

Review

Recent Advances in Renewable Hydrogen Purification Technologies: A General Review

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Abstract

Renewable hydrogen purification is a critical yet often underemphasised step in enabling its use as a clean energy carrier. Hydrogen produced from biomass-based thermochemical and biological routes typically contains CO₂, CO, CH₄, H₂S, and other impurities that must be removed to meet stringent requirements for fuel cell, industrial, and grid-injection applications. This review provides a critical and up-to-date assessment of renewable hydrogen purification technologies, focusing on their suitability for variable and impurity-rich renewable hydrogen streams. Established benchmark technologies, including pressure swing adsorption and cryogenic separation, are described, with emphasis on their operating principles, material innovations, and process integration strategies. Recent advancements in inorganic, polymeric, and mixed-matrix membranes are highlighted, with particular focus on how advanced porous materials enhance selectivity, permeability, and flexibility. Additionally, a comparative techno-economic assessment is presented, evaluating each purification method based on technology readiness level, capital and maintenance costs, energy efficiency, and operational lifespan. By incorporating recent research trends, this approach facilitates the selection and design of purification systems that are not only efficient and scalable but also cost-effective, tailored to both decentralised and centralised renewable hydrogen production.

Keywords: renewable hydrogen; hydrogen purification; pressure swing adsorption; membrane separation; techno-economic assessment

1. Introduction

Hydrogen has emerged as a key energy carrier in the transition to low-carbon energy systems, owing to its high energy density and potential for zero-emissions when produced from renewable resources. However, achieving cost-competitive renewable hydrogen depends critically on effective purification, particularly in biomass-derived and other emerging production pathways, where multicomponent gas streams and trace contaminants complicate separation. This review focuses on recent advances and deployment considerations in renewable hydrogen purification technologies, highlighting performance trade-offs and implementation readiness under realistic feed conditions.

Hydrogen is increasingly recognised as central to decarbonisation strategies across the transport, industrial, and energy sectors due to its high gravimetric energy density and absence of direct carbon emissions at the point of use [1]. However, its overall climate benefit



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depends strongly on the production pathway. The current market remains dominated by fossil-based hydrogen (grey hydrogen), while blue hydrogen integrates carbon capture, and green or renewable hydrogen is produced from renewable electricity or renewable carbon resources [2–4]. In contrast to grey hydrogen derived from natural gas reforming, renewable hydrogen streams obtained from biomass, biogas, or waste gasification are typically more heterogeneous and impurity-rich, containing variable levels of CO₂, CO, CH₄, H₂O, N₂, sulphur species, ammonia, tars, and oxygenated compounds. These compositional characteristics directly influence purification system design, affecting technology selection, sequencing, and operating conditions [5].

Renewable hydrogen can be generated from a wide range of biomass feedstocks through biological or thermochemical conversion pathways. Biological pathways, including dark fermentation and photo-fermentation, as well as photo-biological processes like direct or indirect biophotolysis, operate under mild conditions and utilise renewable substrates. However, they often face challenges such as low conversion efficiencies and high sensitivity to environmental factors. Thermochemical routes, particularly pyrolysis, gasification, and supercritical water conversion, typically achieve higher yields and are more compatible with continuous large-scale operation. These advantages are accompanied by higher operating temperatures, potential catalyst deactivation, and the generation of complex gas mixtures that require extensive downstream purification [6–9].

In contrast to conventional grey hydrogen produced via natural-gas reforming, renewable hydrogen streams derived from biomass gasification, biogas reforming, or waste-to-hydrogen pathways typically exhibit a more heterogeneous and impurity-rich composition. These streams typically contain higher levels of tars, particulates, sulphur species, ammonia, oxygenated compounds, and carbon dioxide. Additionally, they show greater fluctuations in pressure and flow rates. Such differences have direct implications for the design of purification systems, influencing the selection, sequencing, and operating conditions of downstream separation technologies [10].

While numerous reviews have examined the progress of biological and thermochemical hydrogen production in detail [11–14], considerably fewer have focused on the purification stage, despite its critical importance in determining the quality, safety, efficiency, and end-use applicability of renewable hydrogen. Raw gas streams generated from biomass typically contain significant concentrations of CO₂, CO, CH₄, H₂O, N₂, and trace impurities such as H₂S or tars. The presence of these contaminants can adversely affect catalysts, membranes, and electrochemical devices, and therefore, strict impurity limits must be met to comply with the purity standards required for fuel cells, industrial hydrogen applications, and hydrogen distribution networks. Consequently, purification plays a crucial role and often represents a high cost in the renewable hydrogen production process.

Several technologies are currently used for hydrogen purification, including pressure swing adsorption (PSA), cryogenic separation, and membrane-based systems. Each approach offers distinct advantages and limitations in terms of selectivity, energy consumption, scalability, and tolerance to impurities [15–18]. In recent years, research efforts have increasingly focused on adapting these technologies to renewable hydrogen streams, which are typically characterised by fluctuating compositions and the presence of trace contaminants. Significant advances have been reported in the development of novel adsorbents, intensified cryogenic configurations, and next-generation membrane materials, including inorganic, polymeric, and mixed matrix membranes (MMMs). In particular, porous materials such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and their hybrid structures have attracted considerable attention due to their adaptable pore structures and promising separation performance [19–21]. At the system level, progress in process simulation and techno-economic assessment has further contributed to identifying

integrated production–purification schemes that can reduce energy penalties and improve economic feasibility [22].

This review provides a comprehensive overview of recent advancements in renewable hydrogen purification technologies. It covers both conventional and emerging separation approaches, analysing their operating principles, material developments, and potential for integration with biological and thermochemical hydrogen production pathways. In contrast to recent reviews that address hydrogen purification and membrane materials in broader or more generic contexts, the present manuscript explicitly discusses where reported performance claims across studies are not directly comparable due to differences in feed composition, humidity control, and testing temperatures/pressures, and how realistic purification pathways for renewable hydrogen streams are constrained by impurities (e.g., moisture and trace contaminants) and end-use purity specifications. Particular emphasis is placed on evaluating purification technologies under conditions relevant to renewable hydrogen streams, including impurity tolerance, achievable purity, and hydrogen recovery. Key performance indicators, such as capital expenditure, operating costs, technology readiness level (TRL), and specific energy consumption, are systematically compared. By highlighting current limitations, research gaps, and promising hybrid configurations, this review seeks to support informed decision-making and guide the development of efficient, scalable, and robust purification systems for sustainable hydrogen production.

2. Purity Requirements for Renewable Hydrogen Applications

The efficiency, safety, and operational lifetime of hydrogen-based systems are strongly dependent on fuel purity, particularly for electrochemical devices. As discussed in Section 1, renewable hydrogen is produced as a multi-component gas mixture, making purification a critical step in enabling its utilisation across different end-use sectors. Unlike conventional fossil-based hydrogen streams, renewable hydrogen often exhibits greater variability in composition and a higher likelihood of trace contaminants, which directly influences purification requirements and system design [17,23].

Purity specifications are therefore defined according to the intended application, reflecting varying sensitivities to residual contaminants. Among these, proton exchange membrane fuel cells (PEMFC) impose the most stringent requirements, as even trace levels of catalyst poisons can lead to severe performance degradation and irreversible damage. Current international standards, such as ISO 14687:2025 [24] and SAE J2719 [25], require hydrogen purities of at least ≥ 99.97 vol.% for PEMFC, with impurity limits specified at the ppm or ppb level for species such as CO, sulphur compounds, NH_3 , O_2 , and moisture [25,26]. It should be noted that while higher purities (e.g., ≥ 99.999 vol.%) are sometimes reported in the literature for ultra-high-purity hydrogen, a minimum purity of ≥ 99.97 vol.% represents the standard compliance threshold for PEM fuel cell operation [27–31]. Other hydrogen applications exhibit greater impurity tolerance. Solid oxide fuel cells (SOFC), for example, can accommodate higher CO concentrations but remain sensitive to sulphur species. Industrial hydrogen uses, including ammonia synthesis and refinery hydrotreating, typically operate with hydrogen purities in the approximately 95–99.9 vol.% range, where impurity control is primarily dictated by catalyst stability rather than electrochemical performance. Similarly, hydrogen injection into gas grids requires moderate purity levels, with strict control of moisture, oxygen, and sulphur to ensure infrastructure compatibility [32,33].

Representative hydrogen purity requirements for major end-use applications are summarised in Table 1. These specifications provide a reference framework for evaluating renewable hydrogen purification technologies in the subsequent sections, where each separation strategy is assessed not only in terms of hydrogen recovery and energy efficiency,

but also in its ability to meet application-specific purity targets under realistic renewable hydrogen feed conditions.

Table 1. Hydrogen purity standards for key renewable hydrogen end-use applications.

End-Use	H ₂ Purity (vol.%)	Typical Impurity Limits for Key Contaminants	Relevance	Ref.
PEMFC (mobility & stationary)	≥99.97	CO ≤ 0.2 ppm; H ₂ O ≤ 5 ppm; CH ₄ ≤ 100 ppm; O ₂ ≤ 5 ppm; Total sulphur (as H ₂ S) ≤ 4 ppb; NH ₃ ≤ 100 ppb	Most stringent targets due to catalyst & membrane sensitivity	[24,25,27,28]
SOFC	≥99.9	CO ≤ 100 ppm; H ₂ O ≤ 50 ppm; H ₂ S ≤ 100 ppb;	Higher CO tolerance; sulphur still critical	[32,33]
Ammonia synthesis	95–99.9	CO ≤ 10–50 ppm; H ₂ S (Total sulphur) ≤ 10–100 ppb; H ₂ O ≤ 50 ppm;	Sulphur & CO poison catalysts	[34,35]
Refinery hydrotreating	~95–99.9	CO & H ₂ S control required depending on downstream catalysts	Application-specific impurity tolerance	[33,34]
Hydrogen grid injection/blending	~98–99	H ₂ O ≤ 50 ppm; O ₂ ≤ 5 ppm; Total sulphur (H ₂ S) ≤ 10–20 ppb;	Infrastructure compatibility; less severe than fuel cells	[33]
Industrial hydrogen (baseline)	≥95	Typical industrial non-fuel-cell limits	Broad category; use-specific tolerances	[34]

3. Biomass-Derived Renewable Hydrogen Purification Technologies

As outlined in Section 2 and summarised in Table 1, the suitability of renewable hydrogen for applications such as fuel cells, industrial processes, or grid injection is governed by strict, application-specific purity requirements. Meeting these standards requires the effective removal of co-produced gases and trace contaminants from biomass-derived hydrogen streams, making purification a critical downstream step in the renewable hydrogen value chain. In practice, the selection of a purification strategy is determined not only by the target hydrogen purity but also by recovery efficiency, energy demand, scalability, and robustness under variable renewable hydrogen feed conditions.

For clarity, the technologies reviewed in this section are organised into (i) established industrial benchmark technologies and (ii) membrane-based and hybrid technologies that are increasingly relevant for decentralized and small-to-medium-scale renewable hydrogen upgrading. The section concludes with a cross-cutting comparison linking performance metrics, techno-economic indicators, and practical deployment constraints (e.g., pretreatment requirements, impurity tolerance, and scale-up limitations).

3.1. Established Industrial Purification Technologies

3.1.1. Adsorption-Based Purification

Initially designed for hydrogen separation in fossil fuel processes, PSA systems are now being explored for the upgrading of renewable hydrogen streams. This shift is motivated by the varying composition and the presence of trace contaminants in renewable hydrogen, which impose greater demands on the selectivity, durability, and overall integration of adsorbents in the process. Adsorption-based processes are among the most widely used technologies for large-scale hydrogen purification, especially in industrial environments where hydrogen is extracted from natural gas, naphtha, or refinery off-gases. PSA is the most prevalent method, operating by selectively trapping impurities (e.g., CO₂, CO, CH₄, and N₂) on porous materials at high pressure (between 6.5–22 bar), while allowing hydrogen to flow through as the purified output [15]. A variety of adsorbents

are commonly employed, including activated carbon, silica gel, and zeolites. These are chosen based on factors such as adsorption capacity, competitive adsorption behaviour, desorption kinetics, and thermal and mechanical stability, ensuring durability during cyclic operations [36]. For renewable hydrogen streams, these adsorbents must also withstand trace contaminants such as tars, sulphur compounds, and CO_2 , which are often present in biomass-derived gas mixtures, without compromising performance or adsorbent lifespan. Typically, conventional PSA systems achieve hydrogen purities of around 99%. However, recovery rates are often capped at about 80%, primarily due to losses that occur during the depressurisation phase [5]. As a result, although PSA technology can easily achieve industrial-grade purity levels (Table 1), reaching the purity standards necessary for fuel cells often necessitates the use of multi-bed setups or additional polishing processes.

A simplified process flow diagram of a PSA system is depicted in Figure 1, illustrating the cyclical operation that involves high-pressure adsorption, depressurisation (blowdown), countercurrent purge, and subsequent repressurisation stages.

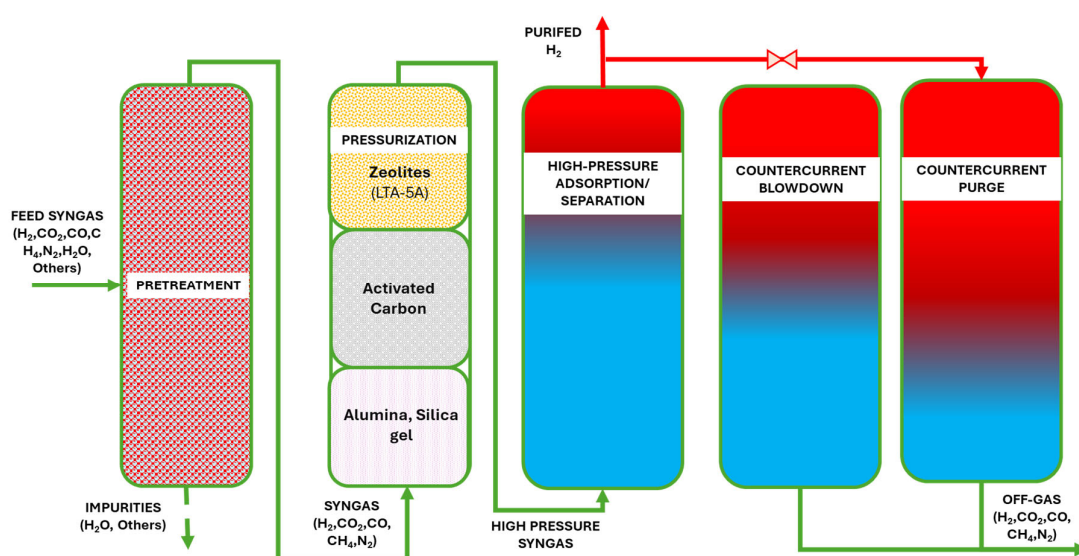


Figure 1. Simplified schematic diagram of a PSA system for hydrogen purification, adapted from [37].

Recent innovations have focused on improving both recovery and purity through advanced cycle configurations and novel adsorbent materials. Vacuum pressure swing adsorption (VPSA), operated at elevated temperatures (200–450 °C) with metal hydride absorbents such as $\text{LaNi}_{4.3}\text{Al}_{0.7}$ or $\text{La}_{0.7}\text{Ce}_{0.3}\text{Ni}_5$, has demonstrated recovery rates as high as 95%, markedly higher than those of conventional PSA systems [36]. Hybrid PSA cycles incorporating steam-rinse or purge stages beyond the dew point have achieved exceptional performance, with reported hydrogen purities of 99.98% and recoveries exceeding 99% [38]. Furthermore, integrating PSA with membrane pre-enrichment stages to form hybrid PSA–membrane systems has yielded combined advantages of high selectivity, reduced adsorbent load, and improved hydrogen recovery (≈ 91 – 92%) [39,40].

To synthesise the operating modes and technological advances described above, a conceptual overview of adsorption-based purification technologies is presented in Figure 2.

Current research is thus directed towards optimising cycle design, improving energy efficiency, and developing next-generation adsorbents such as functionalised zeolites, carbon molecular sieves, and MOFs with enhanced selectivity and stability. These advances, together with integrated purification architectures, are expected to enable cost-effective and scalable solutions for renewable hydrogen upgrading [41,42].

A techno-economic comparison of representative adsorption technologies is summarised in Table 2, outlining key performance and cost indicators relevant to biomass-derived hydrogen purification.

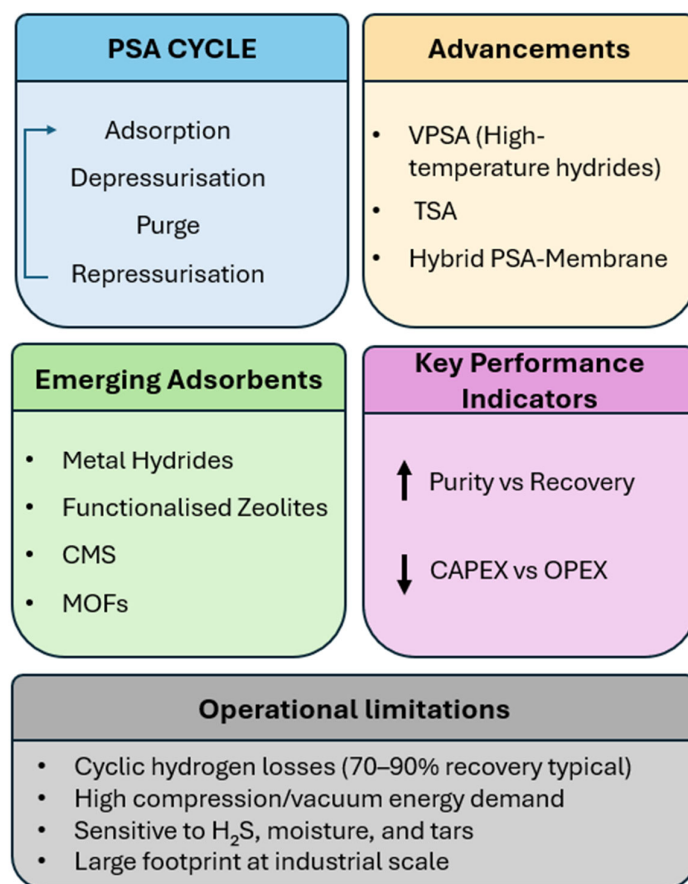


Figure 2. Overview of adsorption-based hydrogen purification technologies.

Adsorption-based systems are advanced technologies commonly used in industrial applications, but they face several challenges when applied to biomass-derived renewable hydrogen. Firstly, PSA and VPSA units often exhibit reduced performance in the presence of tars, sulfur compounds, and moisture. These substances have the potential to irreversibly damage adsorbents, thereby shortening the lifespan of the beds. This issue is particularly relevant for decentralised biomass gasification systems, where feedstock composition can vary significantly. Secondly, while conventional PSA can achieve hydrogen purity of around 99%, the recovery rate typically ranges from 75% to 85% [43]. This results in significant hydrogen losses during depressurisation and purging. Furthermore, the energy required for compression and cyclic regeneration contributes to elevated operational costs, particularly in smaller-scale applications.

Achieving purity levels suitable for PEMFC typically requires multi-bed architectures or downstream polishing processes, which adds complexity to the system and increases capital expenditures (CAPEX). Additionally, issues such as adsorbent ageing, thermal cycling fatigue, and the necessity for periodic replacements create extra maintenance challenges that are often overlooked in techno-economic analyses. These factors emphasise the value of hybrid configurations, such as PSA-membrane or PSA-cryogenic systems, which can help reduce recovery losses, enhance tolerance to impurities, and ensure industrial reliability [44].

Table 2. Techno-economic indicators of adsorption-based hydrogen purification systems.

Technology	TRL	Typical H ₂ Purity (%)	Recovery (%)	CAPEX (€/kW)	OPEX (%/yr)	Specific CAPEX (€/kWh) *	Production Cost (€/kg H ₂)	Ref.
Conventional PSA (zeolite 5A, activated carbon)	9	~99.0	75–85	300–500	3–5	120–250	1.6–2.0	[5,15,36,38,45]
VPSA (metal hydrides, e.g., LaNi ₅ -based)	7–8	99.0–99.9	90–95	400–700	4–6	150–280	1.8–2.3	[36,39,42,45]
TSA (Thermal swing adsorption)	6–7	99.0–99.9	75–90	500–800	5–7	160–300	1.9–2.4	[17,36,40,41]
Hybrid PSA–membrane	6–8	99.0–99.9	91–92	450–900	4–6	180–320	1.5–1.9	[39–42]
MOF-based adsorption (pilot)	4–6	95–99	80–92	800–1200	6–8	200–400	2.0–2.7	[38,41,42]

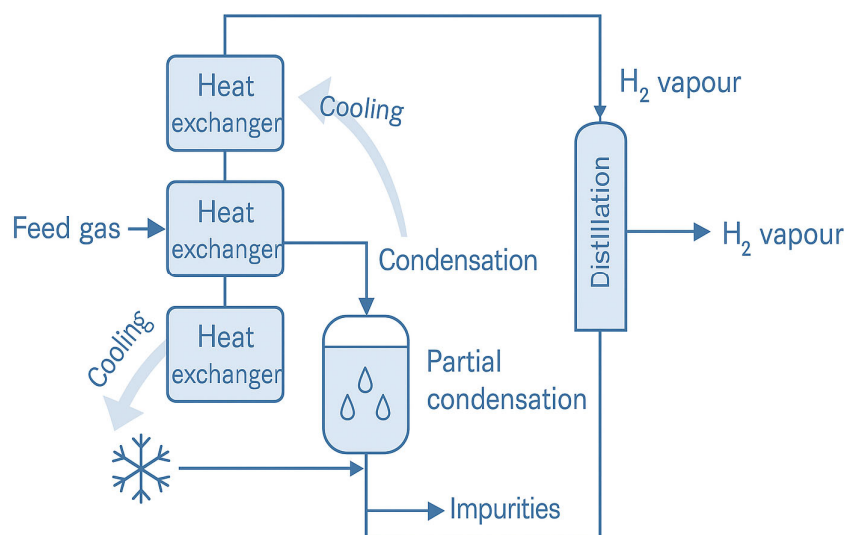
Notes: TRL = Technology Readiness Level (1 = concept, 9 = commercial); CAPEX includes adsorber vessels, compressors, and utilities; costs refer to mid-scale units (50–200 Nm³-H₂/h); production costs exclude upstream H₂ generation; Reported values are literature-derived and may reflect different system boundaries and maturity levels (industrial vs. projected). Multiple references indicate the sources used to compile the reported range.

* Normalised to system scale (1–10 MWh ranges).

3.1.2. Cryogenic Separation

Cryogenic separation constitutes a well-established and industrially relevant route for hydrogen purification, frequently utilised either as a stand-alone system or in combination with PSA and membrane technologies. This process exploits the distinct phase-change behaviour of hydrogen and its accompanying gases at very low temperatures. Cooling of the gas mixture is typically achieved through multistage heat exchangers employing Joule–Thomson expansion, external refrigeration loops, or turbo-expansion of hydrogen-rich streams [46,47].

As illustrated in Figure 3, the separation relies on the selective condensation or solidification of impurities. At cryogenic temperatures, impurities such as CO₂, CO, N₂, and CH₄ reach their boiling or freezing points and are effectively removed from the gas phase. In contrast, hydrogen, which has the lowest boiling point among standard syngas components, remains mainly in the vapour phase. This allows for hydrogen recovery efficiencies exceeding 98%, with product purities typically ranging from 95% to 98% [48,49].

**Figure 3.** Schematic of a cryogenic hydrogen purification process.

As with adsorption-based PSA systems, the variable composition and presence of trace contaminants (hydrocarbons, NH₃, H₂S, or halides) typical of biomass-derived hydrogen streams impose additional demands on feed pretreatment and process integration, making the careful design of cryogenic separation units critical for achieving high-purity renewable hydrogen [17,49,50].

A summary of the critical thermophysical properties that govern cryogenic separation behaviour is provided in Table 3, highlighting the substantial differences in boiling and freezing points between hydrogen and other syngas components [46].

Table 3. Comparison of the various critical properties of the main components of the syngas [46].

Component	Boiling Point (°C, 1 atm)	Freezing Point (°C, 1 atm)	Critical Temperature (°C)	Critical Pressure (bar)
H ₂	−252.9	−259.2	−239.9	13.0
CO	−191.5	−204.9	−139.9	34.9
CO ₂	−78.5	−78.5	30.9	73.8
N ₂	−195.8	−210.0	−146.9	34.0
CH ₄	−161.0	−182.5	−81.9	46.0

Before cryogenic processing, complete removal of CO₂ and H₂O is essential. Their relatively high freezing points make them prone to solidification inside heat exchangers, expansion valves, and distillation towers, which may lead to operational instability or equipment failure [27,51]. To address these challenges, hybrid cryogenic configurations, such as partial condensation combined with CH₄ scrubbing or multistage flash separation, have been developed. Such intensified schemes can achieve hydrogen purities above 99.5%, approaching the requirements of fuel cells [52,53].

Cryogenic separation without distillation offers the advantages of simpler equipment, lower operating cost, and high recovery. However, the achievable hydrogen purity is typically inferior to that of adsorption- or membrane-based systems. Incorporating cryogenic distillation columns significantly enhances purity but incurs penalties in energy demand and capital cost [46,54]. Thus, while cryogenic separation is very effective for hydrogen recovery, achieving fuel-cell-grade purity often requires hybrid or multi-stage arrangements, similar to the multi-bed setups utilised in PSA processes. Consequently, current research trends focus on process intensification, including advanced heat-integration networks, compact heat exchanger technologies, integrated cryogenic–adsorption systems, and synergistic cryogenic–membrane designs, all aimed at improving separation efficiency while minimising refrigeration duty [55,56].

Cryogenic separation is effective for hydrogen recovery and is well-suited to large industrial plants. However, it has some limitations that make it less suitable for small-scale renewable hydrogen production. The main issue is its high energy use for deep refrigeration, which can account for 30–50% of total energy use, depending on the feed and cooling method [44,57]. Additionally, cryogenic systems require thorough pretreatment to remove CO₂ and H₂O, as even small amounts can freeze in the equipment, leading to problems such as blockages [57].

The cost of cryogenic equipment, like turboexpanders, heat exchangers, and distillation columns, is also much higher than that of PSA or membrane systems. This makes cryogenic separation only cost-effective at large scales. Moreover, these systems do not respond well to changes in feed type, limiting their use with variable biomass-derived feeds. To address these issues, researchers are developing hybrid systems that combine cryogenic methods with membrane and adsorption technologies to improve hydrogen recovery, better handle impurities, and reduce refrigeration requirements [44,58].

Adsorption and cryogenic technologies stand out as among the most advanced methods for hydrogen purification, with technology readiness levels (TRLs) of 8–9. These techniques have been widely utilised in various sectors, including refineries, ammonia production plants, and large-scale syngas upgrading operations. Their proven reliability and established supply chains make them appealing choices for centralised renewable hydrogen production. However, their limited flexibility, high energy demands—particularly

with cryogenic systems—and sensitivity to contaminants can hinder their effectiveness for decentralised hydrogen production from biomass. On the other hand, membrane-based systems are generally less developed (TRL 5–8, depending on the material) but offer benefits such as modularity, lower energy use, and better adaptability to changing feed conditions [57]. This difference in development and operation shows that we should evaluate purification technologies based not only on the purity they achieve but also on how and where they will be used, their scale, and the variability of the feed [58].

3.2. Membrane-Based Purification Technologies

Membrane-based gas separation systems have become highly appealing technologies for purifying renewable hydrogen due to their operational flexibility, compact and modular designs, lower energy requirements, and relatively minor environmental impact. In these systems, the permeation of hydrogen is primarily driven by a difference in partial pressure across the membrane, which facilitates the selective transport of gases through the membrane layer. When compared to PSA and cryogenic systems, membrane technologies stand out as particularly well-suited for small- to medium-scale renewable hydrogen production units. These units often experience fluctuations in feed composition and require a system that can effectively handle tars, CO₂, and various trace contaminants.

Several mass transport mechanisms operate in membrane systems, including Knudsen diffusion, surface diffusion, capillary condensation, molecular sieving, and solution diffusion. The significance of each mechanism varies according to the membrane's morphology and material type, leading to unique selectivity and permeability characteristics. As a result, a diverse range of membrane materials has been developed for hydrogen separation, such as organic polymers, inorganic ceramics, metallic thin films, and MMMs that combine both polymeric and inorganic components [12,13].

3.2.1. Polymeric Membranes

Polymeric membranes are widely employed in industrial gas separations due to their mechanical robustness, chemical versatility, and scalable fabrication. However, their intrinsic performance is constrained by the permeability–selectivity trade-off, commonly described by the Robeson upper bound. As shown in Figure 4, most conventional polymers lie below this empirical limit, motivating structural strategies aimed at increasing fractional free volume, enhancing chain rigidity, or tailoring specific gas–polymer interactions to surpass the upper-bound relationship [59,60]. Common polymer families employed in hydrogen-separation membranes include polycarbonate (PC), cellulose acetate (CA), polyethylene (PE), polysulfone (PSf), polyimide (PI), polyetherimide (PEI), and poly(pyrrolone)s [61].

A primary way to classify polymeric membranes is by their glass transition temperature (T_g), which differentiates between rubbery and glassy polymers. When temperatures exceed T_g, the polymer chains gain significant mobility, resulting in a rubbery state that enhances permeability. Conversely, when temperatures fall below T_g, the mobility of the chains decreases, causing the polymer to shift into a glassy, more rigid state. This glassy state is characterised by increased selectivity but reduced permeability [44]. Figure 5 summarises this classification, illustrating the structural and transport properties associated with each category.

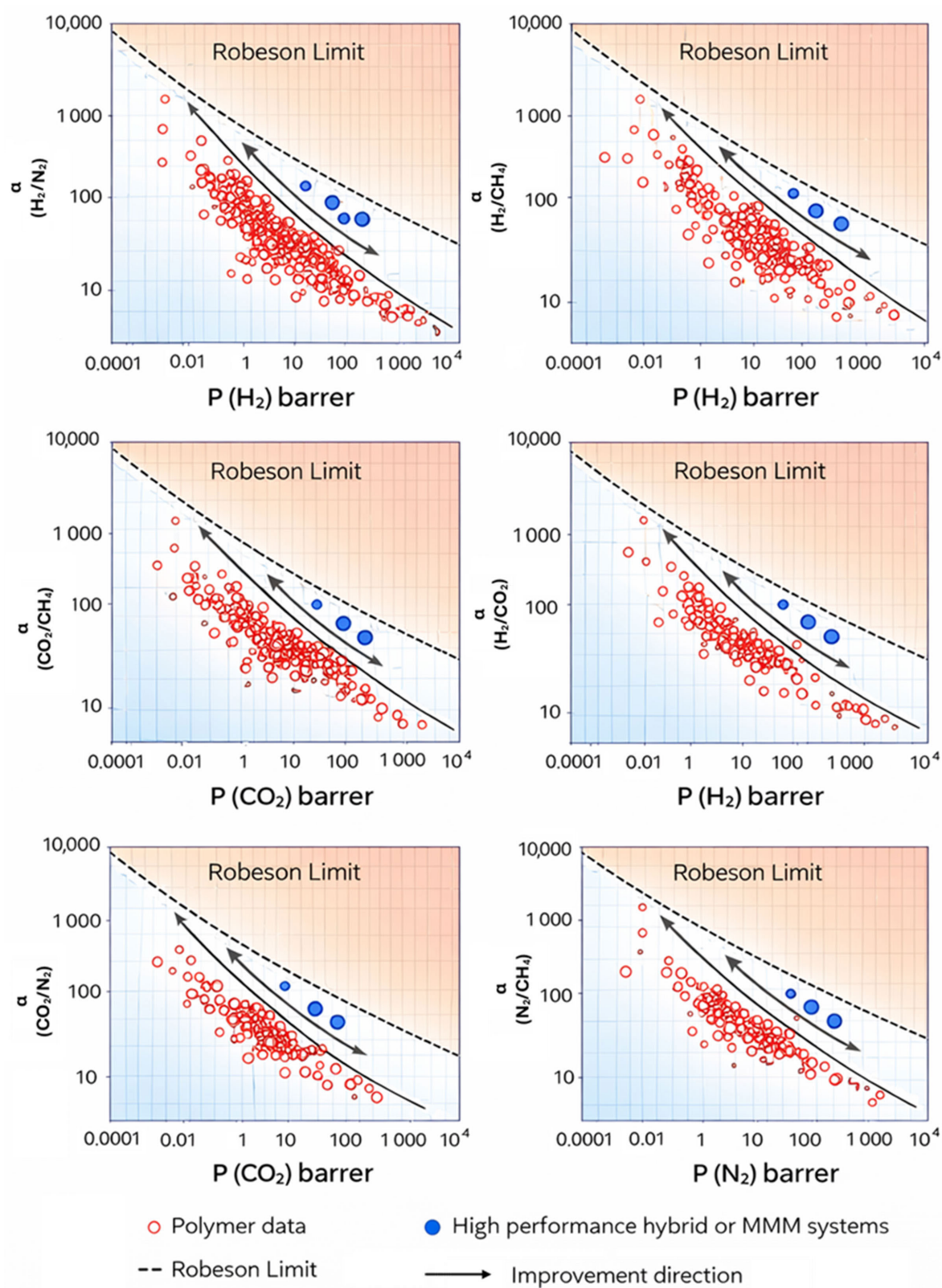


Figure 4. Upper-bound correlation of the main components of syngas [59].

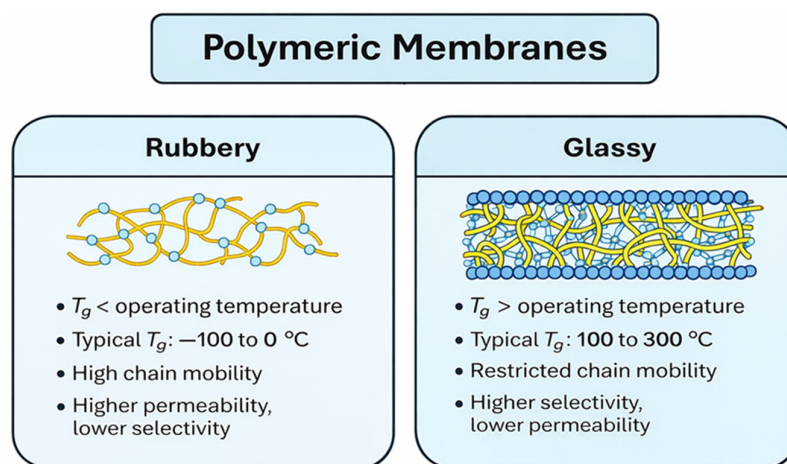


Figure 5. Classification of polymeric membranes based on glass transition temperature (rubbery vs. glassy). T_g values represent typical ranges reported for representative polymer classes and may vary depending on polymer chemistry and processing history.

Rubbery polymers are characterised by low T_g , high chain mobility, and amorphous structures with significant free volume. These features favour gas transport primarily through solution–diffusion, with contributions from surface diffusion and capillary condensation for condensable species. As a result, rubbery polymers are particularly suitable for the separation of organic vapours due to their high solubility for larger and more condensable molecules [62,63]. Representative examples include polyvinyl acetate (PVAc), polydimethylsiloxane (PDMS), styrene–butadiene rubber (SBR), and polyurethane (PU) [64,65]. PDMS-based membranes are widely used for organic vapour separations because of their exceptionally high permeability and strong chemical resistance. However, for small non-condensable gases such as hydrogen, rubbery polymers typically exhibit low selectivity and inferior separation performance compared with glassy polymers [66,67]. This structure favours size-based discrimination of small gases such as hydrogen, particularly relative to CH_4 and N_2 , although competitive CO_2 sorption can reduce effective H_2/CO_2 selectivity in certain systems [61,68,69].

Glassy polymers operate below their T_g and are characterised by rigid, tightly packed chain structures that enhance size-based discrimination between gas molecules. Gas transport in these materials predominantly follows the solution–diffusion mechanism, wherein gases dissolve into the polymer matrix and diffuse through transient free-volume elements between polymer chains [70,71]. Often resulting in improved size-based discrimination relative to CH_4 and N_2 , although CO_2 solubility effects may reduce H_2/CO_2 selectivity in certain systems [62]. Common glassy polymers include polyimides (PIs), polycarbonates (PCs), polysulfones (PSfs), and polyamides (PAs), with PIs and polybenzimidazole (PBI) being among the most established materials for hydrogen purification [72–74]. Aromatic 6FDA (fluorinated dianhydride)-based polyimides exhibit excellent mechanical and thermal stability but are susceptible to CO_2 -induced plasticisation, motivating structural modifications such as incorporation of bulky substituents, cross-linking, or copolymerisation to suppress CO_2 -induced plasticisation [75–77]. PBI membranes, with T_g values near 427 °C, display exceptional chemical resistance and maintain high selectivity at the elevated temperatures typical of biomass-derived syngas streams. Both solid-state melt polymerisation and solution-based synthesis routes enable the fabrication of dense films and hollow-fibre membranes suitable for scale-up [78–80].

A rapidly advancing class of glassy polymers is polymers of intrinsic microporosity (PIMs), first introduced by Budd et al. [73]. PIMs are characterised by rigid and contorted backbone structures that prevent efficient chain packing, creating permanent

sub-nanometre voids that enable rapid gas transport. As a result, these materials exhibit exceptionally high gas permeability. Tröger's-base (TB) PIMs, such as PIM-EA-TB, incorporate highly rigid molecular units that further enhance intrinsic microporosity and have been shown to exceed the Robeson upper bound for H₂/CH₄ separation [81,82]. A key limitation of early PIMs is their susceptibility to physical ageing, which leads to a gradual loss of permeability over time. Recent developments, including PIM-polyimides, ladder-type polymers, and cross-linked PIM derivatives, have significantly improved long-term structural stability and resistance to physical ageing [83,84].

A recurring limitation is that many reported performances are obtained on simplified binary or dry feeds, which reduces comparability and can overstate relevance to renewable hydrogen streams. Long-duration stability under multicomponent and humid conditions remains insufficiently reported to support direct claims of end-use compliance without downstream polishing.

To contextualise the performance of mixed-matrix membranes discussed in the following section, Table 4 summarises typical hydrogen selectivity ranges reported for representative conventional polymer membranes.

Table 4. Typical literature-reported hydrogen selectivity values for representative glassy and rubbery polymer membranes under mixed-gas or relevant separation conditions.

Polymer	Polymer Type	T _g (°C, Typical)	H ₂ /CO ₂ Selectivity	H ₂ /CH ₄ Selectivity	Ref.
Matrimid®	Glassy polyimide	300–315	5–10	80–150	[15–17,85,86]
6FDA–ODA polyimide	Glassy polyimide	~300	8–15	70–120	[15–17,87]
6FDA–DAM polyimide	Glassy polyimide	~290	6–12	60–110	[15–17,87,88]
P84 co-polyimide	Glassy polyimide	~315	6–12	60–100	[18,85,89]
Polysulfone (PSf)	Glassy polymer	180–190	4–8	40–80	[15,16,87]
Polyetherimide (PEI)	Glassy polymer	~215	4–9	35–70	[17,85,88]
PEBAX® 1657	Rubbery block copolymer	~−40	4–8	10–25	[18,19,87]
PDMS	Rubbery silicone	~−120	2–5	5–15	[15,16,87]

3.2.2. Inorganic Membranes

Inorganic membranes are an important class of hydrogen separation technologies and are generally divided into dense and porous architectures, each governed by distinct transport mechanisms. Dense metallic or ceramic membranes separate hydrogen via atomic or proton diffusion, whereas porous inorganic membranes rely on molecular sieving, Knudsen diffusion, and surface interactions within well-defined pore networks [90,91]. An overview of the main inorganic membrane classes, including their materials, separation mechanisms, and key advantages and limitations, is provided in Figure 6.

Dense inorganic membranes include metallic hydrogen-selective membranes and ceramic proton-conducting membranes, both capable of delivering ultra-high-purity hydrogen. Hydrogen transport in these systems is governed by atomic or proton diffusion through the membrane lattice under a chemical potential gradient, enabling high selectivity and flux at elevated operating temperatures [90,91]. Owing to their thermal and chemical robustness, dense inorganic membranes are particularly suited to renewable hydrogen streams with variable composition and high impurity levels, where stable performance is critical for downstream fuel cell applications.

Among dense membranes, Pd-based systems are widely regarded as the benchmark for ultra-high-purity hydrogen separation. Pd catalytically dissociates molecular hydrogen, allowing rapid diffusion of atomic hydrogen through its face-centred cubic lattice [92–94]. Hydrogen transport proceeds via dissociative adsorption, bulk diffusion, and recombination on the permeate side [90,95]. Despite their excellent selectivity, Pd membranes are

susceptible to poisoning by contaminants such as H_2S and CO , which reduce permeability through sulfide or carbide formation [91,94,96]. Alloying Pd with metals such as Ag, Cu, or Ni improves mechanical stability, mitigates hydrogen embrittlement, and enhances resistance to sulfur- and carbon-containing species. In parallel, thin-film fabrication techniques, including electroless plating, magnetron sputtering, and chemical vapour deposition, enable high hydrogen fluxes at moderate operating temperatures ($\approx 350\text{--}500\text{ }^\circ\text{C}$) [18,94]. Surface modification with catalytic metals (e.g., Pt, Rh, Ru) and hybrid Pd-based configurations have further improved tolerance to syngas contaminants without compromising selectivity [93,97,98].

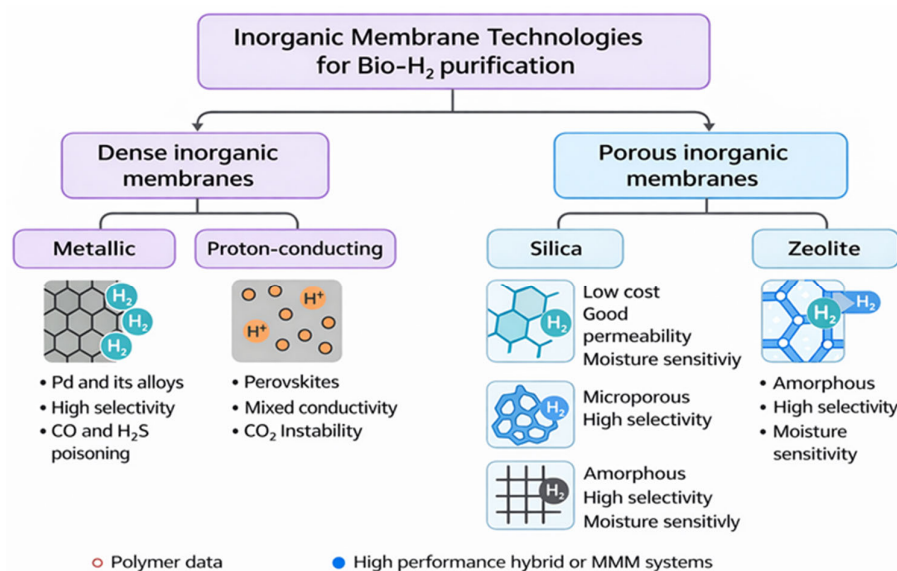


Figure 6. Schematic overview of dense and porous inorganic membrane technologies for renewable hydrogen purification and their key characteristics.

Dense ceramic membranes, including perovskite, pyrochlore, niobate, tantalate, and tungstate oxides, enable hydrogen separation via ambipolar diffusion, involving the coupled transport of protons and electrons through the crystal lattice [99,100]. Perovskite-based materials such as SrCeO_3 , BaCeO_3 , and SrZrO_3 exhibit proton conductivities on the order of $10^{-2}\text{--}10^{-3}\text{ S}\cdot\text{cm}^{-1}$ at $673\text{--}1273\text{ K}$, which can be enhanced through trivalent cation doping (e.g., Y^{3+} , Yb^{3+} , Sm^{3+}) [101–103]. A key limitation of Ce-based perovskites is their susceptibility to CO_2 -induced degradation via carbonate formation. Zr-rich compositions offer improved chemical stability but lower conductivity, leading to the development of mixed cerate–zirconate systems that balance performance and durability [104,105].

Beyond perovskites, rare-earth pyrochlores, niobates, and tantalates exhibit improved CO_2 resistance and thermal stability, making them promising candidates for high-temperature hydrogen separation. However, challenges related to long-term stability and scalable fabrication remain barriers to widespread industrial deployment [106,107]. Key performance metrics and representative studies on dense inorganic membranes are summarised in Table 5.

Porous inorganic membranes consist of a thin selective layer deposited on a mechanically robust support, typically α -alumina, zirconia, glassy carbon, or stainless steel. Gas transport occurs through molecular sieving, surface diffusion, or Knudsen diffusion, depending on the pore size regime of the selective layer: microporous ($<2\text{ nm}$), mesoporous ($2\text{--}50\text{ nm}$), or macroporous ($>50\text{ nm}$) [91].

Table 5. Representative literature data on hydrogen separation performance of dense inorganic membranes under relevant operating conditions.

Membrane (Alloy/Composition)	Support/Form	Preparation Method	T (°C)	Pressure (bar)	Permeance/Permeability (mol·m ⁻² /s·Pa ^{-0.5}) or Flux	Ref.
Dense metal (Pd-based) inorganic membranes						
Pd–Cu (thin layer, composite on porous oxide support)	Porous Al ₂ O ₃ /YSZ support (composite)	Two-step electroless plating (ELP)	300–500	1–6 (varies)	e.g., 9.9×10^{-6} mol·m ⁻² /s·Pa ^{-0.5} reported at 300 °C (Pd–60Cu layer example).	[108]
Pd–Cu (sputtered/composite)	Self- support/thin film	Magnetron sputtering/surfactant- induced ELP	~300	0.5–7	Typical reported permeances: 1×10^{-6} – 1×10^{-5} (depends on thickness). High flux examples reported in literature;	[109]
Pd–Ag (supported/dense film)	Stainless steel or porous oxide support	Magnetron sputtering/ELP	300–400	0.8–2.0	permeance $\sim(1\text{--}2) \times 10^{-5}$ (thin films) depending on microstructure. Recent alloy studies show improved CO/H ₂ S	[110]
Pd–Au and Pd–Ag–Y variants (alloys)	Self-support or supported	Magnetron sputter- ing/metallurgical	350–450	varied	tolerance with moderate flux trade-offs; permeance often 10^{-6} – 10^{-5} (thin films). Reported permeances vary (10^{-6} – 10^{-5}) depending on composition; alloying improves	[16]
Pd–Ru, Pd–Ni (alloyed layers)	Porous oxide support	ELP/Electrodeposition	350–500	varied	mechanical/chemical robustness.	[16]
Membrane composition (dense ceramics/cermets)	Thickness δ (mm) if reported	T (°C)	H ₂ flux/Permeance (reported)	Feed composition (reported)	Ref.	
Dense ceramic (protonic/mixed conducting) inorganic membranes						
SrCe _{0.95} Tm _{0.05} O _{3-δ} (perovskite proton conductor)	0.15 mm	900	H ₂ flux $\approx 9.4 \times 10^{-4}$ mol·m ⁻² /s (reported under 10 mol% H ₂ /He)	10 mol% H ₂ /He	[111]	
SrCe _{0.95} Yb _{0.1} O _{3-δ}	0.05 mm	1000	H ₂ flux $\approx 7.6 \times 10^{-4}$ mol·m ⁻² ·s ⁻¹ (80 mol% H ₂ /He reported)	80 mol% H ₂ /He	[112]	
BaCe _{0.8} Y _{0.2} O _{3-α} (cerate)	-	1045	Reported very high flux in some literature (order 10^{-3} – 10^{-2} mol·m ⁻² ·s ⁻¹ at high temp/thin membranes)	25 mol% H ₂ /He	[111]	
Sr(Ce _{0.6} Zr _{0.4}) _{0.85} Y _{0.15} O _{3-δ}	0.17 mm	795	Reported H ₂ flux values vary; some high flux examples reported (10^{-3} – 10^{-2}) when optimised	Pure H ₂ or H ₂ /He feeds	[112]	
Tungstate/W-based oxides (e.g., La _{5.5} W _{0.8} Re _{0.2} O _{11.25-δ})	0.5–0.9 mm	695–995	H ₂ flux reported across works in 10^{-4} – 10^{-3} range (50 mol% H ₂ /He)	50 mol% H ₂ /He	[112]	
Ni–cerate cermet (Ni– BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3-δ})	0.15 mm	895	H ₂ flux reported up to 5×10^{-3} – 5×10^{-2} in some cermet studies (composition & measurement dependent)	20 mol% H ₂ /N ₂	[113]	
Ta–Y ₂ O ₃ stabilised ZrO ₂	0.5 mm	295	Some dense oxide membranes show high H ₂ flux under pure hydrogen; reported values vary widely	Pure H ₂	[112]	

Silica membranes are among the most extensively studied porous inorganic systems due to their high hydrogen permeability, thermal and chemical stability, and relatively low

production cost. They are commonly fabricated by sol–gel methods, producing amorphous silica networks with high permeance but moderate selectivity, or by chemical vapour deposition (CVD), which yields denser and more selective layers at the expense of flux [114–117]. Doping silica membranes with ZrO_2 or Nb_2O_5 improves mechanical stability and enhances performance under high-temperature reformat conditions [118,119].

Zeolite membranes, composed of crystalline aluminosilicates with uniform microporous channels, offer excellent thermal stability, tunable pore sizes, and high hydrogen selectivity [120,121]. Advances in synthesis techniques, including in situ crystallisation, secondary growth, microwave-assisted hydrothermal synthesis, and dry-gel conversion, have reduced defect densities and improved reproducibility, while post-synthetic functionalisation further suppresses non-selective transport pathways [122,123]. Post-synthetic functionalisation strategies further suppress non-selective transport pathways [124]. Recent studies have shown that MFI-type bilayers and zeolitic imidazolate framework (ZIF) membranes, such as ZIF-8 and ZIF-9 (where MFI refers to the zeolite framework type associated with ZSM-5 and silicalite-1 and characterised by intersecting microporous channels of approximately 0.5–0.6 nm) exhibit high selectivity for H_2/CO_2 and H_2/CO while maintaining their structural integrity under industrial reformat conditions [125–129].

Carbon molecular sieve membranes (CMSMs), produced by controlled pyrolysis of polymeric precursors, possess narrow slit-like micropores and exhibit outstanding H_2/CO_2 and H_2/CH_4 selectivity together with excellent thermal and chemical resistance [130]. Their fabrication typically involves precursor conditioning, carbonisation, and optional post-treatment or CVD-based defect engineering [18,131]. However, brittleness and moisture sensitivity remain practical limitations, motivating the development of hybrid polymer–inorganic membrane configurations [132,133].

A comparative overview of representative porous inorganic membrane systems, including preparation routes, operating conditions, and hydrogen permeance and selectivity, is provided in Table 6.

Table 6. Representative performance data for hydrogen separation using porous inorganic membranes under relevant operating conditions.

Membrane Type	Support	Preparation	Precursor or Modifier	T (K)	ΔP (kPa)	H_2 Permeance ($\times 10^{-8}$ mol $\text{m}^{-2}/\text{s Pa}$)	H_2 Selectivity	Main Gas Pair	Ref.
Silica membranes									
SiO_2 – ZrO_2 composite	$\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$	Sol–gel	BTESE	573	100	9.8×10^2	$\text{H}_2/\text{CO}_2 \approx 10$	H_2/CO_2	[134]
Pure silica thin film	$\alpha\text{-Al}_2\text{O}_3$	Dip-coating + calcination	TEOS	523	200	1.0×10^2	$\text{H}_2/\text{CH}_4 \approx 12$	H_2/CH_2	[135]
$\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$ bilayer	$\alpha\text{-Al}_2\text{O}_3$	CVD	TPMS (Triphenylmethoxysilane)	573	500	1.2×10^2	$\text{H}_2/\text{N}_2 \approx 15$	H_2/N_2	[136,137]
Doped silica									
Nb-doped silica (33 mol %)	$\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$	Sol–gel	BTESE + Nb ethoxide	473	50	5.1	$\text{H}_2/\text{CO}_2 \approx 9$	H_2/CO_2	[137]
Zr– SiO_2 hybrid	$\alpha\text{-Al}_2\text{O}_3$	CVD	TEOS + $\text{Zr}(\text{OPr})_4$	873	100	7.3	$\text{H}_2/\text{CO}_2 \approx 11$	H_2/CO_2	[138]
Zeolite membranes									
CHA-type (High-silica)	$\alpha\text{-Al}_2\text{O}_3$ tube	Ionothermal synthesis	Silica precursor (TEOS)	303–473	100	7.0×10^1	$\text{H}_2/\text{CH}_4 \approx 50$	H_2/CH_4	[139]
SAPO-34	$\alpha\text{-Al}_2\text{O}_3$ tube	Steam-assisted growth	TEOS + AlPO gel	298	100	6.9×10^2	$\text{H}_2/\text{CO}_2 \approx 40$	$\text{H}_2/\text{CO}_2/\text{CH}_4$	[140–142]
DDR zeolite	Clay–alumina tube	Secondary growth	Si–Al gel	303	100	4.0×10^1	$\text{H}_2/\text{CO}_2 \approx 22$	$\text{H}_2/\text{CO}_2/\text{CH}_4$	[143]
SSZ-13 CHA	$\alpha\text{-Al}_2\text{O}_3$ hollow fibres	Secondary growth + dip-coating	Silica gel	473	500	1.8×10^1	$\text{H}_2/\text{CO}_2 \approx 30$	H_2/CO_2	[91,144]
Carbon molecular sieve membranes									
PI-derived dual-crosslinked CMSM	Flat film	Pyrolysis (850 °C, N_2)	Polyimide precursor	298	100	3.5×10^3	$\text{H}_2/\text{CH}_4 \approx 3800$	H_2/CH_4	[145]
GO–polyimide composite CMSM	Flat film	Carbonization + GO dispersion	Polyimide + GO	298	100	5.5×10^2	$\text{H}_2/\text{CO}_2 \approx 32$	H_2/CO_2	[146,147]
Phenol–formaldehyde resin (PFR) CMSM	$\alpha\text{-Al}_2\text{O}_3$ tube	Sol–gel + pyrolysis	PFR precursor	303	1300	1.4×10^2	$\text{H}_2/\text{CO}_2 \approx 25$	H_2/CO_2	[148,149]
Hyperbranched polyimide-derived CMSM	Flat film	Controlled pyrolysis	HPI precursor	308	100	2.0×10^{-2}	$\text{H}_2/\text{CO}_2 \approx 15$	H_2/CO_2	[150,151]

Note: Reported values are literature-derived and may reflect different system boundaries and maturity levels (industrial vs. projected). Multiple references indicate the sources used to compile the reported range.

Reported results vary widely across studies, often reflecting differences in defect control, sealing, and operating history, which complicates cross-comparison. In addition, impurity tolerance and stability under representative renewable-hydrogen conditions are still under-documented, making scale-up realism a key uncertainty.

3.2.3. Mixed Matrix Membranes

MMMs were developed to overcome the inherent limitations of both polymeric and inorganic membranes. Polymeric membranes are constrained by the permeability–selectivity trade-off described by the Robeson upper bound, whereas inorganic membranes, despite their high selectivity and thermal and chemical robustness, often suffer from low permeability or mechanical brittleness. By embedding micro- or nano-structured inorganic fillers within a continuous polymer matrix, MMMs introduce alternative transport pathways that can simultaneously enhance permeability and selectivity, partially decoupling these properties compared with single-phase membranes [152,153].

Among the various fillers employed in MMMs, advanced porous materials such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) are particularly effective due to their highly ordered microporous structures and tunable chemistry. These materials introduce well-defined molecular sieving channels that can favour hydrogen transport over larger molecules such as CO₂ and CH₄, while their functionalised internal surfaces enable selective adsorption effects that enhance solubility-based discrimination. In addition, the rigid crystalline structure of MOFs and COFs can increase the effective fractional free volume of the composite membrane and restrict local polymer chain mobility, thereby mitigating CO₂-induced plasticisation. Through this combination of size-selective diffusion and tailored adsorption interactions, MOF- and COF-based MMMs aim to partially decouple the traditional permeability–selectivity trade-off observed in conventional polymers [154–156].

Realising these performance gains requires precise control over membrane fabrication, as challenges such as filler agglomeration, sedimentation, non-selective interfacial voids, and poor polymer–filler compatibility can compromise separation performance. Key design parameters include filler morphology and size, polymer chain rigidity, filler loading, and interfacial adhesion strategies such as surface functionalisation or cross-linking. The conceptual framework of MMM design is illustrated in Figure 7, highlighting how inorganic fillers, including zeolites, MOFs, COFs, and carbon nanotubes, are integrated into polymer matrices to mitigate the permeability–selectivity trade-off and engineer tailored transport pathways for hydrogen separation.

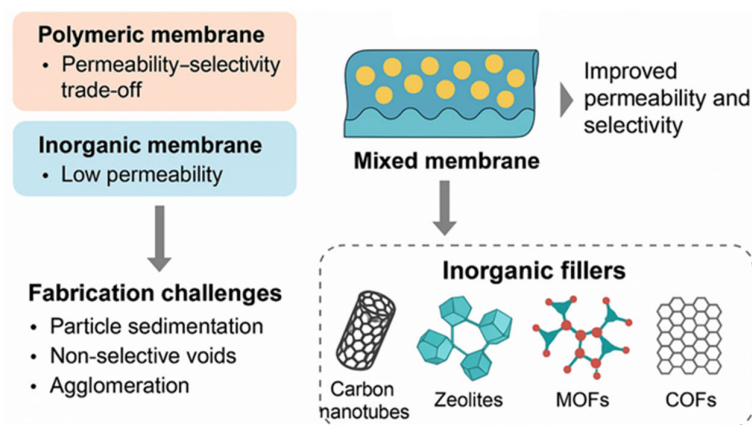


Figure 7. Schematic representation of mixed matrix membranes and their role in overcoming the permeability–selectivity trade-off.

MOFs are the most widely studied fillers for MMM fabrication due to their exceptionally high surface area, uniform microporosity, and chemically modifiable structures. MOFs are crystalline porous materials composed of metal clusters interconnected by organic linkers, which allows for precise control of pore size, topology, and chemical affinity. They can be synthesized using various methods, including solvothermal, microwave-assisted, mechanochemical, electrochemical, and sonochemical routes [157]. When integrated into polymer matrices, MOFs can help reduce physical ageing, mitigate CO₂-induced plasticisation, and introduce selective adsorption sites and fast-diffusion channels. These benefits are especially advantageous for hydrogen-containing mixtures, where preferential hydrogen transport can occur without compromising membrane stability. Some representative MOFs used in MMMs include ZIF-8, ZIF-90, HKUST-1, UiO-66, MIL-53, and MIL-101. Many of these systems successfully exceed the Robeson upper bound for challenging gas pairs such as H₂/CH₄ and CO₂/CH₄, as illustrated in Figure 8.

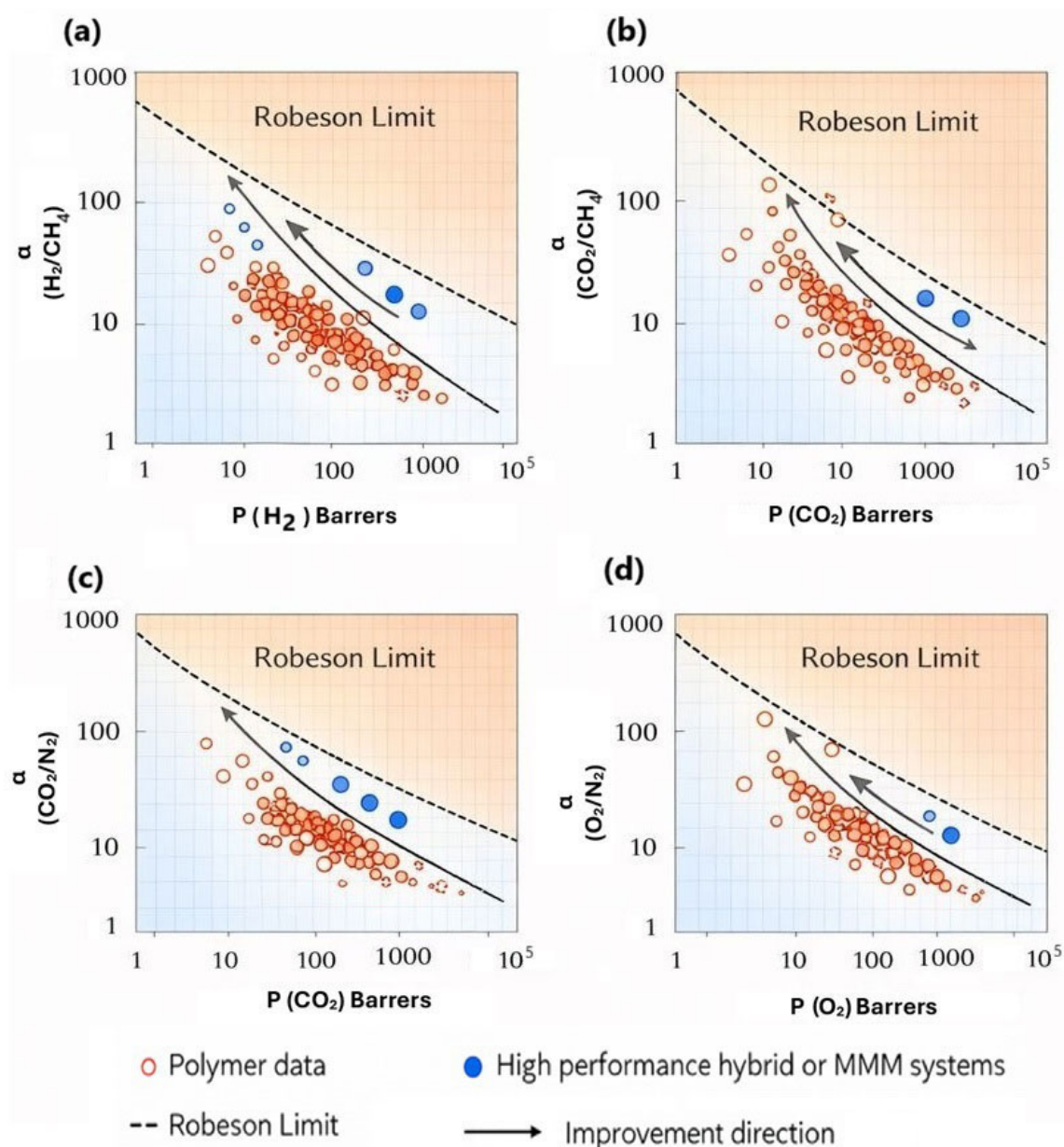


Figure 8. Selectivity–permeability performance of MOF, COF, and MMMs for key gas pairs: (a) separation of H₂/CH₄, (b) separation of CO₂/N₂, (c) separation of CO₂/N₂, and (d) separation of O₂/N₂ [133].

Carbon nanotubes (CNTs), including single-walled (SWCNTs) and multi-walled (MWCNTs) variants, have been extensively investigated as fillers for mixed matrix membranes due to their high aspect ratio, excellent mechanical properties, and high thermal conductivity. Their incorporation generally enhances gas permeability and mechanical robustness by introducing preferential transport pathways within the polymer matrix. However, achieving uniform dispersion and minimising interfacial slippage remain key challenges, as poorly integrated CNTs can reduce selectivity and lead to non-selective transport [157,158]. Zeolites, among the earliest inorganic fillers employed in MMMs, provide rigid microporous frameworks with intrinsic molecular-sieving capability. Despite their high selectivity, their relatively low permeability and high production costs have historically limited their ability to surpass polymeric upper bounds. Recent advances, including surface functionalisation, nanocrystal engineering, and improved polymer–zeolite compatibilisation, have significantly enhanced dispersion and separation performance for H_2 , CO_2 , and CH_4 , renewing interest in zeolite-based MMMs [151,159,160].

More recently, hybrid crystalline systems combining MOFs and COFs have emerged as highly promising MMM fillers. These hybrids integrate the adsorption selectivity and engineered pore environments of MOFs with the rigidity, chemical stability, and π -conjugated backbones of COFs. Their intergrown crystalline architectures create well-defined, size-selective transport pathways that favour rapid hydrogen permeation while effectively excluding CO_2 , CH_4 , and other syngas impurities [133,159]. Figure 9 illustrates the evolution of MOF–COF hybrid membranes from 2018 to 2025, highlighting advances in core–shell architectures, confined-growth deposition, interfacial engineering, and vacuum-assisted assembly that have enabled substantial improvements in permeability, selectivity, and long-term stability.

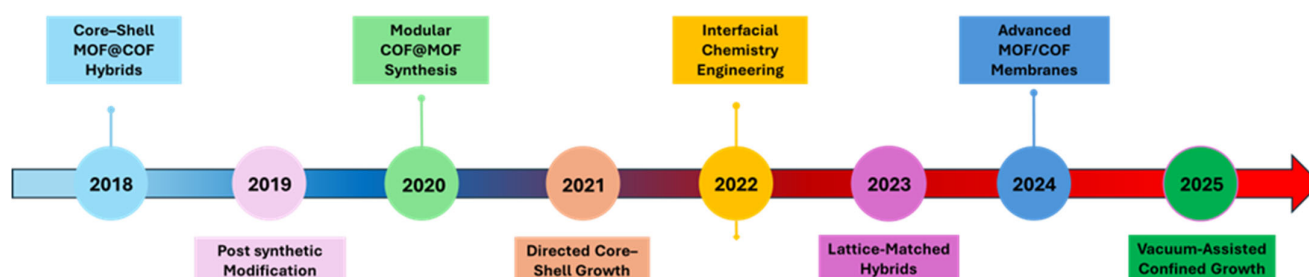


Figure 9. Timeline of MOF–COF hybrid membrane development (2018–2025), emphasising advances in core–shell design, interfacial bonding, and synthesis strategies for hydrogen and syngas purification.

Recent experimental studies have demonstrated the outstanding separation performance achievable with MOF–COF hybrid membranes. For example, ZIF-67–TpPa-155 hybrid films display hydrogen permeances of approximately 3800 GPU, along with H_2/CH_4 selectivity values ranging from 37 to 38. This performance significantly exceeds that of conventional polymeric and zeolitic systems [160–162]. Layered hybrid structures such as COF-300@[UiO-66] also exhibit competitive separation behaviour, achieving H_2/CO_2 selectivity of approximately 12.6 with permeances exceeding 10^4 GPU [163]. Even more impressively, H_2P -DHPH COF–UiO-66 hybrids have been reported to have H_2/CO_2 selectivities approaching 32.9 and permeances of around 1.08×10^5 GPU, ranking them among the highest-performing solid-state membranes available today [164,165]. These results confirm that MOF–COF hybrids are promising candidates for next-generation hydrogen purification, especially in scenarios requiring simultaneously high flux and selectivity under chemically complex syngas conditions.

In addition to free-standing hybrid films, MOF–COF fillers can be incorporated into polymeric matrices to create flexible MMMs. These combinations harness the high selectivity of crystalline fillers while benefiting from the mechanical resilience and processability of polymers. Representative examples include Pebax–Cu(BDC–NH₂)/TpPa membranes and polysulfone-based systems containing UiO-66@TpPa hybrids, both of which exhibit significant improvements in CO₂/CH₄ and H₂/CO₂ separation factors compared to their unmodified polymer counterparts [155,166]. These results highlight the potential of hybrid filler architectures to mitigate the interfacial limitations typically associated with MMMs.

A broader overview of MMM performance relevant to hydrogen purification is provided in Table 7, summarising representative membrane formulations, filler loadings, operating conditions, and separation metrics. The emerging trend toward MOF–COF hybrid MMMs suggests the potential to exceed performance reported for polymer-, zeolite-, or MOF-only technologies at laboratory scale, while industrial deployment remains contingent on demonstrated long-term stability under realistic feeds, robust defect control at module scale, and economically viable manufacturing routes. Many MOF-, COF-, and hybrid-based membranes are reported under idealised or simplified test conditions (often dry or binary mixtures), whereas industrial purification requires stable performance under multicomponent, humid feeds with fluctuating compositions. In addition, evidence on tolerance to biomass-derived trace contaminants (e.g., sulphur species, condensables/organics, and NH₃) and on long-duration operation is still limited. Scale-up realism is further constrained by the need for reproducible large-area defect control, mechanically robust supports and seals, and manufacturing costs associated with MOF/COF synthesis, post-processing, and module fabrication. These factors are not yet captured by permeance or selectivity metrics alone.

Table 7. Summary of published works on H₂ separation using MMMs.

Polymer Matrix	Material	Filler (wt.%)	Feed Composition (Inlet Gas Mixture)	H ₂ Permeance	Selectivity (H ₂ /Other Gas)	Ref.
6FDA–ODA Polyimide	Cu ₃ (BTC) ₂ (HKUST-1) MOF	6	Binary H ₂ /CH ₄ mixed-gas (equimolar unless otherwise specified in [159])	—	240	[167]
Matrimid®	MOF-5	30	Binary H ₂ /CH ₄ mixed-gas (reported mixed-gas tests in [160,161])	—	120	[168,169]
PBI	ZIF-7	50	Binary H ₂ /CO ₂ mixed-gas (composition as reported in [152])	—	7.2	[161]
6FDA–DAM Polyimide	Zr–MOF	16	Binary CO ₂ /CH ₄ mixed-gas (equimolar unless specified in [162])	—	25.4	[170]
Matrimid®	MIL-88B(Fe)	10	Binary H ₂ /CH ₄ mixed-gas (reported in [163])	—	80	[171]
Polyimide (6FDA–ODA)	NH ₂ –CAU-1	20	Binary H ₂ /CO ₂ mixed-gas (reported in [164])	—	32.8	[172]
Polysulfone (PSf)	UiO-66–NH ₂	15	Binary H ₂ /CO ₂ mixed-gas (reported in [165,166])	—	27.0	[173,174]
PEI (Polyetherimide)	Functionalized MWCNT	1	Binary H ₂ /N ₂ mixed-gas (reported in [167–169])	—	3.75	[175–177]
6FDA–TA Polyimide	SWCNT (functionalized)	2	Binary H ₂ /CH ₄ mixed-gas (reported in [166,170,171])	—	88	[174,178,179]
Udel® PES	Zeolite Nu-6(2)	15	Binary H ₂ /CH ₄ mixed-gas (reported in [172])	—	>398	[180]
Matrimid®	Deca-dodecasil 3R zeolite	20	Binary H ₂ /CH ₄ mixed-gas (reported in [172–174])	—	375	[180–182]
PVDF	Zeolite 4A	10	Binary H ₂ /CO ₂ mixed-gas (reported in [126,175])	—	3.5	[132,183]
P84 Co-polyimide	ZCC (Zeolite–Carbon Composite)	1	Binary H ₂ /N ₂ mixed-gas (reported in [176])	—	4.9	[184]
PEBAX® 1657	MXene (Ti ₃ C ₂ Tx)	1	Binary H ₂ /CO ₂ mixed-gas (reported in [177,178])	—	63	[185,186]
GDP polymer	COF (TpPa-1)	40	Binary H ₂ /CH ₄ mixed-gas (reported in [179,180])	165.5 GPU	—	[187,188]
GDP polymer	COF (TpBD)	20	Binary H ₂ /CO ₂ mixed-gas (reported in [181,182])	—	31.4	[154,189]

Table 7. Cont.

Polymer Matrix	Material	Filler (wt.%)	Feed Composition (Inlet Gas Mixture)	H ₂ Permeance	Selectivity (H ₂ /Other Gas)	Ref.
PEBAX® 1657	MXene (Ti ₃ C ₂ Tx)	0.15	Binary H ₂ /CO ₂ mixed-gas (reported in [177,183,184])	—	72.5	[185,190,191]
Pebax® 1657	Cu(BDC-NH ₂)/TpPa (MOF-COF hybrid)	10	Binary CO ₂ /CH ₄ mixed-gas (reported in [127,185,186])	815.9 Barrer	20.3	[133,192,193]
Polysulfone (PSf)	NH ₂ -UiO-66@TpPa-1 (MOF-COF hybrid)	15	Binary CO ₂ /CH ₄ mixed-gas (reported in [187–189])	7.1 Barrer	46.7	[194–196]
Free-standing hybrid film	ZIF-67-TpPa-155 (MOF-COF)	—	Binary H ₂ /CH ₄ and H ₂ /CO ₂ mixed-gas (reported in [154,190,191])	3800 GPU	37–38	[163,197,198]
Layered hybrid membrane	[COF-300]@[UiO-66] (MOF-COF)	—	Binary H ₂ /CO ₂ mixed-gas (reported in [154,155])	13,000 GPU	12.6	[163,164]
Free-standing layered MOF-COF	H ₂ P-DHPh COF/UiO-66	—	Binary H ₂ /CO ₂ mixed-gas (reported in [127,192])	108,341 GPU	32.9	[133,199]

Note: MOF—Metal–Organic Framework; COF—Covalent Organic Framework; MXene—Transition metal carbide/nitride 2D materials; GDP—Glassy dense polymer; GPU—Gas Permeation Unit; PSf—Polysulfone; PEBAX—Poly(ether-block-amide); PBI—Polybenzimidazole; P84—Commercial co-polyimide. Reported values are literature-derived and may reflect different system boundaries and maturity levels (industrial vs. projected). Multiple references indicate the sources used to compile the reported range.

Although many studies report improved selectivity or permeance, reproducibility and scalability remain debated due to filler dispersion and interfacial defects, and stability under humid or multicomponent exposure is rarely demonstrated. This makes MMMs more credible for staged enrichment or hybrid configurations than as a standalone route to stringent purity without polishing.

4. Cross-Cutting Comparison and Deployment Guidance

The practical deployment of renewable hydrogen purification technologies requires a cross-cutting evaluation that goes beyond individual process performance or isolated cost metrics. While Sections 3.1 and 3.2 examined adsorption, cryogenic, and membrane-based purification technologies in detail, real-world implementation demands an integrated assessment of achievable purity, hydrogen recovery, energy demand, technological maturity, and system compatibility under realistic renewable hydrogen feed conditions.

The economic viability of renewable hydrogen production is strongly influenced by the efficiency, scalability, and maturity of the purification system employed. Significant progress has been achieved in hydrogen production from biomass via thermochemical and biological routes. However, purification often remains the most cost and energy intensive step in the renewable hydrogen value chain. This is largely due to the need to separate hydrogen from co-produced gases such as CO₂, CO, CH₄, and trace contaminants, including H₂S and moisture.

To effectively evaluate purification technologies, it is crucial to consider key techno-economic indicators, including capital expenditure (CAPEX), operational expenditure (OPEX), energy intensity, equipment lifetime, and TRL. Importantly, these indicators must be interpreted in the context of variable feed composition, decentralised plant scale, and intermittent operation, which are characteristic of biomass-derived hydrogen systems and differ substantially from conventional fossil-based hydrogen production routes [200,201].

Recent assessments have analysed the maturity and cost structures of purification systems for renewable hydrogen applications, including adsorption, cryogenic, and membrane-based technologies. Although PSA systems can routinely achieve hydrogen purities above 99.9 vol.%, hydrogen recovery is inherently constrained by the cyclic adsorption–desorption mechanism. During depressurisation and purge steps, a fraction of hydrogen remains co-adsorbed or is discharged with the tail gas stream, resulting in typical recovery values between approximately 70 and 90%, depending on feed composition, pressure ratio, and

cycle configuration [57]. Recovery decreases when processing dilute hydrogen feeds, such as biomass-derived reformat streams, where lower H_2 partial pressures reduce adsorption selectivity and increase hydrogen losses during regeneration. Moreover, a fundamental trade-off exists between purity and recovery: achieving higher product purity generally requires more intensive purge or additional pressure-equalisation steps, which can reduce net hydrogen recovery and increase operational complexity. These limitations are particularly relevant for decentralised renewable hydrogen systems, where feed variability further complicates optimisation of recovery and efficiency [202]. Cryogenic separation can achieve hydrogen recoveries exceeding 98% and provides excellent product quality, but suffers from high energy consumption, making it more suited for centralised, large-scale installations [203]. Owing to its high throughput capability and reliance on energy-intensive refrigeration infrastructure, cryogenic separation is generally better suited to centralized, large-scale hydrogen production facilities rather than decentralised biomass-to-hydrogen plants [17]. In contrast, membrane-based technologies, particularly MMMs and emerging hybrid systems combining MOFs and COFs, present compact, modular, and energy-efficient solutions that are more suitable for decentralised renewable hydrogen production. Nevertheless, many membrane systems currently operate at lower TRL compared with PSA or cryogenic separation and may require multistage configurations or hybrid integration to achieve fuel-cell-grade hydrogen purity [160,204–206].

A comparative techno-economic overview of representative purification technologies is presented in Table 8. Reported values are indicative literature-derived ranges and are not fully harmonised, as they reflect different system boundaries, cost normalisation approaches, plant scales, and operating conditions. The compiled ranges include both measured values (industrial/pilot operation) and projected values (model estimates derived from laboratory performance and scale-up assumptions), depending on the underlying source. Unless explicitly stated otherwise in the cited studies, CAPEX/OPEX values are interpreted at the purification-unit level (including directly required auxiliaries such as compression/vacuum and refrigeration where applicable), and may exclude upstream conditioning, hydrogen production, and downstream storage/distribution. The ranges therefore reflect both inter-study variability and uncertainty in scale-up/assumption sets and should be interpreted as order-of-magnitude guidance rather than strict cross-technology ranking.

Table 8. Comparative technoeconomic assessment of renewable hydrogen purification technologies.

Technology	TRL	Typical H_2 Purity (%)	H_2 Recovery (%)	CAPEX (€/kW)	OPEX (%/Year)	Lifetime (Years)	Specific Energy (kWh/kg H_2)	LCOH Contribution (€/kg H_2)	Ref.
Cryogenic separation	7–8	99.9	90–95	1800–2500	4–6	20–25	3.0–3.5	0.8–1.2	[44,207–210]
PSA	9	99.9	70–85	900–1200	3–5	15–20	2.6–3.1	0.7–1.0	[27,202,207,208]
TSA or VPSA	6–8	99.0–99.9	75–90	1000–1500	3–5	15–20	2.8–3.3	0.8–1.1	[15,85,211]
Polymeric membranes	7–8	98–99.9	75–90	600–900	2–4	10–15	1.6–2.3	0.5–0.8	[18,86,89]
Inorganic membranes (Pd-based)	5–7	99.99	85–95	2000–4000	5–8	5–10	2.8–3.6	1.0–1.4	[17,206,207]
MMMs (MOF/COF hybrids)	4–6	99.9–99.99	90–98	800–1500 (projected)	2–4	10–15	1.2–2.0	0.4–0.7	[166,212–214]

Note: Values represent ranges reported for renewable hydrogen or biogas upgrading systems, normalized to 2021–2025 cost levels. Energy demand includes compression, separation, and auxiliary utilities; Reported values are compiled from the cited literature and may reflect different boundaries/assumptions and maturity levels (industrial/pilot data and/or model-based projections). Where multiple references are listed, the entry reflects the envelope of values across those sources.

The comparison highlights that PSA and cryogenic systems are the most technologically mature options (TRL 8–9), widely deployed across industrial hydrogen networks. Nevertheless, their reliance on large compressors, vacuum systems, or refrigeration cycles constrains their suitability for decentralised biomass-to-hydrogen facilities, where fluctuating syngas compositions and lower throughput favour more flexible solutions [215].

Membrane-based systems, encompassing polymeric, inorganic, and hybrid MMM architectures, offer substantially lower energy requirements and simplified process integration. Their modular nature enables direct coupling with gasification, reforming, or fermentation units at small and medium scales [20,216]. Among emerging membrane technologies, MMMs incorporating MOF, COF, or hybrid MOF–COF fillers exhibit particularly promising performance, combining high selectivity with enhanced permeability and reduced energy demand.

Reported reductions in energy consumption and equipment footprint of up to approximately 30% relative to PSA systems have been demonstrated in selected comparative studies, although these values depend strongly on system configuration, scale, and feed composition [160,217,218]. Furthermore, scalable fabrication techniques, including solution casting, electrospinning, and layer-by-layer deposition, together with projected operational lifetimes of 10–15 years, support levelised purification costs below $0.7 \text{ € kg}^{-1} \text{ H}_2$ in prospective decentralised applications [133,154,212].

In addition to purity and efficiency, the practical deployment of hydrogen purification technologies depends strongly on their hydrogen throughput capacity. Commercial PSA units are routinely operated at large scales, typically processing several hundred to tens of thousands of $\text{Nm}^3\text{-H}_2/\text{h}$, making them well-suited for centralised hydrogen production facilities. Cryogenic separation systems are applied at similarly large or higher throughputs, often exceeding $10^4 \text{ Nm}^3\text{-H}_2/\text{h}$, where their high recovery rates and product quality can compensate for the associated energy demand.

In contrast, membrane-based hydrogen purification systems are typically applied at small to medium scales. Polymeric membrane units are often operated at capacities ranging from a few tens to several hundred $\text{Nm}^3\text{-H}_2/\text{h}$ per module, with overall capacity increased through modular replication. Inorganic membranes, including Pd-based systems, are generally demonstrated at pilot to early-demonstration scales, from a few to a few tens of $\text{Nm}^3\text{-H}_2/\text{h}$, reflecting material and fabrication constraints. Emerging mixed-matrix membranes (MMMs), particularly those incorporating MOF or COF fillers, are currently limited to laboratory and small pilot scales, typically below $10\text{--}50 \text{ Nm}^3\text{-H}_2/\text{h}$, although higher throughputs are projected through modular scale-up. These throughput ranges are indicative and depend strongly on feed composition, operating pressure, and system integration; they are provided as order-of-magnitude guidance rather than strict capacity limits.

Figure 10 provides a qualitative, decision-oriented synthesis of the renewable hydrogen purification technologies reviewed in this work. Technologies are positioned based on typical performance ranges reported across multiple studies, considering achievable hydrogen purity under renewable, impurity-rich feed conditions (e.g., biomass-derived syngas) and current deployment maturity. The figure intentionally avoids strict quantitative benchmarking to prevent artificial comparability between industrial, pilot-scale, and laboratory datasets and should therefore be interpreted as deployment-oriented guidance rather than quantitative ranking. Positioning is derived from (i) achievable hydrogen purity under realistic multicomponent feed conditions and (ii) technological maturity expressed as deployment readiness (laboratory, pilot, demonstration, and commercial stages), consistent with the TRL ranges summarised in Table 8. The vertical axis reflects standard hydrogen purity classes (industrial grade $\sim 95\text{--}99\%$, fuel-cell grade $\geq 99.97\%$, high purity $\geq 99.99\%$, and very-high purity $\geq 99.999\%$) based on literature benchmarks and international hydrogen quality specifications. The horizontal and vertical extents of each box represent indicative ranges rather than precise numerical boundaries, capturing variability in feed composition, operating conditions, system integration, and feed complexity (idealised versus multicomponent streams).

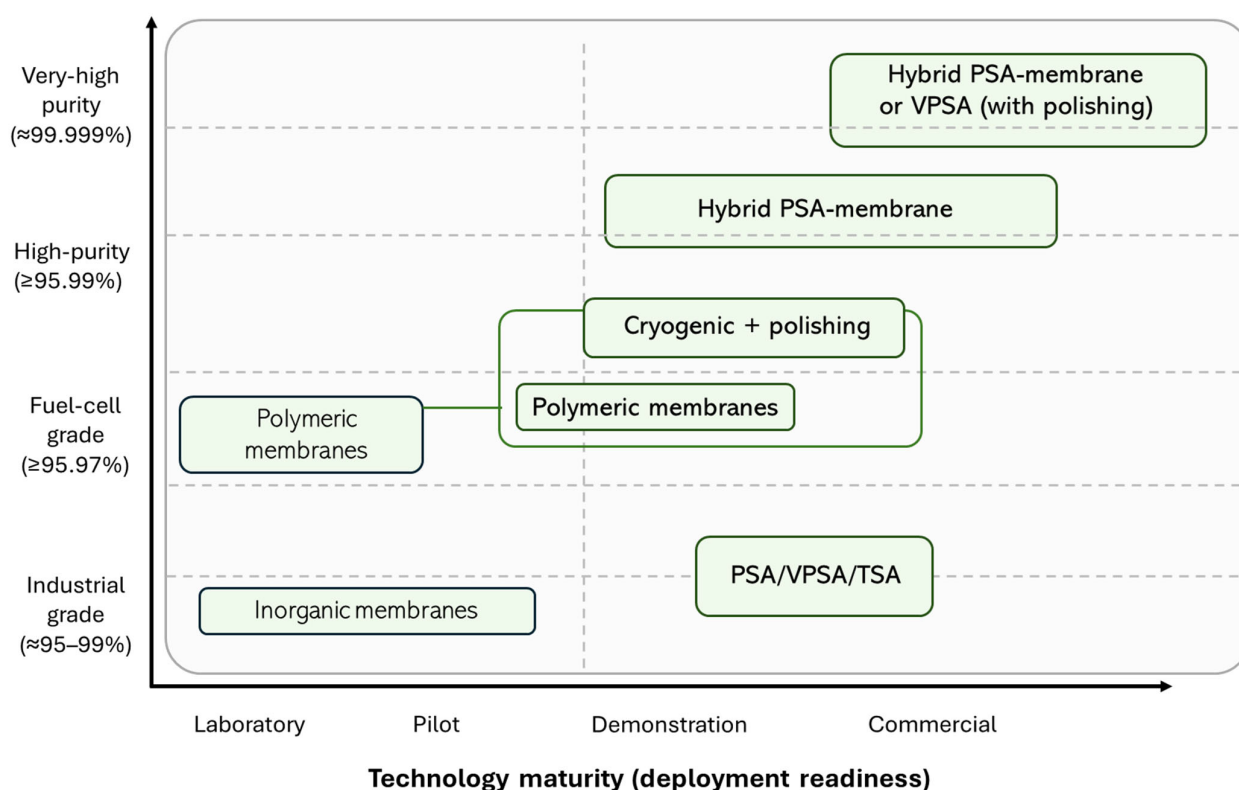


Figure 10. Qualitative comparative positioning of renewable hydrogen purification technologies based on typical performance ranges and technoeconomic data compiled from the literature and summarised in Table 8.

4.1. Advanced Polishing and Post-Purification Technologies

Obtaining fuel-cell-grade hydrogen (≥ 99.97 vol.%) from biomass-derived or reformat-rich sources usually cannot be achieved through a single bulk separation method, such as PSA, cryogenic separation, or membranes. Consequently, additional or combined purification processes are often required to reach the desired purity level (Figure 10). Residual trace impurities, including CO, CO₂, CH₄, O₂, NH₃, and sulphur species, can severely degrade downstream catalysts and PEMFC components [33]. Moreover, the variable composition of syngas, combined with intermittent operation and decentralised production scales, complicates the consistent delivery of ultra-high-purity hydrogen. As a result, advanced polishing and post-purification stages play a critical role in ensuring reliability and compliance with stringent end-use specifications.

To address these challenges, recent research has focused on two complementary polishing approaches: electrochemical hydrogen pumping (EHP) and catalytic polishing reactors (CPRs). EHP operates analogously to PEM electrolysis, selectively transporting protons through a solid polymer electrolyte under a low applied voltage (<0.1 V bar⁻¹) [219]. In addition to purification, EHP inherently enables hydrogen compression, allowing purification and pressurisation to be integrated within a single compact unit. Demonstrations by Xiao et al. [220], and Bagacki et al. [221] have reported purities exceeding 99.999%, energy consumption of 2–3 kWh kg⁻¹ H₂, and operational lifetimes of more than 30,000 h.

CPRs employ noble-metal or mixed-oxide catalysts to oxidise or shift residual CO, hydrocarbons, or trace O₂ at moderate temperatures (150–350 °C). Studies by Alptekin et al. [222] and Rossetti et al. [223] have shown near-complete removal of CO and hydrocarbons under simulated biomass gas compositions. These reactors can be combined with selective adsorbents to target specific trace contaminants such as NH₃, H₂S, or halides, thereby increasing polishing robustness and operational resilience.

Hybrid polishing strategies, such as membrane pre-separation followed by EHP or CPR, are becoming increasingly appealing. By reducing the impurity load entering the polishing stage, these configurations lower energy demand, mitigate catalyst or membrane degradation, and improve overall system efficiency. Preliminary techno-economic studies indicate that hybrid polishing can lower total purification costs by 20–30% compared to configurations that rely solely on PSA [224,225]. Hybrid polishing strategies, such as membrane pre-separation followed by EHP or CPR, are becoming increasingly appealing. By reducing the impurity load entering the polishing stage, these configurations lower energy demand, mitigate catalyst or membrane degradation, and improve overall system efficiency. Preliminary techno-economic studies indicate that hybrid polishing can lower total purification costs by 20–30% compared to configurations that rely solely on PSA [224,225]. A summary of representative techno-economic indicators for advanced hydrogen polishing technologies is presented in Table 9.

Table 9. Techno-economic parameters of advanced hydrogen polishing technologies for integration with renewable hydrogen purification systems.

Technology	Principle	H ₂ Purity (vol.%)	TRL	Typical Scale	CAPEX (€/kg H ₂ d ⁻¹)	OPEX (€/kg H ₂)	Energy Use (kWh/kg H ₂)	Lifetime (Years)	Ref.
EHP	Proton-exchange transport under applied voltage	>99.99	6–7	Modular (10–500 kg H ₂ d ⁻¹): scalable for decentralised or small-scale biorefineries	250–400	0.15–0.25	2–3	8–12	[220,221]
CPR	Oxidation or water-gas-shift of residual CO/O ₂ /hydrocarbons	>99.99	7–8	Industrial (>1000 kg-H ₂ /d ⁻¹)	150–250	0.10–0.20	0.8–1.2 (thermal)	10–15	[222,223]
Cryogenic polishing (hybrid)	Condensation of residual impurities before membrane/EHP	>99.99	5–6	Pilot (50–200 kg H ₂ d ⁻¹): compatible with combined adsorbent polishing for trace NH ₃ , H ₂ S, halides	350–500	0.20–0.30	3–5	8–10	[18,226]
Hybrid membrane + EHP	Dual-stage (membrane pre-separation + electrochemical polishing)	>99.99	5–6	Pilot: modular, suitable for decentralised, small-to-medium scale plants	400–600	0.25–0.35	2.5–3	10	[147,210,219]

Note: Reported values are compiled from the cited literature and may reflect different boundaries/assumptions and maturity levels (industrial/pilot data and/or model-based projections). Where multiple references are listed, the entry reflects the range of values across those sources.

EHP and CPRs function in a complementary manner, with EHP providing efficient high-purity hydrogen separation and compression, while CPRs target the removal of trace chemical impurities. Combining these approaches in hybrid strategies, such as incorporating membrane pre-separation before EHP or CPR, reduces the impurity load on the polishing stage, enhancing energy efficiency, prolonging catalyst and membrane lifetimes, and lowering overall system costs [224,225].

4.2. Integrated Purification Configurations and Sequencing Rationale

In practice, renewable hydrogen purification is rarely achieved using a single separation technology. Instead, integrated purification configurations that combine adsorption, membrane, cryogenic, and electrochemical processes are increasingly adopted to balance hydrogen recovery, energy efficiency, purity, and robustness against feed variability.

Hybrid purification configurations differ in their sequencing logic, degree of process intensification, and suitability for specific gas compositions. The selection of a given configuration is strongly influenced by the impurity profile of the hydrogen stream, target purity level, production scale, and operational dynamics. For example, membrane and PSA configurations enable bulk CO₂ and CH₄ removal upstream, reducing PSA vessel size

and regeneration duty, whereas PSA and membrane arrangements can protect sensitive membrane materials from high contaminant loads.

Cryogenic–membrane hybrids, particularly those involving partial condensation, exploit differences in condensability to remove CO₂, H₂O, and higher hydrocarbons while minimising refrigeration demand relative to stand-alone cryogenic systems. Electrochemical polishing stages can then be integrated downstream to achieve ultra-high purity and compression in a single step, particularly for refuelling or PEMFC applications.

Table 10 summarises the main integrated purification configurations reported in the literature, outlining their process sequences, underlying rationale, and key advantages and limitations. Together, these hybrid configurations illustrate how combining complementary separation principles enables more resilient and energy-efficient purification strategies than single-step approaches.

Table 10. Integrated purification configurations and their rationale.

Configuration	Process Description	Key Advantages	Considerations	Ref.
Class I: Membrane → PSA	The membrane unit provides bulk separation (removing CO ₂ and CH ₄); a downstream PSA delivers final polishing.	Reduces PSA vessel size, adsorbent inventory, and regeneration duty; increases overall H ₂ recovery.	The membrane stage may require pretreatment to prevent fouling; additional compression may be necessary.	[39,227]
Class II: PSA → Membrane	PSA performs coarse purification; the membrane provides final polishing or dehydration.	Effective for high-contaminant feeds; PSA rapidly removes heavy species before membrane exposure.	Trade-offs in compressor duty; risk of membrane fouling if PSA breakthrough occurs.	[228–230]
Membrane ↔ Cryogenic (partial condensation hybrids)	The membrane removes non-condensables while the cryogenic unit condenses CO ₂ , H ₂ O, CH ₄ , and other condensables.	Achieves very high recovery (>95%); reduces refrigeration load compared with stand-alone cryogenic systems.	More complex control strategies are required; sensitive to feed composition variability.	[44,231]
Membrane + EHP	Membrane pre-separation followed by EHP producing ultrapure, compressed H ₂ .	Ideal for small to medium-sized decentralised renewable hydrogen production or refuelling applications; facilitates purification and compression in a compact design.	Currently, lower TRL, long-term durability, and cost targets are still under validation.	[232–234]
Multistage mixed approaches	Combinations such as Membrane → PSA → CPR or Membrane → Cryogenic → Membrane.	Addresses complex feeds (tars, H ₂ S, NH ₃ , halides); increases resilience to variable syngas quality.	Higher system complexity; requires advanced control strategies and optimisation.	[235–237]

Note: Reported information is compiled from the cited literature and may reflect different boundaries/assumptions and maturity levels (industrial/pilot data and/or model-based projections). Where multiple references are listed, the entry reflects the specific information across those sources.

4.3. Evidence from Pilot-Scale and Techno-Economic Case Studies

Beyond conceptual designs and laboratory-scale demonstrations, pilot-scale and techno-economic evidence are essential to assess the practical viability of integrated renewable hydrogen purification systems. Hybrid configurations have addressed to address several operational challenges specific to biomass-derived syngas, including tar formation, moisture condensation, and sulphur poisoning.

Quantitative case studies demonstrate the advantages of hybrid purification configurations over stand-alone technologies. For instance, Naquash et al. [44] reported that a membrane–cryogenic configuration achieved hydrogen purities of approximately 99.99%,

with recovery rates close to 96% and a specific energy demand of around $2.37 \text{ kWh kg}^{-1} \text{ H}_2$, significantly lower than that of conventional cryogenic separation. Similarly, optimisation studies of membrane–PSA sequences have shown reduced adsorbent inventories, smaller PSA vessel sizes, and improved overall recovery, particularly at small to medium production scales ($10\text{--}100 \text{ kg H}_2 \text{ day}^{-1}$), where PSA-only systems are less economically favourable [39].

Despite these advantages, hybrid purification configurations introduce additional complexity, including the need for coordinated control strategies, management of transient behaviour, and increased integration effort. Space requirements and CAPEX may also increase depending on the selected configuration [238,239]. These trade-offs highlight the importance of system-level optimisation when selecting purification strategies for renewable hydrogen applications. A summary of representative pilot-scale performance metrics and techno-economic outcomes for leading hybrid purification configurations is provided in Table 11.

Table 11. Pilot-scale evidence and techno-economic performance of hybrid renewable hydrogen purification configurations.

Hybrid Configuration	Representative Performance Metrics	Techno-Economic Impact	Ref.
Membrane–cryogenic hybrid	H_2 purity $\approx 99.99\%$; recovery $\approx 95.9\%$; energy use $\approx 2.37 \text{ kWh} \cdot \text{kg}^{-1} \text{ H}_2$	Lower refrigeration duty vs. stand-alone cryogenic; high recovery with reduced operating cost	[44]
Membrane–PSA hybrid	Increased recovery; reduced PSA vessel size and adsorbent mass	Lower CAPEX and OPEX for PSA stage; improved efficiency especially at $10\text{--}100 \text{ kg H}_2 \cdot \text{day}^{-1}$	[39]
Membrane pre-cleaning + PSA	Effective removal of CO_2 and heavy hydrocarbons before PSA	Extends adsorbent lifetime and lowers regeneration cost	[228–230]
Cryogenic pre-treatment + membrane	Condensation/removal of tars and H_2O before membrane separation	Reduces membrane fouling; stabilises long-term performance	[44,231]
Multistage hybrid chains (Membrane $\rightarrow$ PSA $\rightarrow$ CPR)	Enhanced removal of trace contaminants (H_2S , NH_3 , hydrocarbons)	Maximises purity and recovery for highly variable biomass-derived streams	[235–237]

Note: Where multiple references are listed, the entry reflects the specific information across those sources.

5. Outlook and Future Perspectives for Renewable Hydrogen Purification Systems

5.1. Ongoing Projects and Demonstrations in Europe

The transition from laboratory-scale concepts to industrially viable renewable hydrogen purification systems is increasingly driven by membrane-centric and hybrid process architectures. Over the past decade, several European research, innovation, and demonstration initiatives have focused on validating advanced membranes, integrated purification topologies, and system-level optimisation under realistic operating conditions. These efforts collectively illustrate the direction in which renewable hydrogen purification technologies are evolving. The shift toward membrane-based and hybrid purification strategies is reflected in a growing number of European research and demonstration projects. These initiatives span laboratory, pilot, and early industrial scales, targeting key challenges such as membrane durability, impurity tolerance, system integration, and cost reduction. Table 11 summarises representative European projects, highlighting their scale, technical focus, and targeted TRL progression. Although Table 12 represents a selective snapshot, it illustrates clear trends toward hybrid membrane–adsorption systems, membrane–cryogenic integration, and pilot-scale validation under industrially relevant conditions. In particular, the HERMES and CARMA- H_2 projects play a central role in advancing membrane

industrialisation by targeting TRL 7 demonstrations and direct coupling with industrial hydrogen streams.

Table 12. European projects that include hybrid or membrane-based hydrogen purification.

Consortium	Project	Scale (Reported)	Key Metrics	Year (Start/Recent)	Ref.
FORTH, UPorto, partners (EU FP7)	HY2SEPS-2 (Hybrid Membrane-PSA)	Pilot/lab → small pilot (project budget ≈ € 1.6M)	Membrane + PSA hybrid design for reformat, optimisation of carbon membranes and layered adsorbents; demonstrates modularity for small-scale units; aims to increase recovery & reduce CAPEX.	2011–2013 (FP7)	[240]
H2SITE, Tecalia, SNAM, TUPRAS + partners (Clean Hydrogen Partnership)	HERMES (Hydrogen Efficient Purification Using Membranes)	Demonstration at industrial sites; prototypes ~100 kg H ₂ /day (TRL7 target)	Scale up Pd-based and carbon molecular sieve membranes; aim <€1/kg purification cost and <3.5 kWh/kg energy; industrial demos in Italy & Türkiye.	2024–2027 (grant 101192352)	[241]
SINTEF and partners	CARMA-H ₂	Pilot/TRL5 → TRL7 planned	Evaluate membrane durability to biogas impurities (focus on H ₂ S tolerance); advancing membranes for biogenic streams.	2024–2025 (active)	[242]
WtE/consortium(WT̄HYIELD AS + partners)	(waste-to-hydrogen)	Industrial demonstration (hundreds of t H ₂ /yr planned)	Waste-to-green H ₂ via gasification + demonstration of purification/upgrading chain for industrial scale. Focus on process integration and modular deployment.	2023–2026 (announced 2024)	[243]
Academic/Industrial consortia (various)	Membrane–Cryogenic integration studies (research projects & pilots)	Lab to pilot	Demonstrated membrane + cryogenic sequences achieving high recovery and reduced energy duty in case studies (process modelling and small pilot tests); validation of hybrid sequences and benchmarking against PSA-only and cryogenic-only systems.	Ongoing academic work (2021–2025)	[44]
Multiple (Horizon/national calls)	HORIZON-JTI CLEAN H ₂ calls (topic on demonstration of purification systems)	Varies	Funding topic explicitly calls for demonstration of purification systems for renewable hydrogen (membranes, electrochemical, thermochemical); supports scale-up and industrial integration of hybrid technologies.	2024–ongoing	[244]

5.2. Key Challenges and Research Directions

Despite the progress achieved through ongoing projects and pilot demonstrations, several cross-cutting technical and non-technical challenges continue to limit large-scale deployment of next-generation renewable hydrogen purification systems. These challenges are particularly pronounced for biomass-derived hydrogen streams, which exhibit high variability in composition and impurity load.

Across technologies, the dominant evidence gaps are the lack of harmonised multi-component testing, limited long-duration ageing datasets, and insufficient reporting of impurity tolerance under representative renewable hydrogen conditions. Apparent con-

flicts between studies frequently trace back to differences in feed composition, humidity control, and performance definitions (purity, recovery, stability window), which should be made explicit when interpreting reported “best performers”. Comparable gaps remain in transparent reporting of scalable module fabrication pathways and cost drivers for emerging membrane materials.

A consolidated overview of the main challenges, together with corresponding research and development priorities identified in recent studies and demonstration activities, is provided in Table 13. The challenges highlighted span material-level limitations, process integration issues, system operation, and broader regulatory and lifecycle assessment considerations.

Table 13. Key challenges and research directions for next-generation renewable hydrogen purification systems.

Challenge	Research & Development Priorities	Ref.
Feed variability and fouling: Biomass-derived syngas contains tars, condensable organics, H ₂ S, NH ₃ , and particulates that foul adsorbents and degrade polymeric/inorganic membranes. Fouling reduces lifetime and increases OPEX.	Develop fouling-resistant materials (e.g., anti-sulphur membranes, protective interlayers); integrate pre-cleaning; evaluate long-term performance in real syngas; conduct long-term testing under real syngas conditions.	[242]
Module scale-up and cost reduction: Outstanding lab-scale performance of MOF, COF, and CMS membranes rarely translates to industrial-scale manufacturing due to reproducibility, defect control, and cost barriers.	Industrial-scale fabrication of defect-free membranes; reproducible roll-to-roll or coating processes; target cost < € 1/kg purified H ₂ for industrial deployment (e.g., HERMES project).	[241]
Control, dynamics, and system integration: Hybrid systems require coordinated operation across multiple separation principles, increasing control complexity, sensitivity to feed swings, and start–stop behaviour issues.	Develop dynamic control strategies; advanced process modelling; validate integrated PSA–membrane and cryogenic hybrids at pilot scale; include predictive maintenance and real-time monitoring.	[39,245]
Standardisation and safety: Lack of harmonised hydrogen purity standards, module certification, and safety protocols complicates cross-border deployment and integration with existing energy systems.	Create unified certification and safety protocols; harmonise purity standards; integrate with EU and international hydrogen roadmaps; develop modular safety assessment procedures for hybrid units.	[246]
System-level LCA and techno-economic assessment: Current LCA/TEA studies rarely include full membrane lifecycle, replacement, and end-of-life handling, leading to incomplete economic and environmental assessments.	Develop full-chain TEA/LCA; include manufacturing impacts; quantify environmental and cost advantages versus PSA/cryogenic alternatives; consider circular economy and recycling strategies.	[241,242]

5.3. Expected Technology Trajectory (2025–2035)

Based on current demonstration activities, industrial roadmaps, and recent techno-economic assessments, the evolution of renewable hydrogen purification technologies over the next decade can be structured into three development horizons: short-, medium-, and long-term. These horizons reflect the anticipated progression from pilot-scale validation to widespread commercial adoption of hybrid purification systems. Table 14 summarises the projected technological, industrial, and economic milestones for renewable hydrogen purification systems over the period 2025–2035, accounting for advances in membrane robustness, hybrid process integration, and cost reduction.

In the short term (2025–2028), the most deployment-ready options remain mature and industrially established separation trains (PSA/VPsA/TSA with appropriate pre-conditioning and polishing), while membranes are most realistically positioned as enrichment or pre-separation units within hybrid pilots rather than as single-step routes to stringent end-use purity. Cryogenic separation is realistically viable mainly for centralised, large-throughput cases or specific feeds where refrigeration integration is advantageous,

given the associated energy and cost burden. In the medium term (2028–2032), wider uptake of modular membrane skids and hybrid configurations (e.g., membrane–PSA and membrane–polishing trains) is credible if long-duration stability under humid multicomponent feeds and tolerance to biomass-derived trace contaminants (notably sulphur species and condensables) are demonstrated beyond pilot scale, alongside reproducible module fabrication at acceptable cost. Advanced MMMs and MOF/COF-enabled systems remain predominantly at laboratory-to-early-pilot maturity for renewable-hydrogen purification, with deployment constrained by impurity tolerance, lifetime evidence under representative conditions, defect-controlled scale-up, and total installed cost.

Table 14. Projected technology trajectory for renewable hydrogen purification systems (2025–2035).

Timeframe	Expected Developments	Milestones	Ref.
Short term (2025–2028)	- Demonstration of membrane prototypes at TRL 6–7 for industrial syngas and biogas streams. - Increasing deployment of hybrid PSA–membrane pilot units achieving lower energy use and CAPEX vs. PSA-only baselines. - Intensive R&D on fouling mitigation, membrane stability, and interlayer protection. - Implementation of early-stage hybrid control strategies for combined membrane–PSA operation.	- HERMES and CARMA-H2 projects delivering pilot-scale validation. - Optimisation of membrane–PSA dynamic control strategies. - First-generation robust anti-sulphur and anti-tar membrane materials.	[241,242]
Medium term (2028–2032)	- Commercialisation of modular membrane skids for decentralised renewable hydrogen production. - Wider adoption of MMMs and MOF–COF hybrids as manufacturing costs decrease and long-term stability is proven. - Increasing attractiveness of membrane–cryogenic hybrids for condensable-rich feeds. - Pilot-scale demonstration of hybrid purification units with integrated process monitoring and optimisation.	- Industrial validation of hybrid sequences with 20–30% energy reduction. - Improved fabrication reproducibility and membrane module standardisation. - Market uptake in waste-to-hydrogen and distributed reforming systems.	[241]
Long term (2032–2035)	- Integrated purification modules (membrane + PSA/polisher + EHP) becoming standard for distributed renewable hydrogen plants. - Widespread commercial deployments enabling large CAPEX reductions at scale. - Purification costs approaching <1 €/kg H₂ in favourable applications due to modularity and improved durability. - Standardisation of performance, safety, and environmental protocols to enable large-scale adoption. - Full-chain TEA/LCA considering lifecycle, recycling, and circular economy aspects for hybrid purification systems.	- Mature supply chains for advanced membrane modules. - Harmonised certification and purity standards enabling large-scale adoption. - Full TEA/LCA optimisation across membrane lifecycles.	[241,242]

5.4. System-Level SWOT Analysis of Renewable Hydrogen Purification Technologies

To synthesise the technological, economic and deployment-related insights discussed in Sections 4 and 5, a system-level strengths, weaknesses, opportunities, and threats (SWOT) analysis is presented in Figure 11.

Strengths High achievable hydrogen purities when combining bulk separation with advanced polishing (EHP, CPR). Modular, compact designs well suited for decentralised and small-to-medium-scale plants. Lower specific energy consumption compared with stand-alone PSA or cryogenic systems in many configurations. Flexible integration with gasification, reforming, and fermentation units.	Weaknesses Lower TRL of advanced membranes and hybrid systems compared with PSA and cryogenic separation. Sensitivity of membranes and catalysts to tars, sulphur species, and moisture without adequate pretreatment. Limited long-term durability data under real biomass-derived syngas conditions. Manufacturing scalability, defect control, and cost of advanced membranes (MOFs, COFs, MMMs).
Opportunities Strong policy support in Europe for renewable and decentralised hydrogen production. Ongoing EU-funded demonstration projects targeting TRL 7–8 for membrane and hybrid systems. Advances in materials science enabling fouling-resistant membranes and improved hybrid integration. Growing demand for fuel-cell-grade hydrogen in mobility and distributed energy applications.	Threats Competition from mature PSA and cryogenic systems with established supply chains. Slow standardisation of hydrogen purity, safety certification, and module qualification. Variability in biomass feedstocks increasing operational risk and maintenance costs. Potential cost overruns or performance gaps during scale-up from pilot to industrial systems.

Figure 11. System-level SWOT analysis of renewable hydrogen purification technologies (with emphasis on membrane-centric and hybrid systems).

Rather than focusing on individual separation technologies in isolation, this SWOT evaluates renewable hydrogen purification from an integrated system perspective, with particular emphasis on membrane-based and hybrid purification configurations. This framework highlights not only intrinsic technological strengths and weaknesses, but also external opportunities and risks that influence large-scale deployment in real-world renewable hydrogen value chains. This perspective is particularly important for decentralized biomass-to-hydrogen systems, where feed variability, scale constraints and integration complexity play a decisive role.

The SWOT analysis confirms that membrane-based and hybrid purification systems offer a strong strategic position for future renewable hydrogen deployment, particularly in decentralized and modular applications. However, their successful transition from pilot to commercial scale will depend on addressing material durability, system integration, and standardization challenges, while leveraging ongoing demonstration efforts and supportive frameworks.

6. Conclusions

The purification of renewable hydrogen is a decisive enabling step for the deployment of low-carbon hydrogen pathways compatible with fuel cells and industrial applications. As demonstrated throughout this review, both biological and thermochemical biomass-based routes produce complex gas mixtures that require extensive upgrading to meet stringent purity requirements, particularly with respect to CO₂, CO, CH₄, H₂S, and other trace contaminants. Irrespective of the production pathway, purification remains among the most energy- and cost-intensive stages of the renewable hydrogen value chain.

Commercially established technologies such as pressure swing adsorption (PSA) and cryogenic separation exhibit high technological maturity (TRL 8–9) and reliably deliver high-purity hydrogen. However, their high energy demand, capital intensity, and limited flexibility constrain their suitability for decentralised or small-scale renewable hydrogen systems. In contrast, polymeric and inorganic membrane technologies offer modularity, reduced specific energy consumption, and lower CAPEX, although challenges related to

long-term stability, plasticisation, and impurity tolerance under variable syngas compositions remain critical.

A central finding of this review is that no single purification technology can be considered universally optimal. Instead, recent advances in MMMs, particularly those incorporating MOFs, COFs, and MOF–COF hybrid architectures, highlight a promising pathway toward next-generation purification systems. These materials demonstrate enhanced selectivity, high permeance, and modifiable pore chemistry, with growing evidence that hybrid membrane-based configurations can approach or surpass the performance of conventional PSA and cryogenic systems under specific operating conditions.

The techno-economic analysis reviewed in this work indicates that integrated hybrid purification strategies, such as membrane–PSA, membrane–cryogenic, and membrane–catalytic polishing configurations, offer clear synergies, enabling reductions in energy consumption, improved impurity management, and enhanced hydrogen recovery. These system-level advantages are particularly relevant for decentralised and small- to medium-scale renewable hydrogen production.

This review demonstrates that future progress in renewable hydrogen purification will rely on intelligent system integration rather than further optimisation of single-step technologies. Priority research directions include the development of fouling- and sulphur-resistant membrane materials, cost-effective fabrication of large-area MMM modules, and the design of standardised, modular purification units. Equally important is the application of harmonised techno-economic and life-cycle assessments to benchmark emerging hybrid systems against established industrial standards. By addressing these challenges, next-generation renewable hydrogen purification systems can achieve the performance, robustness, and cost-effectiveness required for large-scale deployment, thereby supporting the transition toward a sustainable and resilient hydrogen economy.

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Abbreviations

The following abbreviations are used in this manuscript:

BDC	Benzene-1,4-dicarboxylate (terephthalate)
CA	Cellulose Acetate
CAPEX	Capital Expenditure
CMSM	Carbon Molecular Sieve Membrane
CNTs	Carbon nanotubes
COF	Covalent Organic Framework
CPR	Catalytic Polishing Reactor
CVD	Chemical Vapour Deposition
DDR	Deca-dodecasil 3R (zeolite type)

EHP	Electrochemical Hydrogen Pump
ELP	Electroless Plating
GDP	Glassy Dense Polymer
GHG	Greenhouse gases
GPU	Gas Permeation Unit
H ₂ S	Hydrogen Sulphide
IEA	International Energy Agency
LCA	Life-Cycle Assessment
LCOH	Levelised Cost of Hydrogen
MIL	Materials Institute Lavoisier (MOF family)
MMMs	Mixed Matrix Membranes
MOF	Metal–Organic Framework
MXene	Transition-metal carbide/nitride 2D material
OPEX	Operational Expenditure
PBI	Polybenzimidazole
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PEM	Proton-exchange membrane
PEMFC	Proton exchange membrane fuel cells
PFR	Phenol–Formaldehyde Resin
PIM	Polymer of Intrinsic Microporosity
PSA	Pressure Swing Adsorption
PSf	Polysulfone
PVAc	Polyvinyl Acetate
PVDF	Polyvinylidene Fluoride
SOFC	Solid Oxide Fuel Cell
SOC	Solid Oxide Cell
SWOT	Strengths, weaknesses, opportunities, and threats
SWCNT/MWCNT	Single-/Multi-Walled Carbon Nanotube
T _g	Glass Transition Temperature
TEA	Techno-Economic Assessment
TEOS	Tetraethyl Orthosilicate
TRL	Technology Readiness Level
UiO-66	University of Oslo MOF-66
VPSA	Vacuum Pressure Swing Adsorption
YSZ	Yttria-Stabilised Zirconia
ZIF	Zeolitic Imidazolate Framework

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