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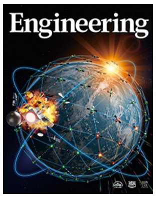

Research
Green Aviation Propulsion—Review

A Comparative Analysis of Conventional Thermal and Electrochemical Reforming Pathways for Hydrogen Production Towards Sustainable Aviation Fuels (SAF)

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A B S T R A C T

H_2 is increasingly recognized as a cornerstone of global decarbonization strategies, including in hard-to-abate sectors, such as aviation. Its large-scale applicability remains limited owing to the limited diversity and maturity of low-carbon production pathways. Approximately 96% of global H_2 production originates from non-renewable sources, primarily through steam methane reforming (SMR), which remains the most commercially established route. Another critical barrier to the substitution of conventional aviation fuels lies in hydrogen storage, as the current volumetric energy density and cryogenic storage requirements render onboard integration impractical for most aircraft configurations. To address these challenges, this study developed a techno-economic and environmental benchmarking framework that compares conventional thermal reforming technologies (SMR, autothermal, and POX) with emerging electrochemical routes (water electrolysis and alcohol electro-oxidation), highlighting their potential roles in the transition toward sustainable aviation fuels (SAF). By normalizing efficiency, energy intensity, CO_2 emissions, and cost ($\mathrm{USD\cdot\ kg^{-1}}$ H_2 and $\mathrm{USD{\cdot}GJ^{-1}}$), this study quantifies the trade-offs that define current and emerging pathways. SMR remains the industrial baseline (70%–85% thermal efficiency, 1–2 $\mathrm{USD{\cdot}kg^{-1}}$ H_2, 9–12 kg $\mathrm{CO_2{\cdot}kg^{-1}}$ H_2), whereas ethanol-based electrochemical reforming operates 0.3–0.9 V below conventional electrolysis, achieving up to 40% lower electrical energy demand ($\sim$2.4 $\mathrm{kW{\cdot}h{\cdot}Nm^{-3}}$ H_2) with near-zero direct emissions. A sensitivity analysis demonstrates that a 60% reduction in catalyst cost or electricity prices below 0.03 $\mathrm{USD{\cdot}(kW{\cdot}h)^{-1}}$ could make electrochemical reforming cost-competitive with SMR. This study consolidates fragmented knowledge into a comprehensive roadmap that links catalyst performance and technology readiness for aviation decarbonization by integrating engineering metrics with policy and infrastructure perspectives to identify realistic transition pathways toward sustainable hydrogen and hybrid aviation fuels.

1. Introduction

Global industrialization and economic expansion have intensified the overall energy demand. Each 1% increase in economic complexity or industrial growth led to an average 1.7% increase in total energy consumption [1]. This relationship indicates that structural transformation, in the absence of sustainable alternatives, tends to reinforce fossil-fuel dependence rather than mitigate it. Therefore, achieving long-term decarbonization requires a systemic transformation of the energy landscape, one that diversifies the energy matrix, scales up renewable deployment, and reforms educational and industrial systems to strengthen efficiency and clean technology innovation. H_2 technologies have emerged as both a technical and strategic response to global energy emission imbalance.

The physicochemical properties of H_2, including its high gravimetric energy density (approximately 120 $\mathrm{kJ{\cdot}g^{-1}}$) and potential for carbon-free utilization, create high expectations for its role in decarbonizing sectors, such as heavy industries and long-distance transportation. H_2 is considered an energy carrier because it does not occur naturally in commercially exploitable quantities on Earth. Although traces exist in geological reservoirs, these sources

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remain insufficient for large-scale utilization [2]. The main challenge for the H_2 economy is to avoid the high carbon emissions of current fossil fuel-based production methods (see Fig. 1(a)), such as steam methane reforming (SMR, 48%), oil reforming (30%), and coal gasification (18%), which produce the vast majority of today's H_2 [3]. This sharply contrasts with the potential of hydrogen as a clean energy vector, making it imperative to shift towards low-emission pathways such as carbon capture utilization and storage (CCUS) [4] or renewable-powered electrolysis [5]. These alternatives align with international efforts to meet global CO_2 reduction targets and achieve net-zero emissions by the mid-century.

The use of H_2 in aviation traces its roots back to the pioneering experiments of Jacques Charles and Robert Brothers, whose hydrogen-filled balloons in 1783 demonstrated the potential for lighter-than-air flight [6]. Since then, the use of propellants has shifted toward liquid hydrogen (LH_2) and liquid oxygen (LO_x) in rockets, where their reactions generate energy [7]. LH_2 offers an energy density approximately 2.5 times greater than that of kerosene; however, achieving equivalent energy output requires roughly four times the fuel volume, demanding major aircraft design modifications for cryogenic storage and integration, which significantly increases structural complexity and operational costs [8], making the transition toward hydrogen-powered aviation a critical step in global decarbonization efforts.

In 2019, aviation accounted for 3.1% of total global CO_2 emissions from fossil fuel combustion. The majority of these emissions originate from long-distance flights (over 1500 km), for which there are few practical alternatives to air travel. Therefore, the advancement of H_2 technologies could play a pivotal role in reducing the sector's carbon footprint, while fostering broader economic opportunities. The aviation fuel market is currently dominated by kerosene-based jet fuel, which has historically served as the primary energy source for almost all commercial aircrafts. More environmentally friendly alternatives such as Sustainable aviation fuels (SAF) have been proposed. SAF refers to renewable liquid fuels produced from biomass, organic waste, or direct CO_2 capture from air. Despite these alternatives, their use represents less than 1% of total aviation fuel consumption [9], mainly because of the high cost of production. A medium- to long-term strategy for aviation decarbonization focuses on the use of H_2 for aircraft propulsion.

To make the use of H_2 as an aviation fuel truly effective, financial balance must be addressed through cost reductions in production, storage, and distribution technologies. Currently, H_2 produced via SMR represents the most cost-effective production pathway, with costs ranging from 1.30 to 1.50 $\text{USD}\cdot\text{kg}^{-1}$ (or 10–12 $\text{USD}\cdot\text{GJ}^{-1}$). H_2 produced through renewable-powered electrolysis offers zero emissions but struggles with higher costs (5.50 $\text{USD}\cdot\text{kg}^{-1}$ or 46 $\text{USD}\cdot\text{GJ}^{-1}$) owing to efficiency limits (50%–60%) and current energy prices [10]. The relatively low cost of SMR makes it the most feasible short-term option for H_2 production. However, its reliance on fossil fuels poses a major challenge in achieving long-term sustainability, particularly given that fossil fuel prices vary considerably across regions. For instance, a 1% increase in the Real Energy Price Index (REPI) can lead to a 0.08%–0.31% reduction in total energy consumption, underscoring the strong sensitivity of energy demand to price fluctuations [1]. Stabilizing energy costs and mitigating exposure to fossil fuel market volatility are critical to ensuring a reliable and economically balanced transition toward renewable energy systems. Electrochemical reforming technologies could help bridge the cost gap if renewable electricity prices fall to approximately 0.03 $\text{USD}\cdot(\text{kW}\cdot\text{h})^{-1}$ and electrolyzer costs decline by 60%–80%, potentially reducing H_2 production costs to about 2.00 $\text{USD}\cdot\text{kg}^{-1}$.

Recent techno-economic assessments and simulation studies have proposed hybrid and electrochemical reforming routes that can bridge this cost gap. For example, thermochemical valorization of refuse-derived fuels (RDF) and electrochemical reforming of organic feedstocks can reduce CO_2 emissions by 25%–30% compared to conventional fossil-based H_2, while maintaining competitive calorific outputs [10,11]. Similarly, Aspen Plus simulations of optimized reforming from scheduled wastes demonstrated that moderate operational conditions (~500 °C, 5 bar (1 bar = 10^5 Pa)) maximize hydrogen yield while minimizing metal contaminants and energy demand, achieving thermal efficiencies above 90% when coupled with heat recovery [12].

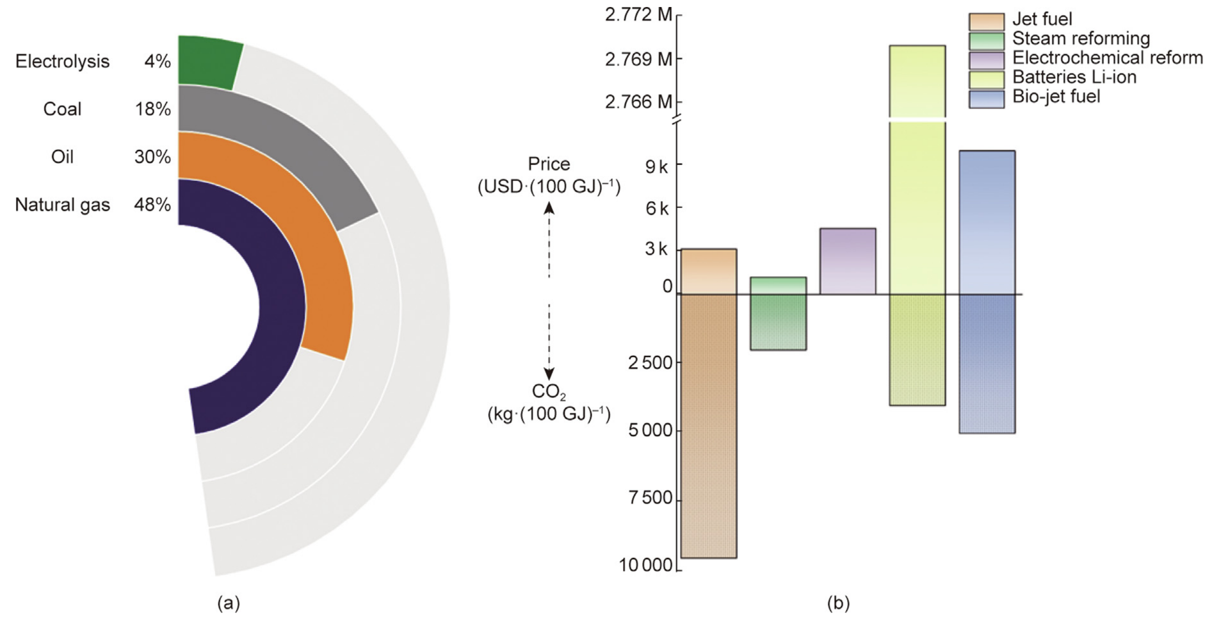

Fig. 1. (a) Global H_2 production by primary source. (b) Comparative assessment of energy cost and CO_2 emissions for different propulsion pathways in an Airbus A320 (100 $\text{GJ}\cdot\text{h}^{-1}$). Values are indicative and include ±20% uncertainty ranges to account for regional variations in fuel price, carbon intensity, and process efficiency.

Fig. 1(b) shows the tradeoffs between implementation costs and carbon footprints across alternative energy solutions for Airbus A320's operational profile, which requires 100 $GJ \cdot h^{-1}$. Steam reforming emerged as the most immediate deployable solution, delivering 100 $GJ \cdot h^{-1}$at 4500 USD with 2000 kg CO_2 emissions, 79% reduction from jet fuel systems. These values remain sensitive to regional energy prices and carbon-intensity assumptions, suggesting that total costs could vary by up to ±20% depending on natural-gas market volatility and local emission-factor baselines. Electrochemical H_2 production demonstrates decarbonization through zero operational emissions. Bio-jet fuels present an environmental-economic paradox, their 10 000 USD cost and 5000 kg CO_2 emissions profile, exposing hidden dependencies on palm oil subsidies that account for 62% of production costs. The lithium-ion battery pathway underscores the fundamental physics barriers. The low specific energy density of current batteries necessitates extensive structural reinforcement, which increases operational costs to approximately 2.7×10^6 USD per 100 GJ. Even under optimistic projections, assuming a two-fold improvement in the gravimetric energy density, cost reductions remain constrained by mass-related design penalties and maintenance requirements.

H_2 role in aviation extends beyond that of direct combustion. Fuel cells enable electrochemical conversion of H_2 and O_2 into electricity, producing only water vapor as exhaust, a contrast to conventional jet engines that emit CO_2 and NO_x. Modern initiatives such as the FlyZero program have demonstrated the feasibility of regional aircraft prototypes powered by H_2 fuel cells [11], which could reduce aviation's carbon footprint by more than 50% in long-haul operations by 2050 [12].

Fuel cells operate by converting the Gibbs free energy (ΔG) of oxidation into electrical work, bypassing thermal cycles and surpassing the classical Carnot limit. The thermodynamic efficiency (η) is often expressed as the ratio between the energy available for electrical work (ΔG) and the total heat of the reaction (ΔH), ($\eta = \frac{\Delta G}{\Delta H}$) [7], bypassing thermal cycles and surpassing the classical Carnot limit. They exist in several configurations, including alkaline fuel cells (AFC), proton exchange membrane fuel cells (PEMFC), solid oxide fuel cells (SOFC), direct methanol fuel cells (DMFC), and direct ethanol fuel cells (DEFC). Each type operates optimally under specific conditions, as illustrated in Fig. 2 [13]. While some fuel cells rely exclusively on pure H_2, others are capable of utilizing alcohols such as methanol or ethanol as fuel sources. In terms of efficiency, conventional heat engines typically reach a maximum theoretical efficiency of approximately 60%, whereas PEMFCs can achieve 80%–86% at temperatures below 100 °C, and SOFCs exhibit comparable efficiencies within the 800–900 °C range [14]. Under practical operating conditions, these efficiencies stabilize near 40% for PEMFCs and 60% for SOFCs, primarily due to mass transport limitations, ionic resistance, and kinetic losses inherent to real-world operations [15].

Maximizing the environmental and economic benefits of H_2-based aviation requires a systemic evaluation of the production routes. This work provides a comparative analysis of conventional thermal reforming technologies (including steam reforming, autothermal reforming (ATR), and partial oxidation (POX)) against electrochemical reforming pathways, such as water electrolysis and the electrochemical reforming of organic feedstocks. The comparative framework encompasses their operating principles, catalytic mechanisms, feedstock requirements, energy efficiencies, and carbon footprints, establishing a foundation for identifying the most scalable, cost-effective, and climate-resilient routes for aviation decarbonization.

2. Conventional reforming technologies

Conventional reforming technologies are an established industrial backbone for H_2 production [16]. Most of the H_2 produced worldwide on an industrial scale comes from steam reforming or as a byproduct of oil refining and chemical compound production. These processes rely on thermal energy (endothermic reactions) to separate H_2 from the carbon in hydrocarbons or alcohols, for example, from methane or ethanol, and involve the reaction of these fuels with steam on the catalytic surfaces to obtain H_2. The use of fossil fuels as feedstock is considered undesirable from the

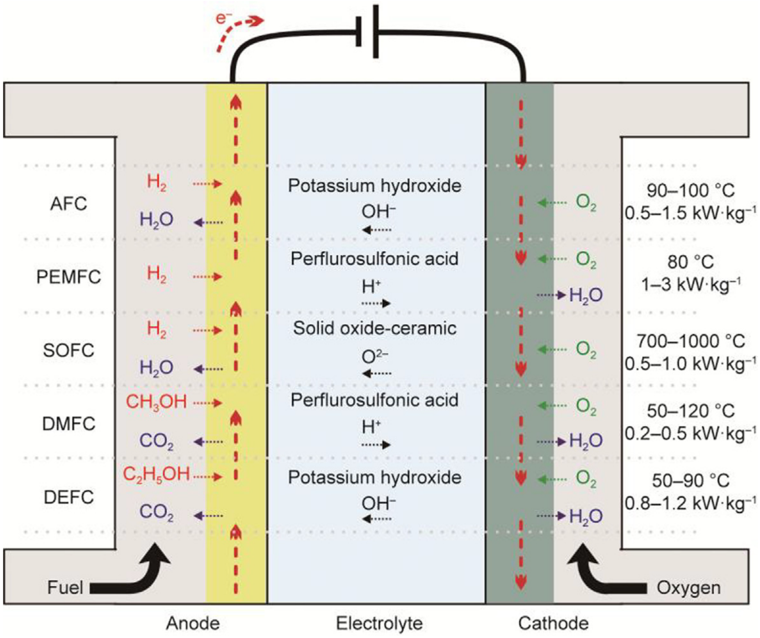

Fig. 2. Comparative overview of fuel cell technologies, highlighting their typical operating temperatures, energy densities, electrolytes, and fuel types. The chart summarizes the main characteristics of alkaline fuel cells (AFC), proton exchange membrane fuel cells (PEMFC), solid oxide fuel Cells (SOFC), direct methanol fuel cells (DMFC), and direct ethanol fuel cells (DEFC). Values represent typical performance ranges and may vary depending on catalyst composition, membrane properties, and system design.

perspective of emerging policies, which often subject these sources to extra taxation, but the technology is well established. These methods are currently the most cost-effective options for large-scale H_2 supply, albeit with significant carbon emissions in their standard configurations. This reality creates a clear conflict for companies with strong commitments to Corporate Social Responsibility (CSR). While cost efficiency is a financial advantage, high carbon emissions are a major drawback, contradicting the environmental aspects, which are the most influential factors in CSR adoption. This conflict is intensified by market pressure since consumer preferences for green technologies are strongly driven by environmental and social factors. Despite environmental limitations, conventional reforming remains the most widely used method for large-scale H_2 production due of its consolidated technological and economic advantages, even as the market shifts toward cleaner solutions.

2.1. Methane reforming

H_2 from natural gas for use in electricity generation has attracted great interest, especially for applications in electrochemical cells. Among all the sources, natural gas composed mainly of methane (CH_4) is the most widely used because of its abundance and the ease with which it can be converted into H_2. The methane-reforming process consists of the following reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2,\ \Delta H = 206\ \text{kJ} \cdot \text{mol}^{-1} \tag{1}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2,\ \Delta H = 247\ \text{kJ} \cdot \text{mol}^{-1} \tag{2}$$

SMR (Reaction (1) is more widely used for H_2 production because it yields a greater amount of H_2 than dry reforming (Reaction (2). Methane reforming with carbon dioxide, known as dry reforming of methane, produces a H_2/CO ratio that is more suitable for the production of methanol, acetic acid, and hydrocarbons [13]. Dry reforming has significant environmental appeal, as it reduces emissions of CO_2 and CH_4 gases that contribute to the greenhouse effect, and is more suitable for chemical energy transmission systems. The main disadvantage of reforming with CO_2 compared with SMR is the risk of catalyst deactivation due to coke formation because of the higher carbon content of the feedstock. Therefore, efforts have been made to develop catalysts that not only exhibit high activity and selectivity but also high stability, indicating resistance to coke deposition [17].

Both reactions are highly endothermic, making it necessary to carry out them at high temperatures. Commercial catalysts are based on Ni supported on α-alumina. Alkaline earth metals (Mg and Ca) are typically introduced into catalyst formulations to increase their stability [18,19]. Nickel-based catalysts, often nickel oxide supported on alumina (NiO/Al_2), are the industry standard because of their acceptable activity and cost-effectiveness. This process is performed industrially in multitubular fixed-bed reactors and currently represents the main global route for H_2 production [20].

From an energetic standpoint, SMR is more favorable than dry reforming, because it involves an additional reaction step beyond the primary reforming process. Specifically, the SMR process continues via the water–gas shift reaction (WGSR), Reaction (3), which further enhances H_2 yield and overall energy efficiency [21]. This reaction occurs exclusively in SMR because this process provides sufficient steam to react with the carbon monoxide produced; in dry reforming, there is no H_2O available for this reaction to take place. The WGSR reaction further increases the overall efficiency of the SMR route by enhancing the selectivity towards H_2 over other reaction products.

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = -41.2\ \text{kJ} \cdot \text{mol}^{-1} \tag{3}$$

The CO produced in the reforming step undergoes a further reaction with steam in the moderately exothermic WGSR reaction to generate additional H_2 and carbon dioxide. To maximize CO conversion and H_2 yield, the WGSR reaction is often carried out in multiple stages, typically a high-temperature shift (HTS) followed by a low-temperature shift (LTS) reactor. The overall SMR reaction, combining reforming and complete WGSR, can be represented as: $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2\ (\Delta H = 164.8\text{kJ}{\cdot}\text{mol}^{-1})$ [22].

As described, SMR faces challenges such as the need for high temperatures, significant energy consumption, and generation of carbon byproducts. Recent technological advancements have focused on overcoming these limitations in order to make the process more efficient and sustainable. Promising innovations include a shift in energy management, where traditional direct heating using fossil fuels is being replaced by methods such as electrified SMR (eSMR), which can be powered by renewable sources to reduce CO_2 emissions [23]. Other developments involve recovering waste heat from industrial processes or using concentrated solar energy to supply the necessary heat, thereby boosting efficiency and lowering fossil fuel consumption [24]. In addition, research has focused on optimizing catalysts and reactors to develop more active and stable catalysts that are resistant to coke formation. Advancements in purification and carbon capture are key topics. New methods such as membrane reactors are being developed to purify H_2 simultaneously with production [25,26], while carbon mineralization offers a path to convert CO_2 into stable carbonates for long-term storage, which is crucial for achieving low-carbon SMR [27]. These advancements collectively represent future opportunities for SMR to become cleaner and more efficient processes aligned with global sustainability goals.

2.2. Different types of feedstocks

In addition to methane, which is the primary source for obtaining H_2 through conventional reforming, other feedstocks are also being studied, as is the case for the industrial route via methanol. This is based on the steam reforming process of methanol over a $Cu/ZnO/Al_2O_3$ catalyst at approximately 300 °C and atmospheric pressure, producing a mixture of H_2, CO, and CO_2. The main reaction involved in methanol steam reforming is: $CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2$[28].

The methanol reforming reaction is of great industrial importance because it enables H_2 production through an easy process, with a low energy cost, and with CO_2 as the only impurity, using liquid reagents that are easy to transport [29,30]. Methanol production still relies on non-renewable fossil raw materials, and overall there will always occurs CO_2 production if not during automotive combustion or during reforming for H_2 production. Additionally, the high toxicity of methanol complicates its handling at fueling stations [20].

In the same way as methanol and methane, ethanol is also considered as a H_2 generator to supply fuel cells in automotive vehicles. Since ethanol comes from a renewable source of fermentation of sugarcane juice or cereals, it is particularly interesting in regions with large-scale production of these crops. The use of ethanol as a substitute for methanol is favored because the CO_2 balance is neutral; that is, the carbon dioxide generated in the reforming reaction is consumed during the production of sugarcane or cereals, thus not contributing to an increase in atmospheric CO_2 [31].

In countries such as Brazil, where ethanol is produced on a large scale and at low cost, it is important to study the replacement of methanol with ethanol [32]. Ethanol steam reforming uses a mixture of vaporized water and ethanol as reactants. This is an endothermic reaction (Reaction (4)) and therefore requires an external heat source.

$$C_2H_5OH_{(g)} + 3H_2O_{(g)} \rightarrow 2CO_{2(g)} + 6H_{2(g)} \qquad \Delta H = 173.5\,\mathrm{kJ{\cdot}mol^{-1}} \tag{4}$$

The combustion of fossil fuels, such as gasoline and natural gas, releases toxic greenhouse gases into the atmosphere, causing many local and global problems. Ethanol, like other forms of biomass, offers the advantage of being renewable within a relatively short period of time and cannot be considered harmful to the atmosphere because its byproducts are neither toxic nor polluting. Moreover, Brazil has enormous agricultural potential for sugarcane production and can export ethanol as an energy source. It has also been shown that the use of ethanol as a H_2 source is economically favorable [32].

Steam reforming of ethanol for H_2 production involves a complex system of multiple reactions, with the purity of H_2 production being affected by many undesirable side reactions. Therefore, the H_2 yield depends in a complex way on process variables such as pressure, temperature, and molar ratio of reactants [33]. To maximize H_2 yield, it is necessary to understand the effect of these variables on the composition of the products. A thorough understanding of the reaction mechanism is essential and ongoing research is actively exploring this aspect. As illustrated in Fig. 3 [33], ethanol steam reforming proceeds through a complex reaction network initiated by $O-H$ bond cleavage in ethanol, forming ethoxy intermediates (CH_3CH_2O). This is followed by sequential dehydrogenation to acetaldehyde (CH_3CHO*) and acetyl species (CH_3CO*). Critical $C-C$ bond scission in these intermediates generates syngas ($CO + H_2$), which CO subsequently converted to CO_2 via the WGSR. However, competing side reactions, including acetaldehyde decomposition (to CH_4 and CO), ethanol dehydration (yielding ethylene, a coke precursor), and methanation (CO/CO_2 to CH_4), significantly reduced H_2 selectivity and promoted carbon deposition [33].

To enhance catalytic performance, multiple factors must be addressed: ① active metal choice (e.g., Ni, Co, Rh) for $C-C$ cleavage and WGSR; ② support properties (e.g., acidity/alkalinity) governing intermediate selectivity; and ③ reaction conditions (temperature, H_2O/EtOH ratio). High temperatures (> 400 °C) favor CH_4 reforming, but risk carbon accumulation. Several studies have achieved promising results with the implementation of ethanol steam reforming, such as the initiative developed in Brazil. A leading project in H_2 research and deployment by the University of São Paulo (USP) is the Green Hydrogen Platform, which aims to pioneer a pilot-scale ethanol steam reforming system capable of producing 4.5 kg of H_2 per hour (approximately 100 $kg{\cdot}d^{-1}$, as shown in Fig. 4) [34]. This study evaluates the potential for reducing greenhouse gas emissions in the USP transportation sector by replacing its diesel bus fleet with hydrogen-powered vehicles. The low-carbon H_2 was produced via ethanol steam reforming. The results show that replacing the fleet can lead to a significant 83% reduction in annual CO_{2-eq} emissions, which is equivalent to 2658 t.

2.3. Oxidative processes: POX and ATR

SMR is the most widely used industrial process for H_2 production [35]. This hydrocarbon-to-hydrogen conversion occurs via three distinct technological pathways: ① steam reforming; ② POX; and ③ ATR. The first method uses steam, making it the most widely adopted industrial method. POX exclusively employs O_2, which is optimized for heavy feedstocks, such as refinery residues. ATR combines steam and oxygen in a single reactor to achieve thermal self-sufficiency through balanced exothermic/endothermic reactions. These three mechanisms can be described by general reactions [36]:

$$\textbf{SMR}: CH_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4H_{2(g)},\ \Delta H > 0 \tag{5}$$

$$\textbf{POX}: C_mH_n + \frac{1}{2}mO_2 \rightarrow mCO + \left(\frac{1}{2}n\right)H_2, \Delta H < 0 \tag{6}$$

$$\textbf{ATR}: C_mH_n + \frac{1}{2}mH_2O + \frac{1}{4}mO_2 \rightarrow mCO + \left(\frac{1}{2}m + \frac{1}{2}n\right)H_2, \Delta H \approx 0 \tag{7}$$

POX is exothermic, operating at 1100–1200 °C to avoid coking, and offers compactness, rapid start-up, and responsiveness. POX can be homogeneous (non-catalytic, tolerant of diverse fuels, but less efficient due to extreme temperatures) or catalytic (lower operating temperatures of 800–900 °C, though sensitive to sulfur content). ATR combines POX and steam reforming, leveraging the exothermicity of POX to drive endothermic steam reforming, resulting in a thermally neutral process. ATR operates at 900–1150 °C and lower pressures than POX with a favorable H_2/CO ratio (~2) [13]. While it eliminates the need for external heat in the steady state, its startup requires energy to reach ignition temperatures, influenced by fuel type and catalyst (noble metals outperform Ni). ATR balances the strengths of steam reforming and POX but shares some of its limitations, such as material constraints and startup energy demands. The thermally neutral operation of ATR eliminates the need for external heat sources, which is a significant drawback of steam reforming, while also avoiding the

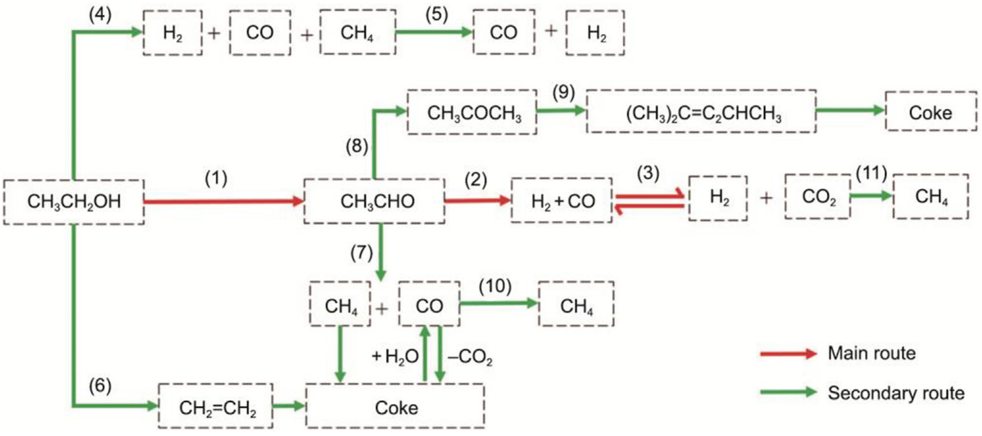

Fig. 3. Reaction network of ethanol steam reforming. Reproduced with permission of John Wiley and Sons [33].

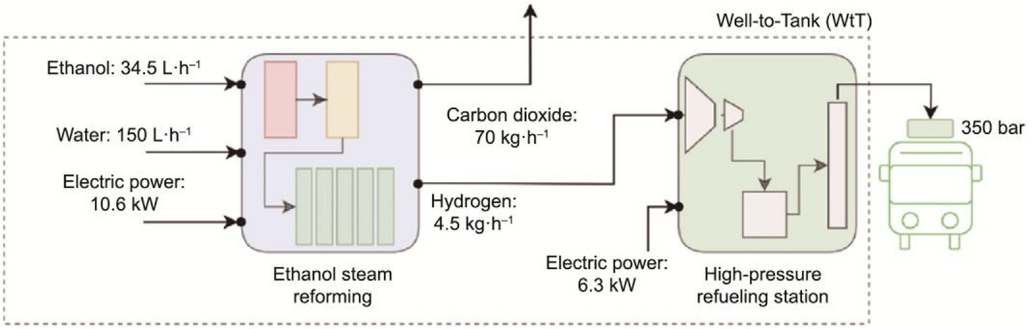

Fig. 4. H_2 production via ethanol steam reforming. In order to mitigate coke formation, the proportion of water used exceeds the stoichiometric amount, with a portion of the water being recovered at the end of the process. Reproduced with permission of Elsevier [34].

post-processing complexity of the WGSR. This streamlined approach directly supports the high-temperature SOFCs selected for aircraft applications, which can utilize ATR syngas output without additional CO cleanup [37]. Though POX offers marginally faster ignition and a more compact footprint, its lower H_2 yield and dependence on pure oxygen ($\geq\geq$ 95% O_2) make it less practical for scalable aircraft integration [15]. ATR is the most balanced solution, harmonizing efficiency, weight savings, dynamic responsiveness, and compatibility with next-generation SOFC-based propulsion systems.

Among these options, ATR emerges as the optimal solution for onboard fuel cell systems in aircraft owing to its unique ability to balance critical operational requirements, as: ① weight and space efficiency: due the combination of exothermic (POX) and endothermic (steam reforming) reactions, eliminating the need for external heat exchangers; ② dynamic performance: achieves 90% syngas output in less than 5 min (vs steam reforming 1–2 h) by leveraging POX-driven ignition and maintains H_2/CO ratio (~2); ③ simplicity: no need for post-processing high-temperature, SOFCs directly utilize ATR's syngas, removing WGSR reactors (saving ~20% subsystem mass) [15].

ATR is the most balanced option for aircraft fuel cell systems, but it has drawbacks such as control complexity, reliance on expensive catalysts (e.g., rhodium), lower efficiency than steam reforming under ideal conditions, miniaturization challenges, and CO emissions, which restrict its use in SOFCs. A possible option would be the combined use of internal combustion engine technology and onboard fuel reforming, leveraging the waste heat of the system to drive the reforming reactions. Fuel reforming leads to a significant reduction in pollutant emissions and a substantial improvement in energy efficiency [38]. Before application, certain limitations must be addressed: ① The process is highly endothermic, requiring a significant amount of heat that cannot always be supplied by the engine's exhaust gases; ② there is a strong tendency for coke formation, which can deactivate the catalyst; and ③ the durability of the catalyst is compromised by carbon deposition, high temperatures, and fuel contaminants. These limitations justify ongoing research into alternatives, such as electrochemical pathways, which offer trade-offs between the dynamic performance and efficiency.

3. Electrochemical reforming technologies

Water electrolysis remains the primary method for "green" H_2 generation, and uses electricity to split H_2O into H_2 and O_2, electrochemical reforming (ECR) has gained significant attention as a complementary approach. In ECR, organic compounds, such as alcohols, polyols, and biomass-derived molecules, are oxidized at the anode, producing H_2 at the cathode. Beyond H_2, valuable byproducts such as carboxylic acids, aldehydes, and ketones are formed, promoting the valorization of organic waste and integrating H_2 production with chemical synthesis in accordance with circular economic principles [39,40].

Recent developments in non-noble transition-metal catalysts have improved their efficiency, selectivity, and stability [41,42]. For industrial-scale applications, a deeper understanding of the reaction mechanisms and optimization of materials and operating conditions such as temperature, electrolyte composition, and applied potential is essential. Thus, ECR complements water electrolysis, enhancing the sustainability of simultaneous H_2 and chemical production.

3.1. Water electrolysis

Water electrolysis is one of the most established and technically mature technologies for producing high-purity hydrogen with zero CO_2 emissions. The electrochemical dissociation of water (H_2O) into molecular H_2 (by the H_2 evolution reaction (HER)) and oxygen (by the oxygen evolution reaction (OER)) occurs through electrochemical reactions at the electrodes, which are separated by an ion-conductive electrolyte. The specific electrochemical half-reactions at the anode and cathode depend on the nature of the electrolyte (acidic or alkaline), leading to different mechanistic pathways and performance characteristics [43].

The main challenge lies in the OER occurring at the anode, particularly in acidic media, and when noble metals are used in the cathode. The OER is a multi-electron reaction (involving the transfer of four electrons) with slow kinetics, which requires high overpotentials to proceed efficiently. This results in high energy consumption for driving the reaction, even when powered by renewable energy sources. The high energy demand to overcome OER overpotentials reduces the overall system efficiency, especially in alkaline and proton exchange membrane (PEM) electrolysis systems. For example, in alkaline electrolysis, the total cell voltage can reach 2.0 to 2.2 V, while in PEM cells, it can range from 1.6 to 2.0 V, values that may significantly exceed the 1.48 V thermodynamic threshold (thermoneutral potential) required to dissociate water [44].

These limitations have largely been attributed to the electrocatalysts used in the OER reaction, which are often based on noble metals such (Ru) and iridium (Ir), which are expensive and scarce materials that are key to achieving high efficiency in these reactions but limit the economic feasibility of large-scale technology [45]. The use of precious metals also causes catalyst degradation. To address this, research has focused on the development of alternative catalysts made from more abundant materials such as iron, cobalt, nickel oxides, and carbon-based materials. These catalysts have shown promising performance, but they still do not match the stability and efficiency of noble-metal-based catalysts [45]. Over time, IrO_2 and RuO_2 catalysts tend to degrade because of the aggressive nature of the OER, resulting in a decrease in cell efficiency and a shortened operational lifespan of the electrolysis system. Energy consumption during electrolysis is not only affected by the catalysts but also by the nature of the electrolyte (acidic or alkaline), which affects the efficiency of ion exchange reactions inside the cell. The use of liquid acidic electrolytes can improve conduction rates but also presents corrosion challenges, whereas alkaline electrolytes are more stable but typically require higher potentials [46].

Despite these challenges, continuous efforts have been made to enhance the energy efficiency and reduce the operational costs through new strategies for catalyst design and process optimization. Recent advances have focused on the development of nanomaterials and low-dimensional structures, such as carbon nanotubes and transition metal nanoparticles, which provide larger surface areas and more active sites for OER reactions [47].

3.2. Electrochemical reforming of organic compounds

ECR is an innovative and increasingly studied strategy for H_2 production, offering a compelling alternative to conventional water electrolysis. In the ECR, carbon-containing compounds such as alcohols (e.g., methanol and ethanol), polyols (e.g., glycerol), carboxylic acids, and other biomass-derived molecules undergo electrochemical oxidation at the anode, while H_2 is simultaneously generated at the cathode via the HER [13]. ECR replaces the OER with the oxidation of organic compounds at the anode, enabling operation at lower voltages (0.2–0.8 V vs standard hydrogen electrode (SHE) below the OER), thus reducing energy losses [48,49]. The oxidation of organic molecules involves complex electron and proton transfers, dehydrogenation, $C-C$ bond cleavage, and the formation of adsorbed intermediates (CO, aldehydes, carboxylic acids), which depend on the molecular structure and catalytic surface [50].

The fundamental principles of the ECR are rooted in electrochemical thermodynamics and kinetics. The oxidation of organic molecules involves complex, multistep electron and proton transfer reactions, which are strongly influenced by the molecular structure of the substrate and physicochemical characteristics of the catalytic surface. At the anode, these processes may include dehydrogenation, $C-C$ bond cleavage, and the formation of adsorbed intermediates such as CO, aldehydes, and carboxylic acids. These pathways depend on the adsorption energies, activation barriers for the bond-breaking steps, and nature of the active sites on the electrode surface [50]. The choice of organic fuel is a determining factor for the efficiency, life cycle, and scalability of ECR. Among the most studied options are methanol, glycerol, and ethanol, all of which present a unique balance of advantages and challenges. To elucidate this balance, Fig. 5 [51–54] presents a visual analysis of the fundamental principles governing the ECR of these alcohols. Part (a) of the figure demonstrates the higher energy efficiency through conceptual polarization curves, whereas part (b) directly compares their thermodynamic potentials to that of water electrolysis. Part (c) summarizes the key life cycle and viability aspects of each fuel using icons.

3.2.1. Methanol

Methanol exhibits the lowest standard oxidation potential (0.02–0.20 V vs SHE), but its application faces the major challenge of catalyst poisoning by the adsorption of carbon monoxide (CO), a reaction intermediate that blocks active sites [55,56]. To mitigate this issue, the most effective catalysts are platinum–ruthenium $(Pt-Ru)$ alloys, in which ruthenium promotes the oxidation of CO adsorbed on the platinum, thereby "cleaning" the catalytic surface and extending the system's lifespan [57,58].

Considering its lifecycle and scalability, methanol presents a paradox. On the one hand, its global production and transportation infrastructure are well established. On the other, over 95% of the world's methanol is "gray"(produced from natural gas), resulting in a high carbon footprint [59]. Therefore, the viability of methanol for green ECR depends on scaling up "green methanol" (from biomass or captured CO_2), which is not yet economically competitive [60].

3.2.2. Glycerol

Glycerol, a biodiesel product, has a higher standard oxidation potential of 0.30 to 0.45 V vs SHE and a practical potential of 0.6 to 0.9 V. Its main advantage is the ability to generate valuable products, such as glyceraldehyde, dihydroxyacetone, and oxalic and glycolic acids, glycerol stands out for its excellent circular economy appeal, transforming a waste stream into value-added products [61–63]. Its oxidation, however, is complex and can follow multiple pathways. The selectivity is influenced by the catalyst: to maximize H_2 production, platinum (Pt)-based catalysts are used; for the co-generation of high-value chemicals, gold (Au) or palladium (Pd) catalysts in alkaline media are more efficient [64].

However, the transition from the laboratory-to the industrial-scale is hindered by two critical factors. The first is feedstock purity: crude glycerol contains impurities that poison the catalysts, requiring costly purification steps [65]. The second is the complexity of product separation: low selectivity generates an effluent with multiple byproducts, making industrial-scale purification a challenge.

3.2.3. Ethanol

Ethanol has the highest standard oxidation potential, between 0.50 and 0.60 V vs SHE, with a practical potential of 0.8 to 0.9 V. One of its greatest advantages is that it provides a source of biomass through fermentation, which has an established infrastructure. The main technical challenge is the efficient cleavage of the $C-C$ bond. The reaction can follow complete oxidation to CO_2(C2 pathway, 12 electrons) or POX to acetaldehyde and acetic acid (C2 pathway, 4 electrons) [54,55,66]. Furthermore, its use in fuel cells can result in an energy savings of 30%–50% compared to water electrolysis [55,67]. The selectivity between these routes depends on the catalyst and pH; in acidic media, platinum–tin $(Pt-Sn)$ alloys are effective, while in alkaline media, palladium (Pd) stands out for its high activity, low cost, and greater tolerance to intermediates [56,68]. Ethanol's decisive advantage for industrial deployment lies in the synergy between its renewable origin and a mature global infrastructure, a combination that mitigates one of the primary hurdles for adoption of new technology [69].

Methanol, ethanol, and glycerol each present unique characteristics that shape their roles in electrochemical reforming for H_2 production, as summarized in Table S1 in Appendix A. Methanol offers the advantage of a low oxidation potential but is hindered by catalyst poisoning and environmental concerns. Glycerol, which is renewable and is capable of yielding diverse valuable products, faces challenges in terms of reaction complexity and feedstock variability. Ethanol stands out as a balanced and practical option, combining a renewable source with manageable oxidation challenges and the added benefits of simultaneous H_2 and chemical production. The choice among these depends on the specific application context, catalyst development, and system design, as summarized in, but the favorable combination of the properties of ethanol is a particularly promising candidate for sustainable and efficient electrochemical reforming. Table 1 [70–72] summarizes

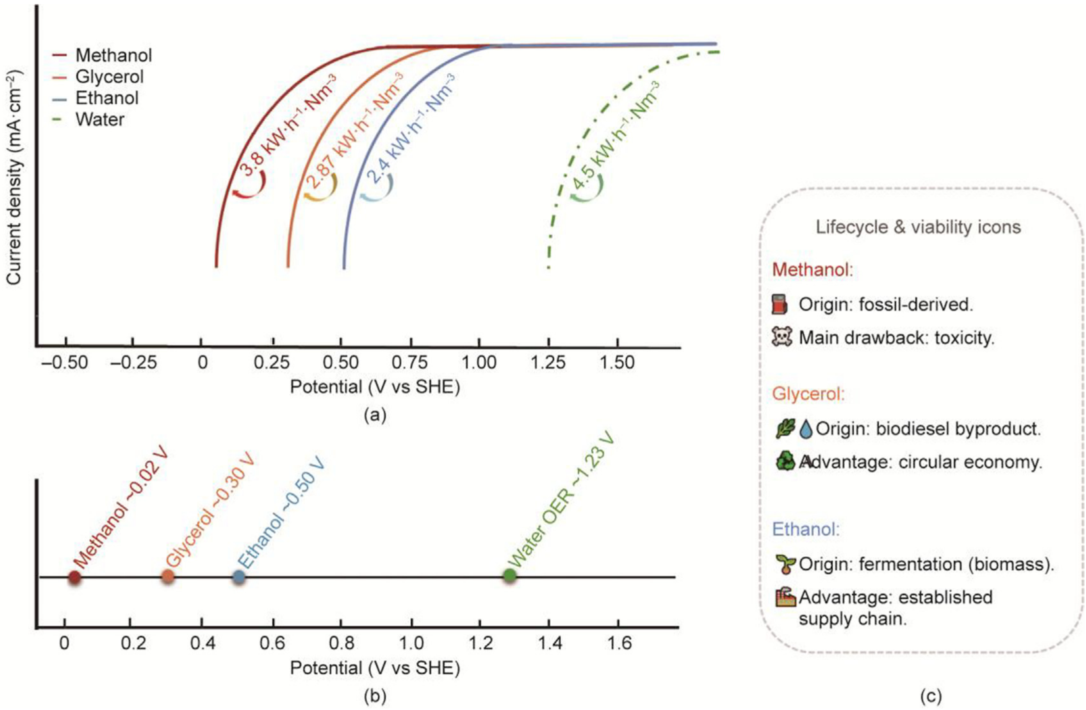

Fig. 5. A multi-faceted comparison of methanol, ethanol, and glycerol for ECR against conventional water electrolysis. (a) Conceptual polarization curves illustrating the lower operational potential (higher efficiency) of alcohol oxidation reactions, with the specific electrical energy consumption for each process highlighted in $\mathrm{kW{\cdot}h{\cdot}Nm^{-3}}$. (b) Thermodynamic potential axis comparing the standard oxidation potentials for methanol, glycerol, and ethanol against the OER benchmark. (c) Icons representing key life-cycle and viability aspects for each alcohol: fossil origin and toxicity for methanol; renewable byproduct origin and circular economy potential for glycerol; and biomass origin and established infrastructure for ethanol [51–54].

Table 1

Comparative summary of the key properties of methanol, glycerol, and ethanol as feedstocks for ECR. The analysis covers the standard oxidation potential of each compound, its primary sources, the value-added products generated at the anode, and the main technical and operational limitations that impact its viability.

Compound	Standard oxidation potential (V vs SHE)	Feedstock source	Byproducts	Valuable products	Key limitations
Methanol [70]	~0.02–0.20	Fossil fuels (mainly)	Strong CO adsorption, catalyst poisoning	formic acid	Toxicity, fossil-derived
Glycerol [71]	~0.30–0.45	Biodiesel byproduct	Complex reaction pathways, product separation	Glyceraldehyde, dihydroxyacetone	Low selectivity, variable supply
Ethanol [72]	~0.50–0.60	Biomass (fermentation)	C – C bond cleavage, CO adsorption	Acetaldehyde, acetic acid	CO poisoning (manageable), incomplete oxidation

the main attributes of each fuel, including analysis of the catalysts and scalability with their respective references.

A fundamental implication of the thermodynamic distinctions between alcohol oxidation and oxygen evolution is the decrease in the cell potential required to operate the system, which in turn reduces energy consumption. Fig. 6 quantifies this advantage, detailing the specific energy consumption (in $\mathrm{kW{\cdot}h{\cdot}(Nm^3)^{-1}}$ of H_2) for H_2 production from the reforming of ethanol, methanol, and glycerol and contrasting these values with the high energy consumption of water electrolysis. Each feedstock undergoes anode oxidation to produce H_2 at the cathode; however, the energy consumption per unit volume of generated H_2 varies significantly. All the reactions exhibited high enthalpy changes, indicating a relatively large energy input, as evidenced by the required reaction energies. Among these, ethanol requires the lowest energy at ~2.4 $\mathrm{kW \cdot h}$ per normal cubic meter ($\mathrm{Nm^3}$) of H_2 produced significantly lower than other feedstocks, making it a promising candidate for efficient H_2 generation. Even when compared to methanol oxidation (which proceeds with a much lower enthalpy change ($\Delta H = +43.8\,\mathrm{kJ}\cdot(\mathrm{mol\,H_2O})^{-1}$)), ethanol retains its advantage in terms of energy efficiency [73], reflecting a lower thermodynamic energy barrier. However, the energy consumption is higher at approximately 3.8 $\mathrm{kW \cdot h \cdot Nm^{-3}}$, which is usually attributed to kinetic limitations and catalyst poisoning effects that hinder efficient conversion [74]. Glycerol shows an intermediate energy demand (2.87 $\mathrm{kW{\cdot}h{\cdot}Nm^{-3}}$), while methanol requires higher operational energy due to catalyst deactivation and complex reaction pathways [75].

An in-depth analysis revealed a complex balance of technical, economic, and environmental factors. Methanol offers chemical simplicity and benefits from a mature infrastructure, but its viability as a source of green H_2 depends on the transition to renewable production routes [60,76]. Glycerol represents the ideal of the circular economy by valorizing an industrial residue but is hindered by significant purification and selectivity challenges that complicate its scale-up [77,78]. Ethanol, in turn, emerges as the most pragmatic and robust candidate for large-scale implementation. It combines the best of both worlds: a renewable and sustainable

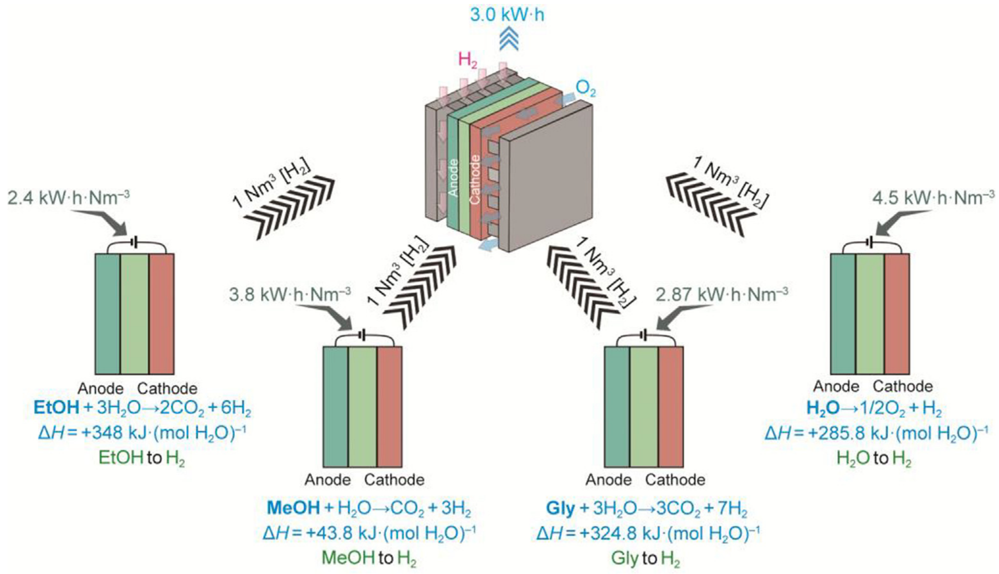

Fig. 6. Specific electrical energy consumption (in kW·h per Nm^3 of H_2) for hydrogen production, demonstrating the energetic advantage of the electrochemical reforming of alcohols (ethanol, methanol, and glycerol) over conventional water electrolysis. The stoichiometric reactions and corresponding enthalpy changes (ΔH) for each process are also shown, highlighting the underlying thermodynamic differences.

source, with a globally established production chain and logistics. Although the complete cleavage of its C – C bond remains a catalytic challenge, its high energy efficiency and ease of scalability are the most promising alternatives for decentralized and sustainable H_2 production via electrochemical reforming [79].

4. Comparative analysis

Conventional thermal reforming supports the current industry with its operational maturity, ECR emerges as a sustainable alternative; however, it still faces critical challenges. Its broader applicability can be attributed to the longer history of technological development related to conventional reforming, as shown in Fig. 7(a). This illustrates the number of scientific publications per year on *Conventional Reforming* (searching specifically for steam reforming) and ECR (searching for electrochemical reforming) from 1970 to 2025 in the Scopus journal database. Conventional reforming has been extensively studied for many decades, with a sharp increase in research activity starting around the year 2000. In contrast, ECR publications began increasing only in the last decade, still representing less than 15% of total reforming studies.

Figs. 7(b) (conventional) and (c) (ECR) map the thematic evolution over time. Conventional reforming was strongly dominated by catalyst development during the first three decades (1975–2005), accounting for approximately 85%–95% of all indexed studies in the field. This overwhelming focus reflects the historical efforts to optimize Ni-based catalysts and reaction conditions in thermal processes. After 2010, the share of catalyst-related publications gradually declined to around 40%–50% as research diversified toward *mechanistic modeling* and *process integration* (~25% after 2015), followed by emerging topics such as *carbon-capture coupling* and *reactor electrification* (~10%–15%). This quantitative reduction aligns with the technological maturity of SMR, where further progress increasingly depends on system-level optimization rather than new catalytic formulations. Fig. 7(c) shows that the distribution of ECR research topics has been considerably more balanced since its emergence. Studies explicitly focused on *electrocatalysts* account for roughly 30%–55% of total publications throughout the analyzed period, with noticeable oscillations peaking around 1995, 2010, and 2020, and alternating dominance among *membrane and cell design*, *reaction mechanisms*, and *alcohol oxidation studies*. These oscillatory patterns, consistent with bibliometric data, indicate that the catalytic core of ECR research has not yet reached the consolidation stage observed in conventional reforming. Instead, the field remains distributed across multiple exploratory fronts, suggesting that the design principles, active-site descriptors, and mechanistic frameworks for electrocatalysts are still under definition and are subject to periodic reorientation as new materials and reaction environments are investigated.

The long developmental history of thermal reforming, particularly SMR, explains its technological maturity and industrial dominance. SMR plants routinely exceed 100 $\mathrm{t\,H_2 \cdot d^{-1}}$, meeting large-scale demands from refineries and chemical industries at costs of 1–2 $\mathrm{USD{\cdot}kg^{-1}H_2}$[80]. This high efficiency is inseparable from its dependence on fossil fuels, generating 7–13 $\mathrm{kg\,CO_{2-eq}\,kg^{-1}\,H_2}$ [81]. Variants such as ATR and POX have emerged to mitigate these impacts. ATR, for instance, integrates catalytic reforming and partial oxidation, achieving thermal efficiencies up to 63% and improved compatibility with CCUS technologies [82].

Water electrolysis powered by renewable energy produces green H_2 with zero direct emission. PEM and solid oxide electrolysis cell (SOEC) can reach electrical efficiencies of 60%–80%, potentially surpassing 100% when SOEC is coupled with residual heat recovery [83]. The specific energy consumption of $\mathrm{4.5\ kW \cdot h \cdot Nm^{-3}}$ remains a barrier to large-scale deployment (Fig. 6). ECR extends this landscape by converting organic molecules into hydrogen and other valuable co-products. However, the selectivity of anodic oxidation is still a major limitation, partial oxidation of complex molecules can yield mixed intermediates, reducing Faradaic efficiency to below 60% in pilot systems [84]. The heavy reliance on precious metal catalysts (Pt in PEM, Ir in SOEC) elevates costs to 3–6 $\mathrm{USD{\cdot}kg^{-1}\,H_2}$ and raises scalability concerns owing to metal scarcity [85]. The International Energy Agency (IEA) projects that partial substitution (40%–60%) of non-platinum catalysts by 2030 could reduce costs, although durability and activity remain technological challenges [80].

Recent techno-economic studies emphasize that the competitiveness of each route is highly sensitive to variations in key assumptions, including the electricity price, catalyst cost, and car-

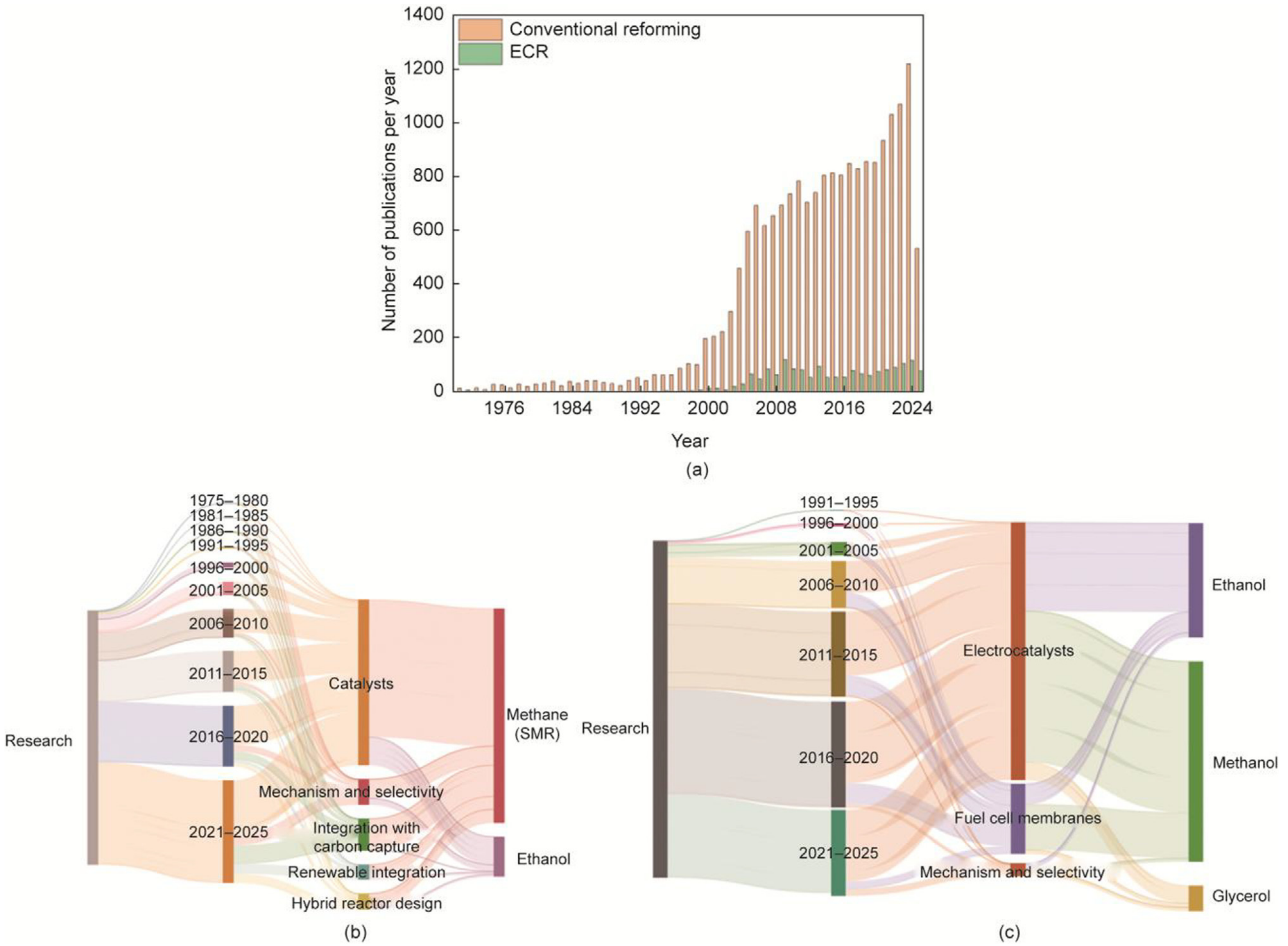

Fig. 7. (a) Annual number of scientific publications related to conventional thermal reforming and ECR between 1970 and 2025, according to the Scopus database. (b) Thematic evolution of research topics in conventional reforming, showing an early predominance of catalyst development (1975–2005) followed by diversification toward mechanism and selectivity, integration with carbon capture, and renewable-assisted reactor design after 2015. (c) Thematic evolution of ECR studies, highlighting a more balanced and oscillatory distribution among electrocatalysts, fuel-cell membranes, reaction mechanisms, and oxidation of alcohols (ethanol, methanol, and glycerol).

bon taxation [86]. When electricity prices exceed 0.08 USD·kW · h^{-1}, electrolysis-based routes become economically unfeasible, reaching 4–7 USD·kg^{-1} H_2, depending on regional energy mixes. Conversely, under scenarios of low renewable electricity costs (≤ 0.03 USD·$(kW·h)^{-1}$) and moderate carbon taxes (≥ 50 USD·t^{-1} CO_2), electrochemical and hybrid systems could achieve cost parity with SMR. This sensitivity highlights how policy-driven variables, such as carbon pricing, renewable incentives, and technological learning rates, can drastically reshape the cost hierarchy among H_2 production routes. For instance, the inclusion of carbon taxes equivalent to 100 USD·t^{-1} CO_2 increases the cost of gray hydrogen from SMR by nearly 30%, narrowing the gap with blue hydrogen and making electrochemical reforming comparatively more attractive for distributed production.

Table 2 [14,71,80,82,87–89,93–97] compares the main characteristics of the thermal and electrochemical H_2 production technologies, including efficiency, CO_2 lifecycle emissions, scalability, and Technology Readiness Level (TRL). This metric, ranging from 1 to 10, classifies technologies from the initial concept to commercial deployment and offers a qualitative indicator of maturity and investment readiness. Conventional technologies such as SMR, ATR, and POX operate at 700–1200 °C using Ni-based catalysts, and exhibit high TRLs (7–10). In contrast, electrochemical methods, including PEM electrolysis and ECR, function below 100 °C and currently range between TRLs 3 and 10, reflecting their emerging status in H_2 production [98,99].

From an environmental standpoint, conventional reforming remains carbon-intensive, producing 9–12 kg CO^2 · kg^{-1} H_2 even with WGSR optimization. Although ATR offers enhanced CCUS compatibility, these systems increase both the capital expenditure (CAPEX) and operational complexity. Ethanol-based thermal reforming can approach carbon neutrality when bioethanol is used, but its efficiency (30%–40%) and cost competitiveness remain limited relative to SMR. These tradeoffs illustrate the persistent challenge of balancing maturity, efficiency, and environmental responsibility.

The ECR of ethanol presents a fundamentally different paradigm. Operating at 50–90 °C, it enables decentralized H_2 generation with drastically lower lifecycle emissions 0.600 to 0.037 kg $CO_{2\text{-eq}}$·$(kW·h)^{-1}$, depending on the electricity mix. When powered by renewable energy and biogenic ethanol, ECR can approach near-zero carbon intensity, thereby offering a fully renewable route. However, TRLs (3–6) and CAPEX (5 000– 20 000 USD·$kW_e{}^{-1}$) remain barriers due to the noble metal and membrane costs. A quantitative comparison between the ethanol reforming routes by Gutiérrez-Guerra et al. [100] highlights these distinctions. Thermal reforming achieves a higher absolute H_2 rate (85.09 vs 0.007462 mol · h^{-1} for ECR), the electrochemical route offers a slightly better H_2 yield per mass of ethanol (0.0434 vs 0.0301 kg H_2 · kg^{-1} C_2H_5OH) and lower energy demand (29.2 vs 32.7 kW·h·kg^{-1} H_2). From an economic and scalability perspective, SMR remains the most competitive option, with a CAPEX of

Table 2
Comparison of conventional and electrochemical reforming pathways for hydrogen production, highlighting operating principles, temperature ranges, efficiencies, and TRL.

	Technology	Operating Principle	Temperature (°C)	Efficiency (%)	TRL	Scalability	CO_2 lifecycle emissions	CAPEX/ OPEX
Conventional Reforming	SMR [80,82,87–89]	Thermocatalytic reforming + WGSR	700–1000	70–85[a]	10	Very high (the dominant technology)	High—9–12 $kgCO_2\cdot kg^{-1}$ H_2	Low/medium—600–1200 $USD\cdot kW^{-1}$ of H_2 (cheapest for large scale)
	Ethanol [90–92]	Thermocatalytic reforming + WGSR	800	30–40[a]	7–9	High (demonstrated, but not on a large scale)	Potentially neutral (depends on the source of the ethanol)	Medium/high (more expensive than SMR)
	ATR [71,80,89]	Thermocatalytic POX + SR + WGSR	900–1050	60–75[a]	7–9	High (commercially mature)	High— ~9–12 kg $CO_2\cdot kg^{-1}$ H_2 similar to SMR (easier to integrate with CCUS)	Medium—800–1500 $USD\cdot kW^{-1}$ of H_2 (CAPEX may be higher than SMR)
	POX [71,80,88,89]	Thermal partial oxidation	> 1200	60–75[a]	9,10	Very high (commercially mature)	High— ~9–12 kg $CO_2\cdot kg^{-1}$ H_2	Medium—800–1500 $USD\cdot kW^{-1}$ of H_2 (requires air separation plant)
Electrochemical Reforming	H_2 Fuel Cells [71,93–95]	Electrochemical water splitting	70–90	40–70[b]	9,10	Demonstration/early commercial (initial commercialization phase)	Low— ~0.60–0.037 kg CO_2-eq.$\cdot(kW\cdot h)^{-1}$	High— ~2000–5000 $USD\cdot {kW_e}^{-1}$ (costs are decreasing)
	DEFC [14,71]	Ethanol electro-oxidation	50–90	40[b]	3–6	Demonstration/early commercial (laboratory validation phase)	Medium— ~0.83–1.25 kg $CO_{2\text{-eq}}\cdot(kW\cdot h)^{-1}$	Very high— ~5000–20 000 $USD\cdot {kW_e}^{-1}$ (based on the cost of precious materials)
	DMFC [88,93,96]	Methanol electro-oxidation	50–120	40[b]	5–7	Prototype/pre-commercial (more mature than DEFC for niche markets)	Low— ~0.20–0.50 kg $CO_{2\text{-eq}}\cdot(kW\cdot h)^{-1}$	Very high— ~5000–20 000 $USD\cdot {kW_e}^{-1}$ (based on the cost of precious materials)
	DGFCs [71,97]	Glycerol electro-oxidation	50–90	33[b]	3–5	Laboratory/ prototype (laboratory validation phase)	Potentially neutral (values not specified)	Very high— ~5000–20 000 $USD\cdot {kW_e}^{-1}$ (based on the cost of precious materials)

TRL: Technology Readiness Level.
[a] Thermal efficiency, based on the higher heating values.
[b] Lower heating value of hydrogen produced divided by the electrical energy to the electrolysis cell.

600– 1200 $USD\cdot kW^{-1}$ H_2 and stable operating expense (OPEX) supported by existing infrastructure and supply chains. On the other hand, ECR is inherently modular and suited for decentralized or on-site production, particularly in regions with abundant renewable electricity and bioethanol. Although still capital-intensive (5 000–20 000 $USD\cdot {kW_e}^{-1}$), expected reductions in electricity costs and improvements in electrocatalyst durability may close this gap in the next decade.

Conventional reforming remains the dominant pathway for current H_2 production, providing the scale and cost efficiency needed to meet industrial demand in hard-to-abate sectors [101]. The reliance on fossil feedstocks and dependence on the CCUS position it as a transitional rather than a sustainable solution. Although still emerging, ECR offers a complementary low-emission pathway driven by renewable electricity and modular design. Its widespread adoption depends on continued policy support, cost reductions, and infrastructure expansion. Together, these technologies define a dual-transition model in which thermal reforming ensures short-term energy security, whereas electrochemical systems enable the long-term decarbonization and localization of H_2 production within a circular and resilient energy framework [102].

Considering the aspects discussed for the aviation sector, the implications of different reforming routes were also assessed in terms of their compatibility with future flight applications and the associated infrastructure. ECR appears to be more suitable owing to its operation under mild conditions and potential for on-site H_2 generation. The conventional reforming routes face major constraints associated with fuel storage and aircraft retrofitting. Even for short-range turboprop aircraft, H_2 storage remains the main limitation owing to its low volumetric density. Achieving the energy required for a 700 nautical miles (NM; 1 NM = 1.85×10^3 m) flight would demand up to 11 times more tank volume and storage densities above 33–35 wt% to maintain the same operating weight, whereas current systems reach only 10–12 wt% and require 700–1000 bar or cryogenic temperatures below 20 K, adding major structural and cost penalties [103]. ECR eliminates the need for H_2 storage entirely, as the reforming process produces H_2 *in situ* from liquid alcohols. These fuels are liquid at ambient conditions (densities of ~790 $kg\cdot m^{-3}$) and can be handled using existing kerosene infrastructure, including pipelines, storage tanks, and refueling systems, with only minor material adaptations. This inherent compatibility significantly reduces the retrofit cost for airports and aircraft while also minimizing the safety and volumetric constraints that make large-scale gaseous or liquid hydrogen storage impractical.

Techno-economic assessments indicate that H_2 infrastructure at large airports may require large capital investments, while ECR deployment involves lower initial costs but higher operational expenses owing to limited biomass feedstock and conversion efficiency. Beyond the economic dimension, H_2 storage introduces substantial safety and operational challenges in airport environments. Owing to its high flammability, low ignition energy, and rapid diffusion, a large-scale H_2 containment requires specialized cryogenic tanks, advanced leak-detection systems, and continuous monitoring to prevent embrittlement or vapor accumulation near refueling areas. The coexistence of H_2 and conventional kerosene logistics increases the risk of cross-contamination and ignition, particularly under adverse weather or maintenance conditions. Furthermore, airports must allocate extensive safety perimeters, redesign underground pipelines and hydrant systems, and train personnel for new emergency protocols [104].

4.1. Future perspectives

SMR demonstrates the highest efficiency and technological maturity, disregarding the carbon footprint, and is the best option for H_2 production. Alternative pathways are also being explored, and biomethane stands out as a promising option, with current research advancing production methods from agricultural residues, including sugarcane bagasse, owing to its high availability in countries like Brazil [105], as well as from sanitary landfills [106]. The first approach is directly linked to the concept of implementing zero-emission integrated biorefineries, which aim to optimize resource use and minimize environmental impacts throughout the entire production chain. For example, although renewable, ethanol production still has an associated greenhouse gas footprint due to methane emissions, and the use of vinasse as a fertilizer can lead to the release of nitrous oxide (NO_2), a potent greenhouse gas. Integrated biorefineries address these challenges by enabling sequential and efficient production of biofuels and biofertilizers from the same biomass feedstock. By valorizing byproducts, such as vinasse, into biofertilizers or other valuable inputs, these systems reduce waste and limit harmful emissions.

The use of ethanol reforming to produce H_2 for fleets beyond pilot projects, such as the initiative at the USP, is crucial for validating their real-world operational feasibility and economic viability. A key focus must also be on improving H_2 production through ethanol steam reforming. Developing more efficient catalysts (as feasible through machine learning applications) [107] and refined reactor designs can significantly increase the energy conversion efficiency and reduce costs. This is highlighted by the study's findings, which show a total energy efficiency (well-to-wheel) of approximately 26.9% for H_2 vehicles, far surpassing the 11.8% for conventional diesel [34]. Furthermore, studies have described the use of H_2 blended with conventional fuels as an alternative to facilitate technological transition. For instance, the addition of H_2 to engines has been shown to reduce vehicle-generated noise and vibration. The combustion quality was also enhanced by the hydrogen-biodiesel mixture. This approach can serve as a viable option to guide technological transitions toward cleaner energy systems [108].

To achieve practical efficiency in the ECR, the development of advanced catalysts capable of addressing challenges such as sluggish kinetics and catalyst poisoning is essential. This requires a detailed understanding of the underlying reaction mechanisms that govern both the kinetics and selectivity. Recent studies have already moved in this direction, exploring theoretical approaches such as microkinetic modeling of methanol electro-oxidation [109], as well as experimental strategies to identify adsorbed intermediates and soluble products using advanced techniques, including differential electrochemical mass spectrometry (DEMS) [35,110–112], Fourier transform infrared spectroscopy (FTIR) [113–115], and surface-enhanced Raman spectroscopy (SERS) [116,117].

Using fuel cells for flights still has a long way to go before they can be applied on a large commercial scale, as countless points still need to be addressed. For example, the establishment of a supply chain, aircraft designs, and operational strategies is consistent with high demand at airports. Although H_2 use is viable in aircraft, some dilemmas still persist. These include storing LH_2, which requires tanks approximately four times larger. This can lead to changes in the aircraft's center of gravity and stability. In addition, cryogenic tank control is necessary, and leaked H_2 can cause global warming through chemical reactions in the atmosphere [118]. With an estimated average consumption of 3–4 liters per passenger per 100 km, there is a high demand, and consequently, a mature technological strategy is needed to supply this demand. Because of the difficulty in miniaturizing the SMR, its installation in aircraft would be unfeasible, leading to a return to confined H_2 storage. The ECR route is the most interesting option because of its high-energy potential, safety, and possibility of miniaturization.

5. Concluding remarks

This review establishes a comprehensive and quantitative analysis comparing conventional thermal reforming and ECR as pathways for sustainable H_2 production, particularly within the aviation sector. By integrating thermodynamic, techno-economic, and life-cycle metrics, this study provides a consolidated roadmap linking catalyst performance, process efficiency, and infrastructure readiness, an aspect not previously addressed in such a unified manner.

The analysis revealed that conventional thermal reforming remains economically dominant but environmentally constrained, while the electrochemical route offers a practical framework for low-temperature, carbon-neutral hydrogen generation. In contrast, ECR operates under mild conditions and enables low-carbon H_2 generation. In the aviation context, the applicability of these routes differs significantly. Conventional thermal reforming, owing to its high operating temperature and centralized nature, is unsuitable for direct use onboard aircraft and requires profound structural redesigns to manage heat, pressure, and storage systems. Therefore, its role is restricted to ground-based production rather than in-flight H_2 generation. ECR, on the other hand, offers a more compatible and flexible alternative. By operating under near-ambient conditions and using liquid as feedstock, ECR allows onboard H_2 production without major modifications to existing aircraft or fueling logistics.

From a technological perspective, ECR is currently limited by its high capital intensity and dependence on noble metal catalysts, which hinders large-scale deployment. Overcoming these barriers requires significant progress in the development of non-precious catalysts and further reduction in renewable electricity costs to improve competitiveness. The performance thresholds include catalyst cost reductions above 60% and electricity prices below $0.03\ \mathrm{USD{\cdot}kWh^{-1}}$. These quantitative boundaries define actionable engineering and policy targets, providing a realistic pathway for transforming ECR from a laboratory-scale concept into commercially viable and sustainable hydrogen production technology.

Overall, this study advances the field by ① establishing a comparative techno-environmental framework that unifies disparate reforming routes, ② identifying ECR as a scalable, low-carbon, and infrastructure-compatible alternative for aviation decarbonization, and ③ outlining measurable conditions for industrial competitiveness. These findings provide not only a scientific basis for catalyst and reactor development, but also a strategic guideline for stakeholders aiming to align H_2 production technologies with the broader goals of carbon neutrality and energy security.

CRediT authorship contribution statement

Leandro Hostert: Writing – original draft, Investigation, Formal analysis, Data curation. **Naiza Vilas-Bôas:** Formal analysis, Data curation. **Julio R. Meneghini:** Writing – review & editing, Funding acquisition. **Edson A. Ticianelli:** Writing – review & editing, Funding acquisition. **Hamilton Varela:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hamilton Varela reports financial support was provided by University of São Paulo. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eng.2025.10.028.

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