Membrane Reactors for Hydrogen Production from Renewable Energy Sources

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Abstract

To create an emission-free energy supply for the future, an increased expansion and integration of renewable energies into the existing energy system is necessary. In this energy transition, hydrogen plays a key role. As a feedstock for synthetic fuels or chemicals, or as a fuel itself, hydrogen alleviates energy fluctuations caused by the highly volatile character of renewable energy sources. In many of the processes to hydrogen, membrane reactors are applied. They combine hydrogen production and separation in one unit and are therefore very compact. In this short review, recent developments in membrane reactors in the framework of renewable energy via two examples, ammonia decomposition and biogas reforming are presented.

Keywords: membrane reactors, renewable energy, hydrogen production, hydrogen purification, ammonia cracking, reforming

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1. Introduction

In 2019, 80.9 % of the world's primary energy consumption was met by fuels from crude oil (30.9 %), coal (26.8 %) and natural gas (23.2 %) [1]. The combustion of these fossil fuels creates CO_2 which is besides methane and nitrous oxide the main greenhouse gas responsible for global warming [2]. To avoid environmental disasters with extreme impacts on ecosystems, human health, agriculture and the economy, the usage of fossil fuels has to

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be reduced significantly [3]. This can only be achieved by comprehensive expansion of renewable resources such as wind-, solar-, and geothermal energy, hydropower and biomass for a CO_2-neutral energy supply. To promote both, rapid expansion and integration of renewables into the energy sectors electricity, heat and transport the Renewable Energies Act (EEG) was established in Germany in 2000 [4]. One of its goals is the fast expansion of wind and solar energy, as well as the power grid with the aim to produce at least 80 % of the electricity from renewable energies by 2030. However, due to local weather and overall seasonal effects, wind- and solar energy have a highly volatile character and the existing energy system is not yet adapted to the occurring mismatch between energy supply and demand.

Power-to-X technologies can alleviate this mismatch. Storage of large amounts of energy over longer periods such as days, months or even years provide synergistic effects for the heat or mobility sector as well as for industry. Electrical energy can be converted into heat by using heat pumps, which is referred to as Power-to-Heat (PtH). Furthermore, electricity can be stored charging electrical vehicles, whereby the battery in the car can also be used to provide power back to the grid when renewable energy sources do not provide enough electricity (Power-to-Power, PtP). The production of synthetic fuels (methane, gasoline, diesel, kerosene, ammonia) or chemicals (methanol, ethylene and ammonia) in Power-to-Fuels (PtF) or Power-to-Chemicals (PtC) applications is useful for large distance transport due to the high energy density of the fuels or with regard to CO_2-neutral products [5]. Hydrogen plays a leading role in all these processes: Firstly, it is often the feedstock for the production of synthetic fuels and chemicals. Secondly, hydrogen can be used as a fuel in the transport sector as well e.g., for stationary power generation in households and industry, and as a chemical energy carrier [6]. In many of the processes to hydrogen, membranes are applied. In terms of process simplification, their integration into chemical reactors, so called membrane reactors, is discussed. The following review is devoted to recent developments of membrane reactors in the framework of renewable energy via two examples, ammonia decomposition and biogas reforming.

2. Membrane reactors: Assembly and configuration

Membrane reactors can be used for hydrogen production from renewable sources in reforming applications or its recovery from chemical hydrogen carriers like ammonia or liquid organic hydrogen carriers (LOHC) [7, 8].

Typically, the membrane acts as an extractor that selectively separates the product from the reaction zone. Through hydrogen partial pressure reduction, the thermodynamic equilibrium conditions are shifted and higher conversions can be achieved or the reaction temperature can be lowered. The latter is particularly beneficial for process heat integration. Depending on the selectivity of the membrane, hydrogen is separated with very high purity. In this way, additional efforts for purification can be avoided, e.g. for fuel cell applications [9, 10, 11, 12, 13].

Membranes must suit to the process, reaction temperature, pressure, reactants and possible interactions between membrane and catalyst must be taken into consideration. There is a wide range of membranes, whose properties, advantages and disadvantages are described in the literature [14, 9, 12, 11]. Inorganic (synthetic) membranes suitable for hydrogen processes are made of materials like carbon, ceramics, zeolite, or metals like palladium, gold, vanadium, silver and their alloys. These membranes operate at temperatures between 300 °C-800 °C, some withstand even up to 1000 °C. However, membranes made of e.g. palladium are expensive, thus they are usually applied on a porous support to reduce the membrane thickness at still high mechanical stability of the membrane. In addition, Pd-alloys (Ag, Cu, Ni and Pt) are often used to improve thermal and mechanical stability, to avoid embrittlement during thermal cycling or to enhance chemical stability against impurities like hydrocarbons and sulphur [15, 10, 16, 17, 18]. One has to keep in mind that a driving force for permeation across the membrane must exist, which is the gradient of the partial pressure between permeate and retentate side [19]. This gradient can either be created by a pressure difference between both sides, or by removing the component on the permeate side by a purge flow or vacuum.

3. Ammonia decomposition

Ammonia is discussed as chemical hydrogen carrier because it can be synthesized using renewable hydrogen and does not contain carbon in its molecule. Compared to hydrocarbons, no capturing of CO_2 is required for a CO_2-neutral synthesis. On the other hand, ammonia requires ultra-pure nitrogen for production [20]. Ammonia has a high hydrogen storage capacity (17.7 wt%) and can be easily liquefied at 20 °C and 8.6 bar [21]. As a fuel for gas turbines or ammonia fuel cells, it can be used directly to generate electrical energy [22, 23]. If hydrogen must be recovered, ammonia can also be split into hydrogen and nitrogen in an endothermic dehydrogenation ($\Delta_\mathrm{f}H^\circ = -20\,\mathrm{kJ\,mol^{-1}}$) [24]. Here, the main challenges are to ensure an effective heat input during the reaction and to separate hydrogen and from nitrogen.

Palladium and its alloys are the dominant materials for hydrogen separation due to their high hydrogen selectivity and permeability of palladium [25, 26, 18]. Jiang et al. compared three types of inorganic membranes for hydrogen production and purification from ammonia decomposition in a packed bed hollow fiber membrane reactor (PBHFMR). The membrane reactor with the dense 1.8 µm Pd/Ag membrane achieved ammonia conversions of $\geq 99.1\,\%$ and showed a high hydrogen selectivity as 99.99 % of the separated permeate consisted of hydrogen. This high selectivity could not be achieved by using a modified MFI zeolite membrane (8 µm on 1.5 mm Al_2O_3) or a carbon molecular sieve (CMS). Nevertheless, for applications where hydrogen quality standards are not that high, a modified MFI membrane with higher hydrogen and nitrogen selectivity might be preferred [27].

Omata et al. investigated ammonia decomposition on a $Ru/Cs_2O/Pr_6O_{11}$ catalyst with integrated hydrogen separation and purification by means of a 100 µm 10 mol % Fe vanadium membrane coated with a 200 nm thick 25 mol % Ag Pd-layer. The vanadium-based alloy serves as a support for the Pd/Ag catalytic layer, which is also a barrier against corrosive gases. Vanadium-based alloys are less expensive and possess higher hydrogen permeability than Pd-based alloys. However, there is still a large barrier to their practical application due to their poor resistance against hydrogen embrittlement, which means that the hydrogen concentration in the metal alloy needs to adjusted carefully [28]. The packed bed membrane reactor (PBMR) of Omata et al. shown in Figure 1 was successfully operated for 125 days, and 79 % of the released hydrogen could be separated from the gas flow at 3 bar. Compared to a reactor without membrane a significant increase in conversion due to hydrogen separation was observed. Hydrogen according to ISO 14687-2:2019 for fuel cells vehicles could be extracted [29].

While Omata et al. used a vacuum pump on the permeate side to increase the driving force for hydrogen separation across the membrane, Park et al. investigated the use of steam as sweep gas to improve the performance of their packed bed membrane reactor [29, 30]. It consisted of a Pd coated tantalum tube (Pd/Ta/Pd) filled with a Ru/La-Al_2O_3 pellet catalyst, which was coupled with a proton-exchange membrane fuel cell (PEMFC) with interjacent gas-liquid-separation. The observed H_2 permeation rate and NH_3 conversion

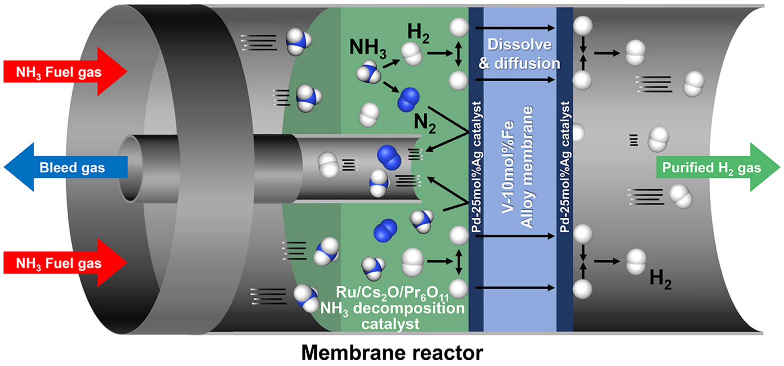
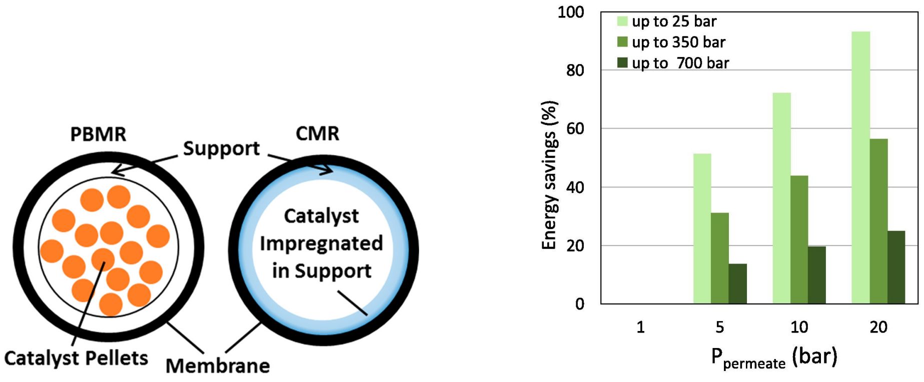


Figure 1: Schematic illustration of the packed bed membrane reactor (PBMR) of Omata et al., reprinted from [29] with permission from Elsevier, Copyright 2022

using steam as a sweep gas was similar compared to the conventional sweep gas nitrogen. However, the use of steam was beneficial as the gas-liquid separator acted as a buffer for ammonia traces in the permeate steam, protecting the fuel cell from damage caused by ammonia slip or membrane failure. Additionally, the humidfied hydrogen could be fed directly into the fuel cell, making additional processing steps for the separation of hydrogen and the sweep gas dispensable [30].

The packed bed membrane reactor (PBMR) is one of the most common membrane reactor configurations. The catalyst is confined in fixed bed configuration and in contact with a permselective membrane [31, 24, 32, 30]. However, this configuration has some disadvantages, as the heat transfer into the catalysis bed and the mass transfer of H_2 to the membrane may be challenging. In addition, abrasion of the membrane can occur in presence of particles. Itho et al. and Zhang et al. have investigated dehydrogenation in catalytic membrane reactors (CMR) [33, 34, 35]. In such reactor configuration, the membrane is either coated with catalyst or made from catalytic material (Figure 2a). Thus, the membrane may also participate in the reaction.

Industrial processes for ammonia cracking use a nickel catalyst and operate at temperatures above 600 °C [36]. The use of ruthenium can lower the reaction temperature [37, 26]. Thus, Itho et al. tried to lower the ammonia cracking reaction temperature below 400 °C by applying a tube-wall catalytic membrane reactor. They coated a ruthenium catalyst onto a porous γ-Al_2O_3 layer inside an externally heated 9 mm wide aluminium tube, to achieve a more uniform and direct heat input. Even without the use of a membrane,



(a) (b)

Figure 2: (a) Schematic illustration of the cross section of a packed bed membrane reactor (PBMR) and catalytic membrane reactor (CMR) from Zhang et al., reprinted from [35] with permission from American Chemical Society, Copyright 2019 (b) Energy savings for hydrogen compression resulting from the production of a pressurized permeate stream, reprinted from Cerillo et al. [32] under Creative Commons license

the tube-wall catalytic reactor (2 wt% Ru) showed a significant improvement in ammonia conversion compared to a 2 wt% Ru/Al_2O_3 packed bed reactor (PBR) due to better heat flux. The integration of a Pd-membrane into the tube-wall catalytic reactor further improved conversion by removing pure hydrogen from the reaction system. Two membrane types were tested, a composite membrane where a 2 µm thick Palladium layer was deposited on a α-Al_2O_3 tube and a 200 µm thick rolled tube composed of $Pd_{77}Ag_{23}$. The integration of the 200 µm $Pd_{77}Ag_{23}$ membrane into the tube reactor increased the reaction rate, however, chemical equilibrium could not be reached. A simulation showed that a further increase in conversion is feasible by decreasing the membrane thickness i.e., increasing the permeability of the membrane. The tube-wall composite Pd-membrane reactor finally achieved nearly 100 % conversion at 375 °C and therefore significantly increased the ammonia conversion [33].

Zhang et al. developed a catalytic membrane reactor (CMR) for ammonia decomposition by embedding a ruthenium catalyst within the outer mesopourous layer of a yttrium-stabilized zirconia (YSZ) tube which was coated with a 6 µm Pd film applied by electroless plating [35]. By placing the catalyst within the porous tube, the distance between catalyst and membrane was reduced, which resulted in an improvement of mass transport and therefore enabled lower reaction temperatures (350 °C-450 °C). Nevertheless, reactor modelling showed that the catalyst performance as well as the hydrogen permeability of the Pd-membrane had to be further increased. Therefore, to improve the permeability, the method of electroless planting was tuned to fabricate thinner membranes. To address the limitation by ammonia decomposition reaction, a commercial 0.5 wt% Ru/Al_2O_3 catalyst served as optimal catalyst system. With this modifications higher ammonia flowrates could be applied while maintaining the same level of ammonia conversion compared to an equivalent packed bed reactor [34, 35].

To the best of our knowledge, most literature sources report the supply of hydrogen at ambient pressure or pressures below 3 bar [33, 29, 34, 31, 24]. However, if the hydrogen is used as a fuel in the transport sector or stored, it needs to be provided at high pressures (up to 700 bar), which makes an additional compression step necessary. To avoid compression costs and CO_2-emissions a high pressure permeate side is desirable. Cerillo et al. tested a packed bed catalytic membrane reactor (PBCMR) for ammonia conversion at elevated permeate pressures up to 15 bar. They observed, that the retentate/permeate pressure ratio determines both hydrogen recovery and productivity and the amount of impurities in the permeate stream increases for higher permeate pressures. However, by providing the H_2-permeate stream at moderate pressures the calculated CO_2 emissions and energy consumption associated to the compression of hydrogen could be noticeably decreased. For example, by increasing the permeate pressure from ambient conditions to 5 bar, the energetic requirements for compressing the hydrogen up to 350 bar can already be reduced by about 30 % (shown in Figure 2b). Furthermore, they investigated the possibility of utilizing the energy of the remaining hydrogen in the retentate to cover the thermal requirements for the process. Without any external energy inputs a maximum a hydrogen recovery of 70-75 % was estimated. Using Aspen plus simulations Cerillo et al. also examined the feasibility of the ammonia decomposition process to produce high purity hydrogen via the membrane reactor compared to a purification via conventional pressure swing adsorption (PSA). Due to the absence of the PSA and the higher pressures of the final H_2 stream after the reactor (3-5 bar) 51 % electric power savings in the membrane-based process could be determined. Based on their findings they calculated a 75 % hydrogen efficiency for a stand alone system for ammonia decomposition and compression to 350 bar [32].

4. Biogas reforming

Biogas, which is produced by anaerobic digestion of biomass, is a regenerative energy source that can be converted into hydrogen via reforming. Typically, it is used in integrated heat and power plants for the simultaneous generation of heat and electricity. In mobility, it is used as a transportation fuel after purification to methane. It primarily consist of methane (60 vol%-70 vol%), carbon dioxide (30 vol%-40 vol%) as well as nitrogen (0.2 vol%), hydrogen sulphide (0 ppm-4000 ppm) and ammonia (100 ppm) [38, 39]. Biowaste generated in private households, vegetable and animal residues from the food and fodder industry as well as agricultural residues are used as a feedstock for biogas production [40]. Some of the main benefits of biogas production are waste recycling with fertilizer as a by-product, reduction of greenhouse gas emissions, reliable production and local availability [39].

Hydrogen can be produced via biogas reforming through auto- or allothermal processes in a wide range of temperatures (650 °C-1000 °C) [38]. Conventional biogas reforming processes are: steam reforming (SR), partial oxidation reforming (POR), dry reforming (DR), auto-thermal reforming (ATR), and dry oxidation reforming (DOR). All of these processes take place in several steps. First, the biogas is desulfurized. Then it is converted to H_2 and CO in a reformer followed by a water gas shift reactor (WGSR) to increase the hydrogen yield. Industrially, the components are separated by pressure swing adsorption (PSA) to recover hydrogen [41].

Membrane reactors are able to combine the reforming, WGSR and hydrogen separation process in one unit. Additionally, some of the main drawbacks of conventional reforming processes, such as the required high reaction temperatures can be eliminated [41]. Due to the selective separation of hydrogen via membrane, membrane reactors can be operated at lower temperatures (400 °C-600 °C), which allows the use of lower-cost materials for reactor construction. Depending on the membrane material, the separated hydrogen either contains traces of other components or can be used in fuel cells [39, 13].

Iulianelli et al. investigated the steam reforming of a synthetic biogas mixture containing H_2S in two different membrane reactors (MR). H_2S is a strong catalyst poison and reduces the permeability and mechanical stability of the Pd-based membrane due to formation of Pd_4S. As Pd/Au-membranes show an increased resistance against H_2S poisoning, Iulianelli et al. studied the effects of an H_2S containing modelled biogas stream (35.03 % CO_2, 59.94 % CH_4, 5.01 % N_2 and 0.02 % H_2S) to a 8 µm thick Pd/Au-membrane, which was deposited via electroless plating technique on a porous α-Al_2O_3 substrate. A self-supported 150 µm thick Pd/Ag membrane was compared. Both membrane reactors (PBMR) were packed with a Rh(1 %)/$MgAl_2O_{4/}Al_2O_3$ catalyst. The Pd/Ag membrane reactor achieved high CH_4 conversions (around 85 %) and seperated pure hydrogen at 400 °C and 2 bar. Nevertheless, due to low hydrogen permeability only 40 % of the hydrogen was recovered. The Pd/Au membrane reactor recovered around 80 % of the produced hydrogen at 550 °C and 1.5 bar. However, the separated permeate flow contained around 50 % of other species than hydrogen, which resulted in low CH_4 conversions (around 25 %) due to low H_2 permselectivity. Regarding the H_2S resistance, a long-term exposure of the membranes showed a significantly stronger and faster decrease of the CH_4 conversion for the Pd/Ag membrane than the Pd/Au membrane. Additionally, the initial hydrogen separation efficiency of the Pd/Ag membrane could not be recovered by treatment with pure hydrogen. In the case of the Pd/Au membrane this was possible [16]. Therefore it can be concluded that there is considerable potential for the use of Pd/Au membranes for the steam reforming of biogas but permselectivity needs to be optimized.

Duran et al. tested a two-zone fluidized bed reactor (TZFBR) with two integrated supported PdAg membranes (layer thickness 76 µm) for methane dry reforming on a Ni−Ce/Al_2O_3 catalyst. This reactor configuration addresses some of the main challenges of biogas dry reforming: Its large energy demand due to the highly endothermic reforming reaction and its strong tendency of coke formation due to methane decomposition and/or the Boudouard reaction via the fluidized bed approach [41]. By supplying the biogas at an intermediate height point into the fluidized catalyst bed and simultaneously supplying an oxidizing agent at its bottom, two zones are created. In the lower zone, the deactivated catalyst is regenerated by coke combustion, while in the upper reaction zone biogas is converted to hydrogen via dry reforming. The Pd/Ag membrane tubes, which are placed inside the reaction zone, are separating hydrogen from the reaction zone and therefore potentially lower the risk of CO_2 conversion with hydrogen to CO and H_2O by reverse water gas shift reaction. The separation of hydrogen via membrane was found to enable lower reaction temperatures and to provide hydrogen suitable for fuel cells. Compared to a similar fluidized bed reactor (FBR) the two-zone fluidized bed reactor with Pd/Ag membranes showed a strong improvement in hydrogen yield. By increasing the fluidized bed height and therefore the effective membrane permeation surface, the hydrogen yield enhanced by up to a factor of 3 in the temperature interval from 475 % to 575 %. Thereby, 70 vol%-80 vol% of the produced hydrogen is separated as permeate. Even though catalyst coking increases with hydrogen removal, enlarging the height of the regeneration zone can counteract via improved catalyst regeneration. For high O_2 and CO_2 concentrations, the coke combustion rate was found to exceed its formation rate. Nevertheless, as O_2 oxidizes the metallic phase of the catalyst and therefore deactivates the catalyst gradually, a reducing atmosphere in the higher zone of the reactor must be ensured [42].

5. Conclusion

Hydrogen plays a key role in the energy transition. As a feedstock for the production of synthetic fuels and chemicals, or as a fuel itself, it alleviates the mismatch between energy demand and supply from renewable energy. Membrane reactors for hydrogen production combine hydrogen production and separation in one unit and can thus be designed to be more compact. Due to the resulting hydrogen partial pressure reduction, the thermodynamic equilibrium condition is shifted and higher conversions can be achieved or the reaction temperature can be lowered. The latter enables the use of lower-cost material and promotes heat integration strategies.

Different membrane reactor configurations, such as packed bed reactors, catalytic membrane reactors and fluidized membrane reactors were presented in this review. For example, Itho et al. and Zhang et al. developed tube-wall catalytic membrane reactors to increase the ammonia conversion in the low-temperature range (325 °C-425 °C) by proving efficient heat supply for the decomposition on the ruthenium catalyst [33, 34, 35]. In the case of biogas dry reforming, Duran et al. addressed the challenge of coke formation by reforming biogas in a two-zone fluidized bed reactor, in which the deactivated catalyst is regenerated in the lower zone by coke combustion [42].

In most reactor configurations, palladium based membranes are employed as they possess a high hydrogen permselectivity. Due to the high cost of palladium, composite membranes are frequently studied. To improve the properties of the Pd-membrane is often alloyed with other materials such as Ag, Cu and Au. For example, Iulianelli et al. investigated a Pd/Au membrane, which should be more resistant to H_2S [16].

The examples above show that some very promising pathways for membrane reactors in hydrogen production are under investigation. Even if they are not yet applicable on an industrial scale and further development is required, there is potential for membrane reactors for hydrogen processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**They used a two-zone fluidized bed reactor with integrated Pd-membrane for biogas dry reforming. This concept is a very interesting, as it addresses the challenge of coke formation during reforming.