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Review

Membrane-Assisted Dark Fermentation for Integrated Biohydrogen Production and Purification: A Comprehensive Review

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Abstract: The aim of this review is to provide a comprehensive analysis of the membrane-assisted dark fermentation process for bioH_2 production and purification. This review initially analyses the need for and the current state of the art in H_2 production through dark fermentation, evaluating the research landscape and the maturity level of the technology. Key factors influencing the dark fermentation process are then examined, along with emerging research trends in membrane-assisted fermentative H_2 production systems. This review subsequently addresses the challenges inherent to dark fermentation and explores potential opportunities to enhance H_2 production efficiency. Special attention is given to membrane technology as a promising strategy for process intensification in bioH_2 production and recovery. Finally, this review provides an in-depth discussion of inorganic membranes, mixed matrix membranes (MMMs), and thin and ultrathin membranes, evaluating each membrane type in terms of its advantages, limitations, and purification performance. This review offers valuable insights into intensifying the dark fermentation process by leveraging membrane technology to enhance bioH_2 production and purification efficiency.

Keywords: dark fermentation; membrane technology; H_2 purification; biogenic off-gas; biorefinery; bioenergy

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1. Introduction

The recent politic, energetic, and environmental crises have triggered the transition to sustainable energy sources to reduce dependence on fossil fuels. This energy transition towards a green circular economy has motivated the creation of international agreements and commitments to meet ambitious targets where it is expected that the carbon dioxide (CO_2) emissions are reduced at least by 55% compared to the year 1990 [1]. For instance, the European Union (EU) has set the most ambitious targets to become the first climate-neutral continent by 2050, and several Action Plans have been established such as the European Green Deal that aims at transforming the EU into a competitive and resource-efficient economy [1]. In this sense, the decarbonization of industrial processes and the transport sector is essential to achieve a circular economy where biofuels are fundamental to meet these ambitious targets. The attractiveness of biofuels relies on their compatibility with existing facilities and equipment from their fossil-based counterparts, which significantly

reduces the initial capital costs and diversifies their applications [2]. Thereby, the EU has significantly incentivized the production and use of gaseous biofuels such as hydrogen (H_2), and since 2020, a H_2 strategy was adopted and reinforced in 2022 by the adoption of the REPowerEU Plan [3]. The H_2 strategy supports the investment, action, demand, research, and cooperation in H_2 production and has set the ambitious target to produce 10 million tons of H_2 by 2030 at the EU level [4]. Under this framework, in March 2023, the EU commission and stakeholders signed a partnership to accelerate the research development of renewable H_2, since this energy sector can contribute to covering 12% of the global energy demand [5].

H_2 has gained great importance due to its high energy content (141.6 kJ g^{-1}), in addition to its versatility of being used as an energy carrier or as a clean fuel [6]. H_2 possesses great advantage over other fuels since it is a non-toxic gas, and its combustion only generates water [7]. Nowadays, H_2 is mainly produced from fossil resources and renewable H_2 production accounts for a small percentage (~4%) of the total H_2 production [6]. Renewable H_2 can be produced via electrocatalytic water-splitting processes, pyrolysis, and gasification of biomass and from biological processes. Biologically produced H_2, better known as bioH_2, stands as the most prominent pathway for H_2 production due to its low energy requirements and the use of organic waste as feedstock [8]. Biological H_2 production processes include biophotolysis, dark fermentation, microbial electrolysis cells, photofermentation, and biological water–gas shift from which dark fermentation is considered the most developed method [8–10].

Dark fermentation has demonstrated high production rates and the advantage of using organic waste such as agricultural waste, industrial waste, and food waste [11,12] and effluents from dairy and paper industries and other carbohydrate-rich wastewaters [13]. The dark fermentation process entails the degradation of complex organic substrates (mainly carbohydrates) into H_2 and volatile fatty acids (i.e., acetic acid, butyric acid, etc.) [14]. Theoretically, the highest bioH_2 production yield is 4 mol H_2 mol glucose^{-1} and 2 mol H_2 mol glucose^{-1} when acetic acid and butyric acid are produced, respectively [10]. However, only 1–2.5 mol H_2 mol glucose^{-1} is produced in practice [15]. In this context, the bioH_2 production rate depends on the substrate characteristics, reactor design, feeding regime, microbial community, and operational conditions [16]. The dark fermentation process, including its state-of-the-art developments, the latest research trends in membrane-assisted fermentative H_2 production, and the challenges in dark fermentation and the associated opportunities for enhancing bioH_2 production, is comprehensively presented in Section 2.

BioH_2 produced via dark fermentation is a gas mixture mainly composed of H_2, CO_2, and moisture [17,18], with H_2 contents typically ranging from 40 to 60% [7,19]. However, for being used as a fuel, bioH_2 must comply with the ISO 14687 [20], which specifies a minimum of 99.97% of H_2 [21]. Thereby, an efficient bioH_2 purification process is necessary to meet this high H_2 purity, especially since the presence of water reduces the efficiency of the separation process [7,18]. Typical bioH_2 purification technologies used industrially are absorption, cryogenic process, membrane separation, and pressure swing adsorption [18,22]. The most appropriate purification technology should account for the initial composition of the gas, volume of the gas to be purified, and the final required composition of the gas [23]. In this context, membrane separation stands as a convenient technology that has been widely studied for bioH_2 purification due to its high selectivity [22,23]. Membrane separation is based on the selective permeability of a fraction of the components in gas mixtures, which results in high selectivity and presents advantages such as high energy efficiency, simple operation, low maintenance costs, minimal utility requirements, absence of moving parts, and compactness and portability of the membrane modules [17].

Even if bioH_2 purification is still in its early stages of development, membrane separation represents a promising technology to achieve high H_2 purity and meet the ambitious 2030 decarbonization targets. In addition, when integrated with dark fermentation systems, membranes facilitate the continuous removal of inhibitory by-products, stabilize microbial activity, and prevent biomass washout. This integration enables higher hydrogen yields and higher microbial densities, even at low hydraulic retention times (HRTs), making the process more efficient and scalable. Thus, membranes play a key role in dark fermentation by enhancing bioH_2 production and purification through efficient gas separation and bioprocess intensification.

In this context, the present review aims at providing a comprehensive overview of membrane-assisted dark fermentation processes for the integrated production and purification of H_2. First, it discusses the need for and current status of bioH_2 production via dark fermentation, analyzing the research landscape and technology maturity level. Then, key factors influencing the dark fermentation process are examined, along with emerging research trends in membrane-assisted fermentative H_2 production systems. Later, this review addresses the challenges associated with dark fermentation and explores opportunities for enhancing H_2 yields. Finally, special attention is given to membrane technology as a promising approach for process intensification in bioH_2 production and purification. This review includes a detailed discussion of inorganic membranes and mixed matrix membranes (MMMs), with each membrane type examined to highlight its respective advantages, limitations, and performance. The novelty of this review lies in its focus on integrating membrane technology with dark fermentation, offering a detailed analysis of how this combination intensifies bioH_2 production and purification.

2. The Need for bioH_2 Production via Dark Fermentation and Current Status

2.1. The Role of Dark Fermentation Technology in the Development of Future Biorefineries

Dark fermentation is an intricate biological process in which various species of bacteria breakdown organic waste and wastewater under anaerobic conditions. This fermentation process generates hydrogen gas (H_2), along with CO_2 and a range of soluble by-products, including organic acids like acetate and butyrate [9]. The dark fermentation process involves different metabolic pathways such as H_2-producing pathways, H_2-consuming pathways, and competing pathways for substrate utilization [24]. These metabolic routes include various types of fermentation, such as ethanol fermentation, propionic acid-type fermentation, lactic acid fermentation, butyric acid-type fermentation, acetic acid-type fermentation, and mixed fermentation. The overall goal is to favor H_2-producing pathways while minimizing the occurrence of non-favorable pathways, thereby maximizing the H_2 production efficiency. The absence of molecular oxygen (O_2) is crucial for the bacteria involved in dark fermentation, as they rely on these anaerobic conditions to metabolize complex organic compounds [25]. The by-products of dark fermentation, especially H_2, have a significant potential for use as a clean and renewable energy source, while other products, such as acetate and butyrate, can serve as precursors for various industrial/biotechnology applications [26]. Dark fermentation is thus a vital technology within the framework of a biorefinery, offering sustainable solutions for waste management while enabling energy recovery. Both the biogenic CO_2 and H_2 produced during the process can be integrated into a biorefinery system, thus contributing to the production of renewable energy and reducing greenhouse gas emissions. Additionally, the fermentation broth, which is rich in organic acids, can be further utilized in various biotechnological applications [26]. This includes the production of biogas, medium-chain fatty acids, bio-oil, bioplastics, and even electricity, alongside other high-value compounds (Figure 1). These additional processes

enhance the overall value of the system, making dark fermentation a key component in the development of a sustainable, circular bioeconomy.

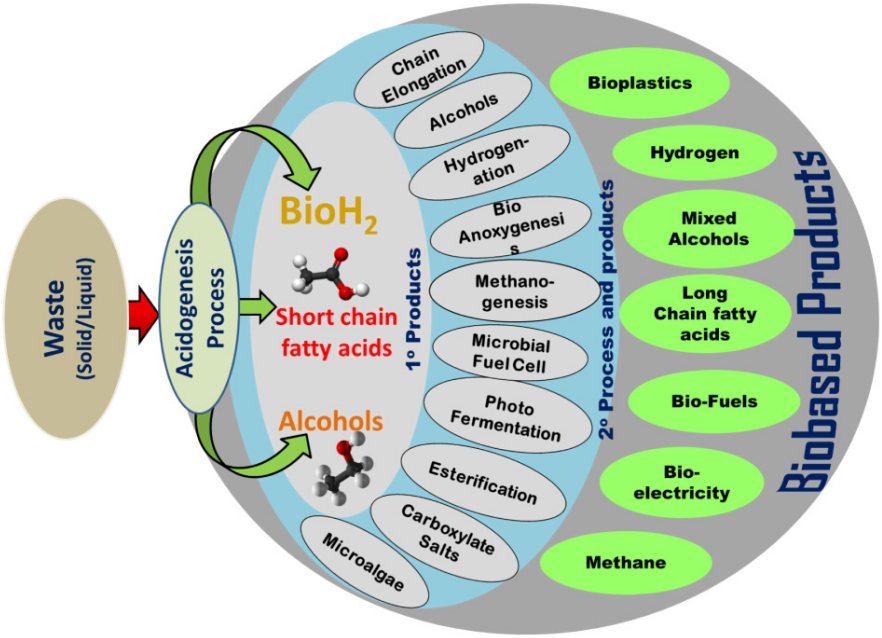


Figure 1. A conceptual framework for acidogenesis applied to bioenergy production and the carboxylate platform for bioproduct applications. Source: Venkata Mohan et al. (2016) [26]. Copyright 2016, with permission from Elsevier.

2.2. Dark Fermentation: Research Landscape and Technology Maturity Level

As shown in Figure 2a, the field of "dark fermentation" has experienced a notable increase in research activity over the past two decades, with the first publications appearing around 2005. Initially, research on this topic was limited, reflecting the novelty and early-stage investigation of microbial processes for bioH_2 production. However, starting around 2010, the number of publications began to rise exponentially, which suggested a growing interest in this renewable energy technology and rapid advances in the field. The exponential growth continued throughout the 2010s, peaking around 2022, when close to 300 publications were produced in a single year. This sharp increase can likely be attributed to heightened global focus on sustainable energy solutions and technological improvements in reactor designs, optimization of microbial communities, and substrate utilization for dark fermentation. In the last five years (2019–2023), the average number of publications per year was approximately 258, showing consistent high interest in the field. China and India have emerged as the leading contributors, with approximately 400 and 300 publications, respectively, thus reflecting their substantial investment in renewable energy research and biotechnology (Figure 2b). Italy follows with around 180 publications, while other notable contributors include Mexico, South Korea, Taiwan, the United States, and France, all of which have produced over 100 documents each on the topic. This global distribution of research activity highlights the widespread recognition of dark fermentation as a promising avenue for renewable energy and marketable products and materials, with significant contributions from both developed and emerging economies. The consistent rise in publications, particularly over the last decade, highlights the growing importance of dark fermentation in global scientific discourse and its potential to contribute to decarbonization solutions in the future. To date, most studies on dark fermentation are at low technology readiness levels (TRLs), focusing on lab-scale research and prototype validation, indicating that dark fermentation is still largely experimental. Dark fermentation research spans from TRL 1 to 6, from concept development to prototype system verification, with few

studies advancing to TRL 7, where pilot systems are demonstrated [27]. Progressing to higher TRLs (TRL 8–9) requires overcoming challenges in scaling, operational stability, and cost-effectiveness. This technological gap highlights the need for further research, innovation, and investment to bring dark fermentation closer to commercial deployment.

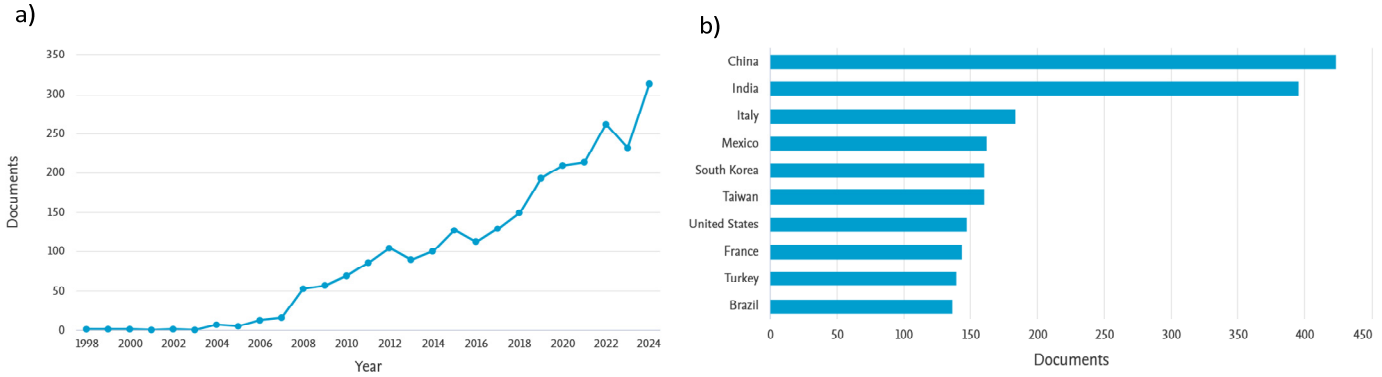


Figure 2. (**a**) Number of documents published on "dark fermentation" by year and (**b**) number of documents published on "dark fermentation" by country or region. Source: Scopus database using the keyword "dark fermentation"; search conducted at the end of October 2024.

It is worth noting that a search conducted on Espacenet, using "dark fermentation" as the keyword, reveals that the patent landscape in this field is heavily focused on enhancing H_2 production through various innovative approaches. A total of 524 patents were identified; Table 1 shows some relevant (application) patents. Commonly, patents explore coupling dark fermentation with other processes, such as photofermentation, to increase yields and efficiency in bioH_2 production. Many inventions integrate microbial electrochemical systems or employ additive materials, such as biochar or graphene-based composites, to optimize dark fermentation performance. Reactor designs are also a recurring theme, as numerous patents propose specialized reactors tailored for fermentative H_2 production. This trend reflects ongoing efforts to make dark fermentation a commercially viable method for sustainable energy production, with significant interest in applying this technology to waste materials and biomass, aligning with global interests in renewable and waste-to-energy technologies.

Table 1. A summary of development approaches for inventions in the dark fermentation field [1].

Development Approach	Patent [1]
Integrated dark fermentation process	IN3532MU2013, CN213416792U, CN116970655A, CN220846099U, US2013217089A1, CN109294882A, US2016186218A1, ES2292312A1, CN104372030A, CN102286537A, CN101760479A, CN117230121A, US2014157777A1
Reactor design	CN117448132A, CN116731828A, US2015111273A1, CN117247825A, WO2019058073A1, CN116814387A, CN217265683U, CN105692895A, CN210367666U, CN220034495U, CN218026060U, CN107488578A
Enhancement additive	CN115992186A, CN115141852A, CN114410695A, CN115215386A, CN117735516A, CN114408981A, CN109626375A, CN109704339A, CN107858379A, CN117487861A, CN111847525A, CN102994559A
Biocatalyst	CN116622562A, CN114703233A, CN117965645A, CN118006694A, CN108707567A, CN112852683A, CN102321671A, CN118028162A, CN116836883A, CN116042478A, CN105462874A, CN104164395A, ES2456776A1, KR20100007210A, JP2012115154A, MX2016014659A

[1] Source: Espacenet, using "dark fermentation" as a keyword; search conducted on 6 November 2024.

2.3. Factors Affecting the Dark Fermentation Process

Figure 3 provides an integrated view of the variables that require careful consideration and control to enhance H_2 production efficiency in the dark fermentation process. The essential factors affecting H_2 production in dark fermentation include inoculum sources, reactor operations, substrate compositions, and operational conditions [24]. Multiple inoculum sources, such as wastewater treatment plant sludge, anaerobic sludge, and compost, are typically used, with pretreatment methods (e.g., thermal, acid, and aerobic treatments) applied to enhance microbial activity and select H_2-producing microbes while killing other undesirable microorganisms (i.e., methanogens). In this context, it is worth mentioning that there is no universal ideal pretreatment, and the pretreatments currently available are not selective enough for beneficial bacteria. The operation regime (i.e., batch, semi-continuous, or continuous) combined with reactor configurations, such as the continuous stirred-tank reactor (CSTR), up flow anaerobic sludge blanket reactor (UASB), and hybrid designs, influences microbial stability and H_2 production performance. Substrate composition, including carbohydrates, nitrogen, and metals, plays a critical role, while inhibitory compounds, such as phenolic acids, may require pretreatment (a detoxification step) to maximize microbial efficiency. Additionally, key operating conditions, including HRT, solid retention time (SRT), organic loading rate (OLR), pH, temperature, oxidation–reduction potential (ORP), and mixing intensity, must be optimized, as they significantly impact microbial metabolism and H_2 production rates. The optimal operational and environmental parameters to maximize H_2 production must be tailored to each specific case, as they are influenced by various factors, including substrate type, microbial community, and system configuration. However, a general guideline for these conditions includes a temperature set either in the mesophilic range (35–37 °C) or thermophilic range (55–60 °C). The pH is commonly maintained between 5.5 and 6.5 to support microbial activity. In continuous systems, the HRT can vary from around 2 h in attached-growth fermenters to 18 h in suspended-growth systems. The OLR range is typically between 90 and 180 g COD/L-d, while the ORP is often controlled within a range of −200 to −500 mV to maintain anaerobic conditions optimal for H_2 production. Finally, gas–liquid transfer rates [28,29], invasive microbiota [30,31], and system perturbations (e.g., fluctuations in temperature, substrate, or pH [32,33]) are also highlighted as important factors to control for optimal H_2 production.

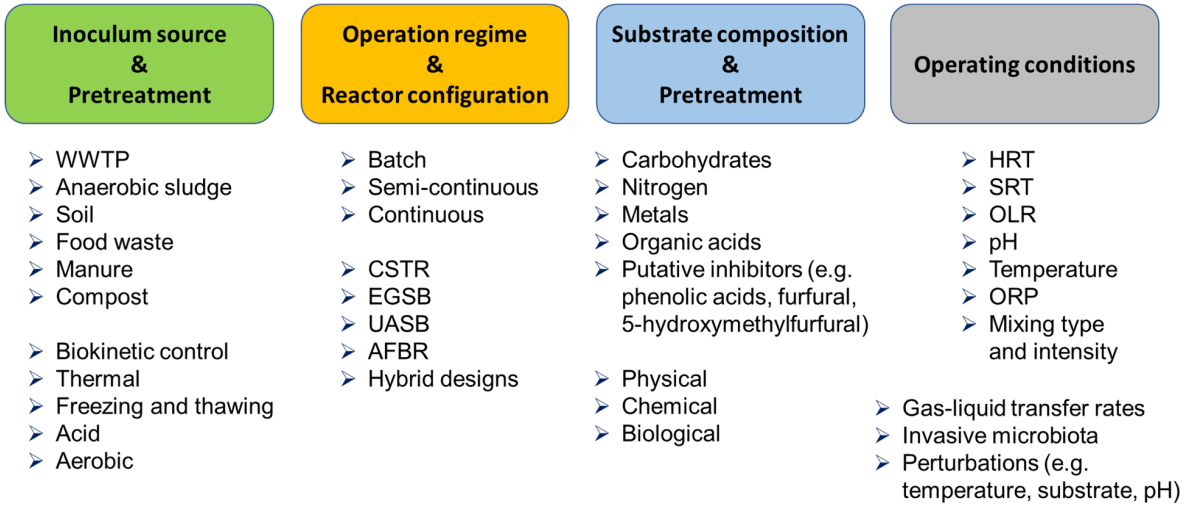


Figure 3. Comprehensive overview of the variables that need careful optimization to enhance the efficiency of H_2 production in dark fermentation. WWTP: wastewater treatment plant; CSTR: continuous stirred-tank reactor; EGSB: expanded granular sludge bed reactor; UASB: up flow anaerobic sludge blanket reactor; AFBR: anaerobic fluidized bed reactor; HRT: hydraulic retention time; SRT: solid retention time; OLR: organic loading rate; and ORP: oxidation–reduction potential.

2.4. Latest Research Trends in the Membrane-Assisted Fermentative H_2 Production

Dark fermentation has been carried out in a range of reactor types, such as the CSTR, packed bed reactor, expanded granular sludge bed, anaerobic fluidized bed reactor, and UASB. Anaerobic membrane bioreactors (AnMBRs), which integrate fermentation with membrane technology, represent a promising alternative to other reactor designs for enhancing fermentative bioH_2 production. AnMBR systems are compact, require minimal physical space, and produce high-quality effluents [34]. Additionally, AnMBRs achieve efficient H_2 production rates while mitigating the buildup of other by-products. AnMBRs also prevent biomass washout, allowing for an increased solid retention time even at low hydraulic retention times, which is essential for effective bioprocessing. AnMBRs have been shown to effectively process high-solid food waste, achieving H_2 yields of up to 111.1 mL H_2 gVS added^{-1} and volumetric H_2 production rates of up to 10.7 L H_2 L^{-1} day^{-1} at an OLR of 125.4 g COD L^{-1} day^{-1} [35]. However, the primary limitations of AnMBRs include high operational costs, membrane fouling, and caking, which can hinder their widespread application [36]. The challenge of membrane fouling has been addressed by employing a hollow fiber module, which enables the continuous extraction of acidogenic off-gas while also supporting biofilm development [37]. In this context, membrane reactor configurations differ according to the placement of the membrane and the approach to phase separation, designed to maximize reactor efficiency and enhance product purity. In terms of membrane placement, both in situ and ex situ configurations are widely implemented. In in situ liquid/gas (L/G) membrane arrangements, the membrane is positioned within the reaction medium itself, which enables the immediate extraction of gasses directly from the fermentation liquid. In contrast, ex situ L/G configurations arrange the membrane outside the main reaction area, often in a separate unit where gasses produced in the reactor are transferred to the membrane module for extraction. Phase separation can be performed through various modes. The solid/liquid (S/L) separation mode allows the membrane to retain solid biomass or suspended particles, concentrating bacterial or solid matter, and can be adapted for in situ or ex situ use depending on the separation location. The liquid/liquid (L/L) mode selectively extracts certain liquid components, such as organic acids, from the fermentation broth, mitigating the inhibitory effects of accumulated metabolites on dark fermentation. Lastly, the gas/gas (G/G) separation mode focuses on gas-phase separation, particularly for H_2 purification or concentration [37].

In the ongoing research, dynamic membrane bioreactors (DMBRs) have emerged as a promising advanced design to significantly enhance H_2 production efficiency. DMBR is a type of bioreactor that uses a biofilm-coated membrane (>10 μm) to retain microbial biomass without immobilization. Unlike traditional membrane bioreactors, a DMBR relies on microorganisms themselves to form a dynamic layer on the membrane, which acts as a filter and support for biofilm development. This self-forming membrane can capture suspended biomass and other particles, promoting high concentrations of microbial communities essential for efficient H_2 production [38,39]. Dynamic membrane modules can be installed either inside (in situ) or outside (ex situ) the reactor chamber [40,41]. The external setup allows for the use of multiple modules and appears to be more advantageous for long-term operation and maintenance [42]. Dynamic membrane modules have primarily been integrated with CSTRs but can also be incorporated into other reactor configurations [40]. The performance of self-forming biofilm is determined by factors such as the concentration, type, shape, and molecular weight of the filtering solution and the cross-flow velocity [40]. In addition, tightly bound extracellular polymeric substances are components of the biofilm matrix that adhere closely to the cells and contribute to the structural stability and integrity of biofilms in the reactor. Higher EPS content has been associated with better biofilm formation using the dynamic membrane module [43]. Here, it should be noted that DMBRs

for fermentative H_2 production are an emerging technology still in the early stages of development, with most studies conducted at the lab scale, highlighting the need for further scale-up and pilot-scale validation. Although still in the early stages, DMBRs have shown promising results in selective biomass retention and stable H_2 productivity, achieving peak H_2 production rates between 26 and 93 L H_2 L^{-1} d^{-1} across various substrates, including glucose [39,44–46], sucrose [47], xilose [48], galactose [43], and complex biomasses containing particulate matter, such as algal biomass [49], food waste [50], and lignocellulosic biomass [51] (Table 2). Here, it should be noted that high-performance dark fermentation reactors capable of sustaining high H_2 productivities have been reported using DMBR. For instance, Sim et al. (2024) reported that a DMBR operated at 2 h HRT with a glucose-based growth medium achieved a volatile suspended solids (VSS) concentration above 20 g/L, along with a H_2 yield of 3.07 ± 0.13 mol H_2 mol hexose consumed^{-1} and a H_2 productivity of 93.6 ± 6.1 L H_2 L^{-1} d^{-1} [52]. Currently, the Environmental Processes and Materials Laboratory, led by Prof. Sang-Hyoun Kim, at the Department of Civil and Environmental Engineering at Yonsei University, is advancing the scale-up of a 500 L DMBR for H_2 production. This project aims at intensifying H_2 output by leveraging mixed microbial cultures, bioaugmentation strategies, and additives such as iron-based materials, biochar, and activated carbon. The research also explores innovative materials for the dynamic membrane module, including carbon nanotubes, to optimize microbial retention (through granulation) and process efficiency [53].

Regarding microbiology, as shown in Table 2, across studies, *Clostridium butyricum* emerged as the dominant hydrogen-producing bacterium due to its ability to metabolize glucose and other substrates such as lactate to H_2 via the butyric and acetic acid pathways [39,43,44]. Biofilm formation on dynamic membranes was significantly enhanced by bacteria such as *Prevotella* spp., *Sporolactobacillus* spp., and *Lactobacillus* spp., which contributed to biofilm integrity and extracellular polymeric substance (EPS) production, ensuring microbial retention and reactor stability [44,50]. Auxiliary species such as *Enterobacter* spp. and *Enterococcus* spp. may support fermentation processes by metabolizing secondary intermediates, while *Anaerostipes* spp., *Bifidobacterium* spp., and *Blautia* spp. have been detected as coexisting bacteria in dark fermentation systems fed with complex substrates such as food waste and lignocellulosic hydrolysates [49,50]. In advanced setups, bioaugmentation with *Clostridium pasteurianum* achieved record-breaking H_2 production (93.7 L H_2 L^{-1} d^{-1}), but required careful management to maintain its population over time [52]. In addition, species such as *Megashaera* spp., *Caproiciproducens* spp., *Ethanoligenens* spp., and *Olsenella* spp. have demonstrated adaptability in systems processing lignocellulosic biomass, algal biomass, and other challenging feedstocks [49,51]. This synergy between different microbial consortia highlights the importance of tailored microbiological strategies in optimizing DMBR performance for sustainable H_2 production.

Table 2. Latest studies on fermentative H_2 production assisted by membrane technology.

Aim of the Study	Substrate	Setup	Remarks	Microbiology	Ref.
To investigate bioH_2 production performance using an external dynamic membrane bioreactor (DMBR) with mixed cultures under mesophilic conditions	Glucose-based synthetic medium (15 g L^{-1})	Lab-scale DMBR with a working volume of 5.5 L. The reactor consists of a continuously stirred reaction zone (5 L) and an external dynamic membrane module (0.5 L) made of polyester screen mesh with a 100 µm pore size.	Peak H_2 productivity of 51.4 L H_2 L^{-1} d^{-1} and H_2 yield of 2.98 mol H_2 mol glucose^{-1} at 3 h HRT. Dynamic membrane retained active H_2-producing bacteria, primarily *Clostridium butyricum*, ensuring stable operation.	*Clostridium butyricum*, *Enterococcus*, *Enterobacter*, *Lactobacillus* spp.	Park et al. (2017) [39]
To investigate kinetic parameters for high-rate bioH_2 production and biofilm formation in a DMBR system	Glucose-based synthetic medium (15 g L^{-1})	Lab-scale DMBR with a total volume of 5.5 L, composed of a CSTR with a working volume of 5.0 L and an external DM module of 0.5 L; polyester mesh with a pore size of 100 µm; operated at HRTs from 12 to 2 h, with mechanical stirring at 150 rpm	Peak H_2 productivity of 48.9 L H_2 L^{-1} d^{-1} and a H_2 yield of 2.8 mol H_2 mol glucose^{-1} at 3 h HRT; transmembrane pressure remained below 1.7 kPa throughout, with high stability in biofilm formation and reactor operation. *Clostridium butyricum* dominated in fermentation liquor, while *Prevotella* spp. was more prevalent on the DM layer.	*Clostridium butyricum* (fermentation liquor), *Prevotella* spp. (biofilm)	Park et al. (2018) [44]
To evaluate the formation and performance of a H_2-producing DMBR under mesophilic conditions	Sucrose-based synthetic medium (10–100 g COD L^{-1})	DMBR with a total volume of 1.0 L and a working volume of 0.8 L. Dynamic membrane developed over monofilament woven polyamide/nylon meshes with openings of 52 and 21 µm submerged in the cross-flow module, with a constant cross-flow velocity of 30 m/h with variable filtration area, ranging from 16.5 to 66 cm^2.	Stable DM filtration and H_2 production achieved at low influent COD concentration (10–30 g COD L^{-1}); optimal HRT of 1 day; permeate flux around 2 L (m^2 h)$^{-1}$	—	Saleem et al. (2018) [47]
To investigate the relationship between dynamic membrane (DM) formation, metabolic flux, and microbial community population	Glucose-based synthetic medium (15 g L^{-1})	DMBR with a working volume of 5.5 L; external screen module with a 100 µm polyester mesh; CSTR, cross-flow external screen module installed for DM development on the screen mesh	60.5 L H_2 L^{-1} d^{-1} (2.39 mol H_2 mol glucose^{-1}); DM formation altered metabolic pathways favoring H_2 production over homoacetogenesis; effective biomass retention due to DM	*Clostridium* and *Sporolactobacillus*	Park et al. (2019) [45]

Table 2. *Cont.*

Aim of the Study	Substrate	Setup	Remarks	Microbiology	Ref.
To examine the effects of alginate immobilization on DM formation and H_2 production	Galactose-based synthetic medium (15 g L^{-1})	DMBR with 5 L working volume CSTR, 150 rpm stirring, and a 0.5 L DM module; 100 µm pore size polyester screen mesh with fermentation liquor recirculated at 10× feed flow rate	Peak H_2 production rate of 26.3 ± 9.7 L H_2 L^{-1} d^{-1}; enhanced biofilm formation, stable operation without washout, increased tightly bound extracellular polymeric substances content, and active DM development	*Clostridium butyricum*, *Lactobacillus*, *Sporolactobacillus*, *Prevotella*, *Enterobacter*, *Enterococcus*	Park et al. (2020) [43]
To investigate the effect of shear velocity on H_2 production and biomass retention in a DMBR system	Glucose-based synthetic medium (15 g L^{-1})	Lab-scale DMBR with 50 µm polyester mesh as a DM module, connected to a CSTR; working volume: 5 L (CSTR), 0.5 L (DM module); HRT 12–3 h; shear velocity 2.4–11.7 m h^{-1}; temperature of 35 °C	Optimal H_2 production (26.6 ± 1.5 L H_2 L^{-1} d^{-1}, 1.8 mol H_2 mol glucose^{-1}) at 6.7 m h^{-1} shear velocity; biomass retention and biofilm stability were enhanced at this shear velocity; severe washout and decreased performance at 11.7 m/h	*Clostridium butyricum*, *Sporolactobacillus*, *Enterobacter*, *Prevotella*	Sim et al. (2021) [46]
To develop a novel liquid/gas hollow-fiber membrane bioreactor (L/G MBR) that integrates in situ gas separation and bacteria retention	Glucose-based synthetic medium (19–54 g L^{-1} d^{-1})	Cylindrical-shaped hollow-fiber membrane module; ultrafiltration polytetrafluoroethylene (PTFE) hollow fibers; working volume of 0.5 L; operated with sweeping gas (N_2 or CO_2) or without sweeping gas	H_2 yield of 0.97 ± 0.09 mol H_2 mol hexose^{-1}; peak H_2 productivity of 2.6 ± 0.3 L H_2 L^{-1} d^{-1}; high resilience of H_2-producing bacteria, which allowed operation without re-seeding over extended periods	*Clostridium*, *Enterobacter*, *Ethanoligenens*, *Sporolactobacillus*	Renaudie et al. (2021) [37]
To evaluate continuous H_2 production from algal biomass using a DMBR system	Red algal biomass (*Eucheuma spinosum*), pretreated to contain 20 g L hexose^{-1}	Lab-scale DMBR with a total working volume of 2 L, consisting of a CSTR with a working volume of 1 L and two DM modules each with a volume of 1 L; DM modules with polyester mesh of 444 µm pore size	Peak H_2 production rate of 21.6 L H_2 L^{-1} d^{-1} at 3 h (1.1 mol H_2 mol hexose^{-1})	*Clostridium* sp., *Anaerostipes* sp., and *Caproiciproducens* sp.	Sim et al. (2021) [49]
To evaluate continuous H_2 production from xylose using a DMBR system	Xilose-based synthetic medium (20 g L^{-1})	Lab-scale DMBR with a 6 L working volume, including two external DM modules with 444 µm pore polyester mesh	Peak H_2 production rate of 30.3 ± 1.2 L H_2 L^{-1} d^{-1} at 3 h HRT; H_2 produced by butyric and acetic acid pathways; *Clostridium* sp. dominated	*Clostridium*, *Enterobacter*, *Lactobacillus*, *Sporolactobacillus*, *Olsenella*	Baik et al. (2022) [48]

Table 2. *Cont.*

Aim of the Study	Substrate	Setup	Remarks	Microbiology	Ref.
To investigate H_2 and CH_4 production from food waste using a two-stage DMBR system	Food waste (Korean standard food waste mixture)	Two-stage DMBR system operated at 37 °C; H_2-DMBR: 2.7 L CSTR with submerged polyester screen mesh (pore size 444 μm); CH_4-DMBR: 10.5 L CSTR with 0.5 L DM module, using the same mesh material	Peak H_2 production rate of 7.1 ± 0.4 L H_2 L^{-1} d^{-1} at 8 h HRT; methane production rate of 0.99 ± 0.02 L CH_4 L^{-1} d^{-1} at 6 d HRT; high microorganism retention facilitated stable H_2 and CH_4 production	*Clsotridium*, *Bifidobacterium*, *Blautia*, *Enterococcus*, *Lactococcus*, *Prevotella*	Jung et al. (2022) [50]
To achieve high-rate H_2 production from lignocellulosic biomass and investigate scalability in a DMBR	Rice straw hydrolysate that is pretreated (0.5% H_2SO_4 at 150 °C for 60 min.), followed by detoxification using powdered activated carbon and calcium hydroxide. The hydrolysate contained glucose (4.1–6.7 g L^{-1}), xylose (10.1 g L^{-1}), and arabinose (1.3–1.7 g L^{-1}).	Contains 3 L and 20 L DMBRs; the DM module used polyester mesh with pore sizes of 220 and 444 μm, and specific filtration area of 7.3 m^2 $(m^3)^{-1}$ for 20 L DMBR.	Peak H_2 production rate of 32.1 ± 0.7 L H_2 L^{-1} d^{-1} and 1.27 ± 0.03 mol H_2 mol hexose equiv. consumed^{-1}; while the 20 L DMBR reached 33.15 ± 0.42 L H_2 L^{-1} d^{-1} and 1.46 ± 0.03 mol H_2 mol hexose equiv. consumed^{-1}.	*Clostridium*, *Megashaera*, *Lactobacillus*, *Olsenella*	Kim et al. (2024) [51]
To investigate high-yield continuous H_2 production through bioaugmentation with *Clostridium pasteurianum* in a DMBR system	Glucose-based synthetic medium (20 g L^{-1})	Laboratory-scale DMBR with a CSTR and a side-stream DM; total working volume: 4.5 L, with DM made of polyester mesh (220 μm pore size)	H_2 yield of 3.1 ± 0.1 mol H_2 mol hexose consumed^{-1} at 2 h HRT; bioaugmentation boosted H_2 production (93.7 ± 6.1 L H_2 L^{-1} $d^{-1)}$; however, as operation continued, the population of *C. pasteurianum* decreased.	*Clostridium pasterurianum*, *Selenomonas bovis*, *Streptococcus equinus*, *Megashaera elsdenii*	Sim et al. (2024) [52]

2.5. Challenges in Dark Fermentation and Opportunities for Enhancing bioH_2 Production

The field of dark fermentation for bioH_2 production faces several critical barriers that limit H_2 yields, production rates, and overall process stability. A major challenge arises from competing microbial groups, such as homoacetogenic bacteria, methanogenic archaea, sulfate-reducing bacteria, propioniogenic bacteria, and lactic acid bacteria [54]. At this point, it should be noted that lactic acid bacteria play a dual role in the dark fermentation process, where their impact on H_2 production depends heavily on process conditions [24,55]. On one hand, lactic acid bacteria can inhibit H_2 production by consuming substrates that would otherwise be used by H_2-producing bacteria, acidifying the fermentation broth due to production of lactic acid, and by excreting bacteriocins. On the other hand, they can significantly enhance process efficiency through various supportive functions. Particularly, lactic acid bacteria contribute to pH regulation, substrate hydrolysis, and oxygen depletion, all of which create a more favorable environment for H_2 producers [24]. Additionally, lactic acid bacteria assist in microbial contamination control and substrate detoxification, allowing H_2-producing bacteria to thrive. By improving biomass retention and facilitating substrate breakdown, lactic bacteria can also help in the optimization of H_2 outcome and overall process stability, underscoring their complex and context-dependent role in dark fermentation [24,56,57].

In addition to microbial competition, operational and environmental conditions can pose significant obstacles to effective dark fermentation. Poor mass transfer conditions can impede the efficient delivery of essential nutrients and the removal of metabolic waste products, which are crucial for optimal microbial performance. Furthermore, maintaining stable operational parameters, such as temperature, pH, and HRT, is essential. However, suboptimal conditions often lead to process instability, fluctuating H_2 yields, and reduced system efficiency. Substrate characteristics also play a key role in the process, as low-biodegradability substrates or those containing inhibitory compounds can significantly hinder microbial activity, resulting in incomplete substrate conversion and, consequently, lower H_2 output. In this context, the production of H_2 from organic waste hinges significantly on selecting suitable feedstocks that promote microbial fermentation while avoiding those that inhibit it. Certain organic wastes, such as cheese whey [25,58–60], vinasse [25,61–63], winery and cassava wastewater [64–66], brewery wastewater [67], lignocellulosic biomass [51,68–71], agro-industrial waste [19,72,73], food waste [11,32,35,50,56,57,74], and the organic fraction of municipal solid waste (OFMSW) [16,75,76], are ideal feedstocks due to their high biodegradability, rich carbohydrate content, and nutrient availability, all of which support the growth of H_2-producing bacteria. These substrates provide the necessary organic matter that facilitates efficient fermentation, making them prime candidates for bioH_2 production. In contrast, various industrial and municipal wastewaters, such as municipal, slaughterhouse, and piggery wastewater, alongside petrochemical, pharmaceutical, pulp and paper, textile wastewater, and landfill leachates, are generally unsuitable for fermentative H_2 production. These feedstocks often contain high levels of inhibitors like heavy metals, complex organic pollutants, and toxic chemicals that impede microbial processes, coupled with low carbohydrate content that fails to sustain H_2-producing bacteria. Additionally, high bacterial loads, acidic conditions, and poor biodegradability further reduce their viability in dark fermentation processes, requiring costly and complex pretreatments to become effective.

By overcoming the above-discussed barriers, the dark fermentation process can be optimized to achieve higher H_2 yields, more consistent production rates, and enhanced stability. However, addressing these bottlenecks still requires a multi-faceted approach, integrating advanced microbial management techniques, precise control over operational parameters, enhancement of substrate quality, and improvements in mass transfer sys-

tems. In this regard, the pretreatment of biocatalysts plays a vital role by enriching the population of H_2-producing bacteria while inhibiting H_2-consuming organisms, ensuring a favorable balance within the microbial community [77]. This approach is complemented by biokinetic control, where conditions such as low pH and shortened HRTs effectively washout methanogens, i.e., microbes that otherwise would consume H_2 [78]. The technique of bioaugmentation further strengthens the process, introducing specialized bacteria that optimize fermentation efficiency and boost H_2 yields [52,79,80]. Equally important is the pretreatment of biomass; by enhancing the biodegradability of substrate, this step makes it more accessible for microbial metabolization, which in turn increases the H_2 output. Co-fermentation, involving the mixing of multiple substrates, is another promising approach, as it improves nutrient composition, enhances buffering capacity, dilutes potential inhibitors, and even supports simultaneous fermentation processes, all of which are conducive to higher H_2 production [25,81,82]. On the other hand, additive supplementation has emerged as a promising approach to enhance fermentative H_2 production. Various materials, such as biochar, magnetite, and iron nanoparticles, are increasingly being explored for their unique properties that can improve microbial activity and electron transfer within the fermentation process [58,69,83]. Another improvement strategy involves fine-tuning operational parameters, such as HRT, pH, and OLR, on a case-by-case basis to unlock the maximum potential of the dark fermentation process. As mentioned above, leveraging lactate-driven dark fermentation, which utilizes lactic acid bacteria to produce H_2 from lactate, adds another dimension of flexibility to the process. Reactor design innovations are particularly transformative, with novel configurations aimed at increasing biomass density (e.g., DMBR) and enhancing the transfer of H_2 from liquid to gas phase, maximizing process efficiency. Finally, continuous end-product removal, such as through membrane-based technology, prevents the accumulation of inhibitory acids, sustaining the fermentation process over longer periods and avoiding productivity bottlenecks [84,85]. However, the number of studies on membrane-assisted dark fermentation remains limited. Further research is needed to optimize designs and validate their performance through practical applications and large-scale implementations. Together, these strategies form a comprehensive and layered approach to advancing fermentative H_2 production, representing significant steps toward scalable, efficient, and sustainable bioH_2 production for future energy needs.

3. Membrane-Assisted Dark Fermentation Process for bioH_2 Recovery

3.1. Membranes as the Latent Alternative for Process Intensification in the Downstream bioH_2 Recovery

One of the most challenging tasks in bioH_2 production comprises its downstream recovery. Due to the low kinetic diameter (ca. 2.9 Å) of H_2 [86], the separation of this gas molecule from other gas molecules (including CH_4, CO_2, N_2) requires highly selective separation techniques. To date, the purification of H_2 has been attempted via pressure swing adsorption [87], fractional/cryogenic distillation [88], membrane gas separation (GS) [89,90], and their possible coupling. Pressure swing adsorption and fractional/cryogenic distillation technologies are used in commercial applications, but they are not commonly cost-effective since they entail a high energy consumption for the separation and purification of H_2. Moreover, none of these processes result in enough purity for the targeted applications in the H_2 economy. In contrast, GS technology is a promising methodology in the field due to its multiple advantages, such as (i) low energy consumption, (ii) high selectivity and efficiency, (iii) the possibility for continuous and long-term operation (depending on the type of membrane and acidogenic off-gas composition), (iv) lower investment cost compared to the other two processes, (v) ease of operation, and (vi) ultimately cost-effectiveness [91–93]. GS is identified for its ability in separating gas mixtures (organic and inorganic gasses) via

molecular sieving of diverse molecules [94,95]. Nowadays, GS finds its main industrial applications in the separation of non-condensable gasses, including N_2 from air; CO_2 from CH_4 [92,96]; and H_2 from N_2, argon, CO_2, or CH_4 [97,98].

When dealing with H_2 separation using pristine polymeric membranes, several polymer materials can be used including sulfonated polyimide, polyimides (e.g., 6FDA-nMPD, 6FDA-DDBT), Hyflon® AD60, Teflon AF-2400, poly(trimethylsilylpropyne) (PTMSP), polydimethylsiloxane (PDMS) [99–101], etc. (Table 3). Among these materials, some polymers tend to provide a high H_2 permeability but low separation efficiency (in terms of selectivity) towards specific gas molecule separation (e.g., H_2/CH_4, H_2/N_2, H_2/CO_2), and vice versa, high selective polymers do not display high permeable properties [102]. Unfortunately, such features have established a limited trade-off relationship (Robeson trade-off), as shown in Figure 4a.

Table 3. Documented H_2 separation performance of several polymeric membranes.

Polymer Type	H_2 Permeability (Barrer)	Selectivity (α)	Ref.
Sulfonated polyimide	52	α (H_2/CH_4) = 325	Tanaka et al. (2006) [103]
Polyimide (6FDA-mMPD)	106	α (H_2/CH_4) = 121	Tanaka et al. (1992) [104]
Polyimide (6FDA-DDBT)	156	α (H_2/CH_4) = 78	Hachisuka et al. (1995) [105]
PTMSP	23,200	α (H_2/CH_4) = 0.99	Nagai et al. (1995) [106]
PTMSP	23,200	α (H_2/N_2) = 2.5	Nagai et al. (1995) [106]
PIM-1	1300	α (H_2/N_2) = 14.1	Budd et al. (2005) [107]
PIM-7	860	α (H_2/N_2) = 20.5	Budd et al. (2005) [107]
PTMSP	13,900	α (H_2/CO_2) = 0.49	Nagai et al. (1994) [108]
PTMSP	23,300	α (H_2/CO_2) = 0.53	Nagai et al. (1995) [106]
Polyaniline	1.7	α (H_2/CO_2) = 23.1	Illing et al. (2005) [109]
Polyimide(1,1-6FDA-DIA)	31.4	α (H_2/CO_2) = 8.0	Rezac and Schöberl (1999) [110]

GS applications require the development of new membranes and membrane processes [97]. To date, it is likely that polymer-based membranes have been consolidated in the field [101,111], and they can be initially used for downstream H_2 recovery. The separation performance of such membranes depends on several factors, such as membrane properties (e.g., free volume), membrane preparation procedure, operating parameters (e.g., thickness, pressure, temperature), and feed gas composition, among others [112–114]. However, today, there are different concepts of membranes, such as inorganic membranes, mixed matrix membranes (MMMs), or composite, ultrathin membranes, which may provide enhanced separation properties. Importantly, most of these membrane designs have already surpassed the Robeson upper bound up to the desired region (see Figure 4b). The following sections address the most promising membrane concepts and types that can assist the bioH_2 purification and recovery, providing their main advantages, drawbacks, and performances.

3.2. Inorganic Membranes

Differently from polymer membranes, inorganic membranes possess multiple advantages, such as defined molecular sieving, long-term durability, high thermal stability (over 200 °C), and chemical stability in a wide range of pH and structural integrity [115,116]. While the main drawbacks of these membranes involve their brittleness, high cost, and the fact that some of them (e.g., based on metal–organic-frameworks) possess low hydrothermal stability [117]. To date, several inorganic membranes, based on silicas, metals, zeolites, metal–organic frameworks, carbon, and graphene oxide, have been introduced as selective interfaces for H_2 separation [90,115,118]. Several commercial dense metal-based membranes, such as vanadium (V), niobium (Nb), and tantalum (Ta), reveal the highest H_2

permeability. However, unlike palladium (Pd)-based membranes, most of these membranes entail the formation of an oxide layer under ambient conditions representing a latent limitation for their application [119]. Pd-based membranes relatively offer high permeation rates (permeabilities between 1 and 1.4 Nm^3 μm m^{-2} h^{-1} $Pa^{-0.5}$) together with good mechanical properties and high H_2 purity [120]. It has been documented that the Pd alloying with other elements (such as Ag, Y and Cu) may tremendously enhance the membrane H_2 permeability and mechanical stability [119]. On the other hand, molecular sieve silica membranes are relatively more recent than Pd membranes, but such ceramic membranes present better mechanical stabilities. Unfortunately, silica membranes display lower selectivity values (e.g., 9–1500 with H_2 permeance between 0.89 and 200 × 10^{-8} mol m^{-2} s^{-1} Pa^{-1}) than Pd ones [108]. In a recent developmental work, Weber et al. (2020) strategically designed a H_2-selective Pd–alumina (Pd/Al_2O_3) tubular composite membrane via the atomic layer deposition (ALD) technique, as shown in Figure 5 [121]. Such membranes showed an exceptional H_2 permeation in the order of 1000 GPU with remarkable H_2 selectivity, e.g., permselectivity values of 23 and 13 for H_2/N_2 and H_2/CO_2 binary separation (at 188 °C), respectively. By understanding the permeation mechanism of the membrane material, it is possible to design outperforming membranes towards H_2 separation considering its very small kinetic diameter. Weber et al. (2020) stated that the high permeation yield can be ascribed to the active contribution of Pd species, which display a strong affinity with H_2 and might concurrently generate PdHx species favoring H_2 permeation. H_2 transport through the composite Pd/Al_2O_3 membrane is eventually a result of complex transport contribution over the present meso/micropores along with the chemical diffusion of (atomic) H_2 across the Pd network [121].

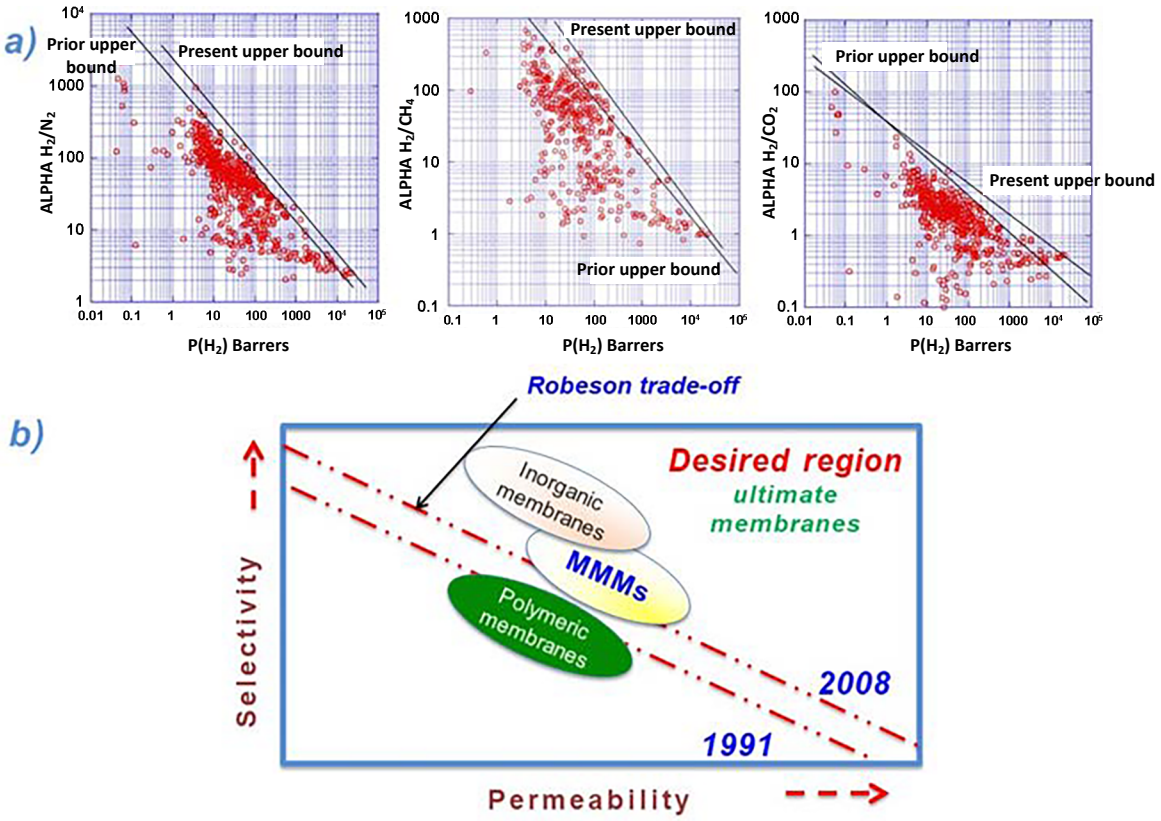


Figure 4. (**a**) Robeson trade-off relationship of several pristine polymeric membranes tested for several H_2 separations [101]. (**b**) Graphical depiction of the current status of several types of membranes (polymeric, inorganic, and mixed matrix membranes) and the desired region for high-performing membranes. Copyright 2008, with permission from Elsevier.

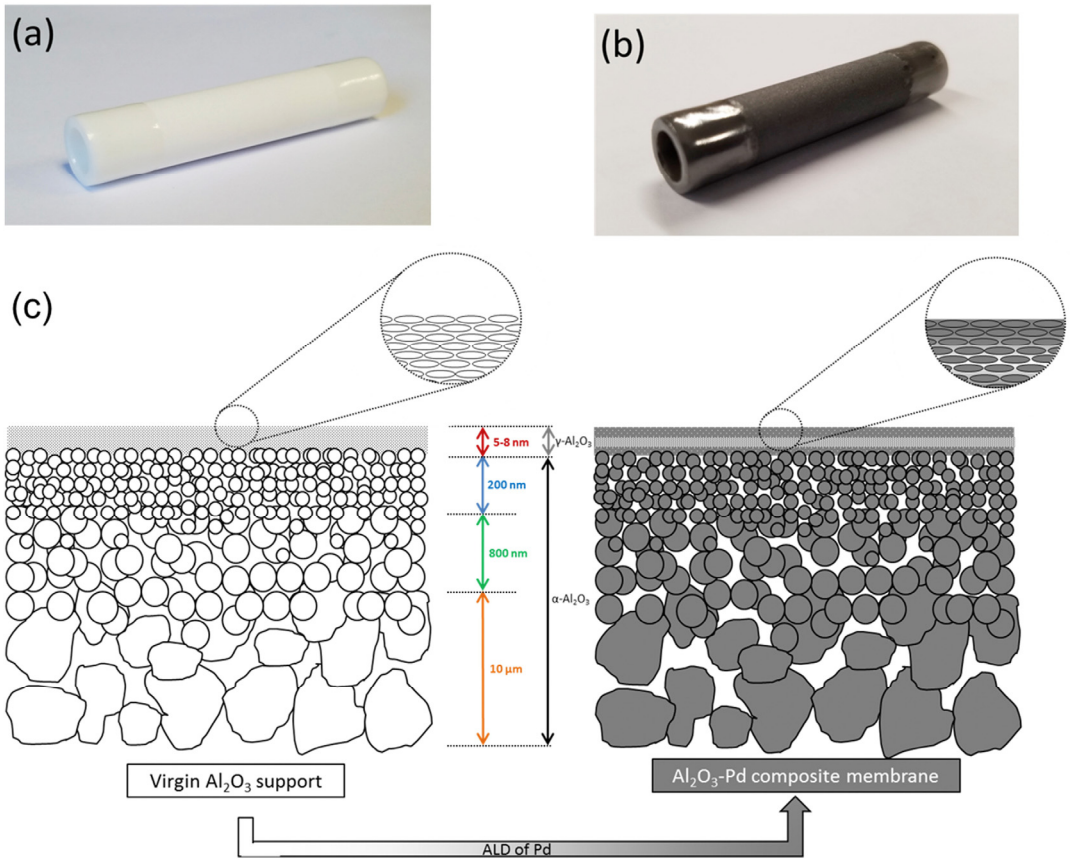


Figure 5. Images and graphical depiction of H_2-selective palladium–alumina (Pd/Al_2O_3) composite membranes. Adapted from Weber et al. (2020) [121]. (**a**) bare alumina membranes, (**b**) Pd-coated alumina membranes fabricated via atomic layer deposition, (**c**) a schematic representation of the pristine asymmetric membrane support, highlighting a magnified view of the γ-Al_2O_3 inner top layer, alongside the Pd/Al_2O_3 composite membrane, illustrating the gradual infiltration of Pd within the γ-Al_2O_3 inner top layer. Copyright 2020, with permission from Elsevier.

3.3. Mixed Matrix Membranes (MMMs)

The concept of MMMs is defined as the combination of polymeric and inorganic materials aiming for the synergistic improvement in polymer membrane properties. Even if polymer membranes have interesting advantages (including low cost, large-scale fabrication, and good quality control), their disadvantages (e.g., weakness, low stability, tendency to denature, and short lifetime), together with their limited separation performance, has led the blending of inorganic materials into polymer membranes. In this regard, specific and highly molecular sieve nanoparticles are preferred to be incorporated into polymer membranes. For instance, two-dimensional zeolitic imidazolate framework-L (ZIF-L) embedded into highly gas-permeable hydroxyl group-containing polyimide has shown an exceptionally effective H_2 separation [122]. Smartly, ZIF-L nanomaterials in the polymer matrix increased CO_2 adsorption concurrently with the restriction of CO_2 transport through MMMs, resulting in a meaningful rise in H_2 selectivity over CO_2. The MMMs (containing 20 wt.%) demonstrated a H_2 permeability of 260 Barrers and ideal H_2/CO_2 selectivity of 13.4 at room temperature. It is important to point out that such membranes displayed a varied performance depending on the ZIF loading (see Figure 6) [122]. In other words, the desired performance of such membranes can be selected according to the need in terms of purity and productivity. The authors highlighted the great potential of these membranes for large-scale fabrication in H_2 separation applications.

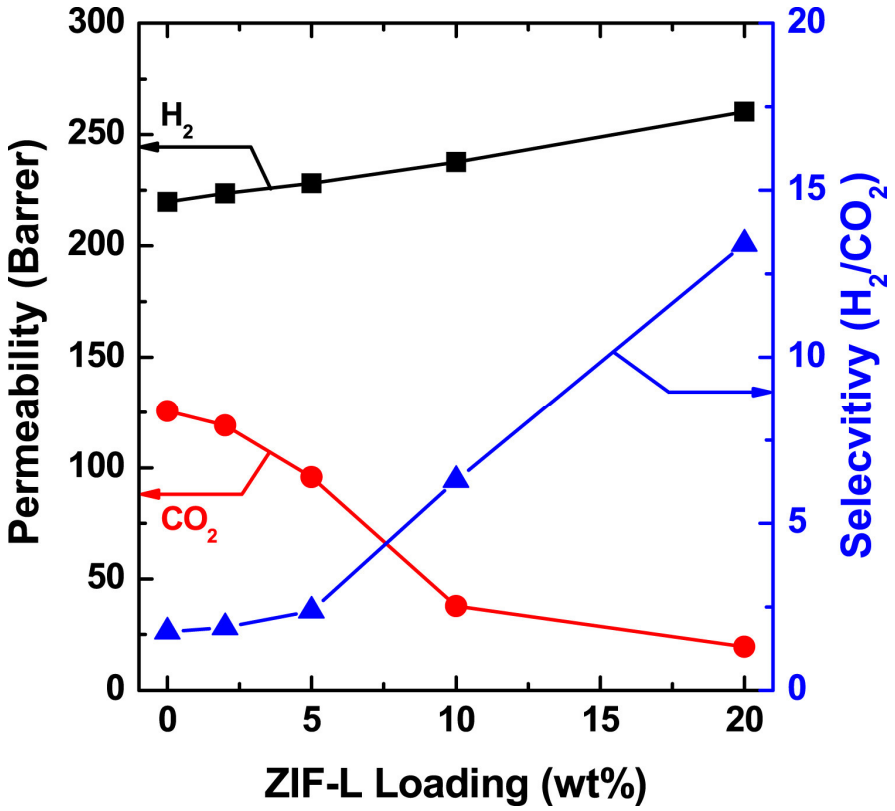


Figure 6. H_2 and CO_2 permeability and selectivity towards H_2/CO_2 of ZIF-L/polyimide MMMs as a function of ZIF-L loading. Taken from Kim et al. (2018) [122]. Copyright 2018, with permission from Elsevier.

ZIF-8 is another MOF material usually sought for improving the intrinsic properties of polymer membranes aimed at molecular gas separations. The interest of this material relies on its excellent hydrothermal stability along with notable resistance in acid and alkali environments [117]. Unfortunately, the lack of interaction between ZIF-8 and polymer phases does not guarantee an exceptional gas separation performance due to the presence of defects and unselective voids. In a timely work, Chen et al. (2020) intentionally improved poly(vinylamine)-ZIF-8 compatibility by modifying the ZIF-8 with tannic acid (which presents a large number of hydroxyl groups) [123]. The physical and chemical interactions at the polymer–filler interface were greatly enhanced as a result of chemical crosslinking among quinone functional groups of oxidized tannic acid and the amino functional groups in poly(vinylamine) via Michael addition mechanism. Interestingly, the obtained membranes (presenting 0.5 g of tannic acid) offered a CO_2/H_2 selectivity of ca. 31 (at a gas pressure of 0.12 MPa), in which CO_2 was the most permeable while hindering H_2 diffusion due to competitive adsorption.

3.4. Thin and Ultrathin Membranes

Thin and ultrathin membranes are recognized to break the trade-off between permeance and selectivity to facilitate ultimate separation [124,125]. In addition to this, several advantages have been denoted, such as a low quantity of selective membrane material (due to the low thickness of selective layers below ca. 1 μm), defect-free structure, and less membrane area needed for a given separation. These ultimate membranes can be either made of inorganic, polymer, or composite materials. For example, ultrathin MOF membranes (sub-10 nm-thick), based on $Zn_2(Bim)_3$ nanosheets, were evaluated for their ability in separating H_2/CO_2 [126]. Interestingly, they showed a separation factor of 166 with H_2 permeance of up to $8{\cdot}10^{-7}$ mol m^{-2} s^{-1} Pa^{-1} at elevated testing temperatures (200 °C) attributed

to the size-exclusion effect. Basically, H_2 molecules (ca. 0.289 nm) can tightly permeate through the apertures (ca. 0.29 nm) of the $Zn_2(Bim)_3$ material, while CO_2 molecules (ca. 0.33 nm) hardly pass. Similarly, high-H_2-performing ZIF-8/ZnO/α-Al_2O_3 nanocomposite membranes were identified as H_2-selective (permeance up to $1.6{\cdot}10^{-8}$ mol$\cdot$ $m^{-2}{\cdot}s^{-1}{\cdot}Pa^{-1}$) in equimolar H_2/CO_2 and H_2/CH_4 gas mixtures having selectivities of 7.8 and 12.5, respectively. Tran et al. (2011) prepared titania (TiO_2) on a γ-Al_2O_3 porous support by coupling with sol–gel methods [127]. The membranes (with a thin TiO_2 layer with thickness around 10 nm) had a H_2 permeance of $12.5{\cdot}10^{-8}$ mol$\cdot m^{-2}$ $s^{-1}{\cdot}Pa^{-1}$ and a H_2/CO_2 separation factor of 5.8. Herein, we can notice that thinner membranes provide higher H_2 permeation rates. More recently, thin ZIF-8 layers (a thickness of about 17 nm) coated on a PVDF hollow fiber support offered high permeable properties for H_2 (up to $215{\cdot}10^{-7}$ mol m^{-2} s^{-1} Pa^{-1}) and H_2 preference in specific separations (e.g., H_2/C_3H_8 = 3400) [128]. These membranes exhibit an impressive separation performance and are able to overcome the Robeson limit for polymeric membranes.

Interesting research, boosting the H_2 separation of the thin-film composite membrane, has been pioneered by blending PVA and PEBAX polymer phases [129]. Thanks to the incorporation of 60 wt.% PEBAX, the resulting membrane apparently revealed an enhancement on both permeability and selectivity, which turn into a surpassed Robeson trade-off. As shown in Figure 7, a better H_2 selectivity (ca. 7) was observed when the PEBAX concentration was higher than 60 wt.% [121]. It is known that the transport of non-condensable gasses (like H_2 and CO_2) is strictly dictated by their diffusion since they do not display any chemical interaction with polymer materials. However, an important point to highlight deals with the membrane crystallinity, e.g., pristine PVA thin membranes presented the highest crystallinity translated to constricted diffusion in rigid polymer networks (Figure 7), but crystallinity was drastically disrupted in the presence of PEBAX into membranes, which allowed a fast permeation of gas molecules. In other words, flexible chains fostered the gas transport due to low resistance, but usually compromising the selective properties.

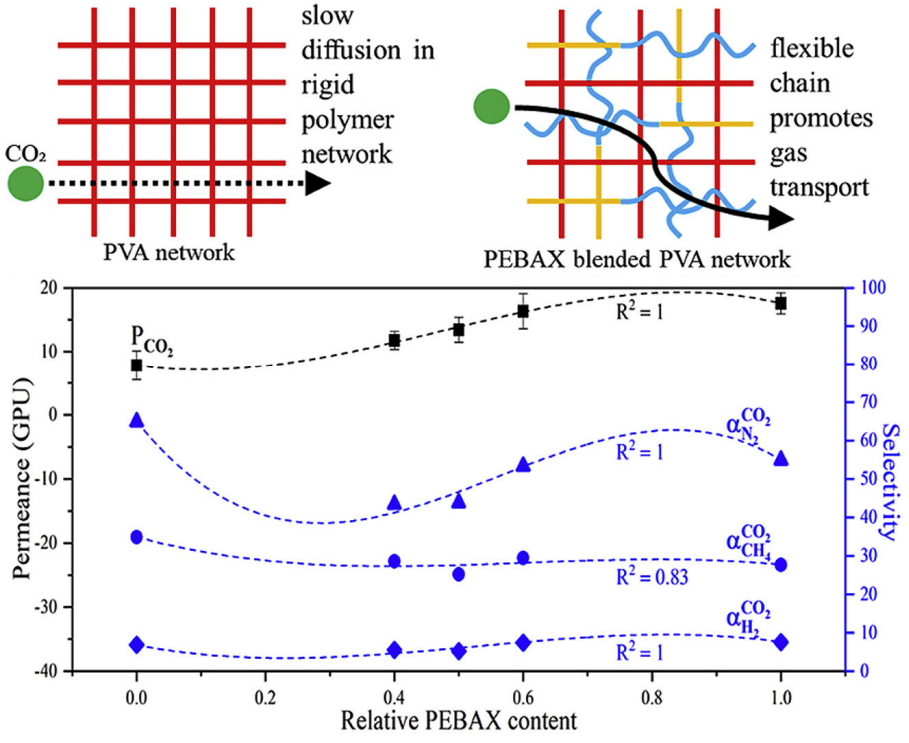


Figure 7. The gas separation performance of the composite membrane as a function of the PEBAX content and the influence of polymeric network motion on the gas transport. Adapted from Wong et al. (2021) [129]. Copyright 2021, with permission from Elsevier.

3.5. Challenges in Membrane-Based bioH_2 Purification and Perspectives

To some extent, membrane gas separation technology meets the basic requirements (permselectivity and permeability) to be considered within process intensification strategies toward the separation and purification of bioH_2 [130]. Obviously, the membrane type, as the key element for the ultimate separation of H_2 from other gas molecules in gas separation, dictates the separation efficiency according to its intrinsic properties and transport mechanism [131,132]. This review has reviewed the different membrane types proposed for such a separation. Importantly, operating parameters (pressure, feed flow, membrane module, etc.) play also an important role during the recovery of this gas molecule. Membrane gas separation needs to be implemented within the downstream processing in an integrated design proposed by Nemestóthy et al. (2020) as depicted in Figure 8 [133]. In a first approximation, Bakonyi et al. (2017) implemented PDMS membranes for separating H_2 and CO_2 fractions from the headspace of the reactor, in which the CO_2-rich gas stream was recycled to the bottom of the bioreactor for liquid phase sparging, proving greater H_2 production (ranging from 8.9 to 9.2 L H_2 L^{-1} d^{-1}) compared to non-assisted continuous stirred tank reactor (between 6.96 and 7.35 L H_2 L^{-1} d^{-1}) under steady-state conditions [134]. This latter approach demonstrates the feasibility of membranes for gas fractions recovery from a bioreactor to improve H_2 production. Unfortunately, further investigation for understanding the mass transfer mechanism on the gas–liquid interface and the physical absorption/desorption of the gasses is needed [134]. The membrane type depends on the H_2 purity requirements, but interestingly, polymer membranes offer high H_2 selectivity, while ultrathin membranes provide high H_2 permeabilities, but the suitable combination of both types of membranes may facilitate a synergistic effect like ZIF-8/PVDF membranes.

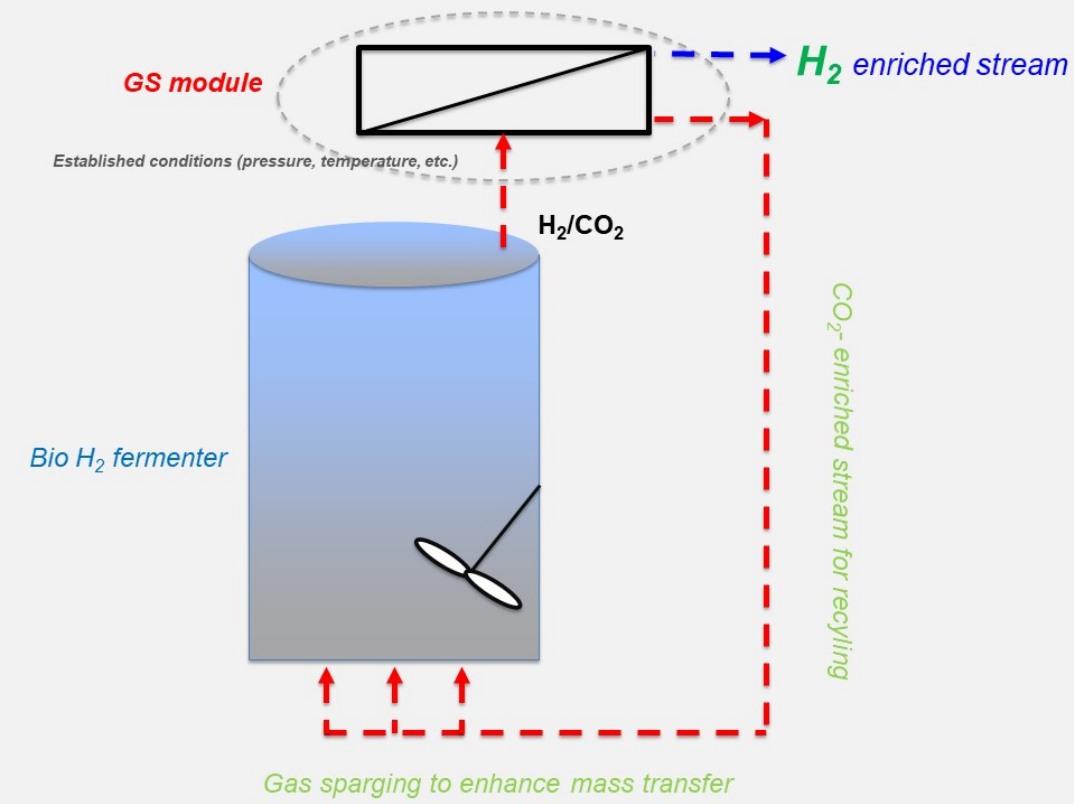


Figure 8. Integrated membrane system for bioH_2 production proposed by Nemestóthy et al. (2020) [133].

So far, regardless of the membrane tested for H_2 separation from H_2-containing mixtures or fermentative systems, most of the research has been conducted testing the membranes in gas binary systems (e.g., H_2/CO_2, H_2/CH_4, H_2/N_2). However, an important aspect that should be considered in further research in the field of bioH_2 production deals with the feed composition. Typically, the feed composition of the inlet gas mixtures consists mainly of H_2 and CO_2, but it also may contain traces of CH_4, water vapor, and hydrogen sulfide, among other volatile organic compounds [135,136]. The feed composition becomes relevant in membrane gas separation since there is competitive absorption at the membrane interface. In other words, the presence of one gas component directly influences the transport of others contained in feed mixtures [92,137]. Therefore, aiming for a better approach in the separation performance of a membrane, researchers should initiate the membrane testing with real gas mixtures, or gas model mixtures, containing most of the components derived from a fermentative process. For instance, the presence of water is a critical factor in membrane separation since a drop in permeance for several gasses has been observed because of the competitive sorption and transport in hydrophobic membranes [138]. Differently, CO_2 permeance can be increased in the presence of water vapor, a phenomenon that has been documented by several studies testing composite HKUST-1-IL-CS/PSf [138] and zeolite A-PTMSP/P84 MMCHF [139] membranes. Among all membrane types, it is likely that Pd-based membranes are at a more advanced stage of development. Pd membranes are able to operate through a sorption–diffusion mechanism, and regardless of their high selective affinity to H_2, they are highly prone to chemical contamination by carbon monoxide (CO), water steam, and sulfur-based compounds [123]. In addition to this, Pd is relatively expensive and not an available metal, limiting its usage in industrial applications.

4. Conclusions

This review provided an in-depth analysis of membrane-assisted dark fermentation for integrated bioH_2 production and purification. Key topics covered include the need for and current advancements in dark fermentation for bioH_2 production, influential factors affecting fermentation efficiency, challenges in the field, and the role of membrane technology in enhancing bioH_2 production and recovery. Additionally, this review examined various types of membranes, such as inorganic membranes, MMMs, and thin and ultrathin membranes, assessing their performance for H_2 separation from other gas molecules (mostly CO_2). The following conclusions are drawn from the analysis of the current advancements in the intensification of membrane-based dark fermentation processes.

1. Dark fermentation represents a promising biological route for sustainable bioH_2 production using organic waste as feedstock, addressing waste management challenges while contributing to renewable energy and decarbonization goals.
2. Membrane-integrated bioreactors significantly enhance dark fermentation processes by enabling continuous gas separation, which reduces product inhibition, stabilizes microbial activity, and increases microbial density, which ultimately boosts H_2 production efficiency. This integration allows for more efficient and steady-state operations, making the production process both scalable and resilient.
3. Membrane-based purification methods, particularly using inorganic and composite membranes, show significant promise due to their high selectivity and permeability, making them ideal for H_2/CO_2 separation. Advanced membrane materials, such as Pd-based and MMMs, provide durable and selective options that address the limitations of traditional methods, offering energy-efficient solutions compatible with the stringent purity requirements for H_2 as a fuel.

4. The development of thin and ultrathin membranes has enabled the enhancement of both permeance and selectivity, breaking traditional trade-offs and positioning membrane technology as a leading choice for bioH_2 purification.
5. Innovative membrane-based dark fermentation systems highlight the transformative potential of process intensification in bioH_2 production. By integrating production and purification into a single system, these technologies enhance process efficiency, reduce product inhibition, and ensure stable, high-purity H_2 output.

In conclusion, membrane-assisted dark fermentation systems hold great promise for improving bioH_2 production and purification, but significant advances are needed to achieve practical implementation. Key areas for development include optimizing system performance, addressing membrane fouling and durability issues, and incorporating innovative materials and designs. Crucially, the design and evaluation of pilot-scale systems is essential to move from laboratory-scale studies to industrial applications, enabling scalable and cost-effective solutions for sustainable energy production.

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