A Review on the Production and Purification of Biomass-Derived Hydrogen Using Emerging Membrane Technologies

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Abstract: Hydrogen energy systems are recognized as a promising solution for the energy shortage and environmental pollution crises. To meet the increasing demand for hydrogen, various possible systems have been investigated for the production of hydrogen by efficient and economical processes. Because of its advantages of being renewable and environmentally friendly, biomass processing has the potential to become the major hydrogen production route in the future. Membrane technology provides an efficient and cost-effective solution for hydrogen separation and greenhouse gas capture in biomass processing. In this review, the future prospects of using gas separation membranes for hydrogen production in biomass processing are extensively addressed from two perspectives: (1) the current development status of hydrogen separation membranes made of different materials and (2) the feasibility of using these membranes for practical applications in biomass-derived hydrogen production. Different types of hydrogen separation membranes, including polymeric membranes, dense metal membranes, microporous membranes (zeolite, metal-organic frameworks (MOFs), silica, etc.) are systematically discussed in terms of their fabrication methods, gas permeation performance, structure stability properties, etc. In addition, the application feasibility of these membranes in biomass processing is assessed from both practical and economic perspectives. The benefits and possibilities of using membrane reactors for hydrogen production in biomass processing are also discussed. Lastly, we summarize the limitations of the currently available hydrogen membranes as well as the gaps between research achievements and industrial application. We also propose expected research directions for the future development of hydrogen gas membrane technology.

Keywords: catalytic membrane reactor; hydrogen; biomass

1. Introduction

Due to continuous population growth and economic development, an increasing amount of energy is being demanded and consumed worldwide. In the meantime, the extensive exhaustion of fossil fuels has caused humanity to face a serious energy crisis and environmental disruptions in recent decades. In particular, the immoderate emissions of greenhouse gas and other combustion pollutants have caused non-negligible consequences, such as global warming and air pollution, threatening the future development of human society. According to the International Energy Agent statistics, the total CO_2 emissions from fuel combustion increased to 32.3 billion metric tons in 2013, a number expected to increase as the non-OECD (Organisation for Economic Co-operation and Development) developing countries are anticipated to consume more energy in the upcoming decades [1]. In this situation, exploring substitute energy resources and sustainable energy systems has become a highly urgent mission facing all countries at this moment.

In response to these stated challenges, many efforts have been devoted to new energy system research and development, and various alternative technologies have been proposed and investigated. Hydrogen energy systems started to attract noticeable attention during the energy crisis of the 1970s and have undergone immense development since then [2–4]. Hydrogen is considered a very promising energy carrier because of its advanced inherent properties, such as its high energy density of 14,300 J/(kg·K), long-term viability, environmentally friendly combustion products, and extensive resources [4–6]. Although hydrogen is the most abundant element on earth, it mostly exists in water and hydrocarbons, where it is bound to oxygen and carbon and hence not naturally ready to use [3–6]. Therefore, different processes have been developed and utilized to produce pure hydrogen from various resources. Among these available hydrogen production processes, the steam reforming reaction (SRR) of natural gas followed by the water gas shift reaction (WGSR) is recognized as the most economical process and is responsible for over 90% of the total hydrogen production at present [7–9]. In the meantime, other promising technologies, including water splitting [10,11] and biomass processing [12–14], are rapidly developing because of their potential to convert clean and renewable energy resources to hydrogen. The application of biomass processing for hydrogen production is urgently needed, not only because of the large supply of renewable resources but also because of the ability to save the environment by utilizing dumped mining and agricultural wastes.

To achieve a successful clean hydrogen energy society, producing hydrogen from a carbon constrained technology, such as biomass, is only the first part of the whole hydrogen energy system. The separation and purification, the storage and delivery and the efficient utilization of the hydrogen gas produced are also very important steps in realizing the benefits of using the hydrogen energy generated from sustainable resources [15]. Among these steps, the separation and purification constitute a critical process in the hydrogen energy system from both the technical and economic perspectives. Currently, various gas separation technologies are readily available for separating hydrogen from the mixed gases produced, and membrane separation technology has shown distinct advantages of low energy consumption, environmentally friendly properties and the attractive potential of serving as a multifunctional membrane reactor [16–18].

To our knowledge, several studies have focused on reviewing the technology of producing hydrogen from biomass processing and there are also some studies emphasizing the development of membranes for hydrogen separation. The objective of this review is to discuss the potential of using different hydrogen separation membranes to produce and purify the hydrogen product derived from biomass processing. In addition to summarizing the recent development of hydrogen separation membranes, including their synthesis methods, hydrogen separation performance, etc., we also aim to assess the technical and economic feasibility of utilizing the available hydrogen separation membranes in biomass processing, which would potentially assist researchers and engineers in choosing the right membrane process for their biomass processing design.

1.1. Hydrogen Energy System

Considering hydrogen's outstanding potential as a clean energy carrier, the hydrogen energy system was proposed and recognized as a permanent solution to the petroleum-based fuel depletion and environmental crisis [19]. In a hydrogen energy system, the energies produced from different primary energy sources (solar, wind, biomass, etc.) are initially transferred to a hydrogen carrier through a variety of reactions (gasification, water splitting and reforming, etc.). The energy carrier hydrogen is then transported, stored and finally utilized by the terminal users, as shown in Figure 1. In this system, hydrogen serves as the intermediary to transfer energy between the energy resource and the energy utilization customers [2–4,20]. Currently, the hydrogen energy system is not only attracting attention from the research perspective, but also several governments have made massive investments to build the infrastructure for realizing a hydrogen energy-driven society. One remarkable event is that the government of Iceland has set the goal of becoming a complete hydrogen-economy country in the year of 2030 by making full use of their geothermal energy through hydrogen energy systems [21].

In addition, the promotion of hydrogen-powered vehicles is encouraged by many counties, such as Japan and China. However, there are four major technical challenges that need to be faced before an efficient hydrogen energy system can be realized, including hydrogen production and purification through a carbon-constrained process, hydrogen delivery and distribution through wide-ranging and well-managed infrastructure, hydrogen storage in reliable and safe plants and hydrogen utilization through an efficient process [15].
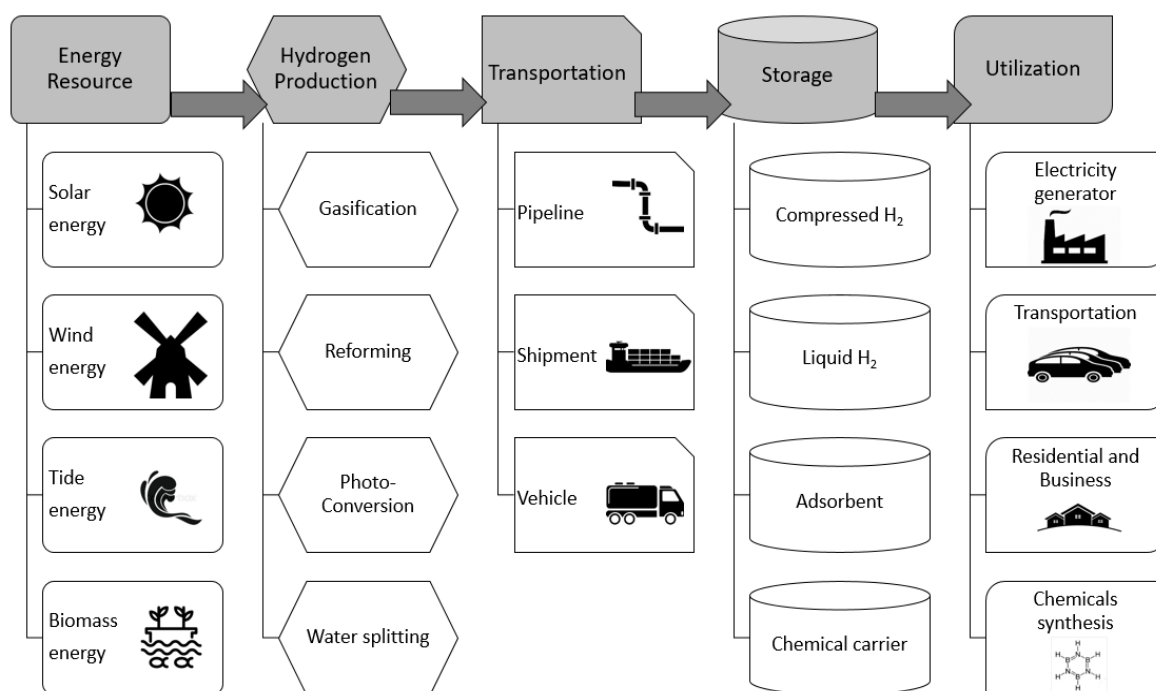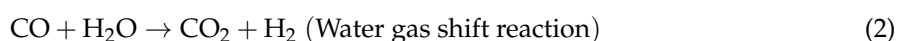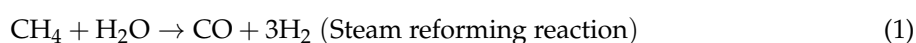

Figure 1. Hydrogen energy system.

Unfortunately, fossil fuel is still the main resource used in the industry to produce hydrogen at this point in time, and over 90% of hydrogen in the US is manufactured from methane through steam reforming and water gas shift reaction (WGSR) processes, as shown in Equations (1) and (2) [4]. In this approach, methane and steam are first used to produce hydrogen and carbon monoxide, and the generated CO can subsequently be converted to carbon dioxide while producing more hydrogen through the WGSR. However, this process is highly reliant on fossil fuel sources and is unsustainable for long-term development [11]. In the meantime, other hydrogen production methods are growing rapidly; water splitting and biomass process are representative examples of these emerging technologies. The new technologies constrain carbon emission either by using a carbon-free process (water splitting) or by reusing carbonaceous waste (biomass) to generate hydrogen [11–14]. In addition, the new technologies could also realize the utilization of local energy sources including solar, tide, geothermal and bio-waste energy rather than being limited by sources of fossil fuel.
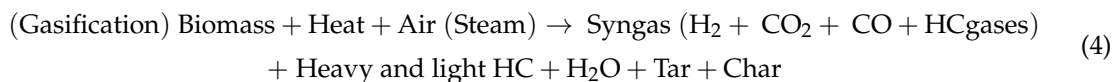
$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ (Steam reforming reaction)} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (Water gas shift reaction)} \tag{2}$$
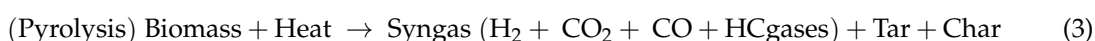
1.2. Hydrogen Production from Biomass

Biomass is one of the most abundant renewable energy resources, formed by fixing carbon from the air and ground during the process of photosynthesis by plants [12–14]. Actually, biomass is one of the stages in the lifecycles of energy and carbon on the earth. There are plenty of biomass

resources in every part of the world, making biomass energies available in almost every corner of this planet [22]. There are four main categories of biomass worldwide that could be utilized, including agriculture waste (crop straw, animal wastes, etc.), forestry waste (logging residuals, sawmill wastes, etc.), energy crops (commercial crops, grass, etc.) and industrial waste (sewage sludge, etc.). In fact, utilizing biomass energy from woody biomass is not a new concept but has been used by human beings for cooking and heating for centuries, accounting for approximately 15% of the current primary energy consumption in the world [23]. However, the low energy efficiency and unmanageable carbon emission of the traditional utilization methods, such as burning, limit the ability of biomass energy to serve as a general energy supply for the modern world. Therefore, finding efficient ways to utilize biomass energy and control the resulting carbon emission stands out as the major challenge for the biomass energy industry [12].

Currently, biomass energy can be produced mainly via two routes: thermochemical and biological processes. The thermochemical route includes combustion, pyrolysis, liquefaction and gasification processes, while the biological route includes direct and indirect bio-photolysis, biogas (methane) production, biological water gas shift reactions, photo-fermentation and dark-fermentation processes [12–14]. However, biological routes are very time consuming and have strict requirements for the feedstocks and reaction conditions. In comparison, thermochemical routes (fast pyrolysis and gasification) are more feasible for hydrogen production because of involving faster reaction processes, having less selective feedstock requirements, and having higher production efficiency (over 50%) and relatively lower cost [24]. The reaction routes of fast pyrolysis and gasification are listed in Equations (3) and (4), and both processes are normally performed at high temperatures, over 800 K, to achieve a higher hydrogen yield. As shown in Equations (3) and (4), the main products of these two processes include gaseous products, liquid products and some solid products. Subsequently, more hydrogen could be produced by converting the other generated gases, such as methane, hydrocarbons and CO through further reactions, as previously noted in Equations (1) and (2) [12–14,24]. In brief, the main products of these feasible biomass processes for hydrogen production are syngas, which is a gas mixture of hydrogen, carbon oxide, carbon dioxide, methane, steam and other species, such as hydrocarbons and hydrogen sulphide. Moving forward, the SRR and WGSR are then carried out to fully convert the CO and CH_4 to hydrogen. Additionally, other products including liquid bio-oil could also be converted to hydrogen following the SRR, although the gaseous phase is more desirable for hydrogen production [14].

$$\text{(Pyrolysis) Biomass} + \text{Heat} \rightarrow \text{Syngas} (H_2 + CO_2 + CO + HC\,\text{gases}) + \text{Tar} + \text{Char} \qquad (3)$$

$$\text{(Gasification) Biomass} + \text{Heat} + \text{Air (Steam)} \rightarrow \text{Syngas} (H_2 + CO_2 + CO + HC\,\text{gases})$$
$$+ \text{Heavy and light HC} + H_2O + \text{Tar} + \text{Char} \qquad (4)$$

Following these reactions, gas separation processing needs to be carried out to (1) obtain the purified hydrogen product for utilization; (2) recycle the unreacted gases, such as CO and CH_4, for further conversion and (3) capture the greenhouse gases, such as CO_2, to prevent their emissions into the atmosphere, thus achieving carbon negativity. The gas separation process plays a very important role in the biomass-derived technology for hydrogen production due to its high impact on the efficiency of the whole system and its economic feasibility, as well as its ability to control the carbon emission and environmental friendliness of the whole biomass system. Despite its economic and environmental impact, the gas separation process must be conducted under harsh conditions of high temperature, high humidity, the presence of acid and sulphur, etc. Hence, a suitable gas separation technology is highly desired and critical for the feasibility of the whole process [15].

1.3. Membrane for Hydrogen Separation

A membrane is a physical barrier that selectively permits specific species to pass through to the permeate side driven by chemical potential (for dense polymeric membranes, this translates into the

difference in fugacities for real gases and in partial pressures for gases where ideal gas behaviour can be assumed), while being able to retain most of the impermeable species at the retentate/feed side [16,17], as shown in Figure 2. After many years of development, membrane separation technology has been extensively applied in many industries, such as water treatment, gas separations, drug delivery, etc. [25]. In particular, membrane-based gas separation technology is currently attracting considerable attention from both academic researchers and industry engineers. Its market is expending very rapidly at over 15% yearly, and its fields of application have included hydrogen production and purification, air separation (oxygen concentrators and nitrogen generators), carbon dioxide capture, vapour removal, etc. [26]. Compared with other gas separation technologies, such as pressure swing adsorption (PSA), membrane gas separation has unique advantages, including simplicity of operation, reduced energy demand, small footprint, continuous operation, etc. [16,17,25,26]. In particular, the utilization of a membrane reactor, a unit combining the catalytic reactor and the membrane separation process, could result in the extra benefits of a shifted reaction equilibrium, higher conversion and concentrated products [27].
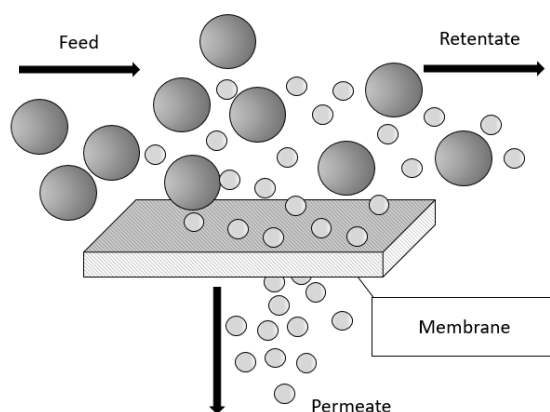

Figure 2. Schematic of membrane separation.

Hydrogen separation and purification is one of the most important applications of gas separation membrane. Basically, there are three main mechanisms for hydrogen separation membranes, as illustrated in Figure 3. In general, there is no separation performance for membranes with relatively large pores (0.1–100 μm) compared with the kinetic diameters of gas molecules, as the gas would non-selectively permeate the membrane under convective flow (Figure 3a). In comparison, gas molecules can be separated based on the inverse square root ratio of the molecular weight through Knudsen diffusion when the membrane pores are smaller than the gas mean free path (Figure 3b), whereas gases could be separated by sieving the large gas molecule out through the molecular sieving mechanism, which is the dominant mechanism of hydrogen separation using microporous membranes. However, the hydrogen separation factor is based on both the solubility and the diffusivity for most nonporous polymeric and dense metal membranes, following the solution-diffusion mechanism [28].

Apart from the permeation mechanisms, the hydrogen separation membrane can also be categorized into the following types based on the materials used, including polymeric membranes, dense metal membranes, microporous (nanoporous) membranes, etc. As shown in Table 1, the various types of membranes significantly differ in terms of their hydrogen separation performance and applicable operation conditions [27,29]. For example, dense mental membranes possess high selectivity for hydrogen over other gases and can be operated at very high temperatures, but they have relatively lower permeability and higher cost. In contrast, the polymeric membranes provide better permeability at a lower capital investment, but most of their applications are limited by their low operation temperatures and relatively lower hydrogen selectivity. Therefore, a comprehensive analysis needs to be performed before selecting an appropriate membrane for a specific application.

Table 1. Types of hydrogen separation membrane. Table adapted with permission of the authors of [29].

Parameters	Membrane Type		
	Polymeric	Microporous	Dense Metal
Typical composition	Polyimide; Cellulose acetate	Silica; Zeolites; Metal-organic frameworks	Palladium; Palladium alloys
Diffusion mechanism	Solution diffusion	Molecular sieving	Solution diffusion
Driving force [†]	Partial pressure difference	Partial pressure difference	Partial pressure difference
Operation temperature	≤110 °C	≤1000 °C	150–700 °C
Relative permeability	Low—moderate	Moderate–high	Low
Typical selectivity	Moderate	Low—moderate	Very high
Relative cost	Low	Low—moderate	Moderate—High

[†] Assumed ideal gas behavior.

Convective flow	Knudsen diffusion	Molecular sieving	Solution diffusion
(**a**)	(**b**)	(**c**)	(**d**)
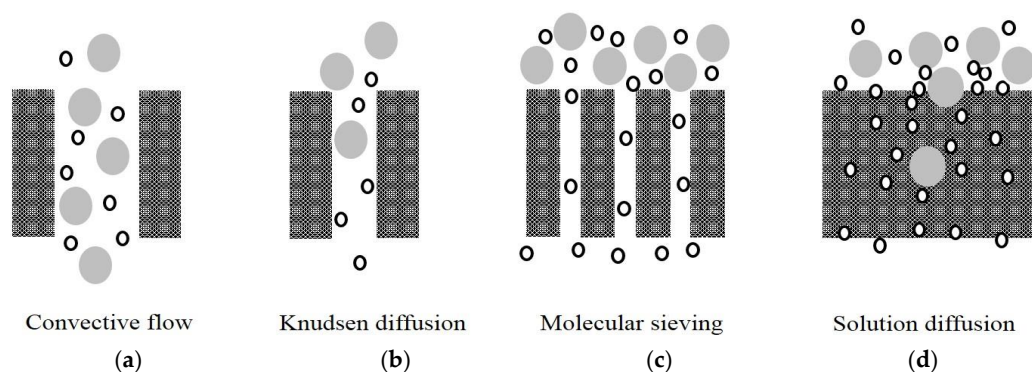
Figure 3. Mechanism for gas separation through (**a**–**c**) porous and (**d**) dense membranes [30]. Black circle and Grey solid circle represent gas molecules with small and large kinetic diameters, respectively.

The permeability and selectivity are the two most important criteria for evaluating the performance of a membrane from the technical perspective, and there has always been a trade-off between these two. Higher permeability could generally yield better productivity, while presuming a higher selectivity could lead to a purer product but could potentially result in poorer productivity. The permeability and selectivity of a membrane would vary under different operation conditions (temperature, pressure, humidity and gas compositions, etc.) [16,17,25]. In addition to the technical performance, the membrane's practical applicability is also a crucial factor for determining the feasibility of a membrane process for a specific industrial application. The practical feasibility, including the robustness, the manufacturing flexibility, the cost, etc., always plays the decisive role when a membrane process or other alternative options are considered [30,31].

For the production and purification of hydrogen derived from biomass processing, the desired hydrogen separation membrane requires considerable technical performance in terms of hydrogen permeability and selectivity, as well as the practical feasibility of being employed under the harsh conditions in the biomass processes. In this study, we will review the development of different types of hydrogen separation membranes and evaluate the practical feasibility of employing the membranes under the conditions of biomass processing for hydrogen production.

2. Polymeric Membranes for Hydrogen Separation

The first concept of a polymeric membrane can be traced back to the 1740s, when Abbe Nolet discovered the phenomenon of water permeation through the animal bladder. However, gas separation polymeric membrane systems could not be commercialized before overcoming the problems of their large-scale manufacture and their poor permeability in the 1980s [16,17,32–36]. Since the first publication of Monsanto's commercial system, the polymeric gas separation membrane has undergone a very fast expansion benefitting from technological improvement and application development.

To date, commercial polymeric gas separation membrane systems have been applied to separate a variety of gas pairs and have been introduced in many industry areas, such as hydrogen recovery, air purification and natural gas purification. The application for hydrogen recovery was the initial target for polymeric gas separation membrane, and in turn, the first large-scale commercial polymeric gas separation membrane system was also employed for hydrogen recovery in the ammonia manufacture industry [33]. Compared with metal and inorganic membranes, polymeric membranes dominate the hydrogen separation membrane market at present [32,35] because of their lower material and manufacturing cost, easy accessibility and mild operation conditions [36].

Currently, the phase inversion process is the primary preparation method for polymeric membranes in the industry. This process enables large-scale membrane manufacturing and makes it possible to produce asymmetric membranes with a thin and highly selective layer on top of the porous supports, which can enhance the permeance of the produced membrane to a great extent [32–34]. Following specific preparation routes, hollow fibres or flat sheet configurations could be spun or casted out and subsequently manufactured into hollow fibres or spiral-wound membrane modules for practical applications [33]. Several reviews have discussed the membrane preparation methods in detail [37–39].

The solution-diffusion model is the dominant gas transport mechanism of polymeric membranes for hydrogen separation [32]. As shown in Equation 5, the gas permeability (P) ina polymeric membrane is equal to the product of the solubility (S) of the gas molecules into the membrane surface and the diffusivity (D) of the gas molecules penetrating in the membrane matrix [40]. Hydrogen has a very high diffusivity coefficient in polymer membrane structures due to its smallest gas molecular size among all the gases, but it has very low solubility because of its weak affinity to all the known polymer materials [32]. From this perspective, the polymeric hydrogen separation membranes could be further divided into two types, hydrogen-selective membranes and hydrogen-rejective membranes [35]. For hydrogen-selective membranes, the principle is to enhance the hydrogen selectivity by maximizing its diffusivity benefits relative to the other gases within the rigid matrix of glassy polymers. In contrast, hydrogen-rejective membranes have a reverse selectivity with respect to hydrogen because they take advantage of the solubility differences among gases but weaken the diffusivity differences with the large free volumes in the rubbery polymer structure [34–36].

$$P \text{ (Permeability)} = S \text{ (Solubility)} \times D \text{ (Diffusivity)} \tag{5}$$

2.1. The Performance of the Polymeric Membrane for Hydrogen Separation

As of today, many polymeric materials have been used for preparing hydrogen separation membranes, including glassy polymers for hydrogen-selective membranes and the rubbery polymer for hydrogen-rejective membranes. The most common hydrogen separation membranes are still made from commercially available polymers, such as cellulose acetate (CA), polysulfone (PSF), polyethersulfone (PES), polyimide (PI), polyetherimide (PEI), etc. [32,41]. Table 2 summarizes the permeation performance of hydrogen and carbon dioxide through several membranes fabricated from conventional polymeric materials [36]. Table 2a indicates that these hydrogen-selective membranes fabricated from commercial polymers such as PES [42], PSF [43] and Polyvinylidene fluoride (PVDF) [44] do not possess the desired H_2/CO_2 selectivity, and moreover, the permeability of these membranes is also not satisfactory, resulting in less than 10 Barrer due to the high diffusion resistance in the rigid glassy polymer chains. In contrast, the hydrogen-rejective membranes (Table 2b) could provide higher permeability because of their high proportion of "free volumes" and macro voids in the structures. However, their CO_2/H_2 selectivity is still unfavourable for the production of the high-purity hydrogen. The Roberson upper-boundary lines, as shown in Figure 4, are compiled to indicate the permeability-selectivity trade-off limits of different gas pairs for the polymeric membranes [45,46]. Figure 4 shows the corrected upper boundary lines for hydrogen and carbon dioxide, which were published in and have has been improved compared with those published in 1991; however, most

membranes fabricated from commercial available polymers are still distant from the attractive region. In recent years, polyimide (PI)—[47,48] and polybenzimidazole (PBI)—[49,50] based membranes are very attractive for hydrogen separation. In addition to their improved performance, these membranes also have promising structural and thermal stabilities under harsh operation conditions.

Table 2. The transport properties of H_2 and CO_2 through some conventional polymeric membranes (**a**) hydrogen-selective and (**b**) hydrogen-rejective. Table modified with permission of the authors of [36].

(a)					
Polymers	**T (°C)**	**P (atm)**	**Permeability (Barrer [a])**		**H_2/CO_2 Selectivity**
			H_2	**CO_2**	
Ethyl Cellulose	30	-	87	26.5	3.28
Polyetherimide	30	-	7.8	1.32	5.91
Polyphenyleneoxide	30	-	113	75.8	1.49
Polysulfone	30	-	14	5.6	2.50
Polymethylpentene	30	-	125	84.6	1.48
Polyimide (Matrimid®)	30	-	28.1	10.7	2.63
Polyethersulfone	35	3.5	8.96	3.38	2.65
Polystyrene	30	1.36	23.8	10.4	2.29
Poly(vinylidene fluoride) (Kynar)	30	1.36	2.4	1.2	2.00
Poly(methyl methacrylate)	30	1.36	2.4	0.6	4.00

(b)					
Polymers	**T (°C)**	**P (atm)**	**Permeability (Barrer [b])**		**CO_2/H_2 Selectivity**
			CO_2	**H_2**	
Polytrimethylsilylpropyne	25	-	79	36.1	2.19
Poly(4-methyl-2-pentyne)	25	-	10700	5800	1.84
Polyphosphazene	30	2.04	250	25	10.00
Poly(tert-butylacetylene)	25	1	560	300	1.87
Poly(amide-6-b-ethylene oxide)	25	4	132	20	6.60
Poly(amide-6-b-ethylene oxide) Pebax® [51]	35	-	220	22	10
Poly(ethylene glycol) diacrylate	23	12	-	83	11.00
Crosslinked PEG copolymer [b]	35	17	-	-	9.40
Crosslinked PEG copolymer [b]	−20	17	410	-	31.00
Polyether	-	-	586	76.6	7.70
Poly(styrene-co-butadiene)	30	-	15.3	7.9	1.94
poly(ethylene oxide)-poly(butylene terephthalate) [52]	30	-	190	-	13
Poly(dimethyl siloxane) (PDMS) [c]	23	1.36	3200	950	3.36

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm / (cm^2 s cmHg); [b] Data obtained from mixed gas CO_2/H_2 (80:20), partial pressure of CO_2 is 17 atm; [c] Data obtained from synthetic syngas mixture.
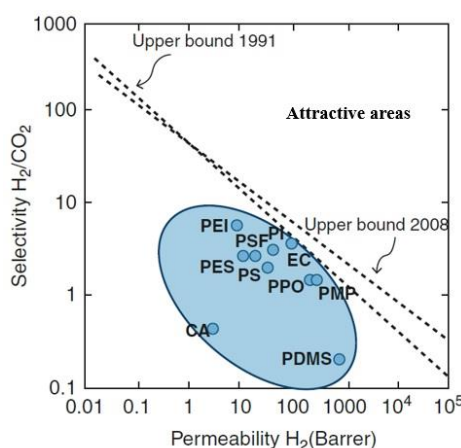

Figure 4. Roberson upper boundary for H_2/CO_2 separation [32,45,46]. The blue area indicates the performance range of the membranes fabricated from commercially available polymers. CA: cellulose acetate; PSF: polysulfone; PES: polyethersulfone; PI: polyimide; PEI: polyetherimide; PDMS: polydimethylsiloxane; PMP: polymethylpentene; PPO: poly(phenylene oxide); PS: polystyrene; EC: ethyl cellulose.

In general, the intrinsic performance of the membranes fabricated from conventional commercial polymers is still insufficient to meet industrial demands in harsh environments. Therefore, many efforts have been made to improve hydrogen separation performance by designing new polymers and modifying existing polymers.

2.2. The Strategy of Improving the Polymeric Membrane

The first strategy is to design new polymer materials to either maximize the diffusivity selectivity for hydrogen-selective membranes or, inversely, to enhance the solubility selectivity for hydrogen-rejective rubbery membranes [35]. Budd and McKeown et al. developed a series of membranes with porous intrinsic micro-porosity (PIMs) polymers for gas separation [53,54]. These PIM membranes had complex and rigid polymer chains with a controllable free volume and microporous structure. Hence, hydrogen could be separated by these membranes through a molecular sieving mechanism, such as that observed in zeolite and MOF membranes. These PIM membranes exhibit noticeable permeability and high selectivity for H_2/N_2 and H_2/CH_4 separations and are located at the desired area in the Roberson upper boundary. Pebax®, a poly(amide-6-*b*-ethylene oxide) polymer introduced by Arkema, has been used to fabricate hydrogen separation membranes with promising gas separation performance for CO_2/H_2 separation [55]. Bondar et al. reported a Pebax® membrane with CO_2/H_2 selectivity of 10 and CO_2 permeability of 220 Barrer in 35 °C. In addition, the CO_2 permeability was enhanced, whereas the hydrogen permeability decreased with increasing pressure, resulting in improved selectivity at higher pressure [51].

The polymer blending strategy is to form an integrated membrane with new prospective benefits by combining the advantages of two compatible polymers. Although the method seems very straightforward from the mixing perspective, the miscibility and interactions between the blending polymers require careful consideration in practice. Chung et al. prepared blended polymeric membranes from PI (Matrimid® 5218) and PBI with various compositions. The best H_2/CO_2, H_2/N_2 and H_2/CH_4 selectivity values of 260, 9.43, and 59.79 were achieved with the composition Matrimid/PBI = 25/75 wt %, whereas the selectivity values of pure Matrimid® 5218 were only 97, 3.88 and 33.33, respectively. The authors attributed the selectivity enhancement to the improvement in diffusivity selectivity obtained by blending the PBI into the PI networks [56]. Peinemann et al. fabricated a composite membrane by blending Pebax® with polyethylene glycol (PEG). The membrane achieved improvements in both permeability and selectivity for CO_2/H_2 separation. They believed that the added PEG reinforced the CO_2 solubility and induced a free volume increase in the Pebax® membrane structure [57].

Chemical crosslinking has been extensively applied to improve the H_2/CO_2 selectivity of polyimide membranes. These diamine-based crosslinking reactions can be post-conducted on almost all aromatic polyimide membranes under mild conditions [36]. Chung's group is the pioneer of exploring the crosslinking post-treatment of polyimide membranes for gas separation [58–60]. According to their reports, the H_2/CO_2 selectivity of the modified polyimide membrane could be significantly increased by over 100 times upon crosslinking with 1,3-diaminopropane (PDA) at 35 °C for only 10 min [61]. However, this crosslinking process also resulted in a significant reduction of hydrogen permeability [58–61] because of increased resistance through the membranes after the polymer chain was restricted.

A mixed matrix membrane (MMM) is constructed from organic polymers and inorganic particles [62]. The strategy of MMM is to enhance polymeric membrane performance, including permeability, selectivity and thermal stability, by embedding inorganic particles, such as zeolites and metal-organic frameworks [62]. In recent years, MMM has been a very popular research topic, and many polymer materials and inorganic particles have been paired in this hybrid membrane. However, there are also some drawbacks of MMMs; for example, the poor affinity between the materials can generate defects and correspondingly poor selectivity. In addition, the complex preparation procedure has been another limiting factor for the large-scale manufacturing of MMM [36]. Yang et al. systematically studied a series of PBI/ZIF (Zeolitic imidazolate framework) MMMs for hydrogen

separation and reported that the embedded ZIF materials (ZIF-7, ZIF-8 and ZIF-90) could enhance the hydrogen permeability by over 100 times without reducing the H_2/CO_2 selectivity. Afterwards, they fabricated these MMMs into a hollow fibre configuration and tested these hollow fibre membranes under industrial application conditions. Their results indicate that PBI/ZIF MMMs have very promising potential for separating hydrogen in reactions such as WGSR [63–65]. Several studies have reviewed the recent development of MMM for gas separation [62,66].

2.3. Current Utilization Status and Future Perspectives for Biomass Processing

Since the first commercial polymeric membrane system was developed for hydrogen recovery by Monsanto in the 1980s [67], the applications of the polymeric membrane system have been extended to many hydrogen separation plants, including gas ratio adjustment for syngas and hydrogen recovery from refinery gases, and they are expected to be utilized for proton-exchange membrane (PEM) fuel cells, biomass processing, etc., in the future [35]. Table 3 provides information on the first commercial polymeric membranes for hydrogen separation. From Table 3, we can see that initially, the main polymers used for hydrogen separation membranes were PSF, CA, PI, etc., and the most common configuration of these membranes was hollow fibre. Currently, many new membrane companies are emerging in the market and providing more diverse polymeric membrane products for hydrogen separation. However, the primary membranes are still made from these conventional commercial polymers, although some of the membranes have been modified through confidential technologies. Detailed information on the currently available polymeric hydrogen separation membrane products has been reported elsewhere [34].

Table 3. Commercial polymeric membranes for hydrogen separation [34,67–69].

Supplier	Membrane Materials	Module Types	Selectivity			Reference
			H_2/N_2	H_2/CH_4	H_2/CO	
Air products	Polysulfone	Hollow fiber	39	24	23	[67]
Air liquid	Polyimide/polyaramide	Hollow fiber	-	-	-	[34]
Ube	Polyimide	Hollow fiber	35.4	-	30	[68]
UOP/Separex	Cellulose acetate	Spiral wound	33	26	21	[69]

In conclusion, the polymeric membrane system possesses some considerable advantages for hydrogen production and purification from biomass processing. First, the polymeric membrane system has been well investigated and commercialized. The currently available polymeric membrane systems on the market could basically meet the demands of separating hydrogen from other biomass-derived gases, such as CO_2, CO, CH_4, etc. In addition, the cost of polymer membrane systems is lower than that of other separation processes due to the ease of polymeric membrane fabrication and the low cost of system operation.

Although several advantages of polymeric membranes in hydrogen separation could be named, polymeric membranes also have significant limitations under some application conditions. First, physical ageing is a natural phenomenon of polymeric membranes and is difficult to avoid. Many polymers, especially glassy polymers, undergo a series of segmental motions over a long-term period, causing the density of the polymer chain to increase and further restricting the membrane structures. As a result, the membrane permeability and selectivity dramatically decrease after a certain time [16,70]. Plasticization is another negative factor when considering polymeric gas separation membranes. Plasticization leads to decreased selectivity and increased permeability because the permeating gases, such as CO_2, have the ability to swell the polymer chain, increasing the free volume and generating defects in the membrane structure [16,33]. Aside from these, several additional practical factors also require consideration before selecting polymeric membranes for hydrogen separation and purification in biomass processing. For example, the polymeric membranes generally exhibit unfavourable selectivity and permeability for hydrogen separation, as shown in Tables 2 and 3.

In particular, the H_2/CO_2 selectivity is lower than or approximately 10 in the available polymeric membranes. These membranes could neither provide qualified hydrogen production nor control CO_2 emission efficiently in one-stage membrane process. Accordingly, multi-stage membrane process is often used in industry in order to enhance the selectivity, despite large membrane areas and expensive operation costs. Although the selectivity can be improved through several modification methods, such as crosslinking, the drawbacks of these methods, such as the dramatic decrease in permeability and complex treatment procedures, make them impractical from the engineering perspective at present. In addition, the poor thermal and chemical stability could be a crucial factor restricting the application of polymeric membranes in biomass processing.

In general, the operating temperature of the glassy polymers must be lower than its glass transition temperatures (T_g), or the membrane will become rubbery and lose its rigid networks. Unfortunately, most conventional polymers have low glass transition temperatures and must usually be operated under 150 °C. However, the glassy polymeric membranes still exhibit better thermal stability and mechanical strength than the rubbery hydrogen-rejective membranes [35,36]. Nevertheless, while PBI and PEI were reported to have higher thermal stability, up to 400 °C, their high price limits the general application of these membranes in the near future. The gas stream could certainly be cooled down to meet the temperature requirements of polymeric membranes, but the overall cost would be increased and heat energy would be lost from this uneconomical cooling process [36].

3. Dense Metal Membranes for Hydrogen Separation

Dense metal membranes are made from the metallic elements of group III-V, such as palladium (Pd), nickel (Ni) and platinum (Pt), and their metallic alloys [71,72]. The most prominent feature of these membranes is their extremely high hydrogen selectivity, and thus they are commonly used for the production of ultra-pure hydrogen [73]. This feature is attributed to the innate ability of the structures of metals and metal alloys to allow hydrogen-selective diffusion while blocking other gases. However, their hydrogen permeability is relatively low compared to other membranes due to the nonporous structures in these metal membranes [71]. Solution-diffusion is believed to be the mechanism of hydrogen permeation through these dense metal membranes. Thus far, several dense metal membranes have been commercialized and extensively used in the semiconductor and LED industries to provide highly purified hydrogen [73]. Among these dense metal membranes, Pd-based membranes have the longest development history and are the most studied dense metal membrane at this time. Pd-based membranes were found to exhibit superior hydrogen solubility on the Pd surface at various temperatures (Figure 5a), resulting in outstanding permeation flux compared with other metal membranes, as shown in Figure 5b [72,74–77].
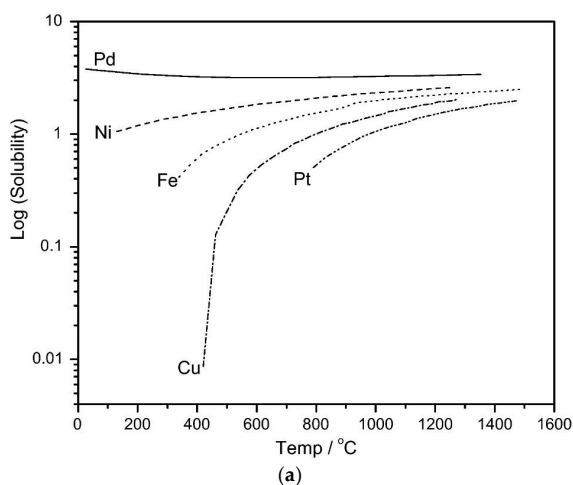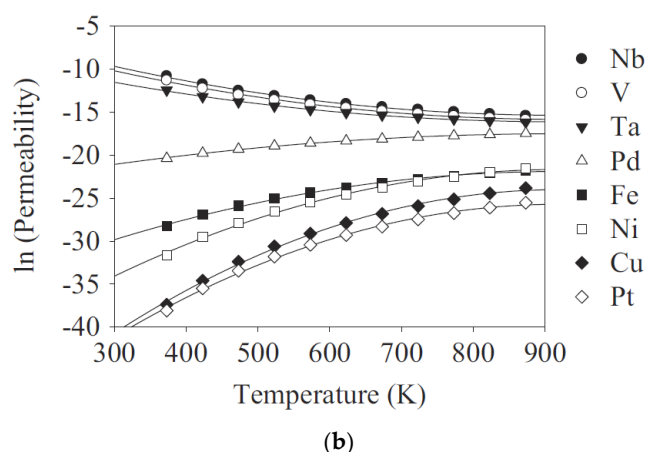

(a)

Figure 5. *Cont.*

(b)

Figure 5. (**a**) The hydrogen solubility in different metals at the pressure of 1 atm at different temperatures [72] and (**b**) the hydrogen permeability in different metals at different temperatures [76]. Figure 5**a** modified with permission of the authors of [72], Figure 5**b** modified with permission of the authors of [76].

A variety of methods have been developed to fabricate dense metal membranes, of which electroless plating (ELP), chemical vapour deposition (CVD) and physical vapour deposition (PVD) are the most common methods employed in laboratory fabrication at present. Herein, ELP is the most popular preparation method for dense metal membranes because of its excellent deposition ability on surfaces of different geometries, the simplicity of its fabrication facility and the lower cost of its manufacturing process. However, the ELP method is a complicated and time-consuming process, making it difficult to precisely control the membrane quality, especially for metal alloy membranes [72]. The principle of CVD preparation is to thermally deposit the metal film on the support by evaporating the volatile metal precursors. The benefits of utilizing the CVD method include the feasibility of large-scale manufacturing, the ability to prepare an ultra-thin membrane layer, better quality control, etc. However, the CVD method cannot precisely control the metal compositions of the alloy membranes, and it is a costly process because of the expensive metal precursors [77]. By using the PVD method, a nanoscale thin membrane layer can be achieved on the support, and the composition of the membrane cross layers can be adjusted accordingly. The PVD method can overcome many drawbacks of the other two methods, and there is no waste generated during the process by bombarding the solid precursors. However, the investment (magnetron sputtering) and maintenance of PVD equipment are very expensive [72,78].

Initially, dense metal and metal alloy membranes were fabricated with a self-supported tubular geometry with a thick wall of 40–100 µm to achieve sufficient mechanical strength. These first dense metal membranes indeed provided very attractive hydrogen separation performance in the early development. However, the overall low permeability and high cost of palladium strictly limited their economical practicality [79]. With regard to the solution-diffusion mechanism, the hydrogen fluxes through these dense metal membranes were dominated by the diffusion rate through the thick membrane walls. To achieve a favourable permeation flux, a supported ultra-thin metal membrane with a robust porous substrate is highly desired. Research and industrial interest has been devoted to these supported metal membranes, and many efforts have been made to produce well-integrated supported metal membranes [72]. At the same time, various porous substrates, such as alumina [80], stainless steel [81], glasses [82], etc., have been used as supports for the metal membranes. However, the fabrication of a defect-free supported metal membrane is a complex task, and many factors need to be considered to produce a reliable membrane. For example, the compatibility between the metal materials and the supports seriously affects the robustness of the membrane, as cracks can form at

high temperatures as the result of different thermal expansion coefficients between the metal materials and the supports [83].

3.1. The Development of Dense Metal Membranes for Hydrogen Separation

Although dense metal membranes could provide "infinite" hydrogen selectivity, they also suffer from several serious problems in practical application. Taking the most common Pd membranes as an example, pure Pd membranes experience a transition from α to β phase when operated with hydrogen at a temperature below 300 °C and a pressure lower than 2 MPa, which is called the hydrogen embrittlement phenomenon. This phase transition phenomenon could lead to volume expansion and internal stress in the membrane structures, ultimately resulting in selectivity loss of the membranes. In addition, palladium membranes are very easily poisoned by chemical contaminants, such as sulphur, carbon monoxide, hydrocarbons, etc., since these contaminants can inhibit hydrogen permeation by forming CH_x species and Pd compounds with S and C on the membrane surface [71–76]. Many attempts have been made to address these problems, and some of the strategies have been proven effective to avoid these failures. To date, alloying different metals is the most practical and universal method to fabricate robust dense metal membranes [71].

There are a multitude of possible alloys from different metallic element pairs, but the Pd-based alloys have attracted the most attention from both the research and engineering perspectives [71]. Among the Pd-based alloys, the Pd-Ag membrane is the most studied in recent decades; the first patent on the Pd-Ag membrane can be traced back to the 1950s [84]. The addition of Ag, on one hand, improves the mechanical strength and stability of the Pd membranes [71]; on the other hand, it can enhance the permeability up to 5 times compared to pure Pd membranes [30,80]. The ELP method has been well developed and widely used for the fabrication of Pd-Ag alloy membranes. Pd-Ag membranes can be fabricated by either simultaneous ELP [80] or sequential ELP [85]. Recently, Tanaka et al. reported an ultra-thin (approximately 1 μm) Pd-Ag membrane produced by a simultaneous ELP method. They reported that the membrane had a H_2 permeance of 9.0—9.4×10^{-6} mol·m^{-2} s^{-1} Pa^{-1} and H_2/N_2 selectivity between 3300 and 2000 at 400 °C. In addition, the membrane performance remained stable for over 100 h under an environment containing CO [80]. However, this Pd-Ag membrane was still sensitive to the presence of sulphur and chloride because Ag could not resist sulphur and chloride poisoning [71]. Apart from Pd-Ag, Pd-Cu and Pd-Au are the other two most thoroughly investigated alloys for hydrogen separation membranes. The Cu alloy is believed to possess the ability to suppress the hydrogen embrittlement phenomenon and to resist poisoning by contaminants (sulphur, CO and CH_4). Additionally, the use of Cu can reduce the cost compared to pure Pd membranes [86,87]. However, the addition of Cu has been reported to significantly inhibit the hydrogen permeation flux [88]. Recently, Vanderspurt et al. examined the hydrogen separation performance of a commercial Pd-Cu alloy membrane manufactured by Power + Energy Inc. and found that the pure hydrogen permeability coefficient of the membrane (1.28×10^{-7} mol·m^{-1} s^{-1} Pa$^{-0.5}$) was comparable to the reported hydrogen permeability coefficient of pure Pd membranes. In addition, they investigated the performance of this commercial membrane by separating a stimulated syngas containing H_2S and found that the membrane had excellent poisoning tolerance with consistent performance over 1000 h at temperatures of 400–500 °C [89]. Pd-Au membranes were also found to exhibit enhanced poisoning resistance compared with pure Pd membranes. Unlike Pd-Cu alloys, the addition of a small amount of Au does not inhibit the hydrogen permeation but instead increases the hydrogen permeation by up to 30% [90]. In addition to the binary alloys, more complex alloys have also been studied with the aim of combining the advantages of different metals [71]. For example, Pd-Ag-Au alloy membranes were fabricated for hydrogen separation by Cornaglia et al. They found that the ternary alloy membrane with the addition of Au and Ag had comparable hydrogen permeance to the pure Pd membrane, while the sulphur poisoning resistance was significantly improved compared with pure Pd and Pd-Ag alloy membranes under testing conditions in the presence of H_2S [91].

In addition to the alloying strategy, other methods have also been developed to improve the stability of dense metal membranes. For instance, Kawi et al. tried to coat a Pd-Ag film layer onto the internal side of a hollow fibre support and compared this internal coating membrane to Pd-Ag alloy membranes with external coating. They found that the internal coating method could significantly improve the mechanical strength of the membrane and limit the structural damage from thermal expansion [92]. Xu et al. synthesized a Linde Type A (LTA) zeolite protective layer over the supported Pd tubular membrane. This composite LTA-Pd membrane efficiently suppressed the inhibition of hydrogen permeance in a propylene/hydrogen mixture at high temperature by using a molecular sieving mechanism to exclude the hydrocarbon molecules from the Pd surface [93]. For more details, some reviews on dense metal membranes have been published elsewhere [71–73,76].

3.2. Current Industrialization Status and Future Perspectives for Biomass Processing

After several decades of research and development, dense metal membrane technology has been commercialized and practically implemented for a variety of industrial applications. Currently, there are some reputable companies and research institutes providing dense metal membrane products and system solutions for hydrogen separation. Information on some available metal membrane products is listed in Table 4. It is worth mentioning that dense metal membranes are recognized as the hydrogen separation membrane with the best potential for the first large-scale industrial application [73,94]. Many pilot-scale demonstration studies are being conducted with newly developed dense metal membranes for hydrogen separation and CO_2 capture. The Center for Inorganic Membrane Studies at Worcester Polytechnic Institute (WPI) has made important progress in developing dense alloy membranes. Prof. Ma and his colleagues have manufactured pilot-scale tubular dense alloy membranes 2 inches in diameter and 6 inches long [30]. The Energy Research Centre of the Netherlands (ECN) is another reputable institute working on metal membrane research, and they have recently successfully demonstrated a pre-pilot-scale Pd-based membrane reactor for CO_2 capture under the EU CO_2 capture project [73]. The Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP) has been dedicated to developing ultra-thin layer dense alloy membranes with poisoning resistance for years. They recently reported the achievement of building a large-scale hydrogen purification plant with composite Pd-alloy membranes, and the performance of the system was found to be stable during long-term operation [73].

Table 4. Available commercial metal membranes for hydrogen separation [30].

Supplier	Material	Dimension Parameters	Applications	Performance
Hysep-Energy research centre of The Netherlands	Pd-Au/YSZ/SS	$0.04/0.1/0.5 \ m^2$	Example: Coal to fuel project in New Zealand	3.5-6 Nm^3/h with 99.5–99.995% hydrogen at 21 Bar pressure difference, from 33% reforming H_2
Power + Energy/United Technologies Research Center	Pd-Cu trimetallic alloy	-	Coal gasification Syngas	0.23 mol/m^2 s with 99.9999% hydrogen
Tokyo Gas	Pd-Y(Gd)-Ag/SS	-	reforming	40 Nm^3/h with 99.99% hydrogen
CRI/Criterion-Shell	Pd and Pd-alloy	OD: 2 inch. L:48 inch	-	40-70 $Nm^3/h \ m^2 \ h^1 \ bar^{0.5}$ with >99% hydrogen
REB	Pd and Pd-alloy	OD: 1/8 inch	fluidized bed membrane reactor	0.2 mol/m^2 s on Pd-Cu alloy membrane at 673K, 3.03 Bar of syngas conditions

Overall, dense metal membranes possess outstanding potential for hydrogen separation in industrial-scale applications. As mentioned above, this type of membrane can provide highly impressive hydrogen selectivity and produce an ultra-pure hydrogen product from a single separation step. In addition, the manufacturing methods of dense metal membranes are not difficult to scale up, and ready-made manufacturing experience of manufacture is well established among the companies proving metal membrane products. Moreover, several large-scale demonstrations have been conducted, and these works have proven the feasibility of using dense metal membranes under practical conditions, while long-term stability experiments are still in operation. In general, as reported from Lin's point

of view, it seems that dense metal membranes have the greatest chance to be first commercialized for large-scale pure hydrogen production from processes such as methane reforming and biomass processing [94].

There are also several challenges to be overcome before dense metal membranes can be widely promoted for hydrogen production from industrial processes, including biomass processing. The first practical concern of employing the dense metal membranes is their weak mechanical and chemical stability. In biomass processing, hydrogen exists as a part of syngas, which also contains CO, CO_2, hydrocarbons, moisture and sulphur compounds. Unfortunately, dense metal membranes are sensitive to these elements and can be damaged after exposure to these gases under certain conditions. Although several methods have been developed to address these instability problems, and some have been reported to be effective ways to enhance the stability, there are always drawbacks accompanying these strategies, such as the significant loss of gas permeability, increased manufacturing expense, etc. In addition, most of these strategies only slow the membrane failure or reduce the permeation inhibition to a certain extent, rather than fully solving the problems. Second, most dense metal and metal alloy membranes are fabricated from noble metals, such as palladium, silver and gold, whose price are always high and are dramatically affected by unpredictable political and market factors. As a consequence, the cost of investing in and maintaining a large-scale dense metal membrane system is tremendous. For these reasons, an ultra-thin selective layer is highly desirable not only to reduce the cost of the metals per area but also to increase the gas permeability, thus decreasing the total membrane area required. Accordingly, more efforts are expected to fabricate ultra-thin and well-integrated metal membrane layers. In short, we think the dense metal membrane possesses practical feasibility for hydrogen production from biomass processing. However, further research and development may give dense metal membrane systems greater economic efficiency for large-scale hydrogen production in the near future.

4. Microporous Membranes for Hydrogen Separation

Membranes with pore sizes smaller than 2 nm are classified as microporous membranes. This type of membrane normally possesses relatively high permeability with considerable selectivity and promising thermal and chemical stability [30]. Gas transport through these membranes mainly proceeds by Knudsen diffusion, surface diffusion and molecular sieving mechanisms. The transportation mechanism is determined by the adsorption characteristics and predominantly the difference between the kinetic diameters of the gas molecules and the pore size of the membranes. The molecular sieving mechanism is the most desirable since the size exclusion effects could result in the best selectivity [94,95]. Microporous membranes can be further divided into two main classes based on their structures, crystalline and amorphous. Crystalline membranes primarily include zeolite membranes and metal-organic framework (MOF) membranes, while silica membranes, carbon membranes and other metal oxide membranes are classified as amorphous membranes [30].

4.1. Zeolite Membranes

The first zeolites were found by the Swedish mineralogist Cronstedt in 1756, and he named the new materials "zeolites", which means boiling stones in Greek. After centuries of development, 229 unique types of zeolite frameworks have been identified, and 40 of them are naturally available minerals on the earth [96,97]. The general formula of these aluminosilicate crystalline minerals is $(SiO_2)_x(AlO_2)_y zMO_x aH_2O$, from which we can see that the main components of zeolites are silicate, aluminium and other metal oxide elements, such as sodium and titanium [98].

Zeolites is an important material in the chemical engineering industry because of its unique regular pore structures and robustness under harsh conditions. Currently, zeolite is extensively employed in commercial catalysts or catalyst hosts for noble metals. In addition, zeolite is a promising adsorbentand has great potential for hydrogen storage, etc. [99,100]. Zeolite is recognized as an ideal membrane material for gas separation because some zeolites have the unique pore aperture

sizes (0.3–1.3 nm) that are comparable to the scale of gas molecules [101,102]. Zeolite membranes are primarily fabricated through hydrothermal reactions within an autoclave reactor in a conventional oven or through microwave-assisted heating. There are two main strategies for zeolite membrane fabrication, in situ growth and seeded secondary growth. During in situ growth, the crystallization solution with or without organic templates is autoclaved with the porous support in a reactor. Then, the obtained green membrane is sintered to remove the organic templates to obtain the final zeolite membrane. In seeded secondary growth, nano-size zeolite particles are seeded onto the support prior to the secondary growth, which is subsequently carried out by immersing the seeded support with the fabrication solutions in the autoclave [103,104]. The bad news about zeolite membranes for gas separation is that although the subject has been investigated for decades, less than 20 zeolites have been successfully fabricated in membrane form, and even more unfortunately, only one zeolite membrane, NaA has been commercialized for industrial dehydration applications at this time [105]. The number of publications on different zeolite membranes, as shown in Figure 6, show that the most popular zeolite topologies for membranes are MFI (ZSM-5 and Silicate-1) and LTA, as these two topologies represent over half of the total publications on zeolite membranes [103].
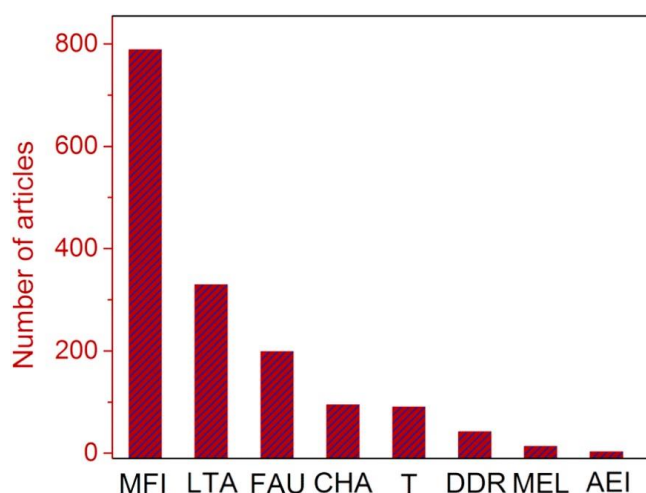

Figure 6. Number of publications for different zeolite topologies in Scopus. (zeolite T is an ERI-OFF intergrowth-type zeolite; MFI contains ZSM-5 and Silicate-1; CHA contains chabazite, CHA and SAPO-34 etc.). Figure modified with permission of the authors of [103].

In the application of hydrogen separation, several types of zeolite membranes, including MFI, LTA, SAPO-34, DDR, etc., have been reported in the last decade. Table 5 compares the kinetic diameters of several gas molecules and the aperture size of some zeolite topologies. From Table 5, we can see that the pore sizes of these zeolites are larger than the kinetic diameters of the gases in syngas. Hence, all these zeolite membranes have relatively low hydrogen selectivity under the Knudsen diffusion mechanism, and their performance is unfavourable for hydrogen separation and purification. Therefore, a modification process for zeolite membranes is necessary to achieve acceptable hydrogen selectivity.

Chemical vapour decomposition (CVD) and chemical cracking decomposition (CCD) are widely used to improve the performance of the ZSM-5 membrane, as these modification methods can result in an impressive improvement in H_2/CO_2 selectivity [106–109]. Lin et al. post-treated ZSM-5 membranes in two steps. First, CVD was carried out to compensate for the defects by sintering tetraethyl orthosilicate (TEOS) into the inter-crystalline gaps. Subsequently, CCD was used to introduce methyldiethoxysilane (MDES) and simultaneously to sinter the MDES to SiO_2 in the pores to reduce the ZSM-5 pore size. The H_2/CO_2 selectivity of the ZSM-5 membrane was significantly improved from 4.3 to 4.92 after CVD and further to 25.3 after CCD. However, the hydrogen permeation decreased by

more than one order of magnitude compared to the as-fabricated ZSM-5 membrane [106]. In addition, that group also prepared a tubular ZSM-5 membrane with the same modification methods and used the modified ZSM-5 membrane to construct a membrane reactor for the water gas shift reaction. This membrane reactor showed good thermal stability during long-term operation at high temperature and in a humid environment [106]. At almost the same time, Dong et al. reported similar work using a modified MFI membrane for a membrane reactor in high-temperature WGSR [108], while Xu et al. used a modified ZSM-5 membrane-based reactor for low-temperature WGSR [109].

Table 5. Comparison between kinetic diameters of specific gas molecules and the aperture pore size of some zeolite topologies.

Gas	Kinetic Diameter (Å)	Zeolites	Aperture Pore Size (Å)	MOFs and ZIFs	Aperture Pore Size (Å)
H_2	2.89	MFI	5.4	ZIF-7	3.0
CO_2	3.3	NaA	4.1	ZIF-8	3.4
N_2	3.64	SAPO-34	0.38	ZIF-22	3.0
CO	3.76	DDR	3.6×4.4	ZIF-90	3.5
CH_4	3.8	NaP-GIS	4.5×3.1	MOF-5	15.6
SF_6	5.5	$AlPO_4$	4.0	HKUST-1	9

In addition to MFI membranes, SAPO-34 membranes have also been extensively studied in recent years. The H_2/N_2 and H_2/CH_4 selectivity of SAPO-34 membranes were reported to be 25 and 7.4, respectively, with H_2 permeance of 2.4×10^{-8} mol/s·m²·Pa at 27 °C and 270 KPa. However, the H_2/CO_2 selectivity was very poor, only 1.3, under the same conditions [110]. Interestingly, subsequent work from Noble's group found that the SAPO-34 membrane had CO_2/H_2 selectivity greater than 100 at −20 °C due to enhanced CO_2 adsorption and inhibited H_2 adsorption at low temperature. However, the CO_2 permeation was still at a relatively low level of approximately 10^{-8} mol/s·m²·Pa [111]. The NaA membrane was fabricated by a microwave-assisted heating method and tested for hydrogen separation from hydrocarbons. The result showed that the NaA membrane had H_2/N_2 and H_2/n-C_4H_{10} selectivity of 3.18 and 11.8, respectively, with a very promising H_2 permeance of 2.13×10^{-6} mol/s·m²·Pa under the testing conditions [112]. DDR (Deca-Dodecasil3R) is a highly siliceous zeolite with a small aperture pore size of 0.36×0.44 nm, as shown in Table 5. Early work reported that a DDR membrane on a porous α-Al_2O_3 support had a low H_2 permeance of 1.1×10^{-10} mol/s·m²·Pa with H_2/CO and H_2/CO_2 selectivity of 11 and 9, respectively, at 500 °C [113]. However, Dong et al. recently published their work on a DDR membrane modified by the liquid phase chemical deposition of tetramethoxysilane (TMOS), and their membrane showed a good CO_2/CH_4 selectivity of 92 and a CO_2 permeance of 2.1×10^{-7} mol/s·m²·Pa at room temperature. However, the H_2 permeation was slower than that of CO_2 after the modification due to the strong CO_2 adsorption, which is not favourable from a hydrogen separation perspective [114]. A P-type zeolite GIS membrane was in situ fabricated on a porous α-Al_2O_3 support and tested for gas separation in Lin's group. The GIS membrane showed a H_2/SF_6 selectivity of 102, which is far better than the Knudsen diffusion separation selectivity, and a H_2/Ar selectivity of 5.29 with a H_2 permeance of 5.71×10^{-7} mol/s·m²·Pa at room temperature. In addition, they reported that the GIS membrane was more stable in a humid environment during a phase transformation process at moderate temperature [104]. An $AlPO_4$ membrane was prepared by Caro's group and had an acceptable H_2/CO_2 selectivity of 11, which is greater than that of the other reported zeolite membranes because of the low CO_2 adsorption on the cation-free LTA zeolite membrane surface. In addition, the $AlPO_4$ membrane provided a H_2/CH_4 selectivity of 146 with a H_2 permeance of 2.63×10^{-7} mol/s·m²·Pa through a molecular sieving mechanism [115].

Generally, the primary benefits of zeolite membranes for hydrogen separation and purification are their hydrothermal stability under the high-temperature and humid conditions that accompany hydrogen production reactions, such as biomass processing. In addition, their moderate to high gas permeability compared to dense metal and polymeric membranes could be another considerable

factor in gas separation applications. However, the application progress of zeolite membranes for gas separation is much slower than predicted, as mentioned above [105]. This delay may be attributed to the difficulty of scaling up zeolite membrane processing, including both the membrane manufacturing and the membrane maintenance on site. Furthermore, the cost of zeolite membranes is relatively high due to the low reproducibility of defect-free zeolite membranes. From the perspective of hydrogen separation in biomass processing, most zeolite membranes are not able to provide satisfactory H_2 selectivity against other syngas components, such as CO_2, CO, etc., because the aperture size of most zeolites is larger than the gas molecule cutoff sizes. Although post-treatment processing could greatly enhance the selective performance, these modification processes significantly increase the expense and further reduce the gas permeation of the zeolite membranes.

4.2. MOF Membranes

Metal-organic frameworks (MOFs) are a class of porous crystalline materials netted with metals or metal clusters as the vertex nodes linked by organic linkers. Apart from its high surface area and structural robustness, the most distinguishing feature of MOFs is their topology diversity with tunable pore sizes. This diversity occurs because their structures can be tailored by assembly from combinations of different metal nodes and organic linkers [116–118]. Since the first prototype MOF-5 was introduced, a variety of MOF materials have been developed. Recently, some of them have been successfully commercialized for gas delivery and food storage. However, the mechanical strength and structural stability of MOF materials are not as good as those of zeolites, because of their coordination network structures with the organic linkers. Herein, ZIF is a subclass of MOF materials consisting of transition metals linked by imidazolate bridging linkers. In ZIF structures, the metal—imidazolate—metal bond has an angle of 145°, which is the same as the Si (Al)-*O*-Si (Al) angle in zeolite structure. Therefore, ZIF materials were found to be more stable than other MOFs due to their zeolitic structures. To date, MOF and ZIF materials have been employed in various application areas, such as separation and adsorption, catalysis, drug delivery, sensors, etc., because of their adjustable porous structures and high surface areas [119–122].

An advantage of MOF membrane research is that the pre-developed facilities for zeolite membrane fabrication could be easily reproduced for preparing MOF membranes [104]. The primary synthesis methods for MOF membranes are also in situ growth and seeded secondary growth, and the other fabrication strategies applied for zeolite membranes, for example, microwave-assisted heating fabrication and post-treatment modification methods, could also be applied to MOF membrane fabrications [123]. However, the synthesis conditions of MOF membranes are milder than those of zeolite membranes, and the time required is shorter. For instance, ZIF-8 membrane can easily be prepared in aqueous solution at room temperature in 6 h [124]. The similarity of fabrication to that of zeolite membranes reduced the barrier to initiating MOF membrane research and could account for the blooming development of MOF membranes in recent years.

In gas separation applications, MOF membranes, especially ZIF membranes, have attracted extensive attention in the last decade. Several studies have been published reviewing ZIF membranes for gas separation and comparing their performance with that of zeolite membranes [105,123,125–127]. The publication numbers on ZIF membranes for gas separation have been organized by Koros et al. as shown in Figure 7, where we can see that the ZIF-8 membrane is the most popular, accounting for over 70% of the total ZIF membrane publications, and almost half of these ZIF membrane publications aimed at hydrogen separation [125]. The pore sizes of several representative MOF materials for hydrogen separation membranes are illustrated in Table 5.

ZIF-8 was reported to have the aperture pore size of 3.4 Å, which was larger only than the kinetic diameters of hydrogen and carbon dioxide. This unique pore size led to the expectation that ZIF-8 membranes could be used to separate hydrogen from other, larger molecular gases, such as CO and CH_4. Caro's group reported their first ZIF-8 membrane for gas separation in 2009. That ZIF-8 membrane showed a hydrogen permeance of 6.04×10^{-8} mol/s·m²·Pa in a single-gas permeation

test at room temperature, with H_2/CO_2 and H_2/CH_4 separation factors of 4.54 and 12.58, respectively. In their study, the hydrogen permeance was relatively low due to the thick ZIF-8 membrane layer, greater than 30 μm thick. In addition, they claimed that the large CH_4 molecule (kinetic diameter of 3.8 Å) could permeate through the membrane because the ZIF-8 structure was more flexible than its natural network during gas permeation, thus resulting in a molecular cutoff of the ZIF-8 membrane that was larger than its ideal pore size [128]. Since then, many studies have been undertaken to investigate the experimental parameters for controlling the MOF and ZIF crystallization process and, in turn, the membrane morphologies [129,130]. At the same time, studies were also carried out to investigate the gas permeation transportation mechanism through MOF membranes. Koros's group proposed that the effective aperture size of ZIF-8 was 4.0–4.2 Å, a conclusion drawn from its sharp cutoff separation performance for propylene (4.0 Å) and propane (4.2 Å) [131]. Lai et al. developed a rapid synthesis method for ZIF-8 nanocrystals in an aqueous system, and subsequently, a ZIF-8 membrane was also fabricated from an aqueous system at room temperature in their group [132,133]. The fabricated membrane was tested for propylene and propane separation for the first time, and a very promising application opportunity for ZIF-8 membrane was found because the propylene/propane separation factor was greater than 50 [124]. Later, ZIF-8 membranes began to be fabricated on hollow fibre supports, and the thickness of the membrane layer was further reduced to approximately 1 μm. Additionally, the hydrogen permeance was significantly improved to 15.4×10^{-7} mol/s·m²·Pa at room temperature, with H_2/CO_2 and H_2/CH_4 separation factors of 3.85 and 11, respectively [134]. Recently, an attempt was made to grow a ZIF-8 membrane on hollow fibre polymeric supports to reduce its fabrication expense by blending the ZIF-8 seeds into the polymer support layers followed by growing the membrane via secondary growth [135].
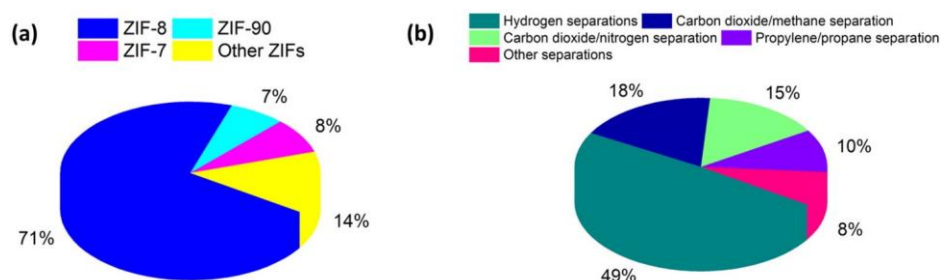

Figure 7. Publication information of ZIF membranes for gas separations. (**a**) ZIF materials and (**b**) application areas of ZIFs. Figure modified with permission of the authors of [125].

Compared with ZIF-8 membranes, ZIF-7 and ZIF-22 membranes could provide better H_2/CO_2 separation factors because of their pore size of 3.0 Å, which lies between the kinetic diameters of hydrogen and carbon dioxide, as shown in Table 5. Li et al. fabricated a ZIF-7 membrane on an alumina plate support through the secondary growth method. That ZIF-7 membrane had H_2/CO_2 and H_2/N_2 separation factors of 13.0 and 20.7, respectively, in a single-gas permeation test at 220 °C, with H_2 permeance of 4.55×10^{-8} mol/s·m²·Pa. In addition, the ZIF-7 membrane structure was found to be stable after operation under simulated WGSR conditions at 220 °C for 50 h [136]. Additionally, the ZIF-22 membrane fabricated in Caro's group showed H_2/CO_2 and H_2/N_2 separation factors of 8.5 and 7.1, respectively, at 323 K, with hydrogen permeance of 2.02×10^{-7} mol/s·m²·Pa [137]. Caro's group also developed a steam-stable ZIF-90 membrane with a thickness of 20 μm on an alumina support for hydrogen separation [138]. The ZIF-90 membrane had a hydrogen permeance of 2.5×10^{-7} mol/s·m²·Pa at 473 K, with H_2/CO_2 and H_2/N_2 separation factors of 7.2 and 12.6, respectively. In addition, the membrane was tested under a steam environment for 24 h, and the H_2/CH_4 separation factor was approximately 15 and was kept stable during long-term operation. MOF-5 and HKUST-1 membranes were also fabricated. However, they had poor hydrogen separation

with only Knudsen diffusion selectivity due to the larger pore aperture sizes in these two framework structures [139,140].

In conclusion, MOF membranes are still in a period of fast development, and more emerging structures are being identified at this time. The structural diversity and tunable pore size are the most attractive properties making MOF membranes a promising candidate for many potential gas separations. As a result, the gas separation performance of MOF membranes is dramatically greater compared with that of other membranes, such as polymer and dense metal membranes. As shown in Figure 8, the H_2/CO_2 separation performance of all the ZIF membranes was predicted to lie in the right upper side of the Roberson Upper Boundary [119]. In addition, the large-scale manufacturing of MOF membranes is not considered difficult because MOF membranes could be fabricated under the relatively mild conditions of an aqueous system at ambient temperature and pressure. However, MOF membranes also face some critical challenges before they can be used in practical industry processes, such as biomass processing for hydrogen production. First, MOF membranes suffer from low hydrothermal stability at high temperatures and in humid environments. Although the MOF and ZIF materials were initially considered to be thermally and chemically stable in various environments [122], recent studies have noted that the stability of these MOF materials and their membranes was not as good as we expected, especially under harsh reaction conditions for long-term operation [141–143]. Second, although MOF membranes possess acceptable overall hydrogen separation performance, the gas permeances are still in the range of 10^{-8}–10^{-6} mol/s·m^2·Pa, which is still relatively low compared with industrial demands. To address this low permeance limitation, efforts have been made to fabricate an ultra-thin membrane with a selective layer several nanometers thick. Yang et al. recently prepared a ZIF-7 membrane with nanometre thickness by using 1-nanometer sheets as the building block, and the membrane showed ultra-high hydrogen permeability and enhanced H_2/CO_2 selectivity [144]. Another challenge is to improve the reproducibility of the gas separation performance of the fabricated MOF membranes. The low reproducibility of these well-integrated crystalline membranes (MOF and zeolite) is the universal challenge from both the research laboratory and manufacturing perspectives. Therefore, the development of reliable fabrication processes with high product reproducibility is another prerequisite for the industrialization of these membranes.
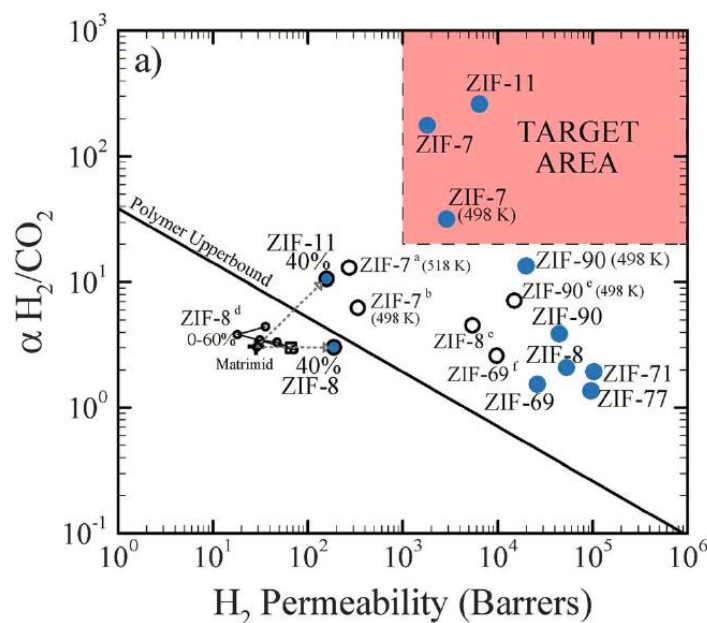

Figure 8. Predicted intrinsic (solid) and experimental (empty) H_2/CO_2 separation performance of ZIF membranes. Figure modified with permission of the authors of [119].

4.3. Other Microporous Membranes

The silica membrane is the most famous amorphous microporous membrane and has been investigated for hydrogen purification for many years. One advantage is that the pore structure of the silica membrane is controllable, and gas separation performance can correspondingly be adjusted [145]. Sol-gel and chemical vapour deposition are the two main methods for silica membrane fabrication. Silica membranes prepared by sol-gel methods often have relatively low selectivity but good permeability, and the pore size of the membrane can easily be adjusted by changing the fabrication conditions. However, this sol-gel process has low reproducibility, and it is difficult to achieve consistent performance [146]. In contrast, silica membranes fabricated from CVD can provide high hydrogen selectivity but correspondingly low permeability. However, the cost of the CVD method is high, and the method is difficult to scale up for commercial manufacturing [145]. Verweij et al. reported their work on high-selectivity high-flux silica membrane fabrication. Their silica membrane was fabricated from optimized conditions. and it possessed hydrogen permeance of 5×10^{-6} mol/s·m^2·Pa at 200 °C in single-gas permeation testing, coupled with H_2/CO_2 and H_2/CH_4 selectivity of 71 and over 4000, respectively [147]. The most crucial concern in employing silica membranes is the instability at high temperature in the presence of water, because such membranes lose permeability and selectivity rapidly after exposure to high-temperature steam due to densification of the pore structures [94]. To date, the most efficient way to overcome this instability is to dope a metal or metal oxide into a silica membrane. Tsuru et al. reported a cobalt-doped silica membrane with hydrogen permeance of 1.8×10^{-7} mol/s·m^2·Pa and H_2/N_2 selectivity of approximately 730 at 500 °C. This membrane performed stable gas separation for 60 h at 500 °C in the presence of steam [148]. Moreover, silica-based membrane reactors have been studied for the low-temperature water gas shift reaction, and the utilization of this membrane reactor was able to shift the limited reaction equilibrium and correspondingly significantly improve the CO conversion and the hydrogen recovery [149,150]. However, the low hydrothermal stability of silica membranes also seriously strained the operation duration of these membrane reactors.

In addition, amorphous metal oxide membranes and carbon membranes have also been developed for hydrogen separation, and both of these membrane types presented some advantages for hydrogen separation. For example, higher H_2 selectivity has been observed for carbon membranes because of the molecular sieving mechanism, while metal oxide membranes usually provide high permeance. Correspondingly, the weaknesses of these membranes are very obvious, namely, low permeability for carbon membranes and low selectivity for metal oxide membranes. These shortages critically hinder the further application of these membranes in the industry [94,151].

5. Membrane Reactors for Hydrogen Separation

The membrane reactor (MR) system is a unit that combines the processes of catalytic reactions and membrane separation. The concept of the membrane reactor was first proposed in the late 1960s, but most of the development progress has been achieved only in the last 20 years. Most of the MR publications and patents were also awarded during this period [152]. The recent rapid development of MR systems could be attributed to the emergence of new membrane materials and membranes with good performance. The development of membranes and membrane materials has further achieved advantages for membrane reactors during practical applications [27]. According to the membrane and catalyst combination methods, MRs can be classified into packed bed membrane reactors (PBMRs) and catalytic membrane reactors (CMRs). As shown in Figure 9, a PBMR is constructed with the packed bed catalytic layer and the membrane separation layer separate (Figure 9a), whereas the membrane surface in a CMR shows catalytic activities for the reactions because these membranes either incorporate the catalyst within their porous structures (Figure 9b) or are self-catalytically active (Figure 9c) [153]. According to their functions, MR configurations can be categorized as extractors, distributors and active contactors, as shown in Figure 10. For example, the MR system configuration for water gas shift reactions is the extractor. By removing the hydrogen produced, the reaction conversions

can be improved through either shifting the thermodynamic equilibrium or enhancing the reaction rate [154,155]. To date, the membrane reactor has been successfully demonstrated for various chemical reactions, including dehydrogenation reactions, hydrogenation reactions, partial oxidation reactions and catalytic decomposition reactions [154]. Clearly, using a membrane reactor can provide many advantages compared with the traditional reaction and separation process, such as the enhancement of productivity, a single step to purified production, easy control of the reactants and a simple process with lower capital cost [15,27].
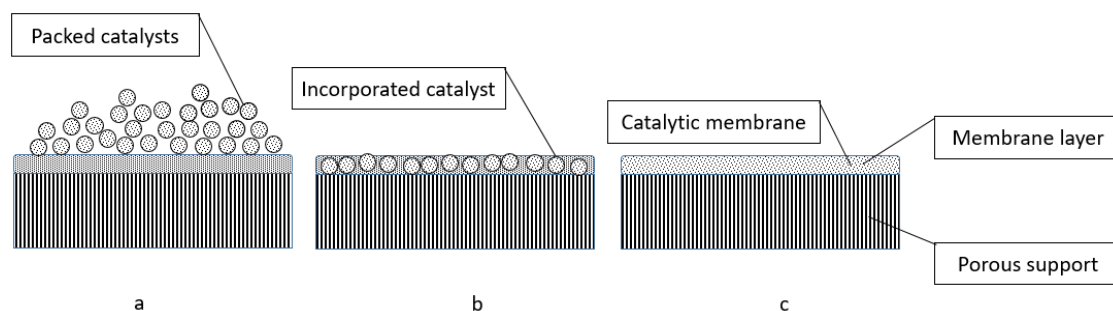

Figure 9. The two membrane reactor types: (**a**) packed bed membrane reactor; (**b**,**c**) catalytic membrane reactors.
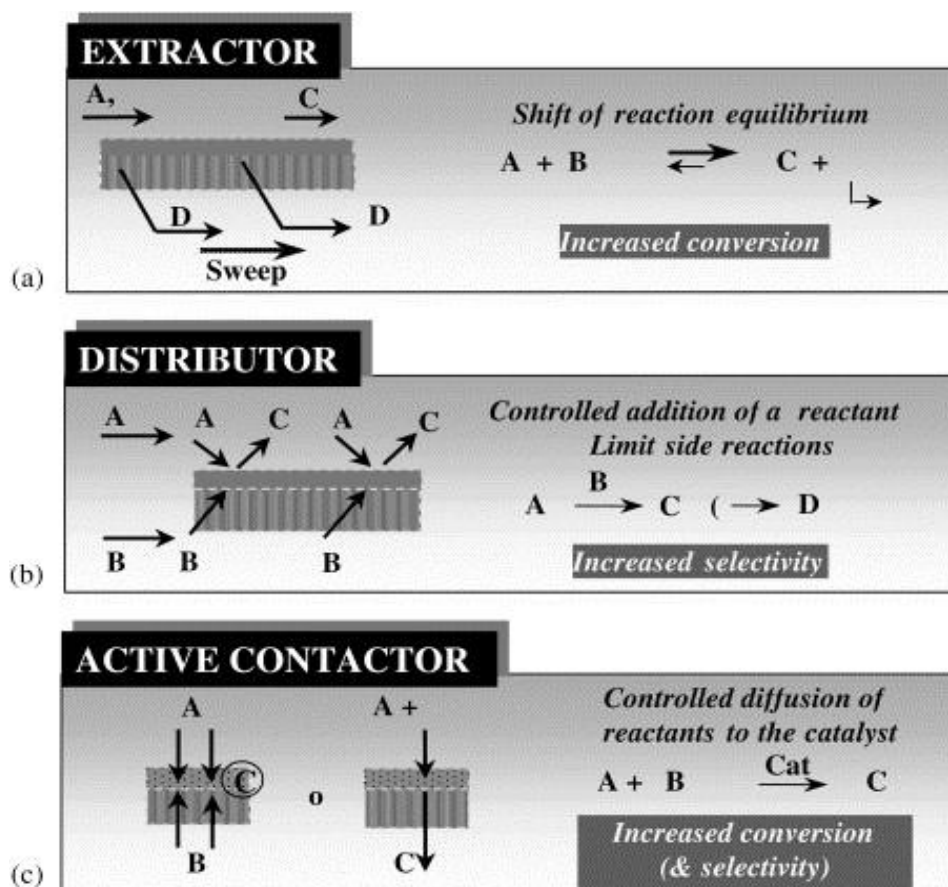

Figure 10. The three main membrane functions of the membrane reactors. Figure modified with permission of the authors of [153].

Membrane reactors for hydrogen production are primarily applied for the steam reforming reaction (SRR) and water gas shift reaction (WGSR) [15]. For SRR and WGSR processes, the MR system can provide the benefits of (1) higher CH_4 and CO conversions with respect to the equilibrium, (2) recovery enhancement of the purified hydrogen; (3) the ability of CO_2 capture, etc. [149,154,155]. Considering the harsh reaction conditions of SRR and WGSR, most membrane reactors for hydrogen production have been constructed with dense metal membranes and some robust microporous membranes. Generally, dense metal membranes have been reported to exhibit better performance than microporous membranes in past studies because of their ultra-high hydrogen selectivity [15]. Apart from the gas separation performance, to select a membrane for MR in a specific application requires a comprehensive feasibility evaluation, ranging from its hydrothermal/chemical stability to its gas permeation capability.

Drioli et al. conducted the water gas shift reaction with a Pd membrane-based catalytic membrane reactor [154]. This Pd membrane was fabricated on a composite alumina support (λ-Al_2O_3/α-Al_2O_3) through the co-condensation method, and the membrane showed hydrogen permeance of 6.25×10^{-8} mol/s·m²·Pa with a H_2/N_2 separation factor of 8.24 at 595 K and 103.6 kPa in the single-gas permeation test. By optimizing the operation parameters, CO conversion of 99.89% could be achieved at 595 K, overcoming the WGSR equilibrium limit (84%) at this temperature. In addition, the membrane was largely stable after two months of operation under the WGSR conditions. Costa et al. reported a cobalt-doped-silica-based membrane reactor for the low-temperature water gas shift reaction [149]. By applying this MR, the hydrogen produced on the permeate side of the MR was two times purer compared with the conventional packed bed reactor. In addition, CO conversion of 12% higher than equilibrium was achieved at 250 °C and at a space velocity of 75,000 h^{-1}. In the stability test, the gas separation performance was well maintained in 2 weeks of operation under the WGSR conditions. Recently, Liguori et al. developed a Pd membrane reactor for the natural gas SRR reaction under low-temperature and low-pressure conditions. The Pd membrane was prepared by the ELP method on a porous stainless steel support and showed infinite H_2/Ar and H_2/He selectivity at 400 °C with a low pressure difference. This membrane reactor recovered a maximum of 82% hydrogen with 100% purity and could successfully convert 84% of the feed methane at 400 °C and 300 kPa.

In addition to the membrane materials and performance, the operating conditions coupling with the engineering design also significantly affect the overall performance of MR systems. Drioli et al. studied the influence of the water/CO molar ratio on the performance of their Pd membrane-based MR in WGSR and reported that increasing the water/CO ratio resulted in higher CO conversion; however, the excess water would block the paths for hydrogen diffusion and seriously decrease the hydrogen permeation [154]. Lee et al. found that the CO conversion and catalytic efficiency could be enhanced when the WGSR was conducted in an MR at high pressure, since the high pressure in the reaction chamber in turn increased the driving force for hydrogen permeation [156]. Costa et al. studied the effect of space velocity (SV) on the MR performance in WGSR and suggested that the CO conversion and hydrogen purity could be improved by increasing SV [149,150]. It is worth mentioning that most of the MRs were operated at a relatively high SV to maximize the H_2 selectivity of the membrane at the low stage cut. However, the high SV also results in decreased energy utilization efficiency and negligible ability to shift the equilibrium limitations in the MR system.

The use of MRs is a very promising strategy to improve the energy efficiency and hydrogen productivity in biomass processing. As mentioned above, syngas, bio-oil and light hydrocarbons generated in pyrolysis and gasification processes, etc., are always realistic intermediates for hydrogen production from biological resources. Thus, the application of MR to biomass-derived hydrogen production is most likely to be employed in the SRR and WGSR after the preliminary biomass conversion. However, the high humidity and contaminant levels (sulphur and heavy hydrocarbons) in syngas are great challenges for MR development in biomass processing. All in all, the development

of robust and high-performance gas separation membranes is the crucial factor determining the application feasibility of MRs.

6. Conclusions and Future Perspective

Hydrogen production from biomass processing is considered one of the potential solutions for the energy crisis. Gas separation and hydrogen purification are a very important process in biomass systems for hydrogen production, and gas separation membranes have been recognized as an efficient and environmentally friendly technology for extracting hydrogen. This comprehensive review covers (1) the technical development of hydrogen separation membranes from different materials and (2) the practical feasibility of using these hydrogen separation membranes for hydrogen production and purification in biomass processing.

First, general information on hydrogen energy systems and the processes for hydrogen production from biomass are introduced. Afterwards, the background of membrane technology for hydrogen separation is presented, and the requirements of membranes for producing hydrogen from biomass are discussed. The development of polymeric membranes for hydrogen separation is reviewed first. We summarize the hydrogen separation performance of various polymeric membranes with different fabrication and modification methods. In addition, the available polymeric membrane products for hydrogen separation are discussed, and their potentials for hydrogen separation in biomass processing are assessed. We conclude that most of the current polymeric membranes could only be used for hydrogen separation at low temperatures. Although the emerging PEI and PBI membranes have been reported to be capable of functioning in high-temperature environments, their high price and moderate gas permeation performance make them economically inefficient for practical applications. In contrast, dense metal membranes exhibit excellent thermal stability and ultra-high hydrogen separation performance. Similar to polymeric membranes, dense metal membranes have also been commercialized and are employed for high-purity hydrogen production in industry. Nevertheless, dense metal membranes also exhibit some problems during the gas separation process, including their hydrogen embrittlement phenomenon at low operating temperatures and their sensitivity to sulphur and carbon poisoning. Accordingly, metal alloying methods have been employed to enhance their structural robustness and to improve their gas permeation performance. Overall, dense metal membranes are believed to have the greatest potential to be employed in large-scale gas separation plants, on the premise of successfully reducing the required capital investment and improving their anti-poisoning ability.

The microporous membranes of zeolite, MOF and silica membranes were also introduced in his review. Both the zeolite and MOF membranes possess unique pore structures for gas separation through either preferred molecular sieving or other mechanisms, such as Knudsen diffusion etc. Unfortunately, the low intrinsic hydrogen selectivity of zeolite membranes make them unfavorable for practical applications, while the poor hydrothermal and chemical stability appear to be critical weaknesses that restrict applications of MOF membrane. In addition, the low reproducibility during the fabrications of the abovementioned crystalline membranes also prevent them from industrial application. By contrast, the gas permeation and separation performance of amorphous silica membrane could be easily controlled by adjusting the pore sizes during the fabrication process. However, the application of silica membrane is restrained due to its structure vulnerability when exposing to steam. Furthermore, the benefit and possibility of employing the membrane reactor for hydrogen production in biomass process was analyzed in this review.

For future development, there are mainly three considerations for improvement of hydrogen separation membranes toward practical applications. Firstly, development of new materials for hydrogen separation membrane is high demanded. Although many materials are applicable for fabricating hydrogen separation membrane as reported in the literature, the performance of these membranes are still not satisfactory for large scale practical applications, especially under harsh operation conditions. Hence, further efforts are required to develop an industrial membrane material,

such as mixed matrix materials, with an improved hydrogen separation performance, enhanced thermal and chemical stability and a low production cost. Secondly, more research efforts are also needed towards more robust membrane fabrication methods. In order to achieve a more permeable membrane with considerable mechanical strength, reliable/reproducible fabrication methods are highly desired for supported membrane with an ultra-thin selective layer. Thirdly, more research attentions are expected to focus on the design and operation of the hydrogen membrane system. The application of gas separation membrane system is always coupled with other processes in the industry. Therefore, many practical parameters in the upstream and downstream processes need to be considered during the membrane system design in order to maximize the membrane performance, as well as the overall system efficiency.

Conflicts of Interest: The authors declare no conflict of interest.

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