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탄소중립형 바이오수소 생산 및 분리막기반 정제 기술 소개

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Biohydrogen Generation and Purification Technologies for Carbon Net Zero

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요 약: 본 총설은 탄소중립 및 에너지순환을 실현하기 위한 재생에너지로부터 그린수소 생산 전략 중 하나인 바이오수소 생산 및 정제법에 관해 소개하고자 한다. 바이오수소는 생물질과 미생물과 같은 재생에너지원을 이용하며, 상온 및 상압 등의 마일드한 실험조건에서 작동하여 에너지소비 및 공정비용이 적게 드는 친환경 공정으로 알려져 있다. 하지만, 이러한 바이오수소를 상업적으로 이용하기 위해서는 해결해야 할 중요한 도전적인 과제가 존재한다. 특히, 바이오수소는 생물반응기내의 복합한 화학반응으로 합성되어, 낮은 수소생산 속도 및 반응기내 다양한 혼합물이 존재하여, 바이오수소 고순도화를 위해서 연속공정 형태의 분리 및 정제 기술이 반드시 필요하다. 이를 위해, 저온 증류법, 압력 흡착법, 분리막법 등을 비롯한 다양한 분리 및 정제 기술이 고순도 바이오수소를 얻기 위해 제안되었다. 본 총설에서는 바이오수소 생산 및 정제 연계화를 위한 비다공성 고분자 분리막의 가능성에 대해 소개하고자 한다.

Abstract: H_2 generation from renewable sources is crucial for ensuring sustainable production of energy. One approach to achieve this goal is biohydrogen production by utilizing renewable resources such as biomass and microorganisms. In contrast to commercial methods, biohydrogen production needs ambient temperature and pressure, thereby requiring less energy and cost. Biohydrogen production can reduce greenhouse gas emissions, particularly the emission of carbon dioxide (CO_2). However, it is also associated with significant challenges, including low hydrogen yields, hydrodynamic issues in bioreactors, and the need for H_2 separation and purification methods to obtain high-purity H_2. Various technologies have been developed for hydrogen separation and purification, including cryogenic distillation, pressure-swing adsorption, absorption, and membrane technology. This review addresses important experimental developments in dense polymeric membranes for biohydrogen purification.

Keywords: *biohydrogen, biohydrogen generation, biohydrogen purification, membrane*

1. Introduction

Hydrogen (H_2) has the highest energy content per unit weight (142 kJ/g), surpassing that of biofuels such as methane, methanol, and ethanol[1]. H_2 is also used for direct combustion in internal combustion engines and fuel cells. H_2 combustion is environmentally friendly as it produces only water. However, carbon-based non-renewable sources such as natural gas, coal, and heavy oil that are used for H_2 production are unsustainable and emit greenhouse gases[2]. Hence, the generation of H_2 from renewable sources such as biohydrogen is attracting increasing interest as a sustainable energy carrier.

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Biohydrogen production needs renewable resources such as biomass and microorganisms to generate H_2. Unlike conventional commercial methods, biohydrogen production needs ambient temperature and pressure, resulting in reduced energy and cost[3,4-6]. The use of these technologies can reduce the generation and release of greenhouse gases such as CO_2 in the environment. However, their commercial and pilot-scale production has not yet been achieved, because scaling up of these technologies poses significant challenges such as low hydrogen yields, unresolved hydrodynamic issues in bioreactors, and the optimization of operating conditions that require further research and development[7]. To overcome these challenges, many laboratories and pilot-scale studies are being conducted to develop the most suitable approach for generating biohydrogen[7].

Generally, H_2 production from biohydrogen occurs via three mechanisms: light-dependent biophotolysis, light-dependent photofermentation, and light-independent dark fermentation[5]. Biophotolysis involves the utilization of sunlight and carbon sources to generate H_2. Photofermentation uses photosynthetic bacteria with organic substrates and light as energy sources. Dark fermentation utilizes carbohydrates such as glucose to produce H_2 along with fermentation byproducts[8].

Unstable and insufficient H_2 production explains why biohydrogen fuel cell systems have not yet been commercialized[9]. For example, proton exchange membrane fuel cells (PEMFCs) require high hydrogen purity of up to 99.99%. Biohydrogen production typically yields mixed biogas containing H_2, CO_2, and possibly small amounts of CO, CH_4, and H_2S. The presence of CO and H_2S is detrimental to the fuel cell stack and reduces PEMFC performance[9]. Hence, it is essential to investigate H_2 separation and purification systems to produce high-purity H_2, with a particular focus on the removal of H_2S and CO_2.

Many hydrogen separation and purification technologies have been developed so far, including cryogenic distillation, pressure swing adsorption (PSA), absorption, and membrane technologies[10-12]. Cryogenic separation cools the mixture to remove unwanted gases and obtain purified H_2; however, it is impractical for small portable hydrogen plants because of limitations in purification and compression. PSA could also be considered for large-scale biohydrogen production in the future. Membrane separation, specifically by using nonporous polymeric membranes, is promising for biohydrogen production[13]. However, scaling up these membranes for large-scale use for H_2 separation and purification requires careful consideration of various factors such as selectivity, durability, and operating conditions. Therefore, further research and development is necessary to advance membrane technology for effective H_2 separation and purification in biohydrogen production.

This review aims to broadly describe general biohydrogen production and purification technologies. It specifically focuses on various polymer membrane gas technologies for H_2 separation and purification.

2. Biohydrogen-generation Methods

Biohydrogen-production technologies can be divided into two categories: light-dependent and light-dependent[7]. Dark fermentation is a light-independent process, whereas biophotolysis and light fermentation are light-dependent. Biophotolysis, which occurs in cyanobacteria and microalgae, involves splitting of water using solar energy and CO_2 as the carbon source. Light fermentation involves the degradation of organic compounds by photosynthetic bacteria in the presence of light[14,15].

Biophotolysis is a simple biohydrogen-production process(Table 1). It uses solar energy and CO_2 to convert water and substrates into oxygen and hydrogen [2]. However, biophotolysis affords relatively low H_2 yields owing to limited light absorption and conversion efficiency in darkness[16,17]. Light fermentation utilizes biomass feedstock such as organic waste and is used as an alternative method for waste treatment and generating renewable energy[18]. Dark fermentation, which does not rely on light energy, is the most profit-

Table 1. Comparison of Three Biohydrogen-production Technologies

	Advantages	Disadvantages	H_2 production rate
Biophotolysis	・H_2 directly produced from absence of water and sunlight. ・Plentiful water as substrate. ・No need for substrate as nutrient.	・Low light conversion efficiency causing low yields of H. ・Need to supply light energy which is limited by cycles of day-and-night if use sunlight source and additional cost if other sources of light used.	0.07 mmol・L^{-1}・h^{-1}
Photofermentation	・The bacteria can utilize the wide spectra of light energy. ・H_2 can be produced by wastewater in this process. ・Organic compounds are completely converted to H_2 and CO_2.	・Low light conversion efficiency causing low yields of H_2. ・Need to supply light energy which is limited by cycles of day-and-night if use sunlight source and additional cost if other sources of light used.	0.16 mmol・L^{-1}・h^{-1}
Dark fermentation	・Produces highest yields of H_2 compared to other biohydrogen production processes. ・No need for light which H_2 can produce all day long. ・A variety of carbon sources can be used such as waste as substrate.	・Additional cost to the process due to the separation unit to separate product mixture of CO_2 and H_2.	64.5 mmol・L^{-1}・h^{-1}

able process, as it yields higher H_2 production than that achieved using the other two processes[19]. However, large-scale H_2 production through dark fermentation requires both fundamental and applied research and development efforts[20].

Direct biophotolysis produces H_2 by utilizing solar energy and algal photosynthetic systems, specifically those of Chlamydomonas reinhardtii (green algae) and Synechocystis (cyanobacteria)[21]. In this process, photosystem I (PSI) absorbs light and transports electrons to ferredoxin, whereas photosystem II (PSII) absorbs light and generates electrons from water. The light absorbed by PSII is essential for the oxidation of water, resulting in the production of electrons, protons (H^+), and oxygen (O_2). These electrons are then transferred through the electron-transport chain using the light energy absorbed in PSI to reach the hydrogenase enzyme. This process does not involve any intermediate CO_2 fixation[21]. Hydrogenases catalyze the recombination of protons and electrons to evolve H_2 gas. The overall reaction of direct biophotolysis, also known as one-stage direct biophotolysis, involves direct production of biohydrogen from water and solar energy through the algal photosynthesis system.

Biohydrogen is generated by photofermentation using photosynthetic bacteria and light energy to convert organic compounds[22]. Photosynthetic bacteria, classified as purple bacteria (purple non-sulfur and purple bacteria) and green bacteria (gliding bacteria and green sulfur), lack PSII; hence, they depend on PSI for photosynthesis during H_2 production[22]. However, similar to biophotolysis, these bacteria are not capable of water splitting. Instead, they use organic acids, such as acetic acid, as electron donors to generate H_2. For instance, purple non-sulfur bacteria produce H_2 in the photofermentation process through nitrogenase enzymes under nitrogen-deficient conditions using organic acids and light energy[22]. Despite extensive research in this field, the practical application of this process is hindered by several technical barriers, including low volumetric production rates, inefficient H_2 production by nitrogenases, low photosynthetic conversion efficiency, and low light conversion efficiency[16-18].

The complex process of dark fermentation comprises a series of biochemical reactions involving various bacteria[7]. H_2 production occurs during hydrolysis and acetogenesis during anaerobic degradation. In the absence of methanogenic bacteria, organic matter is de-

Table 2. Comparison of Three Representative Hydrogen-purification Technologies

Methods	Advantages	Disadvantage
Cryogenic separation	· Suitable for low H_2 feeding concentration · Relatively high H_2 purity and recovery (~99%)	· Energy intensive · Impurites need to be elimanted before feeding into the process
PSA	· Mature industrial process · Proceducs pure H_2 (> 99%)	· Requirement of high energy to operate · Low product recovery
Membranes process	· Simple operation and technology · Higher energy efficiency and low energy consumption	· Relatively low H_2 puritry (< 90%) · Requirement of additional instruments including pre-filter, gas compression, and etc.

graded into H_2, CO_2, and volatile fatty acids (VFAs). To promote H_2 production, the environment must support the growth of H_2 producers and minimize the population of hydrogen consumers[19]. In dark fermentation, feedstock, such as biomass and waste, is subjected to pretreatment to eliminate methanogens and enhance the hydrogen yield[19]. For example, cellulose-containing agricultural waste, when pretreated, undergoes size reduction and delignification, whereas food processing waste may require only physical treatment[23]. Glucose, a preferred carbon source, undergoes glycolysis and breaks down into pyruvate and nicotinamide adenine dinucleotide (NADH) during the early stages of dark fermentation[23].

Dark fermentation is an attractive method for renewable hydrogen production because it can utilize sugars and carbohydrates from various wastes and biomasses as substrates[23]. This process utilizes hydrogen-producing enzymes that generate hydrogen without consuming oxygen. In addition, well-established fermentation reactor technologies and bioprocess controls can be utilized. As the name implies, dark fermentation does not require light energy input. In addition, as this method requires the use of plant-derived carbohydrates, it aligns with the optimized agricultural practices of the developed countries[7].

Dark fermentation also affords some additional advantages for H_2 production, including high efficiency, low cost (as it does not require light energy input), the ability to use diverse substrates (including the low-cost agricultural waste), and the use of stable H_2-producing enzymes because of the absence of oxygen evolution [24-26]. However, it generates a significant amount of byproducts (e.g., butyrate, acetone, and organic acids). Approximately two-third of its substrate produces byproducts, leaving only one-third of the substrate to produce H_2. Additionally, dark fermentation primarily generates mixed biogas containing H_2 and CO_2, along with potential traces of CO, CH_4, and H_2S[22, 29]. To utilize H_2 as a fuel in internal combustion engines or fuel cells, it is necessary to use a separation and purification system to obtain high-purity H_2 gas. CO_2 present in the biogas can negatively impact the fuel cell performance.

3. Biohydrogen-purification Technologies

The purification process for biohydrogen involves treating the impure hydrogen gas by compressing and densely storing it and allowing it to compete with other gases such as gasoline and natural gas. Various technologies, including cryogenic distillation[12], PSA [10], and membrane technologies[11], have been employed for H_2 separation(Table 2).

Cryogenic distillation involves cooling a mixture to low temperatures to remove unwanted gases by liquefaction. This process yields highly purified H_2 because of its low boiling point in the gas mixture. However, it is not suitable for small portable hydrogen purification and compression units. Cryogenic processes are commonly used in large-scale production of hydrogen owing to cost considerations[30]. When applied to biological mixtures containing CO_2, the transitioning of CO_2 from the gaseous state to the solid state at 1 atm

pressure becomes challenging, potentially clogging the system[31]. To overcome this problem, the operating pressure was increased to enable the change of the CO_2 phase from gas to liquid[31]. Therefore, the cryogenic process is conducted at very low temperatures (120 K) and high pressures, making it energy-intensive. In addition, it requires various instruments for compression, refrigeration, and separation, which, however, increases the construction and operational costs[30]. The efficiency of the purification process depends on the partial condensation of the gas mixture at high pressures and low temperatures, typically affording an overall efficiency of 95~98%[32]. Owing to these challenges, the industry is currently moving toward adopting alternative separation systems and moving away from cryogenic methods.

PSA is one of the most extensively employed technologies for H_2 separation[33]. It is considered a cutting-edge technology for producing pure H_2 in the petrochemical industry[34]. The PSA process involves four steps: adsorption, depressurization, blowdown, and pressurization(Fig. 1)[35]. PSA can be applied in medium-to-large industries as well as in pilot and small portable systems, yielding H_2 purities ranging from 99.5 to 99.9%[35]. Primarily used for separating H_2 from other gases including CO_2, the efficiency of H_2 purification in PSA depends on the adsorption capacity of the adsorber at both high and low pressures[36].

In this PSA, gases are selectively adsorbed at high pressures and desorbed at low pressures. Higher pressure enhances H_2 adsorption onto the adsorbent, whereas lower pressure facilitates the detachment of H_2. The purity of H_2 depends on the binding forces between the gas molecules and the adsorbent, making the selection of the adsorbent crucial for achieving effective

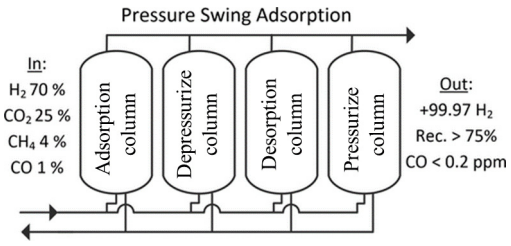

Fig. 1. Illustration of single-stage PSA process.

separation[34]. Various adsorbents have so far been developed, including silica gel, activated carbon, and zeolites[34]. These adsorbents exhibit different capabilities for removing impurities(Table 3)[34]. For instance, silica gel is effective in removing impurities from water vapor, but is ineffective with CO_2 separation. Conversely, activated carbon is suitable for CO_2 removal, but it is less effective for removing water vapor.

Multiple bed absorbers should be used to enhance the purity of adsorbed H_2 in practical applications. This configuration, also known as the polybed PSA process, usually comprises 7~16 beds (depending on the mixture conditions) and a cycle configuration with at least three pressure-equalization steps to maximize H_2 recovery and throughput[34]. The primary focus of the research on polybed PSA systems is the development of an optimal bed-to-bed configuration[37]. Although the PSA system is a well-established technology, the biohydrogen process operates under conditions such as ambient pressure and moderate temperature (~40°C). Consequently, the use of the PSA process is quite challenging for biohydrogen application. As shown in Table 2, PSA is the most widely used technology for H_2 separation, particularly for large-scale production. It is currently being tested for both laboratory and pilot-scale biohydrogen production[38]. If

Table 3. Impurity-elimination Ability of Three Representative Adsorbents

	CO_2	H_2O	N_2	VOC
Silica gel	Good	Excellent	Poor	Moderate
Activated carbons	Good	Very poor	Poor	Moderate
Zeolites	Excellent	Good	Moderate	Good

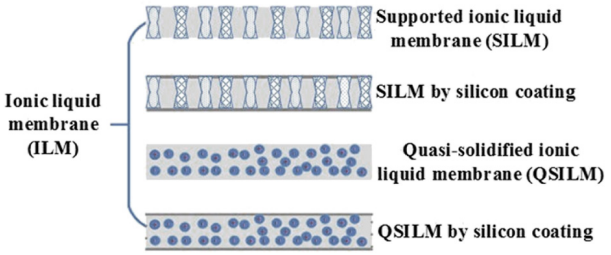

Fig. 2. Schematic draw of ionic liquid membranes.

proven successful on a larger scale, PSA could be used for biohydrogen separation during production.

Membrane technology is a promising technique for the separation and purification of biohydrogen. Membrane systems are advantageous because of their modular nature, fewer operating units, and low energy consumption[39]. Various types of membranes are available for enriching H_2. These membranes can be classified as porous or nonporous. They can also be further divided into organic or inorganic materials. In general, porous membranes have pore diameters of < 2 nm[40-42]. They employ a molecular sieving mechanism as the primary means of separating H_2 from larger species such as CO_2, CO, CH_4, H_2O, and H_2S. Consequently, the size and configuration of the pores play pivotal roles in this separation process, exhibiting enhanced H_2/CO_2 selectivity at elevated temperatures. Zeolite, silica, and carbon-based membranes are the most commonly employed porous membranes[40-42]. However, the precise control of the pore size and shape still remains a major challenge. As an alternative, a porous polymeric membrane incorporating ionic liquids has been proposed as a supporting material to form supported ionic liquid membranes (SILMs), which can be employed for biohydrogen separation [43,44]. One of the key benefits of employing SILMs for biohydrogen separation is the difference in the solubility of various gas components within ionic liquids (ILs) (Fig. 2). This attribute has significant potential for the effective separation of H_2 and CO_2.

The gas-separation efficiency of SILMs strongly depends on the ionic liquid, supporting membrane, and separation conditions[45-47]. In addition, the SILM

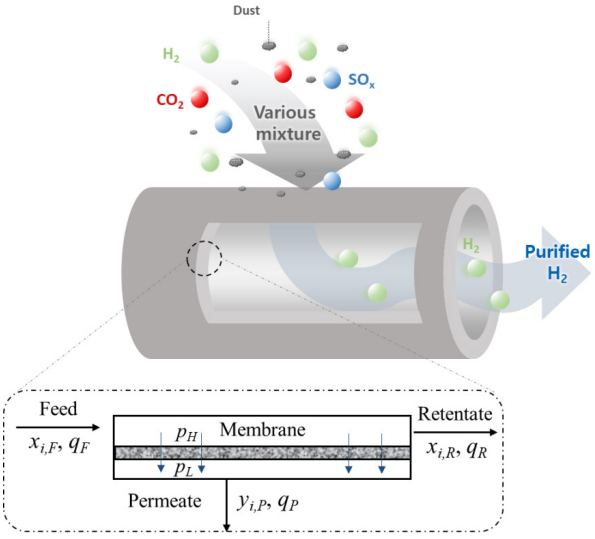

Fig. 3. Illustration of membrane-based H_2 separation. $x_{i,F}$, concentration of feed gas; q_F, feed flow rate; $x_{i,R}$, concentration of retentate gas; q_R, retentate flow rate; $y_{i,P}$, concentration of permeate gas; q_P, permeate flow rate; P_H, high-pressure feed side; P_L, low-pressure permeate side.

configuration resembles that of dense polymeric membranes, with separation based on the gas mixture diffusivity and solubility that are affected by pressure and temperature[47]. Increasing the transmembrane pressure gradient enhances gas permeability, but may cause IL loss, defects, or leakage. Thus, it is crucial to study the effect of transmembrane pressure, which determines the critical displacement pressure based on the pore structure, IL interface tension, and contact angle, to improve the mechanical durability[48,49].

Traditionally, researchers tend to use dense membranes for H_2 separation[50-53]. Nonporous metallic membranes, such as palladium, exhibit exceptional H_2-separation performance; however, their high operating temperatures (approximately 400°C) are not favorable for biohydrogen separation[50,51]. Therefore, the development of metallic membranes specifically for biohydrogen purification is crucial, because it could reduce the material cost and improve the separation efficiency under biohydrogen-operating conditions. Other dense membranes, particularly polymeric materials, are also promising candidates for biohydrogen separation (Fig. 3). These materials demonstrate reasonable sepa-

Table 4. Comparison of Membrane Performance of Representative Membrane Materials

Materials	Conventional polymers	Advanced polymers	Carbon molecular sieve (CMS)	Mixed matrix membranes (MMM)
Mechanism	Solution-diffusion	Solution-diffusion	Molecular sieving	Solution-diffusion molecular sieving
Examples	CA, PSf, PI	PIM-1, TR-polymer	PI-derived CMS	Polymer + MOF (COF, GO, etc…)
Performance	-	+	++	+
Long-term stability	+	-	-	+
Scale-up	++	++	+	+

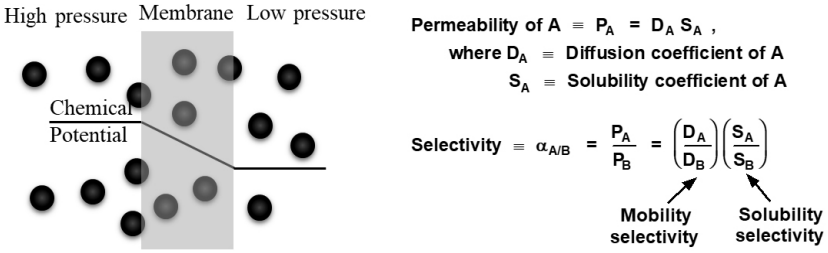

Fig. 4. Simplified schematic image of dense polymeric films based on solution-diffusion model.

ration properties in similar biohydrogen-separation systems, which operate at ambient temperature and pressure[54,55]. Furthermore, their low costs align well with the biohydrogen-production process, making them potentially useful technologies for biohydrogen separation.

4. Polymeric Membranes for Biohydrogen Separation

Various materials have been proposed for producing dense membranes(Table 4). Promising results have been observed with the testing of organic membranes (polymers) for the separation of H_2/CO_2 mixtures (Table 5)[54,55]. Typically, these membranes operate under conditions similar to those required for biohydrogen production (ambient temperature and pressure). In addition, their low costs make them promising technologies for biohydrogen separation.

Nonporous polymeric membranes generally facilitate mass transfer based on the solution-diffusion model [56,57]. Considering the transport mechanism, two material design approaches have been proposed(Fig. 4): one focuses on diffusion-dominant materials, while the other involves the synthesis of solution-dominant materials. Interestingly, H_2 and CO_2 have distinct preferences for transport mechanisms[55]. H_2 transport relies on diffusion, whereas CO_2, a condensable gas, is transported based on its solubility[57,58]. Some recent studies have suggested the possibility of using unique membrane materials that combine both features, that is, they can allow diffusion and solubility-based separation[59,60]. Most materials allow this possibility. The selectivity of polymeric membranes significantly affects the gas-separation efficiency. In H_2-selective polymeric membranes, H_2 extensively permeates the membrane, impeding the passage of other components, including that of CO_2 [57,58]. High selectivity is achieved when H_2 exhibits high diffusivity, while CO_2 has low solubility[57,58].

Despite exhibiting different dominant transport behaviors, both H_2 and CO_2 are fast-permeating gases [61]. Therefore, the primary objective of polymeric membranes is to enhance the H_2/CO_2 selectivity. The nature of the polymer used allows for the production of membranes with either sorption selectivity for CO_2

Table 5. H_2 and CO_2 Permeabilities and H_2/CO_2 Separation Coefficients of Dense Polymer Films

Polymers	Permeability		Selectivity	Refs.
	H_2	CO_2	H_2/CO_2	
Polyimide (Matrimid® 5218)	n.s.	n.s.	2.7	[55]
UBE polyimide module	n.s.	n.s.	2.36	[66]
Polysulfone	12.1	6.1	2.0	[62]
Polyethersulfone	8.96	3.38	2.65	[63]
Polystyrene	23.8	10.4	2.3	[62]
Polymethylmethacrylate	2.4	0.6	4.0	[62]
6F-PBI	997.2	192.7	5.2	[64]
m-PBI	76.8	3.3	23	[64]

or diffusion selectivity for H_2[61]. Generally, polar rubbery polymers exhibit the maximum sorption selectivity for CO_2 and minimal diffusion selectivity for H_2, resulting in an overall selectivity of up to 10 for CO_2 over H_2. In contrast, highly rigid glassy polymers such as polybenzimidazole (PBI) maximize the diffusion selectivity, favor H_2, and can achieve an overall selectivity of 10–20 for H_2 over CO_2(Table 5)[55].

The feed temperature and pressure play significant roles in gas diffusion through membranes. Theoretically, a higher pressure difference between the feed and the permeate sites results in an increased flux and selectivity[65], offering an opportunity to enhance the separation efficiency without requiring drastic material changes. For instance, a commercial Matrimid® membrane demonstrates feed-partial pressure-dependent separation properties in terms of gas mixture permeability and selectivity[55]. The operating temperature is another critical factor influencing the selectivity and permeability of membranes during gas mixture separation [66,67]. The theoretical transport mechanism indicates that gas diffusion into the membrane is directly proportional to the operating temperature because of the increased molecular-diffusion activation energy[66,67]. Additionally, higher temperatures reduce gas solubility in the membrane, favoring diffusion-selective transport, as observed for H_2-separation membranes. A study utilizing a H_2-selective polyimide membrane showed higher separation factors as the operating temperature increased from 21 to 65°C[67]. However, determining the optimal temperature for H_2/CO_2 gas mixture separation is crucial, because both components exhibit different gas-transport behaviors.

5. Organic-based Membrane Reactor for Biohydrogen Separation

A membrane contactor (MC) employed to enhance mass transfer between gas and liquid phases upon contact. These devices facilitate mass transfer between the target gas and the absorbing liquid by utilizing a membrane. Consequently, MCs effectively merge membrane and absorption separation methods. A MC system comprises circularly operated membrane absorber and desorber units. The gas separation mechanism is the same as the present absorption-desorption separation system, but the difference is the presence of a membrane segregating gas and liquid phases in each separation unit. For H_2/CO_2 mixtures, the feed gas enters the absorption unit, where CO_2 permeates the polymeric membrane and pure H_2 exits as retentate. Absorbed CO_2 moves to the desorption unit, passes through the membrane, and exits the system. The liquid absorbent returns for continuous operation.

In general MC polymeric membranes are porous, however their use poses challenges due to bubble formation and liquid penetration, causing contamination. As an alternative, non-porous polymeric membranes of-

fer greater potential because of higher mass transfer coefficients, resistasnce to feed pressure, and no contamination. Notably, Polyvinyltrimethylsilane (PVTMS) membrane displays high gas permeability, ideal for biohydrogen separation[68]. Furthermore, PVTMS and potassium carbonate (K_2CO_3) achieve efficient CO_2 removal in MC systems, extending to CH_4/O_2 mixtures. When used different liquid absrobents such as monoethanolamine, this system achieves higher CO_2 separation efficiency (99%) than K_2CO_3 solution (57%) in PVTMS membrane-based MCs[69]. As a result, chemical absorbents like MEA and K_2CO_3 offer better mass transfer, practicality, and eliminate the need for additional compression systems seen in physical absorbents.

The MC system's integration with biohydrogen production has been explored. Beggel *et al*. demonstrated a 99% CO_2 separation efficiency from real biogas (H_2/CO_2 mixture) and obtained 90% pure biohydrogen with 10% CO_2 by coupling an MC with photofermentation. They employed batch separation due to the slow biogas production rate of the photofermenter, achieving high purity biohydrogen. However, MC's adoption is less prominent compared to NPPM in this context[7].

6. Conclusions

Production of biohydrogen from renewable sources is vital for sustainable energy production. Biohydrogen production can be performed through biophotolysis, photofermentation, and dark fermentation. However, challenges related to low hydrogen yields and optimization of operating conditions need to be first addressed. Furthermore, the production of high-purity H_2 suitable for application in H_2-combustion engines and fuel cells requires efficient separation and purification systems. Cryogenic distillation is cost-intensive and unsuitable for small-scale applications. PSA offers high H_2 purity. Membrane technology affords various advantages, such as low energy consumption and modularity, making it a promising option for biohydrogen separation and purification. The study results show that dense polymeric membranes are promising candidates, although they require further research and development for large-scale application.

Acknowledgments

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