage technologies exist: compression and cryogenic hydrogen storage, hydride hydrogen storage, and porous media hydrogen storage. Table 9 compares several hydrogen storage methods.

3.2.1 Compression and cryogenic hydrogen storage

Currently, the most prevalent hydrogen storage methods are gaseous and liquid hydrogen storage [149]. Gaseous hydrogen storage involves compressing hydrogen into storage tanks at high pressures ranging from 17 MPa to 70 MPa [150]. Common stationary high-pressure gaseous hydrogen storage vessels include seamless storage vessels and multifunctional layered stationary storage vessels [151].

Liquid hydrogen storage entails liquefying and storing hydrogen at low temperatures, around 20 K [152]. Special vessels are necessary to maintain adiabatic conditions under high pressure and to prevent liquid hydrogen from vaporizing when temperatures exceed boiling points [153]. Liquid hydrogen has a high energy density, approximately 3.2 times that of compressed hydrogen at the same volume and 30 MPa [152]. However, the cryogenic hydrogen liquefaction process is highly energy-intensive, and it is challenging to avoid hydrogen loss due to evaporation, resulting in high liquid hydrogen costs [154].

3.2.2 Hydrogen storage based on hydride

Liquid organic, inorganic chemical, and solid metal hydrides are promising hydrogen storage technologies [155]. For residential and commercial buildings, Liquid Organic Hydrogen Carriers (LOHC) are favorable, with exhaust temperatures around 80°C. LOHC integration with CHP systems can enhance overall efficiency [156].

Methylcyclohexane, a low-cost liquid cycloalkane with high hydrogen density, is a potential hydrogen storage material [54]. However, its toxicity, high dehydrogenation temperature, and enthalpy increase energy consumption. Liquid organic heterocyclic compounds containing nitrogen and boron can reduce hydride dehydrogenation enthalpy [157], but their thermal stability is inadequate [158].

Hydrous hydrazine (H_2NNH_2) and other inorganic nitrogen boron hydrogen complexes are also promising. Hydrazine hydrate, a room-temperature oily liquid, decomposes by catalysts. It offers high hydrogen content, easy recharging, and compatibility with existing infrastructures. However, high decomposition temperature and potent toxicity are concerns [155].

Solid metal hydrides, like magnesium hydride (MgH_2), are highly feasible. Hydrogen molecules combine with metal under specific pressures (3-30 bar) to form metal hydrides. Some, like sodium borohydride, have limited hydrogen storage capacity at low temperatures and pressures. Metal hydrides require hydrogen purity, as impurities harm performance and can react with moist air [159].

Ammonia is another hydrogen storage material with a high content (17.8wt%), offering theoretical hydrogen conversion efficiency near 90%. However, the current focus is on direct ammonia production for hydrogen rather than conversion for storage [160].

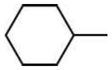
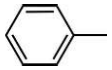
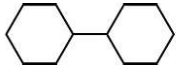
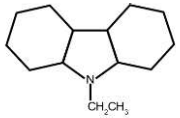
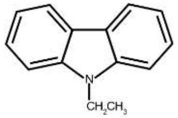
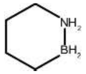
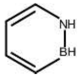
3.2.3 Hydrogen storage based on porous media

Hydrogen storage using nano-materials, metal-organic frameworks, and other porous media is an alternative technology that adsorbs hydrogen molecules through high specific surface area and porosity [161]. Nano-material-based storage avoids excessive metal hydride issues, and nanostructured materials are more stable [162]. However, challenges include potential nanostructure collapse during repeated hydrogen uptake and release cycles, and the need to improve hydrogen storage capacity [163].

Metal-organic frameworks offer low-cost, lightweight, and excellent thermal and chemical stability [164]. Rapid hydrogen adsorption and desorption on pores can be achieved by pressure or heating, and this method has been extensively studied [165]. Some hydrogen storage methods demand higher surface areas and larger free volumes [166]. For instance, large-scale underground hydrogen storage in porous media necessitates strict terrain requirements [167].

Table 9

Comparison of hydrogen storage methods [155, 168, 169].

Type	Storage materials	Pressure / temperature	Dehydrogenation temperature	Hydrogenated form	Dehydrogenated form	Hydrogen content (g/L)	Hydrogen content (wt%H_2)
Compression hydrogen storage	Tank	10Mpa, 20°C	-	-	-	7.8	100
	Tank	35MPa, 20°C	-	-	-	24	100
	Tank	70MPa, 20°C	-	-	-	39	100
Cryogenic hydrogen storage	Tank	0.1MPa, -253°C	-	-	-	71	100
Liquid organic chemical hydrides	Methylcyclohexane [170]	-	195-400			47.4	6.2
	Bicyclohexyl [171]	-	260-320			64.2	7.3
	Dodecahydro-*N*-ethylcarbazole [172]	-	150-170			54	5.8
	1,2-BN-cyclohexane [173]	-	>150/<80			48	4.7
Inorganic chemical hydrides	Ammonia borane [174]	-	100,150,>500	NH_3BH_3+$2H_2O$	NH_4B_2	153	19.6(9.0)
	Hydrous hydrazine	-	>300	$N_2H_4 \cdot H_2O$	N_2	80.26	8.0
Solid metal hydrides	Magnesium hydride [175]	-	300	MgH_2	$Mg(OH)_2$	110	7.6
	Hydrogen storage alloy	-	25°C	$LaNi_5H_6$	$LaNi_5$	-	1.4
		-	280	$MgNiH_4$	Mg_2Ni	-	3.59
Nano-materials	Layered Mg/Ni composites [176]	5MPa, 350°C	-	-	-	-	1.425
Metal-organic framework	Cu based-MOF [164]	5MPa, -196°C	-	-	-	-	4.3-8.6
		5Mpa, 25°C	-	-	-	-	0.34-1.03
	MOF-5 [177]	5MPa, -196°C	-	-	-	-	4.5

3.3 Hydrogen transportation

Besides direct hydrogen storage steel cylinder transportation, compressed gaseous hydrogen is primarily conveyed to grid-connected hydrogen-powered applications via tube trailers. The trailer tube material impacts storage performance and cost [178]. Cryogenic liquid hydrogen is transported using liquid hydrogen tankers, with temperature fluctuations during transit requiring attention. Both transportation modes have stringent safety requirements. Tube trailers offer relatively low transport efficiency, making them suitable for short-distance or low-volume transportation. Liquid hydrogen tankers provide higher storage capacity, ideal for medium-distance transport. For large-scale and long-distance hydrogen transportation, pipelines are highly economical. However, the cost of installing new hydrogen pipelines is substantial [179].

Consequently, some researchers propose using existing natural gas pipeline networks for hydrogen transport. Dodds et al.[180] investigated the feasibility of converting the UK gas networks for hydrogen transmission, finding that high-strength steel gas pipelines were susceptible to hydrogen embrittlement, while polyethylene pipelines were suitable for low-pressure hydrogen transport. Currently, projects in the US [181] and EU [182] are laying hydrogen pipelines or modifying natural gas pipelines. DNV's H_2 Pipe Joint Industry Project aims to develop the world's first guidelines for hydrogen transport in existing and new offshore pipelines. Future stable development of hydrogen pipeline transportation requires more legal policies.

Additionally, hydrogen storage in the form of hydrides poses challenges. Organic and inorganic chemical hydrides' toxicity necessitates leakage risk assessment during transport [183]. While metal hydrides are safe and stable, the cost increase resulting from added weight must be considered during transportation.

3.4 Emerging technologies for CHP systems

Regarding hydrogen production, fossil fuel-based methods are still widely used. For example, Hou et al. [184] developed a PEMFC-CHP system that uses methanol-reforming to produce hydrogen, and the power generation capacity can reach 115.84 kW, which can meet the electricity and heating demands of small industrial parks. Alternatively, hydrogen production can be combined with the supply of raw materials and the use of hydrogen for energy, forming a self-sufficient system. For instance, biogas can be produced through cow farms and biogas plants. Hydrogen can be obtained through biogas reforming to supply energy for the CHP system to generate electricity and heat the cow farm and biogas plant [185]. This method is mature and has been applied successfully.

In hydrogen CHP systems, using renewable energy sources to generate electricity for electrolyzing water to supply hydrogen often leads to uncertainty. The production of interrelated electricity and heat in the system should also be considered. Therefore, uncertainty management is crucial for CHP systems in the power grid [186]. Meanwhile, electrolyzing water not only produces hydrogen but also oxygen. This portion of electrolytic oxygen must be treated for its corrosive hydroxides before use [187]. Furthermore, for biomass fuel, on-site hydrogen production can be combined with the use of waste heat from the CHP system to produce biofuels via pyrolysis [11]. Or, residual gases from biomass hydrogen production can be used as additional fuel for the CHP system to improve its economic efficiency [188].

Regarding hydrogen storage, gaseous and liquid hydrogen storage technologies are already relatively mature. However, gaseous hydrogen has a low volumetric energy density (1/3000 that of gasoline), and liquid hydrogen requires complex cooling and insulation equipment, with leakage occurring during storage. Therefore, constructing a hydrogen storage system in a CHP system requires storing hydrogen with higher volumetric energy density, lower safety risks, and cooling requirements. Metal hydride storage [189] and LOHCs [190], as emerging hydrogen storage technologies, have higher storage densities and reduced risks of leakage and pressure fluctuations. However, their maturity is currently low and requires higher costs, so their practical application still needs further discussion. As for MOFs for hydrogen storage, there have been no reported applications in CHP systems to date. Furthermore, appropriate hydrogen storage strategies are still a consideration in CHP systems [191].

In addition to directly utilizing the produced hydrogen, injecting hydrogen into existing natural gas pipelines to obtain hydrogen-enriched natural gas blends is also a viable method for hydrogen utilization. For such blended fuels, internal combustion engines typically use hydrogen contents of less than 50%; gas turbines do not have strict requirements for hydrogen content in the blended fuel and can use pure hydrogen or pure methane; for fuel cells with low tolerance, such as AFCs or PEMFCs, pure hydrogen is required.

4 Discussions

Although hydrogen and CHP systems have garnered significant interest, existing literature reveals research gaps and challenges. Hydrogen has vast development potential, but fully hydrogen-dependent economic and energy systems have yet to be realized. Inadequate infrastructure development and the high cost of renewable hydrogen and equipment constrain hydrogen-based CHP systems' growth.

4.1 System design

The design of CHP system infrastructure, spatial planning, and geographic positioning of hydrogen production facilities are crucial for efficient hydrogen utilization in hydrogen-based CHP systems, ensuring sustainability, cost-effectiveness, and reliability. CHP system design must prioritize stability and reliability. Besides, simpler designs are preferable to avoid installation difficulties, extra costs, and excessive auxiliary equipment. The design process must consider local climate, policies, system costs, maintenance, energy supply, and output. Additionally, tailoring the design to hydrogen's unique requirements and considering safety measures and appropriate materials are essential to prevent hazards related to storage and transport, such as leaks or embrittlement.

Spatial planning determines optimal locations for hydrogen production facilities, storage sites, CHP plants, and distribution network layout, minimizing energy losses during transportation, reducing costs, and ensuring efficient hydrogen distribution. The location of hydrogen production facilities significantly impacts CHP systems' efficiency and cost-effectiveness. Positioning facilities near CHP plants or end-users can minimize transportation costs and energy losses. In some cases, decentralized hydrogen production sites may be more effective and strategically located to serve multiple CHP plants or distributed energy systems.

The economic benefits of hydrogen CHP systems depend on various factors, including electricity costs, fuel costs, system design, equipment costs, and the operational efficiency of the CHP system. Electricity costs in the installation area affect the system's competitiveness, and the higher electricity costs will make CHP systems more attractive alternatives. Fuel costs directly impact operating expenses, and the higher costs will reduce competitiveness. System design, encompassing size, configuration, and integration with other energy resources, greatly influence economic performance. The system's economic feasibility is affected by equipment costs for prime movers, heat recovery components, and auxiliary parts. Power-to-heat ratios and operational strategies also play a significant role in influencing the overall efficiency of CHP systems. Optimizing the power-to-heat ratio ensures that electrical and thermal energy demands are satisfied effectively, maximizing the system's efficiency and reducing energy wastage. Effective operational strategies can enhance the system's performance, increase its reliability and lifespan, and reduce the overall costs associated with its operation.

4.2 Technical challenges

Compared to traditional fuels, hydrogen has the potential to improve thermal efficiency and reduce CO_2 emissions, excessive hydrogen content can lead to abnormal combustion, high NO_x emissions, and poor thermal efficiency in ICE-CHP systems. The current technology prefers a hydrogen ratio below 50%, with effective methods to reduce NO_x emissions and an optimal fuel-hydrogen content ratio. For hydrogen turbines, GTCC systems are the best example of CHP systems, but the efficiency of the GT-CHP system is affected by ambient temperature. The development of hydrogen turbine-based CHP systems is limited by hydrogen cost and embrittlement. Different types of fuel cell technologies, including AFC, AEMFC, PEMFC, and SOFC, each have their own advantages and challenges. For example, AFC's liquid alkaline electrolyte has poor tolerance to CO_2 and carries a risk of leakage, which affects performance. AEMFCs have a relatively low level of technological maturity, with improvements still needed in ion transport efficiency, stability, and lifespan. PEMFCs require high fuel purity and a low tolerance for CO and CO_2, and using precious metal catalysts (such as platinum) results in higher costs. The high operating temperature of SOFCs presents challenges in material selection and system reliability, and they also require longer startup times and higher manufacturing costs.

The article explains that fuel cells are gradually replacing ICEs in stationary distributed energy applications and transportation. Fuel cells offer higher efficiency, greater flexibility, easier maintenance, and lower CO_2 emissions compared to ICEs in electricity systems. For stationary applications of FC-CHP systems, the main fuel is rich-H_2 gas obtained by natural gas reforming or by water electrolysis using renewable energy sources such as solar and wind energy. Besides, PEMFCs are predominantly utilized in daily start-stop operation CHP systems, while SOFCs are employed for continuous operation. In addition, fuel cells can be integrated with thermoelectric generators to optimize CHP system performance. For transportation applications of FC-CHP systems, the heat can be recovered by heat exchange or adsorption refrigeration technology to adjust vehicle temperature. PEMFCs are suitable for vehicles because of their small size, low operating temperature, and low noise. Compact SOFC stacks can also be used as power units or range extenders for vehicles or aircraft.

Most hydrogen currently used in CHP systems comes from natural gas reforming emitting CO2. Steam reforming is fast but energy-intensive, with a low conversion rate. Autothermal reforming requires temperature control and high oxygen levels. Existing hydrolysis hydrogen production methods face limitations in efficiency, cost, and technical expertise. Combining water electrolysis hydrogen production equipment with solar, wind, or nuclear power plants can reduce hydrogen production energy demand. Hydrogen production from biomass consumes less energy but involves complex raw materials and requires purification. Using blended fuels rather than pure hydrogen is a more economical solution for CHP system costs during the transition period. Additionally, hydrogen storage methods, such as hydride-based storage, offer advantages over compressed and cryogenic hydrogen storage. Still, difficulties with dehydrogenation, excessive mass, and high cost remain obstacles to widespread application.

5 Conclusions

This review investigates prevalent and potential technologies for hydrogen-based CHP systems. The characteristics of hydrogen as a primary energy source are discussed, and the structure, associated technologies, and current projects of hydrogen CHP systems, including engines, turbines, and fuel cells, are analyzed. With their high efficiency and low emissions, fuel cells are promising candidates to replace engines and turbines, but they currently face high costs. Moreover, hydrogen-powered CHP systems generally exhibit better performance and lower emissions than their fossil fuel-powered counterparts. Utilizing blended fuels, created by mixing hydrogen with other fuels, can serve as a transitional solution from fossil fuels to pure hydrogen fuels. Further development of current hydrogen production and storage technologies is necessary to enable large-scale commercial applications.

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