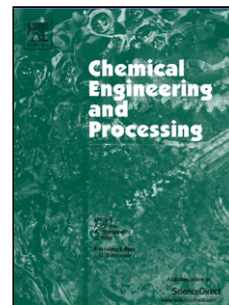


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Palladium membranes applications in reaction systems for hydrogen separation and purification: A review

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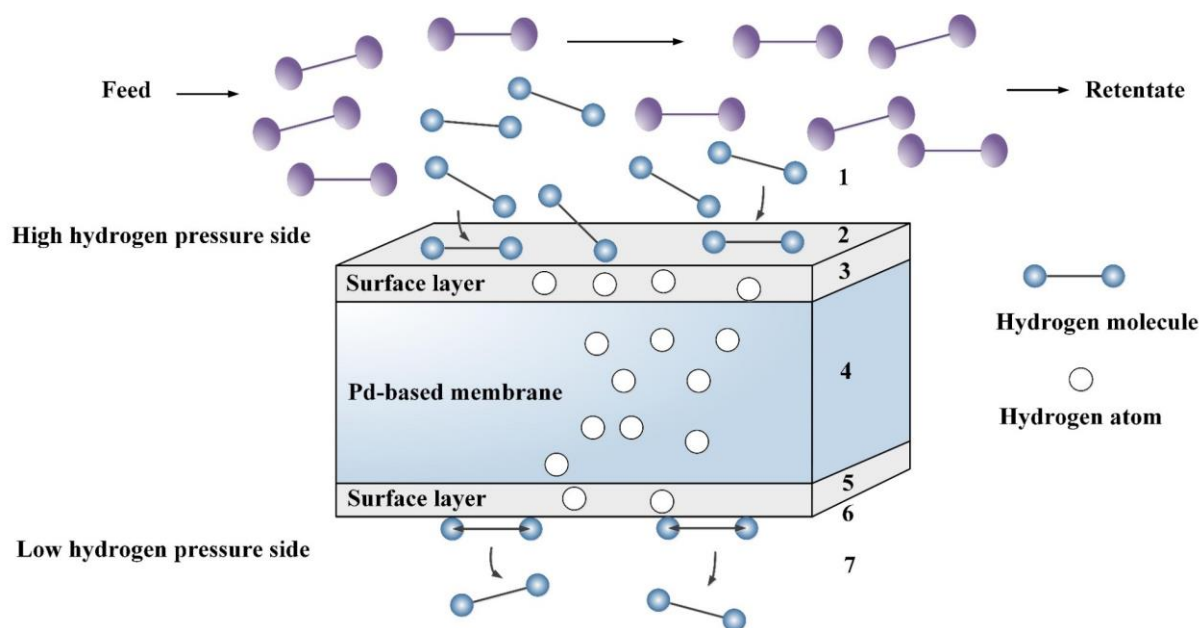
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Graphical Abstract:



Highlights:

- Diffusion of hydrogen through palladium membranes are evaluated
- The ability of Pd-alloy membrane reactors in the removal of hydrogen from various reactions is investigated
- Palladium membranes preparation and characteristic, and different types of membrane reactors are discussed in detail
- Some essential ideas for the improvement of future membrane technology are proposed

Abstract

Application of palladium-based membrane technology in chemical reactions is currently focused on producing ultrapure hydrogen. Due to the environmental concerns and undesirable side effects of greenhouse gases, hydrogen has great potential as an alternative future fuel. Pd-alloy membranes have demonstrated tremendous potential for the hydrogen extraction in hydrogen-dependent reactions. Numerous studies have been done investigating the diffusion of hydrogen through palladium membranes. In this review, the ability of Pd-alloy membrane reactors in the removal of hydrogen from water gas shift, steam reforming, and dehydrogenation reactions is evaluated. This review is divided into several sections including palladium membranes, Pd-alloy membranes, composite Pd-based membranes, and their preparation methods. Moreover, the hydrogen permeation rate, Sieverts' law, Damkohler-Peclet product design parameter, and various membrane reactors will be discussed in detail. There is also an overview of the last-decade researches on Pd-based membrane reactors. Finally, some essential ideas for the improvement of future membrane technology are proposed.

Abbreviations

ATR	Autothermal reforming
CFBMMR	Cascading fluidized-bed membrane methanol reactor
CMR	Catalytic membrane reactor
CR	Conventional Reactor
CVD	Chemical vapor deposition
Da	Damkohler number
DME	Dimethyl ether
DR	Dry reforming
EAR	Ethanol autothermal reforming
ECN	Energy research centre of the Netherlands
ELP	Electroless plating
ESR	Ethanol steam reforming
FTS	Fischer– Tropsch synthesis
FBMR	Fluidized bed membrane reactor
FBCMR	Fluidized bed catalytic membrane reactor
Flat-MR	Flat membrane reactor
FMR	Fixed bed membrane reactor
HVOF	High velocity oxy-fuel spraying
IMFBR	Inert membrane fluidized bed reactor
IMPBR	Inert membrane packed bed reactor
IMR	Inert membrane reactor
ITM	Institute membrane technology
KT RMM	Kinetics technology reformer and membrane module
MSR	Methanol steam reforming
MMR	Microstructured membrane reactor
MOCVD	Metal-organic chemical vapor deposition
MPSS	Macroporous stainless steel
MR	Membrane reactor
MRF	Membrane reformer
MRL	Membrane reactor loop
MTMR	Multi tubular membrane reactor
OSR	Oxidative steam reforming
PBCMR	Packed bed catalytic membrane reactor
Pe	Peclet number
PFR	Plug Flow Reactor
PG	Porous glass
PBMR	Packed bed membrane reactor
PSA	Pressure swing adsorption
PSMR	Permeative-stage membrane reactor
PVD	Physical vapor deposition
RFTMR	Radial flow tubular membrane reactor
SMR	Spherical membrane reactor
SR	Steam reforming
SRM	Steam reforming of methane

SSMR	Staged-separation membrane reactor
WGS	Water gas shift
WHSV	Weight Hourly Space Velocity

Keywords: Membrane reactor; Pd-alloy membrane; Hydrogen permselective membrane; Composite Pd-based membrane; Hydrogen production

1 Introduction

Due to limitation of fossil fuel sources and global warming, hydrogen is introduced as an alternative renewable energy. Use of hydrogen, as the lightest chemical element, offers ways to minimize greenhouse emissions, reduce air pollution, diversify energy supply, and reduce noise [1]. Large amount of hydrogen is being used as a basic raw material in the petrochemical industries. Especially, hydrogen has recently drawn tremendous attention as a green energy source in areas such as fuel cells. The hydrogen industry has aimed the diversification of feedstock and hydrogen production processes. Gaseous hydrocarbons such as methane, butane, kerosene, alcohols (e.g., methanol and ethanol), ketones and ethers (e.g., dimethyl ether) are the main feedstock in hydrogen production processes such as reforming reactions, partial oxidation reactions, and decomposition reactions. These reactions occur in the presence of a steam or carbon dioxide which is obtained through separation and purification processes [2-4].

According to international union of pure and applied chemistry (IUPAC), membrane reactor (MR) comprises of a reaction chamber along with a membrane to add reactants or to remove products of the reaction. MRs are examples of combining two processes, such as membrane separators and a chemical reactions in one stage [5, 6].

1.1 Scope of the current review

The main purpose of this study is to present a comprehensive research area encompassing hydrogen permselective membrane reactors with particular focus on palladium-based membranes. This review is divided into several sections including palladium membrane reactors, reactor types, classification of various reactions for hydrogenation, and Pd-alloy based on deposition methods. Introducing important parameters that can affect permeation rate and Sieverts' law validity and an overview of the last decade researches on Pd-based membrane reactors are of other issues we have covered in order to shed light on the current trend of research. Finally, some new ideas are proposed to improve the performance of permselective membrane reactors for further investigations.

1.2 Evolution of membrane reactors

Figure 1(a) shows all the cited publications used in the present work by the years 2000-2017 and 34 publications before that period. Figure 1(b) demonstrates the trend of all publications on Pd-based membranes for hydrogen purifications during the same period (there are also 119 publications before 2000). As can be seen, tremendous amount of research work has been carried out since 2000. In this paper, most of the work related to membrane reactors for production of hydrogen was done starting in 2004.

Fig 1

1.3 Membrane reactors

In 1784, the word "membrane" (meaning pellicle, capsule, diaphragm and thin parchment in Latin) was proposed by Nollet for the first time. He applied membrane for separation of liquid mixtures such as alcohol and water [7]. The first successful application of polymeric membrane systems for separating hydrogen from ammonia purge gas streams was

conducted in 1970's. Nowadays, application of hydrogen permselective membrane systems are widely developed in various industrial processes, involving reforming, gasification, or petrochemical processes [6]. For efficient use of hydrogen permselective membranes, a high hydrogen permeation flux should be allowed with a high selectivity. Resistance against temperature degradation and poisoning as well as sufficient sealing in the reactor are two other important features that a membrane should possess [8].

In highly supercritical gases (i.e., carbon monoxide, nitrogen and methane), hydrogen can be separated easily using polymeric membranes owing to its extremely high diffusivity to all other molecules except helium. When hydrogen solubility factor is not so significant, the diffusion contribution overcomes and overall high selectivity will gain. For instance, in some polyimide and polyaramide membranes, hydrogen/methane selectivities of about 200 have been reported [9]. In spite of the fact that membranes are widely used in industries in low temperature conditions for many years [10], the high temperature stability can be considered as an obstacle that limits the application of these membranes in hydrogen production reactors. However, there are several methods and figures in the literature [11-13], that apply membranes in high temperatures with some modifications. For industrial scale in high temperatures, long time thermal stability of membranes is vital, especially in steam methane reforming processes [11].

Membrane reactors are superior to conventional reactors (CRs) for the following reasons [9]:

- High conversion of equilibrium limited reactions.
- The possibility of controlling the interaction between two reactants using membrane.

- Reduction of capital cost by combining two units (catalytic reactor and down-stream separation processes) into one.
- Easy maintenance of the stoichiometry of the reaction.
- The possibility of dividing the reactor and membrane into two individual segments for individual reactions (i.e. oxidative and hydrogenation reactions).

1.4 Membrane types

Membranes are categorized into three main groups including hybrid, organic and inorganic membranes. Organic membranes are classified into polymeric and biological membranes, while inorganic membranes are subdivided into metallic and ceramic (porous and non-porous) ones. Moreover, from porosity viewpoint, membranes are classified into non-porous and porous groups, the latter of which is divided into micro-porous or molecular sieve (pore sizes < 2 nm), meso-porous (2-50 nm) and macro-porous (>50 nm) membranes [14].

Hydrogen separation membranes can be categorized into the following classes: polymeric, porous and dense metal membranes such as palladium based membranes (extremely high hydrogen permeable with infinitely selective toward hydrogen) and proton conducting membranes [15].

Porous membranes for hydrogen separation can be divided into meso-porous ceramic membranes and micro-porous ones. For meso-porous ceramic membranes, the main feature is the low selectivity with Knudsen diffusion as its dominant transport mechanism. The separation mechanism for micro-porous ceramic membranes is more complex and is prevailed by selective adsorption and molecular sieving at low and high temperatures respectively, with a complex mix of two processes at intermediate conditions [14, 16, 17].

Proton conducting membranes as one of hydrogen separation membrane categories, are subdivided into dense ceramic and composite ceramic metal (cermet) membranes. Although dense ceramic membranes are low permeable, they can give an extremely high purity of H₂ stream at temperatures as high as 1173 K, because of proton transport mechanism.

To gain a high hydrogen flux, it is essential to have high values for electronic and protonic conductivities. Perovskite and non-perovskite membranes are two different types of dense ceramic membranes [14, 15]. There is no need to an external electrode for perovskite type membranes due to the mixed ionic and electronic conductivity of these materials. However, limited permeability and low thermal and chemical stability are considered as the most common defects of dense ceramic membranes [18].

The overall classification of membranes based on their material and different types of hydrogen separation membranes are shown in Fig. 2 and 3, respectively.

Figure 2

Figure 3

2 Palladium membranes

Dense metal membranes have potential to transport hydrogen in a dissociative form, and consequently give a theoretically unbounded selectivity [19]. Numerous studies have been done on various metals as candidates for hydrogen permeable membranes. The following trend in decreasing order of hydrogen permeability through various metals is reported in Fig. 4.

Figure 4

Generally, metals such as vanadium, niobium, and tantalum are called refractory metals with an order of magnitude higher permeability in comparison with palladium at lower temperatures. These metals are more inexpensive and possess greater tolerance at high temperatures compared with palladium. Nonetheless, fabrication of these metal membranes (as single components) has been stopped, because in the exposure to hydrogen, they lose flexibility in the presence of 6.9 bar hydrogen at room temperature, a process named hydrogen embrittlement. In addition, poor surface properties of the metals (i.e. creation of surface oxide layers), which decreases hydrogen transport, is another factor limiting their use [21-23].

Among these, palladium (Pd) membranes has recently received considerable attention for the following reasons: excellent permeability, high tolerance to hydrocarbon flows and self-catalyzing the H_2 dissociation reactions. Another important feature of Pd membrane is its excellent resistance to hydrogen embrittlement and catalytic ability for hydrogen recombination [19, 24]. Hydrogen diffusion through Pd lattice is fast due to its capable for hydrogen dissociation into monatomic hydrogen [25]. Also Pd absorbs approximately 600 order of magnitude hydrogen per its volume, while Pd structural integrity as well as its physical properties remain unchanged [26]. Palladium has the atomic number 46 and $[Kr]4d^{10}$ electron configurations. Pd density and its melting point are 12.023 g cm^{-3} and 1828 K respectively [25].

2.1 Pd-alloy membranes

Although palladium is the best candidate for fabricating hydrogen separation membranes, its use is limited by some major drawbacks; pure Pd is likely to embrittle at temperatures and pressures below 573 K and 2MPa, respectively [19, 27]. Furthermore, palladium is subjected to deactivation by deposition of carbonaceous impurities (temperatures

higher than 723 K) and to irreversible sulfur poisoning. High cost of commercial Pd foils ($>25\mu\text{m}$ in thickness) is another limiting factor that affects pure palladium usage [19, 28].

As an efficient membrane requires a long lifetime under operating conditions and pure palladium cannot satisfy this requirement, it should be alloyed with other metals, including aluminum, copper, indium, molybdenum, nickel, platinum, rhenium, rhodium, ruthenium, silver, titanium and tungsten [19].

Pd alloy with these metals possess a lower critical temperature. Consequently they can operate at lower temperatures without hydrogen embrittlement (embrittlement occurs in pure palladium by repeated hydrogen sorption and desorption cycling). Pd alloys have also indicated higher catalytic activity than pure palladium. Moreover they are resistance to H_2S poisoning and thermal cycling. Literature showed that some Pd alloys such as 23% Ag, 6% Ru, 40% Cu, 5% Au are more permeable than pure Pd [29]. In the study of Sakamoto et al. $\text{Pd}_{95-x}(\text{Y}(\text{Gd}))_x\text{Ag}_5$ with $x = 6.3$ were found to be the most permeable to hydrogen with the permeability of 2-2.5 times higher than Pd-24%Ag [30].

Pd-based membranes technologies are currently developed based on high hydrogen permeability, reasonable thermal stability, and proper mechanical strength [31].

2.2 Composite Pd-based membranes

Hydrogen separation membranes are commonly made of thermally stable inorganic compounds, which can be categorized into two types based on their structures: (1) self-supporting Pd-based membranes, and (2) composite Pd-based membranes (made of a thin selective layer) deposited on porous supports composed of ceramic or stainless steel [32]. The first group gives a very high selectivity for hydrogen, however shows low hydrogen fluxes due to small diffusion coefficients for gases in solids. Moreover, for mechanical stability of

these membranes, higher thickness (in the 100 μm range) is needed which subsequently results in an expensive noncommercial membrane [32-34].

Although, porous membranes offer less operating cost with high fluxes, they exhibit relatively low hydrogen selectivity [32]. This is due to hydrogen separation is mainly controlled by Knudsen diffusion [34] and hence it is only on the influence of molecular size [35]. Table 1 shows different Pd-alloy composite membrane efficiencies for hydrogen separation.

Table 1

The main development in the membrane technology was production of composite membranes made of a thin metallic film with thickness in the ranges of 1-10 μm deposited on porous substrates [32] providing both high flux and mechanical strength of support [19]. Figure 5 demonstrates hydrogen partial pressure distribution along the structure of the composite membrane (a three layer membrane support) [51].

Figure 5

In the following sections, porous membranes as palladium supports will be discussed and then two major porous supports, (porous ceramic supports and porous metallic supports) will be explained in more details.

2.2.1 Porous supports

For porous membranes, the gas transport mechanisms depend on pressure, temperature, pore size to mean free path length ratio and the membrane surfaces [52]. As a result, to describe gas transport behavior, the following diffusion mechanisms are used: Knudsen diffusion (mesopores), surface diffusion (mesopores and micropores), capillary

condensation (mesopores), laminar flow or viscous flow (macropores and mesopores) and molecular sieving (macropores and mesopores) [18, 53].

The gas transport mechanism in a commercial porous membrane (pore sizes > 4 nm) at elevated temperatures and low pressures is primarily governed by Knudsen diffusion [34]. When temperature is high, permselectivity increases by reduction of pore sizes and transportation through the membranes can be controlled by pressure with macropores or big mesopores, because under these conditions adsorption is not significant, capillary condensation and surface diffusion do not participate [18]. When membrane pore sizes is much greater than gas molecules, Molecular sieving cannot be accomplished. In this case, the portion of viscous flow, consequence of the difference in pressure across the pores is negligible [34].

2.2.1.1 Ceramic supports

Non-metallic substrates with pore size ranges of 5-200 nm are placed in a broad group named, porous ceramic supports. Alumina is commonly used as a ceramic material in the preparation of Pd composite membranes for the following features: reasonable mechanical and thermal stability, widespread usable in different compositions and modifiable by using intermediate layers [54, 55].

In general, ceramic supports is divided into a supporting, a middle layer and a top layer. Supporting layer as composition of large ceramic grains exhibits a good mechanical strength with a low resistance to gas transport. The top layer offers a smaller grains to approach a relatively smooth surface. For reduction of gas transport resistance, a sufficiently low thickness of top layer is required. For this purpose, an intermediate layer with middle size grains is employed to join the supporting and top layer [56].

A homogeneous surface features, particles with a diameter less than the top layer thickness and a monotonic pore size distribution are accounted as a proper support characteristics. The underlying support with a relatively surface roughness provides a good mechanical stability without any cracks formation [54].

In the study of Pereira et al. on Pd–Ag based membranes on ceramic supports (α - Al_2O_3), the gas permeation test indicated that the membrane is selective toward H_2 . A schematic of their experimental apparatus for hydrogen permeation test is shown in Fig. 6 [57].

Figure 6

2.2.1.2 Metal supports

Porous metal supports have a pore size in the ranges of 0.2-100 μm . As the thermal expansion coefficient of these substrates is close to palladium [58], less stress in thermal processes is applied to them. Therefore it is recommended to use them as a support material [59, 60]. Non-monotonic pore distribution and non-homogeneous surface of porous metal supports are two obstacles to gain a thin Pd film on the surface [22], which cause defects or pinholes on Pd alloy membrane surfaces. Therefore to have defect-free selective layers, much thicker palladium films is required for porous metal supports in comparison with ceramic supports [21].

Among different porous metal supports, stainless steel is the best candidate for the development of commercial filters, owing to its good weldability, high physical strength and cracking resistance, accessibility, and cost effectiveness [32, 61].

Pd–Ag metallic supported membranes for high temperature applications was experimentally investigated by Fernandez et al. The results indicated significantly high permselectivity of H_2/N_2 at 673–873 K [12, 57]

3 Preparation methods for composite membranes

Numerous studies have been devoted to alternative methods of Pd and Pd-alloy deposition on different materials. Film porosity, grain size and adhesion controlled by film deposition methods, can effect on hydrogen permeability, membrane life time and permselectivity [22].

A variety of techniques such as electroless plating (ELP) [62], physical vapor deposition (PVD) [15], chemical vapor deposition (CVD) [41], pyrolysis [34], micro-emulsion technique, pore plugging by liquid impregnation [8], electroplating[16], solvated metal atom deposition and high velocity oxy-fuel spraying (HVOF) [22] are available for Pd deposition. The main methods to date which have produced satisfactorily composite membranes include electroless plating, metal-organic chemical vapor deposition (MOCVD) and PVD magnetron sputtering [8] which would be explained specifically in the following sections.

3.1 Electroless plating (ELP)

Electroless plating (ELP) is a heterogeneous oxidation-reduction reaction (known as autocatalytic deposition process) [62], involving metal deposition at the solid-liquid interface without using electrical energy [63].

ELP reduces metallic salt complexes on a support material surface [27]. An activation step is provided by seeding the surface with metal crystallites to initiate plating and to warrant the adherence of the film. The electroless plating is initiated by metal nucleation sites

through accelerating of reducing agent decomposition in the plating bath [22]. Conventional electroless plating consists of: (a) seeding a support surface with Pd fine particles via sensitization [64] (e.g. with stannous chloride [34]) and activation [64] (e.g., with palladium chloride [34]), and (b) Pd layer plating on top of the activated surface. The initial rough surface of support can be smoothed by the deposition of intermediate layers (Fig.7) [64].

Figure 7

Successful electroless plating cannot be simply attained by adding a reducing agent to metal ion solution. In practice, the pH of the solution alters during plating and thus will affect the rate of deposition. Hence, a buffer needs to be added in the plating bath to stabilize the pH of solution. The temperature of plating bath is also an important operating parameter that can extremely affect the rate of deposition [62]. Pd alloys synthesis by this method leads to disparate reduction potential of the metallic ions and subsequent of uneven deposition. This occurs for Pd-Ag alloys where dendritic growth is observed. However this challenge can be prevailed by adjusting reactant concentrations [65].

An interesting adjunct to the electroless plating method is the plating with osmosis. Essentially this method involves electroless plating on the outside surface of the membrane, by simultaneous circulating of a high osmotic pressure solution through the tube-side of the membrane. By osmotic pressure, the water in the plating solution permeates into the high osmotic pressure solution. This increases the concentration of Pd complexes in the substrate pores, leading to denser films of Pd. This has been shown to be capable of repairing pinholes in the Pd layer, which may appear after the first electroplating deposition [66].

3.1.1 Advantages and disadvantages of electroless plating

Electroless plating is rather low cost due to the simple equipment required and the absence of electrical source. It also supplies monotonic dense coatings on both conducting and non-conducting surfaces. Moreover, it has the ability of covering supports with complex geometries [15, 16]. Also, this method performs the co-deposition of Pd and Ag through simple preparation processes. Hence, the alloying can be conducted at low temperature during annealing process [67].

ELP is more complicated and takes more time because there are several pre-treatment stages such as activation and sensitization before accomplishment of final plating of the desired metal [65]. Using of extremely poisonous chemicals and formation of hazardous liquid wastes are another drawbacks of ELP[22].

3.2 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) or metal-organic chemical vapor deposition (MOCVD), is a process using thermal decomposition of one or several volatile precursors to create thin films on a substrate [68]. The chemical reaction is an essential characteristic of the method. Within obtaining composite metal membrane, the organometallic substance is generally sublimed in a separate vessel, swept using an inert gas and reacted with a gas such as hydrogen or thermally decomposed on the desired surface [69].

The MOCVD process can be affected by the following parameters: substrate quality (defects) and temperature, precursor quality, hydrogen content in the deposition atmosphere, precursor amount loaded in the MOCVD reactor and sublimation temperature [70].

3.2.1 Advantages and disadvantages of chemical vapor deposition

Adjusting the film thickness (generally $>3\mu\text{m}$) and providing high film quality and reasonable adhesion on the membrane substrate are some particular challenges in electroless

plating. Therefore, there is a considerable interest focused on advancement of dense supported Pd membranes by vapor phase processes, such as CVD [41].

In spite of CVD technique can be applied to fabricate thin films, it requires costly Pd precursors (i.e., $\text{Pd}(\text{C}_3\text{H}_5)_2$, $\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_5)$ and $\text{Pd}(\text{C}_5\text{H}_5)_2$) of good thermal stability and high volatility. In addition, high purity constituents and high-vacuum ($<0.1\text{mmHg}$) conditions are required in this method [71]. Another drawback of the method is that CVD tends to give lower fluxes and also produces smaller values of the H_2/N_2 selectivity in comparison with electroless plating [8], and also the film may be polluted with organometallic elements such as carbon [41].

3.3 Physical vapor deposition (PVD)

PVD stands for physical vapor deposition as a coating method. In this technique, the solid source is vaporized by gaseous plasma or a high temperature vacuum. Then the target atoms are bombarded with energetic particles to coat the entire substrates with thin films through condensation [34, 72]. PVD and CVD are the same techniques except that in PVD the precursors are generally in the elemental state (as a pure metal), so chemical decomposition reactions do not occur in the surface while in CVD, the precursors are in the vaporized state (as a chemical compounds) [70]. Representative techniques in PVD are thermal evaporation, pulsed laser evaporation, magnetron sputtering and also sputtering with an electron beam, laser or ion gun [8, 15, 70, 73, 74].

Pereira et al. employed MS (magnetron sputtering) as a type of PVD method for the Pd-Ag thin film membrane synthesis. In this technique Pd and Ag targets are bombarding with energetic argon particles and then neutral metal atom species are repulsed, which

consequently condense on the support. The support is heated and rotated between both inclined magnetrons during the process (see Fig. 8) [57].

Figure 8

3.3.1 Advantages and disadvantages of physical vapor deposition

PVD is superior to ELP, because of its environmentally friendly nature, no liquid waste from chemical baths is produced [75]. Although PVD are implemented to coat thin, uniform metal and metal alloy films, it is unable to easily coat the interior part of tubes [22, 76], and thus this method can be applied only for supports with a flat substrate geometry. This shortcoming severely limits the range of practical applications [27]. Also, it suffers from low efficiency and high cost due to the expensive high vacuum equipment required [16].

4 The effect of various parameters on permeation rate

Mass transfer in Pd membranes is a complicated process, can be affected by many factors. In order to verify the behavior of palladium membranes under different conditions, it is essential to demonstrate the effect of various parameters on these membranes. Some of the key factors such as operating conditions, thickness of the membrane, direction of the permeation and air pre-treatment will be discussed in the following sections. In addition, the effect of gases presented in the feed mixture on permeation rate and the mechanisms will be covered in more details.

4.1 Operating conditions

Wei et al. showed that in the absence of chemical reactions, pressure is likely to increase hydrogen flux and decrease its selectivity, while augmentation of temperature leads to an increase in both hydrogen flux and selectivity. However, from the durability point of

view, too high temperatures can shorten the membrane life [61, 75]. Yolcular also observed the same result for Pd/TiO₂ composite membranes [31]. The results of Wei et al. experiments are shown in Fig. 9 (a, b).

Figure 9 (a, b)

The influence of sweep gas on hydrogen permeation was verified by Li et al. [51] and Didenko et al. [77]. Sweep gas reduces the hydrogen partial pressure on the permeation side by dilution, which causes increasing of H₂ transport rate. Although sweep gas improves the membrane performance, additional cost associated with its operation must be justifiable. Minimum sweep gas flow rate should be capable to enhance at least 10% augmentation in average H₂ flux with reasonable operational cost [51].

4.2 Thickness of the membrane

Generally, to obtain high hydrogen separation flux, the Pd membranes are desired to be as thin as possible to speed up the diffusion step [61]. However the thin membrane thickness should guarantee a reasonable sufficient mechanical strength to be self-standing [31]. However, the preparation of a thin defect free Pd membrane is still a concern. Many investigations have been devoted to find more efficient ways of membrane preparation. As previously mentioned, it is beneficial to apply a substrate as a mechanical support with the ultimate goal of producing a thin film of Pd with sufficient mechanical strength [22, 32]. It is necessary to mention that the surface roughness of the support must be reasonably small. Hence, ceramic supports with smaller surface roughness in comparison to porous metal supports are advisable to be applied [21, 22]. In addition, CVD and PVD techniques are among preparation methods with the highest capability of producing a thin Pd based

membrane [22, 41]. Moreover, a thin layer coating of Pd provide an unreactive surface and as an efficient catalyst dissociates hydrogen into the atomic form [22].

4.3 Direction of hydrogen permeation

Goto et al. surveyed the effect of hydrogen diffusion direction on permeation rate of a composite palladium membrane under two ways, namely ‘CP mode’ and ‘PC mode’. In the ‘CP mode’, hydrogen direction is from the ceramic support to the palladium film, while in the ‘PC mode’ hydrogen direction is in the reverse way. The results demonstrated higher permeability rate for the CP mode [78]. Liang and Hughes showed that hydrogen permeation direction is strongly as a function of feedstock. Higher permeability rate for pure hydrogen is from the support to metal film, while a hydrogen/nitrogen mixture, the opposite results was achieved [79]

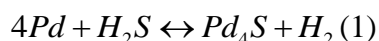
4.4 Air pre-treatment

The influence of air pre-treatment on the membrane performance was investigated experimentally. It was found that the oxygen pre-treatment activates the Pd-Ag surface and eliminate carbonaceous surface impurity by oxidation reactions which can directly affect hydrogen permeability [56].

4.5 The effect of various impurities

In this section, the effect of various impurities on the performance of palladium membranes will be explained in details.

H₂S as highly corrosive gas can react with pure Pd to form a thick Pd₄S film on the Pd surface by the following reaction:



Although hydrogen can be decomposed by Pd₄S surface, it severely retards hydrogen permeation [16, 80] and also reduces the mechanical strength of the membrane [81].

Another mechanism regarding H₂S presence is the adsorption of its molecules on the surface of palladium. For steam reforming of methane or methanol the fractional surface coverage of H₂S depends on the ratio P_{H_2S}/P_{H_2} . So the removal of produced hydrogen will be in favor of the H₂S adsorption, and thus affect the catalytic activity of palladium. For this case the effect of low amounts of H₂S can be minimized at a higher temperature or using a platinum protective layer [8].

For the Pd-alloy membranes, although H₂S reduces the hydrogen flux, the mechanism is completely different. For example, the Pd₄₇Cu₅₃ alloy creates an extremely thin Pd-Cu-S layer which is impermeable to hydrogen [16], but its impermeability is lower than that of pure Pd owing to lower H₂S binding tendency of Cu than Pd [82]. In order to investigate the capability of Pd alloys in controlling the effect of H₂S on permeability, O'Brien and Howard designed an experiment with PdCu other than pure Pd. The results indicated that PdCu membrane loses its permeability towards hydrogen within about 5min, while pure Pd is still active for six hours [81].

For N₂ mixtures, Pizzi et al. recognized that the absolute value of H₂ permeance is certainly lower with respect to pure H₂ permeation [56]. This is mainly because of the dilution of the feed mixture that further results in lower driving force exerted on the system [83]. Hence, purifying the feed mixture from inert component of nitrogen can greatly improve the efficiency of palladium membranes.

Carbon monoxide blockage includes two main mechanisms: (1) CO molecules are adsorbed at the same sites of metal surface for hydrogen atoms, consequently H₂ adsorption

would be directly blocked [83, 84]. In this case, even a small amount of CO can affect the hydrogen permeability [85, 86]. (2) CO adsorbed on the membrane surface influence on transition state energy of hydrogen dissociation [83]. The adsorbed CO can then decompose to carbon atoms which can diffuse through Pd to produce palladium carbide [87].

When Pd is heated in the presence of oxygen or air in temperature ranges of 673-1123 K, a dense PdO film is created. In this case, increasing temperature can cause an increase in PdO layer thickness which results in even lower permeation rate [35]. Also, water formation in the presence of oxygen coverage for adsorbed hydrogen is possible which subsequently reduces hydrogen permeation rate caused by small hydrogen coverage [86].

The effects of individual components of CO and O₂ have been discussed above. However, the co-adsorption of both molecules has not been considered. In this situation, carbon dioxide formation reaction in the presence of CO is replaced with water formation reaction. Based on the ratio of CO/O₂ and the temperature, the blocking caused by CO+O₂ can be either higher or lower than that caused by pure O₂ [86].

According to Gielens et al. [87] a considerable decrease in hydrogen flux is expected in the presence of steam. This is due to a competitive adsorption would be arises between water and hydrogen molecules which leads to decreasing the number of active sites and further reduction of H₂ flux [87, 88]. However, this phenomenon is reversible. Moreover, it was shown that hydrogen fluxes in the mixtures of H₂/H₂O is lower than H₂/N₂ mixtures at the same operating conditions [87-90].

5 Sieverts' law

Hydrogen permeation through Pd membranes is described by a solution-diffusion mechanism. Hydrogen diffusion from a high to a low pressure zone occurs in the following steps (Fig. 10) [24, 91, 92]:

- Transferring of H₂ molecules to metallic membrane surface
- Reversible H₂ chemisorption on the metal surface
- Reversible atomic hydrogen dissolution at the membrane surface
- Atomic hydrogen diffusion within metal lattice (generally rate limiting step)
- Atomic hydrogen association at the metal surface
- Hydrogen molecular desorption from the surface of metal
- Transferring of H₂ molecules from the membrane surface

Figure 10

If atomic hydrogen diffusion through the metal lattice is the rate controlling step, and $H/Pd < 1$, Sieverts' law would be applied [93]. This law which is only valid at low pressure hydrogen, thick membranes and moderate temperatures is given in following equation [94]:

$$J_{H_2} = \pi_{H_2} \left[\left(P_{H_2}^{Feed} \right)^{0.5} - \left(P_{H_2}^{Permeate} \right)^{0.5} \right]$$

Where J_{H_2} is the hydrogen flux through the membrane, π_{H_2} is the proportionality factor and P is the hydrogen partial pressure either on the retentate side or on the permeate side [6].

In the above equation π_{H_2} can be evaluated from Arrhenius law, which is bounded to high temperatures [94], and can be described as below [61]:

$$\pi_{H_2} = \pi_{H_2}^{(0)} \exp(-E_a / RT)$$

Where $\pi_{H_2}^{(0)}$, E_a , R and T represent the pre-exponential factor, the apparent activation energy, the universal gas constant and the absolute temperature respectively.

For estimation of hydrogen flux even for the case when hydrogen diffusion within metal lattice is not the only rate-limiting step, the following modification is suggested [93]:

$$J_{H_2} = \pi_{H_2}^{(n)} \left[\left(P_{H_2}^{Feed} \right)^n - \left(P_{H_2}^{Permeate} \right)^n \right]$$

Where n is an empirical exponent, which can be obtained by a nonlinear regression. This parameter has its own physical meaning that represents the rate determining step in the permeation process of hydrogen through Pd-based membranes.

Pure H_2 flux in Fig. 11 proves the validity of Sieverts' law, which means that diffusion of hydrogen atoms through Pd-Ag membrane is the rate limiting step. However, in the presence of N_2 , hydrogen flux confirms Sieverts' law only at low pressures and deviates at high pressures [56].

Figure 11

6 Damkohler-Peclet product design parameter

There are two main factors affecting the performance of plug flow reactor (PFR): reaction rate and the rate of the reactants fed per catalyst volume. Their ratio gives the so-called Damkohler number (Da) [95]:

$$Da = \frac{(\text{reactor volume}) \times (\text{maximum reaction rate per unit volume})}{(\text{inlet flow rate})} \quad (5)$$

For membrane reactor, another rate (the permeation rate of the fast gas) is also added, which can be termed as the Damkohler-Peclet product:

$$Da \times Pe = \frac{(\text{maximum reaction rate per unit volume})}{(\text{maximum permeation rate per unit volume})} \quad (6)$$

It is explained that if the permeation rate is too low (i.e., the product $Da \times Pe$ is very high), the membrane efficiency is low and the reactor performs like a PFR with the feed gas as reactant. On the other hand, if the permeation rate is too high (i.e., the product $Da \times Pe$ is very low), the shell and tube sides will equilibrate rapidly [96], and no driving force results for permeation. In practice, the latter is unlikely to occur with selective membranes such as Pd-Ag because of the dense non-porous nature of the deposited layer. It has been noted that for optimum performance of a membrane reactor, the product $Da \times Pe$ should lie between 0.1 and 10 [8].

The effect of catalyst activity as an important factor is reflected in the Da value. In the low reaction rates, equilibrium is not achieved and product removal by the membrane will not change the ultimate reaction yield. In other words, slower reactions are not helped by membrane reactor as they are kinetically limited (low Da) [96].

The Damkohler-Peclet product can be used as a design parameter. In order to change $Da \times Pe$, without simultaneously changing Da , the membrane area can be changed while holding the reactor volume constant. Thus to increase the $Da \times Pe$, the membrane area must be decreased. Alternatively, to decrease $Da \times Pe$, the membrane area per reactor unit volume must

be increased. To achieve the latter, the use of multi-tubular membrane systems is appropriate, while for the former the use of single tube membranes with catalyst in the annular space is more suitable [8].

7 Membrane reactor configurations and process classification

Integration of reaction and separation processes in one unit is able to cope several problems arising in chemical reaction engineering, [95] however the operating conditions of membrane reactors are relatively complicated due to combination of chemical reactions with membrane permeation process [96].

The membrane reactors can be categorized into two basic categories according to the catalytic behavior of membrane. Membranes can be inert or they can act as the reaction catalyst (they can be either inherently catalyst or impregnated by catalyst). The former is called inert membrane reactor (IMR) and the latter is named catalytic membrane reactor (CMR). Both IMRs and CMRs can be either packed with catalyst or the catalyst can be fluidized in the tube side. This results in different membrane reactor configurations including inert membrane packed bed reactor (IMPBR), inert membrane fluidized bed reactor (IMFBR), packed bed catalytic membrane reactor (PBCMR), and fluidized bed catalytic membrane reactor (FBCMR) [18, 34, 67].

The abovementioned reactors are used in a variety of membrane geometries. Currently planar and tubular membranes are commonly used for gas separation process. In research and development, planar membranes are frequently used, while tubular membranes are the most preferred choice for industrial applications because of their high surface area-to-volume ratio [15].

In the last decade, researchers have focused on reactors including H₂ permselective palladium membranes [2, 6, 9, 23, 97-105], polymeric catalytic membranes [106], auto-thermal membranes [107], zeolite membranes [108], ceramic membranes [109, 110], carbon membranes [111, 112], inert membranes [112], and dense membranes [41]. Fixed bed, packed bed, fluidized bed and slurry membrane reactors are four major types of hydrogenation reactors, which will be discussed in the following sections.

7.1 Fixed bed membrane reactors

Currently chemical process researches are concentrated on the conducting hydrogenation or dehydrogenation reactions in the membrane reactors which fixed bed membrane reactor (FMR) is the simplest one among them.

This type of membrane reactor, two main operations are simultaneously performed: the reactions are shifted toward the desired products and one or more reactant(s) or product(s) are removed from the reaction side [35]. Fixed bed membrane reactors are considered as units consisting of large cylinders as well as jacketed or shell and tube reactors in which a membrane or a hollow tube is located. The reactions take place on the catalyst surface packed in the annulus [113].

Finding a proper configuration for augmentation of desired products has been studied widely. The enhancement of operating condition for hydrogen separation from the reaction mixture was always the main concerns of the researchers. Several types of reactor with various modes of operation (i.e., lower pressure drop configurations, coupled reactors, etc.) have been recommended. Before investing in development of a pilot plant stage, complicated mathematical models are used essentially to describe the basic parameters of such novel configurations. In addition in order to save time and money, successful commercialization of

such novel configurations will be achieved through exploration of pilot plant optimal conditions by model development.

Based on feedstock flow pattern and the reactor structure, fixed bed reactors are categorized as below:

- Axial-flow, tubular reactor
- Radial-flow, tubular reactor
- Axial-flow, spherical reactor

7.1.1 Axial-flow, tubular membrane reactor

Figure 12 shows an axial-flow, tubular membrane reactor configuration for simultaneous dimethyl ether (DME) and benzene synthesis. This system has three concentric tubes in which DME synthesis and dehydrogenation of cyclohexane occur in the inner (first) and outer (second) tubes respectively. A hydrogen permselective membrane is located as the wall between second and third tubes to remove hydrogen from the second one. Sweeping gas flowing through permeation side transmits the permeated hydrogen. A palladium-silver alloy with the thickness of 6 mm deposited on a thermo stable support is employed. Hydrogen flux permeated through membrane obeys half-power pressure law (Sievert's law). Hydrogen recovery yield as well as cyclohexane conversion were obtained 2.86 and 99.9% respectively.

The results indicate the feasibility of thermally coupled membrane reactor for both DME and hydrogen production [114]. Thermally coupled reactors are multifunctional reactors in which exothermic reaction, as a heat source, provides the required heat of endothermic one in a single vessel. Synthesis of multiple products, improvement of productivity, decreasing the reactor size and beating the thermodynamic limitation of the reactions are all the advantages with coupling reactors [115]. However, experimental studies under common operating conditions are required to prove the accuracy of the model used to

describe these configurations. There are several studies in the literature focused on axial-flow, membrane reactors [116-125].

Figure 12

Figure 13 shows a membrane dual-type reactor configuration for Fischer–Tropsch synthesis (FTS). The first reactor is called water-cooled reactor and the second one is referred as the gas-cooled reactor. Synthesis gas is first preheated in tube side of the second reactor and then enters the first reactor to convert partially into hydrocarbons. The outlet gas of the first reactor is sent to shell side of the second one to complete the reactions. In order to gain relatively high conversion of synthesis gas to light hydrocarbon, a Pd membrane coated the wall of the tubes of the second reactor is used to permeate hydrogen from the reaction side since there is difference in hydrogen partial pressure. In extremely high exothermic reactions such as FTS, a temperature jump may occur in the first part of reactor. Membrane dual-type reactors are more able to control temperature compared to conventional one. This is due to the inlet feed in the second reactor has lower hydrogen, because of hydrogen permeation through the membrane. As a result, heat of reaction will reduce and a lower temperature peak with a better products distribution will be achieved. In this membrane reactor, C₅₊ selectivity increases and undesired products (i.e., methane and carbon dioxide) are reduced. The results also indicated higher hydrogen permeation rate in counter-current mode of operation compared to co-current one [126]. Rahimpour et al. [127] considered a conventional two-stage methanol synthesis reactor using a hydrogen-permselective membrane. Syngas partially converts to methanol in the first reactor while in the second one the reaction heat is used to preheat the feedstock of the first reactor. A Pd–Ag membrane was employed in the wall of the tubes of the second reactor in order to improve the overall CO conversion to methanol. Rahimpour and Bayat [128] considered a cascade membrane methanol reactor in the presence of catalyst deactivation. The wall of tubes in the both reactors were coated with Pd–Ag

membrane. The results showed 4.7% increasing methanol production yield during 1400 days of operation in this configuration compared to conventional dual type methanol reactor.

Figure 13

7.1.2 Radial-flow, tubular membrane reactor

Radial-flow, reactors have the advantage of low pressure drop across the bed and high reaction yield. The design of radial-flow, tubular membrane naphtha reactor is shown in Fig. 14. In this configuration, for a uniform flow distribution the naphtha feed and sweep gas predominately flows radially in tube and shell sides. There is a collector pipe consisted of two concentric cylinders. The inner tube is used to collect the sweeping gas while the outer tube collects the final products. The cross-section area of this configurations is divided into some subsections. Pd–Ag membrane layer used as the walls of the gaps between these subsections, permeates hydrogen from the reaction side. Permeated hydrogen in the shell side is carried by the sweeping gas. Sweep gas pressure, membrane thickness, length to diameter ratio, the ratio of permeation angle to the reaction angle, etc. were chosen as decision variables to increase aromatic and hydrogen yields. In optimized conditions, hydrogen and aromatic yields were enhanced 11.60% and 8.90% respectively. Although reaction yields significantly increase in this reactor, the cost evaluation needs to be verified [129]. Iranshahi et al. [130] studied an optimized radial-flow moving bed membrane reactor for catalytic naphtha reforming process. Insertion of hydrogen permselective membrane in this configuration in the optimal conditions, increases aromatics and hydrogen production rates, and reduces light end products respect to the conventional process. Farsi et al. [131] proposed radial flow moving bed hydrogen-permselective membrane reactors for isobutene production. Compared to conventional configuration, isobutene production rate was enhanced about 3.7%.

Figure 14

7.1.3 Axial-flow, spherical membrane reactor

The advantages of this configuration in comparison with tubular reactors are significantly lower pressure drop, lower manufacturing costs owing to small wall thickness, higher production capacity and lower recompression cost [132, 133].

Implementation of a membrane layer for hydrogen removal was investigated in spherical reactors. A spherical membrane reactor (SMR) for naphtha reforming process is illustrated in Fig. 15. There are two concentric spheres in SMR configuration. The inner sphere is covered with a Pd-Ag membrane layer. Feed and sweeping gas enters axially through the inner and outer sphere respectively. Hydrogen produced during the reaction permeates to shell side and then is carried by the sweeping gas. Based on Le Chatelier's principle, the equilibrium is shifted toward the desired products, hence, higher products' yields will be achieved in this configuration compared to conventional one [134]. Iranshahi et al. [135] proposed a combination of tubular membrane and spherical reactors for conventional naphtha reforming process. The results indicated a remarkable increase in aromatic (8.01%) and hydrogen (9.81%) production rates in this optimized configuration.

Figure 15

7.2 Packed bed membrane reactors

Numerous studies have been carried out on palladium based permselective membranes along with a packed bed of catalyst [6]. The most common configuration of packed bed is tubular. Catalysts can be packed either in tube (Fig. 16(a)) or in the shell side (Fig. 16(b)), whilst the sweep gas flows on the other side of the packed catalysts [136].

Figure 16

Figure 16: Packed bed membrane reactor with catalyst packed (a) in the tube and (b) in the shell side [136]

The transport process through packed bed membrane reactors is because of considerable difference in partial pressures of hydrogen between the reaction and permeation sides [6], resulting in less membrane surface area required for hydrogen separation [15]. The mass transfer driving force is caused by two factors: use of vacuum or sweep gas [6, 22, 34]. Vacuum industrial applications would be too costly, and although using a sweep gas requires a further separation step, it is of great interest among researchers [137]. The sweep gases can be either reactive (e.g. carbon monoxide, air or oxygen) or inert (e.g. N₂, steam or helium), based on their chemical nature with respect to the reaction [6, 8, 138]. Among these, steam has the superiority of being available on-site and can be easily separated from the permeated hydrogen. Use of air or oxygen as a reactive sweep gas produces water as a product on the permeation side, and although it may facilitate the permeation of hydrogen, it produces a byproduct of little value [8].

Along with advantages that this type of membrane reactor possesses, there are also some disadvantages that must be considered. One defect of hydrogen permeation through the membrane is the bed-to-wall mass transfer limitations (a phenomenon called concentration polarization), which is possible in packed bed membrane reactors (PBMRs), as it specifies the membrane area needed for a certain hydrogen recovery.

Lower selective layer thickness increases transmembrane flux (due to reduction of resistance), however the external mass transfer would be one of the slowest elementary steps, subsequently concentration polarization occurs. Concentration polarization phenomena can severely influence the membrane performance in a way that the Sieverts' law cannot be

applied for prediction of hydrogen permeation. For that reason, a systematic approach is needed to find the polarization level for accurate design of membrane equipment [139]. Caravella et al. [139] showed that the concentration polarization is reduced with membrane thickness, upstream hydrogen mole fraction, turbulence and downstream total pressure, while augments with upstream total pressure and temperature. Nakajima et al. indicated that increasing feedstock gas linear velocity and decreasing the reactor diameter vessel makes the flow boundary layer on the membrane thin, which subsequently reduces the concentration polarization [140].

The second important drawback of PBMRs is the pressure drop along the reactor, which bounds the size of catalyst particle to be used. To decrease the pressure drop, particles with large sizes are required, but this hinders the intra-particle mass transfer, which is manifested as increased membrane area needed for a certain conversion/recovery [15].

Temperature control is another limiting factor in association with PBMR. Reduction of temperature on the membrane surface results in a lower hydrogen flux through the membrane [61, 75], while temperature increasing leads to membrane surface cracking and subsequently reduction of permselectivity [15]. In order to overcome deterioration and detachment of the Pd-based layer from the support, the membrane material must sustain a large axial temperature gradient [141]. PBMRs also possess some disadvantages including radial concentration and temperature gradients, difficulties in the removal of reaction heat, low specific surface area of the membrane and inflexibility with respect to the arrangement of membranes and cooling tubes [75].

7.3 Fluidized bed membrane reactors

Another kind of membrane reactor for hydrogenation is fluidized bed membrane reactor (FBMR), in which a bundle of hydrogen-selective membranes is placed in a catalytic bed, operating in the turbulent, bubbling or fast fluidization regime (Fig. 17). However, most of the experimental work on FBMR were conducted in the bubbling flow regime [15, 108-113, 136, 137, 139, 141-146].

Figure 17

The application of vertical tubes in bubbling fluidized bed is more common in comparison with horizontal tubes due to its considerable impact on the bed hydrodynamics, ease of construction and its wear-decreasing impact. However more selective removal of product can be achieved in the horizontal arrangement of membranes [8, 75].

FBMRs have the merit of isothermal conditions along the tube due to the movement of catalyst particles [8, 118, 145]. This possibility of isothermal operation avoids strain on the membrane, produces uniform permeation rates [8], and allows the reactor to operate autothermal reforming (ATR) of hydrocarbons. Methane autothermal reforming in a packed bed membrane reactor is actually difficult because of hot-spots creation at the reactor inlet which may result in melting the membrane. This problem often occurs in fluidized bed assisted membrane reactor [145]. In these types of reactor, bubble-to-emulsion phase mass transfer is considered as an important mass transfer limitation which affects the reactor performance. As the mass transfer coefficient between emulsion and bubble phases decrease, a larger gas slip via the bubble phase as well as less conversion would be achieved. As a matter of fact increasing the reactor length can increase bubble diameter, which results in an increase in bubble-to-emulsion phase mass transfer limitation and consequently a decrease in the reactant conversion. A method to overcome this problem is reduction of the bubble diameter by inserting staggers at different reactor heights (i.e., staging the fluidized bed

reactor) [141]. Great tube-to-bed heat transfer in FBMRs provides a safe operation even for extremely high exothermic reactions [75].

FBMR offers the advantages of both membrane and fluidized bed reactor, including isothermal operation, negligible pressure drop, flexible arrangement of membrane package, improved fluidization behavior owing to compartmentalization, reduction of average bubble size, small internal spacing, and optimal concentration profiles due to controlled dosing or withdrawal. On the other hand, FBMRs suffer from disadvantages including the erosion of reactor internals and catalyst attrition due to vigorous particle motion created by gas bubbles in the bed and difficulties in reactor construction and membrane sealing at wall [75, 146-151].

A fluidized-bed membrane reactor for production of methanol and hydrogen is depicted schematically in Fig. 18. This configuration consists of three concentric tubes. Methanol synthesis occurs in the inner one as a fluidized-bed reactor and also as a heat source of the endothermic side. Cyclohexane dehydrogenation to benzene is carried out in the second tube coated by a Pd-Ag membrane layer. Hydrogen produced by dehydrogenation of cyclohexane diffuses into the permeation side (outer tube). The performance of this configuration was also compared with thermally coupled membrane reactor at the same operating conditions. The results demonstrate that the hydrogen recovery yield and benzene production of FBMR increases about 5.6% and 8.52% relative to that of thermally coupled membrane reactor. This is because of low pressure drop and negligible mass and heat transfer limitations in fluidization processes. The results demonstrate the advantages and the feasibility of this novel configuration for pure hydrogen production [1].

Figure 18

Figure 19 demonstrates a cascading fluidized-bed membrane methanol reactor (CFBMMR) configuration. Both reactors are fluidized-bed using small catalyst size. The outlet gas from the first reactor (water cooled) is sent to the bottom of the second one (gas-cooled reactor) to fluidize the catalyst bed. Also the synthesis gas leaving the second reactor enters the bottom of the first reactor. A hydrogen permselective membrane is used in the second reactor as the walls of tubes. The performance of CFBMMR was compared with an industrial dual-type methanol reactor and the results showed 9.53% in methanol production yield in the proposed configuration. [152]. Rahimpour et al. [153] and Bayat and Rahimpour [154] simulated a cascade fluidized-bed membrane reactor for FTS and methanol synthesis respectively.

Figure 19

7.4 Slurry bubble column membrane reactor

The slurry bubble column membrane reactor suggested here consists of a water-cooled (a fixed-bed reactor) and gas-cooled reactor (slurry bubble column reactor). In a gas-cooled reactor, an inert liquid is used to absorb and transfer heat of reaction.

Dispersed catalyst particles flow upward through the liquid phase. A schematic of this configuration is presented in Fig. 20. The tubes wall of slurry bubble column reactor is coated with a Pd membrane to add hydrogen to the reaction side in order to gain a higher conversion of synthesis gas. This configuration is an appropriate reactor type for high temperature process relative to conventional and membrane FTS reactors [155]. The work presented is still theoretical in nature but does show some potential for application. Practical design, implementation and fabrication of such a reactor will present a range of challenges which a developer will need to recognize and acknowledge.

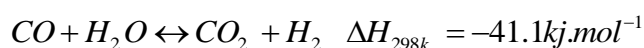
Figure 20

8 Classification of alternative reactions for hydrogen production using Pd-based membranes

There are a great number of reactions to generate hydrogen in membrane reactors including water gas shift, autothermal reforming, steam reforming, partial oxidation and dehydrogenation reactions. Lack of adequate research on various aspects of these chemical reactions and their influence on permeation parameters necessitates more attention. In the following sections, some aspects of the two main hydrogen production reactions will be discussed.

8.1 Water-gas shift process (WGS)

Water gas shift (WGS) reaction occurs in some industrial processes, such as catalytic steam reforming of hydrocarbons, coal gasification, and production of ammonia. In accordance with Eq. 7, WGS is an exothermic reaction with no change in the number of moles. The forward reaction is favored in low temperatures and is not affected by the pressure changes. But in Pd-based MR, operating in high pressure leads to increasing of hydrogen permeation rate and since the reaction is shifted towards products formation, the bed temperature would be reduced. Moreover, the amount of required catalyst for a certain conversion decreases and the blocking effect of the Pd membrane surface sites at $T < 623\text{ K}$ is reduced [23, 53, 156-158].



Higher feed space velocities which provide a lower residence time, negatively affect CO conversion as well as H_2 permeation through the Pd membrane. For more permeation

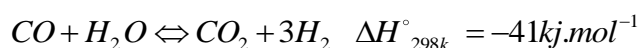
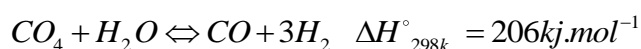
through membrane, a sweep gas is often applied. However additional separation stage downstream would be required [157, 159, 160].

In water gas shift membrane reactor (WGSMR), the co-current mode of operation reduces the thermal effects in membrane reactor through declining temperature rise in the reaction side. This occurs as a results of heat transferring with the permeation side as a cooling medium of the reactor. In the countercurrent scheme, the reaction ignition is facilitated because of preheating effect of permeated stream, however a high temperature rise may occurs in reactor bed which is a source of instability [159].

In Fig. 21, production and purification of hydrogen based on WGSMR is shown [161].

Figure 21

Hydrogen is produced via steam reforming, partial oxidation, and autothermal reforming of fossil fuels (including natural gas, naphtha and light oil) and alcohols with a high level of energy conversion [162]. Among these, the steam reforming of hydrocarbons, which supplies the half of hydrogen produced in the world, requires more attention. In steam reforming of methane following reactions occurs [138]:



These reactions are highly endothermic equilibrium limited. Therefore for higher methane conversion, the process is required to perform at high temperatures, which means high energy consumption and a costly external high temperature heat exchange equipment [8, 138, 163].

Practitioners and researchers have shown that fabrication of metal membrane reformer for both hydrogen separation and production in only one unit particularly in steam reforming process must be considered as an imperative task for highly pure hydrogen generation [164-168].

Steam reforming of methane (SRM) is considered as the most important chemical process for hydrogen production and it can operate with stability even at low hydrogen partial pressure [8, 22, 138, 141, 169, 170]. In the steam reforming of heavier hydrocarbons such as liquefied petroleum gas, naphtha, and kerosene, the performance of membrane reformer may decline due to carbon deposition on the catalyst and/or palladium membrane [171].

Traditional SRM process includes of several steps such as primary and secondary reformers, feed gas preheating and pretreatment, high and low temperature shift converters, CO₂ removal and methanation units. Also a pressure swing adsorption (PSA) unit is required to gain a high hydrogen purity [88, 171]. By combination of hydrogen perm-selective membranes and steam reformer, the number of process units as well as the total reactor volume are decreased. Moreover under conditions of low temperatures, a higher hydrogen yields and methane conversions would be achieved [141, 172].

In addition in order to change the operating temperature is offered for shifting WGS reaction towards CO₂ and H₂ production, hydrogen removal from the reaction side also facilitates the equilibrium shifting of the reaction [87, 138]. As can be seen in Fig. 22 the membrane reactor can integrate these steps in only one reactor [2].

Figure 22

In autothermal reforming process, methane is partially oxidized in the presence of air or pure oxygen to provide the required reaction energy for in situ steam reforming [151, 164].

The possibility of performing of methane ATR in packed bed membrane reactors in isothermal and adiabatic mode of operation was investigated. The energy consumption by the reforming reaction in isothermal operation may be balanced by heat generated during combustion and water gas shift reactions, while in adiabatic operation, incredible high temperature gradients appear [151]. Figure 23 shows a membrane reactor for autothermal methane reforming [173].

Figure 23

8.2 Dehydrogenation process

Selective unsaturated alcohols dehydrogenation is the main process in the production of fine chemicals (i.e., unsaturated aldehydes in the synthesis of fragrances and pharmaceuticals). Selective dehydrogenation of hydroxyl groups in the presence of hydroxyl groups and carbon-carbon double bonds as reactive chemical structures bonds in unsaturated alcohols is too difficult because it leads to hydrogenation of both hydroxyl groups and carbon-carbon double bonds [174]. Hydrogen perm-selective membrane reactors such as Pd membrane reactors are interesting candidates for applications in dehydrogenation reactions, because the reaction shifts in favor of hydrogen production, which is withdrawn from the reaction side to permeation side [6, 175-181].

Palladium membrane reactors have the capability to promote dehydrogenation of cyclohexane to benzene [182], propane [77, 178, 179, 182] and isobutene [36, 183] and n-butane [77] and methylcyclohexane [31]. Hydrogen permeable membrane reactors have shown to be useful in the selective dehydrogenation of unsaturated alcohols to unsaturated aldehydes, due to the removal of produced hydrogen during dehydrogenation, which results

in more progress of the reaction. Table 2 presents some theoretical and experimental investigations on Pd-alloy membrane assisted in different types of reactor configuration.

Table 2

9 Recent development by research groups and companies

Recently, Italian groups have been at the forefront of research into membranes for hydrogen separation, particularly on thin film Pd-based alloy membranes. Angelo Basile is a senior researcher at ITM of the Italian national research council (CNR). His research area includes membrane for gas separation [50, 229-231], inorganic membrane reactors [232-236], modelling and simulation aspects [237-240]. Adolfo Iulianelli, as a researcher at the ITM-CNR works on membrane reactors [240-242], fuel cells [243-245], gas separation [246, 247] and hydrogen production from reforming reactions of renewable sources through inorganic membrane reactors [234, 248, 249]. Naotsugu Itoh at Utsunomiya University works mainly on functional membranes [250-252] and innovative chemical and separation processes [197, 253-256]. J. Douglas Way in Colorado University focused on application, study, and synthesis of new materials such as metals, microporous oxides and ionic polymers for use in novel separation processes include inorganic membranes and catalytic membrane reactors for fuel cells, applied to energy, environmental and chemical processing applications [21, 257-259].

The world's pioneering pilot scale membrane reformer (MRF) had built by Tokyo Gas and Mitsubishi Heavy Industries [260]. A very high purity hydrogen (99.999 %) can be produced in this reformer with a production capacity of 20 Nm³/h of H₂. Tokyo Gas then developed the first 40 Nm³/h-class MRF system in 2003 and then modified it for higher efficiency. The improved system with a high efficiency of 81.4% higher heating value in hydrogen

production proves the great potential of the MRF system for hydrogen production on a practical scale. Moreover, the purity of hydrogen produced was over 5 N, as required for hydrogen refuelling stations [261].

Another pioneering work had started since 1990 in Canada at the University of British Columbia and the University of Calgary for H₂ production by Pd based membrane reactors. Adris et al. constructed a pilot scale using a fluidized bed membrane reactor to maximize pure H₂ production with a capacity of 6 Nm³/h [262]. The common projects between Calgary and UBC have resulted to the foundation of Membrane Reactor Technologies Limited (MRT), which focuses on the commercial development of reformers [263].

Kinetics Technology reformer and membrane module (KT RMM) pilot plant was constructed in 2009 in Italy and the objective is studying the integration of hydrogen membranes in a real steam reforming environment. Generally, steam reforming processes are run at 850–900°C, which are above the working temperatures for Pd alloy membranes. So the pilot plant was built with two stages reformers and membrane separation units for a capacity of 20 Nm³/h of pure hydrogen [264].

10 Overview of recently researches on Pd membrane reactors

In this section, the outlook of researches done in 2004-2016 is presented. Despite numerous publications in these years in the Pd membrane reactor field, there is no opportunity of describing all papers. Therefore, it is sufficient to mention only two or three of the most important papers published per year.

In 2004, a novel Pd-membrane reactor configuration for methanol production was proposed by Rahimpour and Ghader [202]. Their study indicated that decreasing the feed flow rate, as the most important parameter, led to increasing the methanol production. In

2005, Schmidt et al. [265] carried out an experimental investigation on the selectivity of partial hydrogenation of unsaturated substrates in a membrane reactor. Abashar and Al-Rabiah [195] simulated a bench-scale membrane reactor for ethane dehydrogenation using a Pd-based membrane. Figure 24 shows a schematic of the composite Pd–Ag membrane reactor for this process. Aparicio et al. [196] designed and sized a palladium membrane reactor for H₂ production via dry reforming of methane. 95% H₂ production yields and a lower carbon deposition in the catalysts were achieved by the membrane reactor operation. In 2006, Basile et al. [266] studied pure hydrogen production of in methanol steam reforming (MSR) reaction by a flat Pd-Ag membrane reactor. Tosti et al. [267] produced a Pd-Ag thin wall tubes with 10 mm diameter and 150 mm length for application in both permeators and membrane reactors in order to produce highly pure hydrogen. In 2007, Sato et al. [197] conducted an experimental study about selective dehydrogenation of unsaturated alcohols via a hydrogen permeable Pd membrane reactor. Gallucci et al. [198] surveyed the dependency of temperature and hydrogen flux pressure on methane conversion and hydrogen recovery through the dense palladium membrane reactors. In 2008, Tosti and coworkers [268] performed an experimental investigation on palladium-silver thin wall tubes produced via diffusion welding. The results demonstrated the capability of these thin wall tubes for ultra-pure hydrogen production though the production rate strongly depends on the mechanical design of the membrane modules. Barbieri et al. [269] had an experimental investigation on an innovative Pd-alloy membrane reactor in order to analyze WGS reaction. Rahimpour et al. [98] investigated the removal of ammonia from purge syngas of an ammonia plant using a double pipe Pd-Ag membrane reactor. Chiappetta and coworkers [99] developed a two-dimensional mathematical model for WGS reaction. It was found that choosing appropriate values for sweep gas flow rate, feed temperature and pressure has a positive influence on hydrogen permeation, conversion and temperature distribution. In 2009, Parvasi et al. [187]

investigated Pd-Ag membrane methanol loop reactors by a set of ordinary differential as well as auxiliary correlations to evaluate the overall processes efficiency. Some advantages of catalytic membrane reactors were described by Lukyanov et al. [14] as below:

- Catalytic membrane reformers have the merits of high energy efficiency ($\geq 80\%$), good dynamic behavior, compact dimensions, and low temperature requirement of carbon reforming.
- Combination of catalytic membrane reactors with autothermal reforming are suggested due to their lower complicated heat supply at the reforming zone.
- They operation life of the reforming catalysts is high compared with catalytic membranes.

Figure 24

Brunetti et al. [100] studied improving features of a simulated reformat stream using a Pd-alloy membrane reactor and showed that the Pd-based membrane reactor can successfully overcomes the thermodynamic constraints of a traditional reactor. Khademi et al. [33] investigated methanol and benzene production in a hydrogen-permselective membrane reactor. Westermann and Melin [270] presented a completed review on flow-through catalytic membrane reactors. In 2010, Tosti et al. [199] carried out an experimental study on a membrane process for pure hydrogen production in ethanol steam reforming. In the study of Bernardo et al. [200] on methane steam reforming with hydrogen permselective Pd-membrane reactors, the results indicated that in situ separation of H_2 in the reaction side using steam as sweep gas and retentate stream as a heating utility leads to energy saving and clean technologies. Chiappetta et al. [271] evaluated the feed pressure and studied the effect of catalyst volume, gas hourly space velocity, membrane surface area and methane loading in

feed on the membrane reactor performance. Tosti [105] presented an overview of Pd-based membrane for pure hydrogen production. Pd-based membrane synthesis methods, design of membrane reactor modules and the various processes for pure hydrogen production by alcohols and hydrocarbons reforming were described in his paper. In 2011, Rahimpour et al. [191] studied a novel application of Pd-based membrane for hydrogen production in a wastewater treatment loop of urea plant. The effect of pre-reforming on the performance of Pd-alloy membrane reactors was investigated by Miyamoto et al. [2]. Santucci and coworkers [103] focused on the capability of a Pd-Ag membrane reactor in oxidative steam reforming of ethanol for ultrapure hydrogen production.

In 2012, Mardanpour et al. [194] developed a numerical solution for the enhancement of dimethyl ether synthesis using a hydrogen permselective Pd-based membrane in fluidized bed reactors. In 2013, Wei et al. [61] prepared a 4 μ m thickness Pd/Ag/PSS membrane by suction-assisted electroless plating technique. The permeation tests were conducted at 623, 673, 723 and 773 K and at the presence of pinholes at 773 K, the membrane became unstable. In 2014, Straczewski et al. [272] developed a thin Pd membranes supported on large porous tubes for a steam reformer. In their work, the concept of coupling membrane tube with the reformer-burner-unit (Fig. 25) was designed and tested. The burner was placed in the center, surrounded by the 1st reformer stage. This stage was in contact by the 2nd reformer stage, enclosed by the porous support tube with the membrane coating. There is a permeate chamber between the membrane and the outer housing. Abo-Ghander et al. [273] considered dehydrogenation of ethylbenzene and hydrogenation of nitrobenzene in a palladium hydrogen-selective-membrane reactor. The results indicated that intraparticle diffusion resistances were significant, as they not only retard the chemical reactions, but also the driving forces for permeation, as well as the heat transfer.

Figure 25

In 2015 Hani et al. applied Pd-Ru composite membrane to perform SMR upon a catalyst with base of Ni in high temperature [11]. Al-Mufachi et al. improved the hydrogen permeability by deposition of Pd thin film on to both feed and permeate sides of Pd-Cu membrane as illustrated in Fig. 26 [274]. Piskin et al. used a third element (Ti) into Pd-Ag membranes to check whether a reduction in their Pd content was possible or not. The results showed reduction of Pd in this three-component membrane Ag-Ti-Pd [275].

Figure 26

In 2016 Wang et al. investigated H diffusion through Pd-Y alloy membrane. They found that in the case of increasing atom fraction Y, H permeability is increased due to the effect of H₂ solubility increasing is more than reduction of diffusion constant [276]. Dias Silva et al. developed a dynamics mathematical model for steam reforming of methane process in both types of conventional and membrane reactor. 12.35% increasing of conversion in much lower temperature was obtained in the membrane reactor compared to the conventional one [277].

11 Future work

Numerous researches in the field of catalytic membrane reactors have presented in the literature providing useful information. But as the membrane reactor technology is not yet well commercialized, there is no comprehensive information on the cost of this technology. More researches must be conducted on finding an alternative membrane with higher permeability and selectivity during a long period of time at harsher operating conditions. In order to improve membrane technology, some essential investigations will be alluded in following lines:

- Fabrication of a thin defect free membrane with high flux and long term stability in various ranges of operating conditions
- Investigation of membrane permeability for hydrogen removal from potential coal gas contaminants such as HCl, NH₃ and trace metals
- A more detailed economic analysis of the membrane reactors
- Reduction of required membrane area and pressure vessel size by increasing the efficiency of membrane modules
- Optimal use of membrane reactors for minimization of catalyst and hardware cost
- Maximization of hydrogen recovery by a membrane with high separation factor
- Development of a process technology for hydrogen separation in the presence of a mixed gas feed stream for carbon capture
- Energy penalty minimization for CO₂ capture via process integration
- Use of high stable palladium alloys to tolerate severe process conditions, abrupt startups and shutdowns, and contaminants in feed streams
- Investigation on a less expensive and high stable alternative membrane material instead of palladium
- Improvement of the durability, reliability and stability of the membrane tubes at common operating conditions
- Investigation on the operating parameters such as feedstock composition and flow rate, pressure and temperature on hydrogen production reactions.
- Taking into account the impact of inhibitors and poisons on reaction rate modeling

12 Conclusion

This review paper deals with catalytic membrane reactors in order to combine the catalytic reaction and down-stream separation for ultrapure hydrogen production from hydrogen gas streams using palladium based membranes. Due to some disadvantages of the pure Pd-membrane, it is recommended to alloy palladium with other metals, particularly with silver to enhance hydrogen permeability. Also, Pd-alloy membranes supported on stainless steel are more superior to other metals for hydrogen separation from the reaction side, owing to their high permeability and 100% selectivity for hydrogen transport. In order to maximize Pd-based membrane efficiency, some useful suggestions are listed in the future work section. A great deal of studies has been reported during 2004-2016 with the concept of membrane reactor. Augmentation of product yield/selectivity and thermodynamically shifting the reactions are the main superiorities of the membrane reactors. This work emphasizes on various hydrogen generation reactions and different types of Pd-based membrane configuration as an appropriate reference for authors.

References:

- [1] M. Rahimpour, M. Bayat, Production of ultrapure hydrogen via utilizing fluidization concept from coupling of methanol and benzene synthesis in a hydrogen-permselective membrane reactor, *international journal of hydrogen energy* 36 (2011) 6616-6627.
- [2] M. Miyamoto, C. Hayakawa, K. Kamata, M. Arakawa, S. Uemiya, Influence of the pre-reformer in steam reforming of dodecane using a Pd alloy membrane reactor, *international journal of hydrogen energy* 36 (2011) 7771-7775.
- [3] T. Takeguchi, Y. Kani, T. Yano, R. Kikuchi, K. Eguchi, K. Tsujimoto, Y. Uchida, A. Ueno, K. Omoshiki, M. Aizawa, Study on steam reforming of CH₄ and C₂ hydrocarbons and carbon deposition on Ni-YSZ cermets, *Journal of Power Sources* 112 (2002) 588-595.
- [4] E. Nikolla, J. Schwank, S. Linic, Promotion of the long-term stability of reforming Ni catalysts by surface alloying, *Journal of catalysis* 250 (2007) 85-93.
- [5] W. Koros, Y. Ma, T. Shimidzu, Terminology for membranes and membrane processes, *J. Membr. Sci* 120 (1996) 149-159.
- [6] R. Dittmeyer, V. Höllein, K. Daub, Membrane reactors for hydrogenation and dehydrogenation processes based on supported palladium, *Journal of Molecular Catalysis A: Chemical* 173 (2001) 135-184.
- [7] J.A. Nolle, *Leçons de physique expérimentale*, Guerin 1784.
- [8] R. Hughes, Composite palladium membranes for catalytic membrane reactors, *Membrane Technology 2001* (2001) 9-13.
- [9] G. Lu, J.D. Da Costa, M. Duke, S. Giessler, R. Socolow, R. Williams, T. Kreutz, Inorganic membranes for hydrogen production and purification: a critical review and perspective, *Journal of colloid and interface science* 314 (2007) 589-603.
- [10] R. Gardner, R. Crane, J. Hannan, Hollow Fiber Permeator for Separating Gases, *Chemical Engineering Progress* 73 (1977) 76-78.
- [11] H.W.A. El Hawa, S.N. Paglieri, C.C. Morris, A. Harale, J.D. Way, Application of a Pd–Ru composite membrane to hydrogen production in a high temperature membrane reactor, *Separation and Purification Technology* 147 (2015) 388-397.
- [12] E. Fernandez, J.A. Medrano, J. Melendez, M. Parco, J.L. Viviente, M. van Sint Annaland, F. Gallucci, D.P. Tanaka, Preparation and characterization of metallic supported thin Pd–Ag membranes for hydrogen separation, *Chemical Engineering Journal* (2015).
- [13] E. Fernandez, K. Coenen, A. Helmi, J. Melendez, J. Zuñiga, D.P. Tanaka, M. van Sint Annaland, F. Gallucci, Preparation and characterization of thin-film Pd–Ag supported membranes for high-temperature applications, *International Journal of Hydrogen Energy* 40 (2015) 13463-13478.
- [14] B. Lukyanov, D. Andreev, V. Parmon, Catalytic reactors with hydrogen membrane separation, *Chemical Engineering Journal* 154 (2009) 258-266.
- [15] F. Gallucci, E. Fernandez, P. Corengia, M. van Sint Annaland, Recent advances on membranes and membrane reactors for hydrogen production, *Chemical Engineering Science* 92 (2013) 40-66.
- [16] K. Yeung, S. Christiansen, A. Varma, Palladium composite membranes by electroless plating technique: relationships between plating kinetics, film microstructure and membrane performance, *Journal of Membrane Science* 159 (1999) 107-122.
- [17] S. Tennison, Current hurdles in the commercial development of inorganic membrane reactors, *Membrane Technology 2000* (2000) 4-9.
- [18] A. Julbe, D. Farrusseng, C. Guizard, Porous ceramic membranes for catalytic reactors—overview and new ideas, *Journal of Membrane Science* 181 (2001) 3-20.

- [19] S.K. Gade, P.M. Thoen, J.D. Way, Unsupported palladium alloy foil membranes fabricated by electroless plating, *Journal of Membrane Science* 316 (2008) 112-118.
- [20] B.D. Morreale, The influence of H₂S on palladium and palladium-copper alloy membranes, University of Pittsburgh, 2006.
- [21] C.A. Wolden, K. Adeyemo, R.H. Vervuurt, M. Ostwal, J.D. Way, Mechanistic studies of hydrogen transport through Mo₂C/V composite membranes, *Journal of membrane science* 427 (2013) 150-154.
- [22] S. Paglieri, J. Way, Innovations in palladium membrane research, *Separation & Purification Reviews* 31 (2002) 1-169.
- [23] A. Basile, F. Gallucci, S. Tosti, Synthesis, characterization, and applications of palladium membranes, *Membrane science and technology* 13 (2008) 255-323.
- [24] F. Shi, *Reactor and Process Design in Sustainable Energy Technology*, Elsevier 2014.
- [25] N. Al-Mufachi, N. Rees, R. Steinberger-Wilkens, Hydrogen selective membranes: a review of palladium-based dense metal membranes, *Renewable and Sustainable Energy Reviews* 47 (2015) 540-551.
- [26] T. Graham, On the absorption and dialytic separation of gases by colloid septa, *Philosophical transactions of the Royal Society of London* 156 (1866) 399-439.
- [27] S. Yun, S.T. Oyama, Correlations in palladium membranes for hydrogen separation: a review, *Journal of membrane science* 375 (2011) 28-45.
- [28] J. Tong, Y. Matsumura, H. Suda, K. Haraya, Thin and dense Pd/CeO₂/MPSS composite membrane for hydrogen separation and steam reforming of methane, *Separation and Purification Technology* 46 (2005) 1-10.
- [29] V. Gryaznov, Hydrogen permeable palladium membrane catalysts, *Platinum Metals Review* 30 (1986) 68-72.
- [30] Y. Sakamoto, F. Chen, M. Furukawa, M. Noguchi, Permeability and diffusivity of hydrogen in palladium-rich Pd-Y (Gd)-Ag ternary alloys, *Journal of alloys and compounds* 185 (1992) 191-205.
- [31] S. Yolcular, Hydrogen recovery from methylcyclohexane as a chemical hydrogen carrier using a palladium membrane reactor, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 38 (2016) 2148-2152.
- [32] R. Checchetto, N. Bazzanella, B. Patton, A. Miotello, Palladium membranes prepared by rf magnetron sputtering for hydrogen purification, *Surface and Coatings Technology* 177 (2004) 73-79.
- [33] M. Khademi, A. Jahanmiri, M. Rahimpour, A novel configuration for hydrogen production from coupling of methanol and benzene synthesis in a hydrogen-permselective membrane reactor, *international journal of hydrogen energy* 34 (2009) 5091-5107.
- [34] J. Zaman, A. Chakma, Inorganic membrane reactors, *Journal of Membrane Science* 92 (1994) 1-28.
- [35] E. Gobina, K. Hou, R. Hughes, Ethane dehydrogenation in a catalytic membrane reactor coupled with a reactive sweep gas, *Chemical engineering science* 50 (1995) 2311-2319.
- [36] W. Liang, R. Hughes, The catalytic dehydrogenation of isobutane to isobutene in a palladium/silver composite membrane reactor, *Catalysis Today* 104 (2005) 238-243.
- [37] A. Li, W. Liang, R. Hughes, Characterisation and permeation of palladium/stainless steel composite membranes, *Journal of Membrane Science* 149 (1998) 259-268.
- [38] P.P. Mardilovich, Y. She, Y.H. Ma, M.H. Rei, Defect-free palladium membranes on porous stainless-steel support, *AIChE journal* 44 (1998) 310-322.
- [39] S. Uemiya, Y. Kude, K. Sugino, N. Sato, T. Matsuda, E. Kikuchi, A palladium/porous-glass composite membrane for hydrogen separation, *Chemistry Letters* 17 (1988) 1687-1690.

- [40] G. Xomeritakis, Y. Lin, Fabrication of a thin palladium membrane supported in a porous ceramic substrate by chemical vapor deposition, *Journal of Membrane Science* 120 (1996) 261-272.
- [41] M.C. Iliuta, B.P. Grandjean, F. Larachi, Methane nonoxidative aromatization over Ru-Mo/HZSM-5 at temperatures up to 973 K in a palladium-silver/stainless steel membrane reactor, *Industrial & engineering chemistry research* 42 (2003) 323-330.
- [42] F. Roa, J.D. Way, Influence of alloy composition and membrane fabrication on the pressure dependence of the hydrogen flux of palladium-copper membranes, *Industrial & engineering chemistry research* 42 (2003) 5827-5835.
- [43] F. Gallucci, L. Paturzo, A. Famà, A. Basile, Experimental study of the methane steam reforming reaction in a dense Pd/Ag membrane reactor, *Industrial & engineering chemistry research* 43 (2004) 928-933.
- [44] J. Tong, L. Su, Y. Kashima, R. Shirai, H. Suda, Y. Matsumura, Simultaneously depositing Pd-Ag thin membrane on asymmetric porous stainless steel tube and application to produce hydrogen from steam reforming of methane, *Industrial & engineering chemistry research* 45 (2006) 648-655.
- [45] Y. Huang, R. Dittmeyer, Preparation of thin palladium membranes on a porous support with rough surface, *Journal of Membrane Science* 302 (2007) 160-170.
- [46] R. Sanz, J. Calles, D. Alique, L. Furones, S. Ordóñez, P. Marín, P. Corengia, E. Fernandez, Preparation, testing and modelling of a hydrogen selective Pd/YSZ/SS composite membrane, *international journal of hydrogen energy* 36 (2011) 15783-15793.
- [47] C. Su, T. Jin, K. Kuraoka, Y. Matsumura, T. Yazawa, Thin palladium film supported on SiO₂-modified porous stainless steel for a high-hydrogen-flux membrane, *Industrial & engineering chemistry research* 44 (2005) 3053-3058.
- [48] K.S. Rothenberger, A.V. Cugini, B.H. Howard, R.P. Killmeyer, M.V. Ciocco, B.D. Morreale, R.M. Enick, F. Bustamante, I.P. Mardilovich, Y.H. Ma, High pressure hydrogen permeance of porous stainless steel coated with a thin palladium film via electroless plating, *Journal of membrane science* 244 (2004) 55-68.
- [49] M.L. Bosko, F. Ojeda, E.A. Lombardo, L.M. Cornaglia, NaA zeolite as an effective diffusion barrier in composite Pd/PSS membranes, *Journal of Membrane Science* 331 (2009) 57-65.
- [50] S. Liguori, A. Iulianelli, F. Dalena, P. Pinacci, F. Drago, M. Broglia, Y. Huang, A. Basile, Performance and long-term stability of Pd/PSS and Pd/Al₂O₃ membranes for hydrogen separation, *Membranes* 4 (2014) 143-162.
- [51] X. Li, A. Li, C.J. Lim, J.R. Grace, Hydrogen permeation through Pd-based composite membranes: Effects of porous substrate, diffusion barrier and sweep gas, *Journal of Membrane Science* 499 (2016) 143-155.
- [52] H. Hsieh, R. Bhavé, H.L. Fleming, Microporous alumina membranes, *Journal of membrane science* 39 (1988) 221-241.
- [53] K. Babita, S. Sridhar, K. Raghavan, Membrane reactors for fuel cell quality hydrogen through WGSR—review of their status, challenges and opportunities, *international journal of hydrogen energy* 36 (2011) 6671-6688.
- [54] J. Sanchez, T. Tsotsis, A. Burggraaf, L. Cot, *Fundamentals of inorganic membrane science and technology*, Elsevier, Amsterdam, The Netherlands, 1996.
- [55] A. Li, J.R. Grace, C.J. Lim, Preparation of thin Pd-based composite membrane on planar metallic substrate: Part II. Preparation of membranes by electroless plating and characterization, *Journal of Membrane Science* 306 (2007) 159-165.

- [56] D. Pizzi, R. Worth, M.G. Baschetti, G.C. Sarti, K.-i. Noda, Hydrogen permeability of 2.5 μm palladium–silver membranes deposited on ceramic supports, *Journal of Membrane Science* 325 (2008) 446-453.
- [57] A.I. Pereira, P. Pérez, S. Rodrigues, A. Mendes, L. Madeira, C. Tavares, Deposition of Pd–Ag thin film membranes on ceramic supports for hydrogen purification/separation, *Materials Research Bulletin* 61 (2015) 528-533.
- [58] D.R. Lide, *CRC handbook of chemistry and physics*, CRC press 2004.
- [59] J. Shu, A. Adnot, B. Grandjean, S. Kaliaguine, Structurally stable composite Pd–Ag alloy membranes: Introduction of a diffusion barrier, *Thin Solid Films* 286 (1996) 72-79.
- [60] S.-E. Nam, K.-H. Lee, Hydrogen separation by Pd alloy composite membranes: introduction of diffusion barrier, *Journal of Membrane Science* 192 (2001) 177-185.
- [61] L. Wei, J. Yu, Y. Huang, Silver coating on porous stainless steel substrate and preparation of H₂-permeable palladium membranes, *International Journal of Hydrogen Energy* 38 (2013) 10833-10838.
- [62] M. Kitiwan, D. Atong, Effects of porous alumina support and plating time on electroless plating of palladium membrane, *Journal of Materials Science & Technology* 26 (2010) 1148-1152.
- [63] Y. Cheng, K. Yeung, Effects of electroless plating chemistry on the synthesis of palladium membranes, *Journal of Membrane Science* 182 (2001) 195-203.
- [64] O. Altinisik, M. Dogan, G. Dogu, Preparation and characterization of palladium-plated porous glass for hydrogen enrichment, *Catalysis Today* 105 (2005) 641-646.
- [65] R. Bhandari, Y.H. Ma, Pd–Ag membrane synthesis: the electroless and electro-plating conditions and their effect on the deposits morphology, *Journal of Membrane Science* 334 (2009) 50-63.
- [66] A. Li, W. Liang, R. Hughes, Repair of a Pd/ α -Al₂O₃ composite membrane containing defects, *Separation and purification technology* 15 (1999) 113-119.
- [67] J. Okazaki, T. Ikeda, D.A.P. Tanaka, K. Sato, T.M. Suzuki, F. Mizukami, An investigation of thermal stability of thin palladium–silver alloy membranes for high temperature hydrogen separation, *Journal of membrane science* 366 (2011) 212-219.
- [68] G. Xomeritakis, L. Yue-Sheng, CVD synthesis and gas permeation properties of thin palladium/alumina membranes, *American Institute of Chemical Engineers. AIChE Journal* 44 (1998) 174.
- [69] E. Feurer, H. Suhr, Thin palladium films prepared by metal-organic plasma-enhanced chemical vapour deposition, *Thin Solid Films* 157 (1988) 81-86.
- [70] G. Xomeritakis, Y. Lin, Fabrication of thin metallic membranes by MOCVD and sputtering, *Journal of membrane science* 133 (1997) 217-230.
- [71] C.-S. Jun, K.-H. Lee, Palladium and palladium alloy composite membranes prepared by metal-organic chemical vapor deposition method (cold-wall), *Journal of Membrane Science* 176 (2000) 121-130.
- [72] D.M. Mattox, *Handbook of Physical Vapor Deposition (PVD) Processing*, Film Formation, Adhesion, Surface Preparation and Contamination Control, 1998, and.
- [73] D.M. Mattox, Physical vapor deposition (PVD) processes, *Metal Finishing* 97 (1999) 410-423.
- [74] A.-L. Thomann, J. Rozenbaum, P. Brault, C. Andreazza-Vignolle, P. Andreazza, Pd nanoclusters grown by plasma sputtering deposition on amorphous substrates, *Applied Surface Science* 158 (2000) 172-183.
- [75] S. Deshmukh, S. Heinrich, L. Mörl, M. van Sint Annaland, J. Kuipers, Membrane assisted fluidized bed reactors: potentials and hurdles, *Chemical Engineering Science* 62 (2007) 416-436.

- [76] H. Klette, R. Bredeesen, Sputtering of very thin palladium-alloy hydrogen separation membranes, *Membrane Technology* 2005 (2005) 7-9.
- [77] L. Didenko, V. Savchenko, L. Sementsova, P. Chizov, Some peculiarities of dehydrogenation of propane and n, *Petroleum Chemistry* 56 (2016) 459-464.
- [78] S. Goto, S. Assabumrungrat, T. Tagawa, P. Praserttham, The effect of direction of hydrogen permeation on the rate through a composite palladium membrane, *Journal of Membrane Science* 175 (2000) 19-24.
- [79] W. Liang, R. Hughes, The effect of diffusion direction on the permeation rate of hydrogen in palladium composite membranes, *Chemical Engineering Journal* 112 (2005) 81-86.
- [80] C.P. O'Brien, A.J. Gellman, B.D. Morreale, J.B. Miller, The hydrogen permeability of Pd 4 S, *Journal of membrane science* 371 (2011) 263-267.
- [81] C.P. O'Brien, B.H. Howard, J.B. Miller, B.D. Morreale, A.J. Gellman, Inhibition of hydrogen transport through Pd and Pd 47 Cu 53 membranes by H₂ S at 350 C, *Journal of Membrane Science* 349 (2010) 380-384.
- [82] C. Ling, D.S. Sholl, First principles investigation of metal sulfides as membranes in hydrogen purification, *Journal of Membrane Science* 329 (2009) 153-159.
- [83] G. Barbieri, F. Scura, F. Lentini, G. De Luca, E. Drioli, A novel model equation for the permeation of hydrogen in mixture with carbon monoxide through Pd–Ag membranes, *Separation and Purification technology* 61 (2008) 217-224.
- [84] J. Boon, J. Pieterse, F. van Berkel, Y. van Delft, M. van Sint Annaland, Hydrogen permeation through palladium membranes and inhibition by carbon monoxide, carbon dioxide, and steam, *Journal of Membrane Science* 496 (2015) 344-358.
- [85] F. Gallucci, F. Chiaravalloti, S. Tosti, E. Drioli, A. Basile, The effect of mixture gas on hydrogen permeation through a palladium membrane: experimental study and theoretical approach, *International Journal of Hydrogen Energy* 32 (2007) 1837-1845.
- [86] H. Amandusson, L.-G. Ekedahl, H. Dannetun, The effect of CO and O₂ on hydrogen permeation through a palladium membrane, *Applied Surface Science* 153 (2000) 259-267.
- [87] F. Gielens, R. Knibbeler, P. Duysinx, H. Tong, M. Vorstman, J. Keurentjes, Influence of steam and carbon dioxide on the hydrogen flux through thin Pd/Ag and Pd membranes, *Journal of Membrane Science* 279 (2006) 176-185.
- [88] A. Li, W. Liang, R. Hughes, The effect of carbon monoxide and steam on the hydrogen permeability of a Pd/stainless steel membrane, *Journal of Membrane Science* 165 (2000) 135-141.
- [89] J. Catalano, M.G. Baschetti, G.C. Sarti, Influence of water vapor on hydrogen permeation through 2.5 μm Pd–Ag membranes, *International Journal of Hydrogen Energy* 36 (2011) 8658-8673.
- [90] K. Hou, R. Hughes, The effect of external mass transfer, competitive adsorption and coking on hydrogen permeation through thin Pd/Ag membranes, *Journal of Membrane Science* 206 (2002) 119-130.
- [91] A. Mahecha-Botero, T. Boyd, A. Gulamhusein, N. Comyn, C.J. Lim, J.R. Grace, Y. Shirasaki, I. Yasuda, Pure hydrogen generation in a fluidized-bed membrane reactor: experimental findings, *Chemical Engineering Science* 63 (2008) 2752-2762.
- [92] G. Berkheimer, R. Buxbaum, Erratum: Hydrogen pumping with palladium membranes [*J. Vac. Sci. Technol. A* 3, 412 (1985)], *Journal of Vacuum Science & Technology A* 3 (1985) 2044-2044.
- [93] A. Caravella, F. Scura, G. Barbieri, E. Drioli, Sieverts law empirical exponent for Pd-based membranes: critical analysis in pure H₂ permeation, *The Journal of Physical Chemistry B* 114 (2010) 6033-6047.

- [94] N.D. Deveau, Y.H. Ma, R. Datta, Beyond Sieverts' law: a comprehensive microkinetic model of hydrogen permeation in dense metal membranes, *Journal of membrane science* 437 (2013) 298-311.
- [95] F. Keil, *Modeling of process intensification*, John Wiley & Sons 2007.
- [96] R. Mallada, M. Menéndez, *Inorganic membranes: synthesis, characterization and applications*, Elsevier 2008.
- [97] D. Mendes, S. Sá, S. Tosti, J.M. Sousa, L.M. Madeira, A. Mendes, Experimental and modeling studies on the low-temperature water-gas shift reaction in a dense Pd–Ag packed-bed membrane reactor, *Chemical engineering science* 66 (2011) 2356-2367.
- [98] M. Rahimpour, A. Asgari, Modeling and simulation of ammonia removal from purge gases of ammonia plants using a catalytic Pd–Ag membrane reactor, *Journal of hazardous materials* 153 (2008) 557-565.
- [99] G. Chiappetta, G. Clarizia, E. Drioli, Theoretical analysis of the effect of catalyst mass distribution and operation parameters on the performance of a Pd-based membrane reactor for water–gas shift reaction, *Chemical Engineering Journal* 136 (2008) 373-382.
- [100] A. Brunetti, G. Barbieri, E. Drioli, Upgrading of a syngas mixture for pure hydrogen production in a Pd–Ag membrane reactor, *Chemical Engineering Science* 64 (2009) 3448-3454.
- [101] K. Sato, S. Hamakawa, M. Natsui, M. Nishioka, T. Inoue, F. Mizukami, Palladium-based bifunctional membrane reactor for one-step conversion of benzene to phenol and cyclohexanone, *Catalysis Today* 156 (2010) 276-281.
- [102] G. Barbieri, F. Scura, A. Brunetti, Mathematical Modeling of Pd- Alloy Membrane Reactors, *Membrane Science and Technology* 13 (2008) 325-400.
- [103] A. Santucci, M.C. Annesini, F. Borgognoni, L. Marrelli, M. Rega, S. Tosti, Oxidative steam reforming of ethanol over a Pt/Al₂O₃ catalyst in a Pd-based membrane reactor, *international journal of hydrogen energy* 36 (2011) 1503-1511.
- [104] G. Marigliano, G. Barbieri, E. Drioli, Equilibrium conversion for a Pd-based membrane reactor. Dependence on the temperature and pressure, *Chemical Engineering and Processing: Process Intensification* 42 (2003) 231-236.
- [105] S. Tosti, Overview of Pd-based membranes for producing pure hydrogen and state of art at ENEA laboratories, *International Journal of Hydrogen Energy* 35 (2010) 12650-12659.
- [106] L. Brandão, L.M. Madeira, A.M. Mendes, Propyne hydrogenation in a continuous polymeric catalytic membrane reactor, *Chemical Engineering Science* 62 (2007) 6768-6776.
- [107] R. Petersen, J. Cadotte, M. Porter, *Handbook of industrial membrane technology*, Noyes Publication, New Jersey (1990).
- [108] E. McLeary, J. Jansen, F. Kapteijn, Zeolite based films, membranes and membrane reactors: Progress and prospects, *Microporous and Mesoporous Materials* 90 (2006) 198-220.
- [109] M. Vospernik, A. Pintar, G. Berčič, J. Levec, Experimental verification of ceramic membrane potentials for supporting three-phase catalytic reactions, *Journal of membrane science* 223 (2003) 157-169.
- [110] W. Yu, T. Ohmori, T. Yamamoto, A. Endo, M. Nakaiwa, T. Hayakawa, N. Itoh, Simulation of a porous ceramic membrane reactor for hydrogen production, *International journal of hydrogen energy* 30 (2005) 1071-1079.
- [111] G. Szejner, M. Sheintuch, Application of a carbon membrane reactor for dehydrogenation reactions, *Chemical engineering science* 59 (2004) 2013-2021.
- [112] A. Lapkin, S. Tennison, W. Thomas, A porous carbon membrane reactor for the homogeneous catalytic hydration of propene, *Chemical engineering science* 57 (2002) 2357-2369.

- [113] F.A. Silva, C.E. Hori, A.M. da Silva, L.V. Mattos, J. Múnera, L. Cornaglia, F.B. Noronha, E. Lombardo, Hydrogen production through CO₂ reforming of CH₄ over Pt/CeZrO₂/Al₂O₃ catalysts using a Pd–Ag membrane reactor, *Catalysis Today* 193 (2012) 64-73.
- [114] M. Farsi, M. Khademi, A. Jahanmiri, M. Rahimpour, Optimal conditions for hydrogen production from coupling of dimethyl ether and benzene synthesis, *international journal of hydrogen energy* 36 (2011) 299-310.
- [115] F. Samimi, S. Kabiri, A. Mirvakili, M. Rahimpour, The concept of integrated thermally double coupled reactor for simultaneous production of methanol, hydrogen and gasoline via differential evolution method, *Journal of Natural Gas Science and Engineering* 14 (2013) 144-157.
- [116] M. Rahimpour, E. Pourazadi, A comparison of hydrogen and methanol production in a thermally coupled membrane reactor for co- current and counter- current flows, *International Journal of Energy Research* 35 (2011) 863-882.
- [117] M. Khademi, M. Rahimpour, A. Jahanmiri, Differential evolution (DE) strategy for optimization of hydrogen production, cyclohexane dehydrogenation and methanol synthesis in a hydrogen-permselective membrane thermally coupled reactor, *international journal of hydrogen energy* 35 (2010) 1936-1950.
- [118] M.R. Rahimpour, Z.A. Aboosadi, A.H. Jahanmiri, Differential evolution (DE) strategy for optimization of methane steam reforming and hydrogenation of nitrobenzene in a hydrogen perm- selective membrane thermally coupled reactor, *International Journal of Energy Research* 37 (2013) 868-878.
- [119] M. Rahimpour, A. Mirvakili, K. Paymooni, Hydrogen as an energy carrier: A comparative study between decalin and cyclohexane in thermally coupled membrane reactors in gas-to-liquid technology, *international journal of hydrogen energy* 36 (2011) 6970-6984.
- [120] R. Vakili, M. Rahimpour, R. Eslamloueyan, Incorporating differential evolution (DE) optimization strategy to boost hydrogen and DME production rate through a membrane assisted single-step DME heat exchanger reactor, *Journal of Natural Gas Science and Engineering* 9 (2012) 28-38.
- [121] M. Bayat, M. Rahimpour, Simultaneous utilization of two different membranes for intensification of ultrapure hydrogen production from recuperative coupling autothermal multitubular reactor, *international journal of hydrogen energy* 36 (2011) 7310-7325.
- [122] F. Samimi, S. Kabiri, A. Mirvakili, M. Rahimpour, Simultaneous dimethyl ether synthesis and decalin dehydrogenation in an optimized thermally coupled dual membrane reactor, *Journal of Natural Gas Science and Engineering* 14 (2013) 77-90.
- [123] M. Rahimpour, Z.A. Aboosadi, A. Jahanmiri, Synthesis gas production in a novel hydrogen and oxygen perm-selective membranes tri-reformer for methanol production, *Journal of Natural Gas Science and Engineering* 9 (2012) 149-159.
- [124] M. Abashar, Modeling and simulation of an integrated multi-shell fixed bed membrane reactor with well-mixed catalyst pattern for production of styrene and cyclohexane, *Chemical Engineering and Processing: Process Intensification* 50 (2011) 931-939.
- [125] M. Farsi, A. Jahanmiri, Methanol production in an optimized dual-membrane fixed-bed reactor, *Chemical Engineering and Processing: Process Intensification* 50 (2011) 1177-1185.
- [126] M. Rahimpour, A. Forghani, A.K. Mostafazadeh, A. Shariati, A comparison of co-current and counter-current modes of operation for a novel hydrogen-permselective membrane dual-type FTS reactor in GTL technology, *Fuel Processing Technology* 91 (2010) 33-44.

- [127] M. Rahimpour, M. Baktash, B. Vaferi, S. Mazinani, Reduction in CO emissions along a two-stage hydrogen-permselective membrane reactor in methanol synthesis process, *Journal of Industrial and Engineering Chemistry* 17 (2011) 198-207.
- [128] M. Rahimpour, M. Bayat, A novel cascade membrane reactor concept for methanol synthesis in the presence of long- term catalyst deactivation, *International journal of energy research* 34 (2010) 1356-1371.
- [129] D. Iranshahi, E. Pourazadi, K. Paymooni, M. Rahimpour, Utilizing DE optimization approach to boost hydrogen and octane number in a novel radial-flow assisted membrane naphtha reactor, *Chemical engineering science* 68 (2012) 236-249.
- [130] D. Iranshahi, M. Jafari, R. Rafiei, M. Karimi, S. Amiri, M.R. Rahimpour, Optimal design of a radial-flow membrane reactor as a novel configuration for continuous catalytic regenerative naphtha reforming process considering a detailed kinetic model, *International Journal of Hydrogen Energy* 38 (2013) 8384-8399.
- [131] M. Farsi, A. Jahanmiri, M. Rahimpour, Optimal conditions of isobutane dehydrogenation in radial flow moving bed hydrogen-permselective membrane reactors to enhance isobutene and hydrogen production, *Chemical Engineering and Processing: Process Intensification* 75 (2014) 126-133.
- [132] F. Samimi, M. Bayat, D. Karimipourfard, M. Rahimpour, P. Keshavarz, A novel axial-flow spherical packed-bed membrane reactor for dimethyl ether synthesis: simulation and optimization, *Journal of Natural Gas Science and Engineering* 13 (2013) 42-51.
- [133] F. Samimi, M. Bayat, M. Rahimpour, P. Keshavarz, Mathematical modeling and optimization of DME synthesis in two spherical reactors connected in series, *Journal of Natural Gas Science and Engineering* 17 (2014) 33-41.
- [134] M.R. Rahimpour, D. Iranshahi, K. Paymooni, E. Pourazadi, Enhancement in research octane number and hydrogen production via dynamic optimization of a novel spherical axial-flow membrane naphtha reformer, *Industrial & Engineering Chemistry Research* 51 (2011) 398-409.
- [135] D. Iranshahi, M. Rahimpour, K. Paymooni, E. Pourazadi, Utilizing DE optimization approach to boost hydrogen and octane number, through a combination of radial-flow spherical and tubular membrane reactors in catalytic naphtha reformers, *Fuel* 111 (2013) 1-11.
- [136] W. Jin, X. Gu, S. Li, P. Huang, N. Xu, J. Shi, Experimental and simulation study on a catalyst packed tubular dense membrane reactor for partial oxidation of methane to syngas, *Chemical Engineering Science* 55 (2000) 2617-2625.
- [137] E. Kikuchi, Membrane reactor application to hydrogen production, *Catalysis Today* 56 (2000) 97-101.
- [138] W. Yu, T. Ohmori, S. Kataoka, T. Yamamoto, A. Endo, M. Nakaiwa, N. Itoh, A comparative simulation study of methane steam reforming in a porous ceramic membrane reactor using nitrogen and steam as sweep gases, *International Journal of Hydrogen Energy* 33 (2008) 685-692.
- [139] A. Caravella, G. Barbieri, E. Drioli, Concentration polarization analysis in self-supported Pd-based membranes, *Separation and Purification Technology* 66 (2009) 613-624.
- [140] T. Nakajima, T. Kume, Y. Ikeda, M. Shiraki, H. Kurokawa, T. Iseki, M. Kajitani, H. Tanaka, H. Hikosaka, Y. Takagi, Effect of concentration polarization on hydrogen production performance of ceramic-supported Pd membrane module, *International Journal of Hydrogen Energy* 40 (2015) 11451-11456.
- [141] F. Gallucci, M. Van Sintannaland, J. Kuipers, Theoretical comparison of packed bed and fluidized bed membrane reactors for methane reforming, *international journal of hydrogen energy* 35 (2010) 7142-7150.

- [142] M. Rahimpour, Enhancement of hydrogen production in a novel fluidized-bed membrane reactor for naphtha reforming, *international journal of hydrogen energy* 34 (2009) 2235-2251.
- [143] M. Rahimpour, F. Rahmani, M. Bayat, Contribution to emission reduction of CO₂ by a fluidized-bed membrane dual-type reactor in methanol synthesis process, *Chemical Engineering and Processing: Process Intensification* 49 (2010) 589-598.
- [144] Y.-M. Lin, M.-H. Rei, Study on the hydrogen production from methanol steam reforming in supported palladium membrane reactor, *Catalysis Today* 67 (2001) 77-84.
- [145] T. Tiemersma, C. Patil, M. van Sint Annaland, J. Kuipers, Modelling of packed bed membrane reactors for autothermal production of ultrapure hydrogen, *Chemical Engineering Science* 61 (2006) 1602-1616.
- [146] M. Abashar, Coupling of steam and dry reforming of methane in catalytic fluidized bed membrane reactors, *International Journal of Hydrogen Energy* 29 (2004) 799-808.
- [147] A.-E.M. Adris, J.R. Grace, Characteristics of fluidized-bed membrane reactors: scale-up and practical issues, *Industrial & engineering chemistry research* 36 (1997) 4549-4556.
- [148] M. Rahimpour, M. Dehnavi, F. Allahgholipour, D. Iranshahi, S. Jokar, Assessment and comparison of different catalytic coupling exothermic and endothermic reactions: a review, *Applied Energy* 99 (2012) 496-512.
- [149] A. Adris, S. Elnashaie, R. Hughes, A fluidized bed membrane reactor for the steam reforming of methane, *The Canadian Journal of Chemical Engineering* 69 (1991) 1061-1070.
- [150] A. Adris, C.J. Lim, J. Grace, The fluidized bed membrane reactor system: a pilot scale experimental study, *Chemical Engineering Science* 49 (1994) 5833-5843.
- [151] A. Adris, C. Lim, J. Grace, The fluidized-bed membrane reactor for steam methane reforming: model verification and parametric study, *Chemical Engineering Science* 52 (1997) 1609-1622.
- [152] M. Rahimpour, M. Bayat, F. Rahmani, Enhancement of methanol production in a novel cascading fluidized-bed hydrogen permselective membrane methanol reactor, *Chemical Engineering Journal* 157 (2010) 520-529.
- [153] M. Rahimpour, M. Bayat, F. Rahmani, Dynamic simulation of a cascade fluidized-bed membrane reactor in the presence of long-term catalyst deactivation for methanol synthesis, *Chemical Engineering Science* 65 (2010) 4239-4249.
- [154] M. Bayat, M. Rahimpour, A novel cascade fluidized-bed reactor assisted by hydrogen permselective membrane concept for improving gasoline productivity and selectivity in Fischer–Tropsch synthesis: A simulation study, *Journal of Natural Gas Science and Engineering* 13 (2013) 20-29.
- [155] M. Rahimpour, S. Jokar, Z. Jamshidnejad, A novel slurry bubble column membrane reactor concept for Fischer–Tropsch synthesis in GTL technology, *Chemical Engineering Research and Design* 90 (2012) 383-396.
- [156] D. Wang, W. Teo, K. Li, Preparation and characterization of high-flux polysulfone hollow fibre gas separation membranes, *Journal of membrane science* 204 (2002) 247-256.
- [157] D. Mendes, V. Chibante, J.-M. Zheng, S. Tosti, F. Borgognoni, A. Mendes, L.M. Madeira, Enhancing the production of hydrogen via water–gas shift reaction using Pd-based membrane reactors, *international journal of hydrogen energy* 35 (2010) 12596-12608.
- [158] A. Basile, A. Criscuoli, F. Santella, E. Drioli, Membrane reactor for water gas shift reaction, *Gas separation & purification* 10 (1996) 243-254.
- [159] M. Adrover, A. Anzola, S. Schbib, M. Pedernera, D. Borio, Effect of flow configuration on the behavior of a membrane reactor operating without sweep gas, *Catalysis Today* 156 (2010) 223-228.

- [160] R. Chein, Y.-C. Chen, J. Chung, Parametric study of membrane reactors for hydrogen production via high-temperature water gas shift reaction, *International Journal of Hydrogen Energy* 38 (2013) 2292-2305.
- [161] D. MENDES, C. MIGUEL, V. GOMES, A. MENDES, L. MADEIRA, DEVELOPMENTS ON PdSBASED MEMBRANE REACTORS FOR HYDROGEN CLEANSUP VIA WATERSGAS SHIFT REACTION, (2011).
- [162] A. Shigarov, V. Meshcheryakov, V. Kirillov, Use of Pd membranes in catalytic reactors for steam methane reforming for pure hydrogen production, *Theoretical Foundations of Chemical Engineering* 45 (2011) 595-609.
- [163] J.R. Lattner, M.P. Harold, Comparison of conventional and membrane reactor fuel processors for hydrocarbon-based PEM fuel cell systems, *International Journal of Hydrogen Energy* 29 (2004) 393-417.
- [164] S. Uemiya, Brief review of steam reforming using a metal membrane reactor, *Topics in Catalysis* 29 (2004) 79-84.
- [165] A. Basile, F. Gallucci, A. Iulianelli, S. Tosti, CO- Free Hydrogen Production by Ethanol Steam Reforming in a Pd–Ag Membrane Reactor, *Fuel Cells* 8 (2008) 62-68.
- [166] A. Iulianelli, A. Basile, An experimental study on bio-ethanol steam reforming in a catalytic membrane reactor. Part I: temperature and sweep-gas flow configuration effects, *international journal of hydrogen energy* 35 (2010) 3170-3177.
- [167] A. Iulianelli, S. Liguori, T. Longo, S. Tosti, P. Pinacci, A. Basile, An experimental study on bio-ethanol steam reforming in a catalytic membrane reactor. Part II: Reaction pressure, sweep factor and WHSV effects, *international journal of hydrogen energy* 35 (2010) 3159-3164.
- [168] A. Santucci, F. Borgogni, S. Cordiner, E. Traversa, S. Tosti, Low temperature ethanol steam reforming in a Pd-Ag membrane reformer, *ECS Transactions* 6 (2008) 29-35.
- [169] S. UEMIYA, S. MISHIMA, I. MIYAZAKI, R. YOSHIIE, H. MORITOMI, M. NISHIMURA, Fabrication of Supported Palladium Membrane for Membrane Reformer, (2004).
- [170] M. Appl, *Modern production technologies, ammonia, methanol, hydrogen, carbon monoxide*, CRU Publishing Ltd, 1997.
- [171] M. Sjardin, K.J. Damen, A. Faaij, Techno-economic prospects of small-scale membrane reactors in a future hydrogen-fuelled transportation sector, *Energy* 31 (2006) 2523-2555.
- [172] C.S. Patil, M. van Sint Annaland, J. Kuipers, Fluidised bed membrane reactor for ultrapure hydrogen production via methane steam reforming: Experimental demonstration and model validation, *Chemical Engineering Science* 62 (2007) 2989-3007.
- [173] J.R. Lattner, M.P. Harold, Comparison of methanol-based fuel processors for PEM fuel cell systems, *Applied Catalysis B: Environmental* 56 (2005) 149-169.
- [174] T. Sato, H. Yokoyama, H. Miki, N. Itoh, Dehydrogenation of unsaturated alcohols with CuO/ZnO catalysts, *Kagaku Kogaku Ronbunshu* 32 (2006) 274-280.
- [175] G. Saracco, H. Neomagus, G. Versteeg, W. Van Swaaij, High-temperature membrane reactors: potential and problems, *Chemical engineering science* 54 (1999) 1997-2017.
- [176] N. Itoh, Y. Kaneko, A. Igarashi, Efficient hydrogen production via methanol steam reforming by preventing back-permeation of hydrogen in a palladium membrane reactor, *Industrial & engineering chemistry research* 41 (2002) 4702-4706.
- [177] N. Itoh, W. Xu, S. Hara, K. Kakehida, Y. Kaneko, A. Igarashi, Effects of hydrogen removal on the catalytic reforming of n-hexane in a palladium membrane reactor, *Industrial & engineering chemistry research* 42 (2003) 6576-6581.

- [178] P. Quicker, V. Höllein, R. Dittmeyer, Catalytic dehydrogenation of hydrocarbons in palladium composite membrane reactors, *Catalysis today* 56 (2000) 21-34.
- [179] K. Kusakabe, S. Fumio, T. Eda, M. Oda, K.-I. Sotowa, Hydrogen production in zirconia membrane reactors for use in PEM fuel cells, *International journal of hydrogen energy* 30 (2005) 989-994.
- [180] J. Tong, Y. Matsumura, Pure hydrogen production by methane steam reforming with hydrogen-permeable membrane reactor, *Catalysis today* 111 (2006) 147-152.
- [181] A. Basile, L. Di Paola, F. Hai, V. Piemonte, *Membrane reactors for energy applications and basic chemical production*, Elsevier 2015.
- [182] H. Weyten, J. Luyten, K. Keizer, L. Willems, R. Leysen, Membrane performance: the key issues for dehydrogenation reactions in a catalytic membrane reactor, *Catalysis today* 56 (2000) 3-11.
- [183] M. Sheintuch, R.M. Dessau, Observations, modeling and optimization of yield, selectivity and activity during dehydrogenation of isobutane and propane in a Pd membrane reactor, *Chemical Engineering Science* 51 (1996) 535-547.
- [184] H.W.A. El Hawa, S.-T.B. Lundin, N.S. Patki, J.D. Way, Steam methane reforming in a Pd Au membrane reactor: Long-term assessment, *International Journal of Hydrogen Energy* (2016).
- [185] K. Ghasemzadeh, R. Zeynali, F. Ahmadnejad, A. Babalou, A. Basile, Investigation of Palladium Membrane Reactor Performance during Ethanol Steam Reforming using CFD Method, *Chemical Product and Process Modeling* 11 (2016) 51-55.
- [186] S. Tosti, C. Rizzello, F. Borgognoni, N. Ghirelli, A. Santucci, P. Trabuc, Design of Pd-based membrane reactor for gas detritiation, *Fusion Engineering and design* 86 (2011) 2180-2183.
- [187] P. Parvasi, A.K. Mostafazadeh, M. Rahimpour, Dynamic modeling and optimization of a novel methanol synthesis loop with hydrogen-permselective membrane reactor, *international journal of hydrogen energy* 34 (2009) 3717-3733.
- [188] D. Mendes, S. Tosti, F. Borgognoni, A. Mendes, L.M. Madeira, Integrated analysis of a membrane-based process for hydrogen production from ethanol steam reforming, *Catalysis Today* 156 (2010) 107-117.
- [189] W.-H. Lin, Y.-C. Liu, H.-F. Chang, Hydrogen production from oxidative steam reforming of ethanol in a palladium–silver alloy composite membrane reactor, *Journal of the Chinese Institute of Chemical Engineers* 39 (2008) 435-440.
- [190] M. Rahimpour, S. Ghader, Enhancement of CO conversion in a novel Pd–Ag membrane reactor for methanol synthesis, *Chemical Engineering and Processing: Process Intensification* 43 (2004) 1181-1188.
- [191] M. Rahimpour, H. Mottaghi, M. Barmaki, Hydrogen production from urea wastewater using a combination of urea thermal hydrolyser–desorber loop and a hydrogen-permselective membrane reactor, *Fuel Processing Technology* 91 (2010) 600-612.
- [192] G. Barbieri, A. Brunetti, G. Tricoli, E. Drioli, An innovative configuration of a Pd-based membrane reactor for the production of pure hydrogen: experimental analysis of water gas shift, *Journal of Power Sources* 182 (2008) 160-167.
- [193] M. Abdollahi, J. Yu, P.K. Liu, R. Ciora, M. Sahimi, T.T. Tsotsis, Ultra-pure hydrogen production from reformat mixtures using a palladium membrane reactor system, *Journal of membrane science* 390 (2012) 32-42.
- [194] M.M. Mardanpour, R. Sadeghi, M.R. Ehsani, M.N. Esfahany, Enhancement of dimethyl ether production with application of hydrogen-permselective Pd-based membrane in fluidized bed reactor, *Journal of Industrial and Engineering Chemistry* 18 (2012) 1157-1165.

- [195] M. Abashar, A. Al-Rabiah, Production of ethylene and cyclohexane in a catalytic membrane reactor, *Chemical Engineering and Processing: Process Intensification* 44 (2005) 1188-1196.
- [196] P. Ferreira-Aparicio, M. Benito, K. Kouachi, S. Menad, Catalysis in membrane reformers: a high-performance catalytic system for hydrogen production from methane, *Journal of catalysis* 231 (2005) 331-343.
- [197] T. Sato, H. Yokoyama, H. Miki, N. Itoh, Selective dehydrogenation of unsaturated alcohols and hydrogen separation with a palladium membrane reactor, *Journal of membrane science* 289 (2007) 97-105.
- [198] F. Gallucci, M. De Falco, S. Tosti, L. Marrelli, A. Basile, The effect of the hydrogen flux pressure and temperature dependence factors on the membrane reactor performances, *International Journal of Hydrogen Energy* 32 (2007) 4052-4058.
- [199] S. Tosti, F. Borgognoni, A. Santucci, Multi-tube Pd–Ag membrane reactor for pure hydrogen production, *international journal of hydrogen energy* 35 (2010) 11470-11477.
- [200] P. Bernardo, G. Barbieri, E. Drioli, Evaluation of membrane reactor with hydrogen-selective membrane in methane steam reforming, *Chemical Engineering Science* 65 (2010) 1159-1166.
- [201] S. Assabumrungrat, K. Suksomboon, P. Praserttham, T. Tagawa, S. Goto, Simulation of a Palladium Membrane Reactor for Dehydrogenation of Ethylbenzene, *Journal of chemical engineering of Japan* 35 (2002) 263-273.
- [202] M. Rahimpour, S. Ghader, Theoretical Investigation of a Pd- membrane Reactor for Methanol Synthesis, *Chemical engineering & technology* 26 (2003) 902-907.
- [203] J. Zaman, A. Chakma, A simulation study on the thermal decomposition of hydrogen sulfide in a membrane reactor, *International journal of hydrogen energy* 20 (1995) 21-28.
- [204] A. Basile, L. Paturzo, A. Vazzana, Membrane reactor for the production of hydrogen and higher hydrocarbons from methane over Ru/Al₂O₃ catalyst, *Chemical Engineering Journal* 93 (2003) 31-39.
- [205] S. Tosti, A. Basile, G. Chiappetta, C. Rizzello, V. Violante, Pd–Ag membrane reactors for water gas shift reaction, *Chemical Engineering Journal* 93 (2003) 23-30.
- [206] K. Sato, T.-a. Hanaoka, S.-i. Niwa, C. Stefan, T. Namba, F. Mizukami, Direct hydroxylation of aromatic compounds by a palladium membrane reactor, *Catalysis today* 104 (2005) 260-266.
- [207] C. Yazhong, X. Hengyong, W. Yuzhong, G. XIONG, Application of coprecipitated nickel catalyst to steam reforming of higher hydrocarbons in membrane reactor, *Chinese Journal of Catalysis* 27 (2006) 772-777.
- [208] A. Basile, S. Tosti, G. Capannelli, G. Vitulli, A. Iulianelli, F. Gallucci, E. Drioli, Co-current and counter-current modes for methanol steam reforming membrane reactor: experimental study, *Catalysis today* 118 (2006) 237-245.
- [209] A. Brunetti, A. Caravella, G. Barbieri, E. Drioli, Simulation study of water gas shift reaction in a membrane reactor, *Journal of Membrane Science* 306 (2007) 329-340.
- [210] O. Iyoha, R. Enick, R. Killmeyer, B. Howard, B. Morreale, M. Ciocco, Wall-catalyzed water-gas shift reaction in multi-tubular Pd and 80wt% Pd–20wt% Cu membrane reactors at 1173K, *Journal of membrane science* 298 (2007) 14-23.
- [211] N. Itoh, S. Watanabe, K. Kawasoe, T. Sato, T. Tsuji, A membrane reactor for hydrogen storage and transport system using cyclohexane–methylcyclohexane mixtures, *Desalination* 234 (2008) 261-269.
- [212] S.A.S. Rezai, Y. Traa, Equilibrium shift in membrane reactors: A thermodynamic analysis of the dehydrogenative conversion of alkanes, *Journal of Membrane Science* 319 (2008) 279-285.

- [213] G. Manzolini, S. Tosti, Hydrogen production from ethanol steam reforming: energy efficiency analysis of traditional and membrane processes, *international journal of hydrogen energy* 33 (2008) 5571-5582.
- [214] S.-H. Cheng, H.-J. Chen, H. Chang, C.-K. Chang, Y.-M. Chen, Multi-objective optimization for two catalytic membrane reactors—methanol synthesis and hydrogen production, *Chemical Engineering Science* 63 (2008) 1428-1437.
- [215] A. Caravella, F.P. Di Maio, A. Di Renzo, Optimization of membrane area and catalyst distribution in a permeative-stage membrane reactor for methane steam reforming, *Journal of Membrane Science* 321 (2008) 209-221.
- [216] A. Li, C.J. Lim, J.R. Grace, Staged-separation membrane reactor for steam methane reforming, *Chemical Engineering Journal* 138 (2008) 452-459.
- [217] A.K. Mostafazadeh, M. Rahimpour, A membrane catalytic bed concept for naphtha reforming in the presence of catalyst deactivation, *Chemical Engineering and Processing: Process Intensification* 48 (2009) 683-694.
- [218] L. Bortolotto, R. Dittmeyer, Direct hydroxylation of benzene to phenol in a novel microstructured membrane reactor with distributed dosing of hydrogen and oxygen, *Separation and Purification Technology* 73 (2010) 51-58.
- [219] A. Iulianelli, S. Liguori, V. Calabrò, P. Pinacci, A. Basile, Partial oxidation of ethanol in a membrane reactor for high purity hydrogen production, *International Journal of Hydrogen Energy* 35 (2010) 12626-12634.
- [220] F. Gallucci, M.V.S. Annaland, J. Kuipers, Pure hydrogen production via autothermal reforming of ethanol in a fluidized bed membrane reactor: a simulation study, *international journal of hydrogen energy* 35 (2010) 1659-1668.
- [221] A. Di Carlo, A. Dell'Era, Z. Del Prete, 3D simulation of hydrogen production by ammonia decomposition in a catalytic membrane reactor, *international journal of hydrogen energy* 36 (2011) 11815-11824.
- [222] D. Iranshahi, E. Pourazadi, K. Paymooni, M. Rahimpour, A. Jahanmiri, B. Moghtaderi, A dynamic membrane reactor concept for naphtha reforming, considering radial-flow patterns for both sweeping gas and reacting materials, *Chemical engineering journal* 178 (2011) 264-275.
- [223] R. Koc, N.K. Kazantzis, Y.H. Ma, A process dynamic modeling and control framework for performance assessment of Pd/alloy-based membrane reactors used in hydrogen production, *international journal of hydrogen energy* 36 (2011) 4934-4951.
- [224] C. Yu, H. Xu, An efficient palladium membrane reactor to increase the yield of styrene in ethylbenzene dehydrogenation, *Separation and Purification Technology* 78 (2011) 249-252.
- [225] M. Rahimpour, S. Mazinani, B. Vaferi, M. Baktash, Comparison of two different flow types on CO removal along a two-stage hydrogen permselective membrane reactor for methanol synthesis, *Applied energy* 88 (2011) 41-51.
- [226] A. Basile, P. Pinacci, A. Iulianelli, M. Broglia, F. Drago, S. Liguori, T. Longo, V. Calabrò, Ethanol steam reforming reaction in a porous stainless steel supported palladium membrane reactor, *international journal of hydrogen energy* 36 (2011) 2029-2037.
- [227] R. Koc, N.K. Kazantzis, Y.H. Ma, Process safety aspects in water-gas-shift (WGS) membrane reactors used for pure hydrogen production, *Journal of Loss Prevention in the Process Industries* 24 (2011) 852-869.
- [228] F. García-García, L. Torrente-Murciano, D. Chadwick, K. Li, Hollow fibre membrane reactors for high H₂ yields in the WGS reaction, *Journal of membrane science* 405 (2012) 30-37.

- [229] A. Iulianelli, C. Algieri, L. Donato, A. Garofalo, F. Galiano, G. Bagnato, A. Basile, A. Figoli, New PEEK-WC and PLA membranes for H₂ separation, *International Journal of Hydrogen Energy* (2017).
- [230] E. Drioli, G. Golemme, A. Basile, S.M. Zhang, Polyorganophosphazene Membranes for Gas Separation: Preparation, Characterization and Transport Properties, *Key Engineering Materials*, Trans Tech Publ, 1992, pp. 611.
- [231] V. Violante, E. Drioli, A. Basile, Catalytic ceramic membrane reactor design for hydrogen separation from inert gas via oxidation, *Journal of membrane science* 104 (1995) 11-17.
- [232] K. Ghasemzadeh, R. Zeynali, A. Basile, Theoretical study of hydrogen production using inorganic membrane reactors during WGS reaction, *International Journal of Hydrogen Energy* 41 (2016) 8696-8705.
- [233] V. Piemonte, D. Di Paola, M. De Falco, A. Iulianelli, A. Basile, Hydrogen production using inorganic membrane reactors, *Advances in hydrogen production, storage and distribution*. Cambridge, UK: Woodhead Publishing (2014) 283-316.
- [234] A. Iulianelli, S. Liguori, P. Pinacci, P. Morrone, A. Basile, Inorganic membrane reactor for hydrogen production through bio-ethanol reforming processes, ethanol: production, cellular mechanisms and health impact. Nova Science Publishers (2012) 79-102.
- [235] A. Iulianelli, S. Liguori, T. Longo, A. Basile, Inorganic membrane and membrane reactor technologies for hydrogen production, *Hydrogen Production: Prospects and Processes* (2012) 377-398.
- [236] A. Iulianelli, A. Basile, Hydrogen production from ethanol via inorganic membrane reactors technology: a review, *Catalysis Science & Technology* 1 (2011) 366-379.
- [237] M. De Falco, M. Capocelli, A. Basile, Selective membrane application for the industrial one-step DME production process fed by CO₂ rich streams: Modeling and simulation, *International Journal of Hydrogen Energy* 42 (2017) 6771-6786.
- [238] K. Ghasemzadeh, E. Andalib, A. Basile, Modelling Study of Palladium Membrane Reactor Performance during Methan Steam Reforming using CFD Method, *Chemical Product and Process Modeling* 11 (2016) 17-21.
- [239] A. Aghaeinejad- Meybodi, K. Ghasemzadeh, A.A. Babaluo, P. Morrone, A. Basile, Modeling study of silica membrane performance for hydrogen separation, *Asia- Pacific Journal of Chemical Engineering* 10 (2015) 781-790.
- [240] K. Ghasemzadeh, P. Morrone, S. Liguori, A. Babaluo, A. Basile, Evaluation of silica membrane reactor performance for hydrogen production via methanol steam reforming: modeling study, *International Journal of Hydrogen Energy* 38 (2013) 16698-16709.
- [241] A. Iulianelli, M. Alavi, G. Bagnato, S. Liguori, J. Wilcox, M.R. Rahimpour, R. Eslamlouyan, B. Anzelmo, A. Basile, Supported Pd-Au membrane reactor for hydrogen production: Membrane preparation, characterization and testing, *Molecules* 21 (2016) 581.
- [242] A. Iulianelli, S. Liguori, J. Wilcox, A. Basile, Advances on methane steam reforming to produce hydrogen through membrane reactors technology: A review, *Catalysis Reviews* 58 (2016) 1-35.
- [243] A. Iulianelli, S. Liguori, Y. Huang, A. Basile, Model biogas steam reforming in a thin Pd-supported membrane reactor to generate clean hydrogen for fuel cells, *Journal of Power Sources* 273 (2015) 25-32.
- [244] A. Iulianelli, I. Gatto, F. Trotta, M. Biasizzo, E. Passalacqua, A. Carbone, A. Bevilacqua, G. Clarizia, A. Gugliuzza, A. Basile, Electrochemical characterization of sulfonated PEEK-WC membranes for PEM fuel cells, *International Journal of Hydrogen Energy* 38 (2013) 551-557.

- [245] A. Iulianelli, P. Seelam, S. Liguori, T. Longo, R. Keiski, V. Calabro, A. Basile, Hydrogen production for PEM fuel cell by gas phase reforming of glycerol as byproduct of bio-diesel. The use of a Pd–Ag membrane reactor at middle reaction temperature, *international journal of hydrogen energy* 36 (2011) 3827-3834.
- [246] K. Briceño, A. Iulianelli, D. Montané, R. Garcia-Valls, A. Basile, Carbon molecular sieve membranes supported on non-modified ceramic tubes for hydrogen separation in membrane reactors, *international journal of hydrogen energy* 37 (2012) 13536-13544.
- [247] K. Briceño, D. Montané, R. Garcia-Valls, A. Iulianelli, A. Basile, Fabrication variables affecting the structure and properties of supported carbon molecular sieve membranes for hydrogen separation, *Journal of membrane science* 415 (2012) 288-297.
- [248] G. Bagnato, A. Iulianelli, A. Sanna, A. Basile, Glycerol Production and Transformation: A Critical Review with Particular Emphasis on Glycerol Reforming Reaction for Producing Hydrogen in Conventional and Membrane Reactors, *Membranes* 7 (2017) 17.
- [249] A. Iulianelli, F. Dalena, S. Liguori, V. Calabrò, A. Basile, Membrane reactors for steam reforming of glycerol and acetic acid, Ch. 9, *Membrane reactors for energy applications and basic chemical production*. Woodhead (2015) 249-266.
- [250] T. Matsui, T. Watanabe, K. Matsuzawa, M. Kakeno, N. Okumura, I. Sugiyama, N. Itoh, K. Kaibuchi, PAR3 and aPKC regulate Golgi organization through CLASP2 phosphorylation to generate cell polarity, *Molecular biology of the cell* 26 (2015) 751-761.
- [251] Y. Nakayama, N. Nakamura, T. Kawai, E. Kaneda, Y. Takahashi, A. Miyake, N. Itoh, A. Kurosaka, Identification and expression analysis of zebrafish polypeptide α -N-acetylgalactosaminyltransferase Y-subfamily genes during embryonic development, *Gene Expression Patterns* 16 (2014) 1-7.
- [252] H. Orita, N. Itoh, Simulation of phenol formation from benzene with a Pd membrane reactor: ab initio periodic density functional study, *Applied Catalysis A: General* 258 (2004) 17-23.
- [253] N. Nagai, Y. Hasegawa, N. Itoh, F. Mizukami, Fabrication of Microporous Separation Membrane using Boehmite Nanofibers, *KAGAKU KOGAKU RONBUNSHU* 39 (2013) 514-519.
- [254] Y. Yoshino, Y. Ando, H. Taguchi, N. Itoh, Selection of CVD precursors for improving high-temperature stability of porous silica membrane for hydrogen separation, *Kagaku Kogaku Ronbunshu* 34 (2008) 242-248.
- [255] Y. Yoshino, T. Suzuki, H. Taguchi, M. Nomura, S.-i. Nakao, N. Itoh, Development of an all-ceramic module with silica membrane tubes for high temperature hydrogen separation, *Separation Science and Technology* 43 (2008) 3432-3447.
- [256] Y. Yoshino, B.N. Nair, H. Taguchi, N. Itoh, Silica and Silica-Metal Membranes for Hydrogen Separation and Membrane Reactors, *The 2005 Annual Meeting*, 2005.
- [257] H.W.A. El Hawa, S.-T.B. Lundin, N.S. Patki, J.D. Way, Steam methane reforming in a Pd Au membrane reactor: Long-term assessment, *International Journal of Hydrogen Energy* 41 (2016) 10193-10201.
- [258] P. Jha, L.W. Mason, J.D. Way, Characterization of silicone rubber membrane materials at low temperature and low pressure conditions, *Journal of membrane science* 272 (2006) 125-136.
- [259] F. Roa, J.D. Way, R.L. McCormick, S.N. Paglieri, Preparation and characterization of Pd–Cu composite membranes for hydrogen separation, *Chemical Engineering Journal* 93 (2003) 11-22.
- [260] L. Paturzo, A. Basile, E. Drioli, High temperature membrane reactors and integrated membrane operations, *Reviews in Chemical Engineering* 18 (2002) 511-552.

- [261] H. Yakabe, H. Kurokawa, Y. Shirasaki, I. Yasuda, Operation of a palladium membrane reformer system for hydrogen production: the case of Tokyo Gas, *Palladium Membrane Technology for Hydrogen Production, Carbon Capture and Other Applications: Principles, Energy Production and Other Applications* (2014) 303.
- [262] A.-E.M. Adris, J.R. Grace, C.J. Lim, S.S. Elnashaie, Fluidized bed reaction system for steam/hydrocarbon gas reforming to produce hydrogen, *Google Patents*, 1994.
- [263] C. Patil, Membrane reactor technology for ultrapure hydrogen production (PhD Thesis) Vol, PhD, University of Twente, Enschede, The Netherlands (2005) 245.
- [264] G. Iaquaniello, E. Palo, A. Salladini, B. Cucchiella, Using palladium membrane reformers for hydrogen production, *Palladium Membrane Technology for Hydrogen Production, Carbon Capture and Other Applications: Principles, Energy Production and Other Applications* (2014) 287.
- [265] A. Schmidt, R. Haidar, R. Schomäcker, Selectivity of partial hydrogenation reactions performed in a pore-through-flow catalytic membrane reactor, *Catalysis today* 104 (2005) 305-312.
- [266] A. Basile, G. Tereschenko, N. Orekhova, M. Ermilova, F. Gallucci, A. Iulianelli, An experimental investigation on methanol steam reforming with oxygen addition in a flat Pd–Ag membrane reactor, *International journal of hydrogen energy* 31 (2006) 1615-1622.
- [267] S. Tosti, A. Basile, F. Borgognoni, L. Bettinali, C. Rizzello, Pd membrane reactor design, *Desalination* 200 (2006) 676-678.
- [268] S. Tosti, A. Basile, L. Bettinali, F. Borgognoni, F. Gallucci, C. Rizzello, Design and process study of Pd membrane reactors, *International Journal of Hydrogen Energy* 33 (2008) 5098-5105.
- [269] G. Barbieri, G. Marigliano, G. Perri, E. Drioli, Conversion-temperature diagram for a palladium membrane reactor. Analysis of an endothermic reaction: methane steam reforming, *Industrial & engineering chemistry research* 40 (2001) 2017-2026.
- [270] T. Westermann, T. Melin, Flow-through catalytic membrane reactors—principles and applications, *Chemical Engineering and Processing: Process Intensification* 48 (2009) 17-28.
- [271] G. Chiappetta, G. Barbieri, E. Drioli, Pd/Ag-based membrane reactors on small scale: Assessment of the feed pressure and design parameters effect on the performance, *Chemical Engineering and Processing: Process Intensification* 49 (2010) 722-731.
- [272] G. Straczewski, J. Völler-Blumenroth, H. Beyer, P. Pfeifer, M. Steffen, I. Felden, A. Heinzl, M. Wessling, R. Dittmeyer, Development of thin palladium membranes supported on large porous 310L tubes for a steam reformer operated with gas-to-liquid fuel, *Chemical Engineering and Processing: Process Intensification* 81 (2014) 13-23.
- [273] N.S. Abo-Ghander, F. Logist, J.R. Grace, J.F. Van Impe, S.S. Elnashaie, C.J. Lim, Heterogeneous modeling of an autothermal membrane reactor coupling dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline: Fickian diffusion model, *Chemical Engineering and Processing: Process Intensification* 77 (2014) 50-65.
- [274] N. Al-Mufachi, S. Nayeibossadri, J. Speight, W. Bujalski, R. Steinberger-Wilckens, D. Book, Effects of thin film Pd deposition on the hydrogen permeability of Pd 60 Cu 40 wt% alloy membranes, *Journal of Membrane Science* 493 (2015) 580-588.
- [275] F. Pişkin, H. Akyıldız, T. Öztürk, Ti modified Pd–Ag membranes for hydrogen separation, *International Journal of Hydrogen Energy* 40 (2015) 7553-7558.
- [276] D. Wang, T.B. Flanagan, K. Shanahan, Diffusion of H through Pd–Y alloy membranes, *Journal of Membrane Science* 499 (2016) 452-461.
- [277] J.D. Silva, C.A.M. de Abreu, Modelling and simulation in conventional fixed-bed and fixed-bed membrane reactors for the steam reforming of methane, *International Journal of Hydrogen Energy* (2016).

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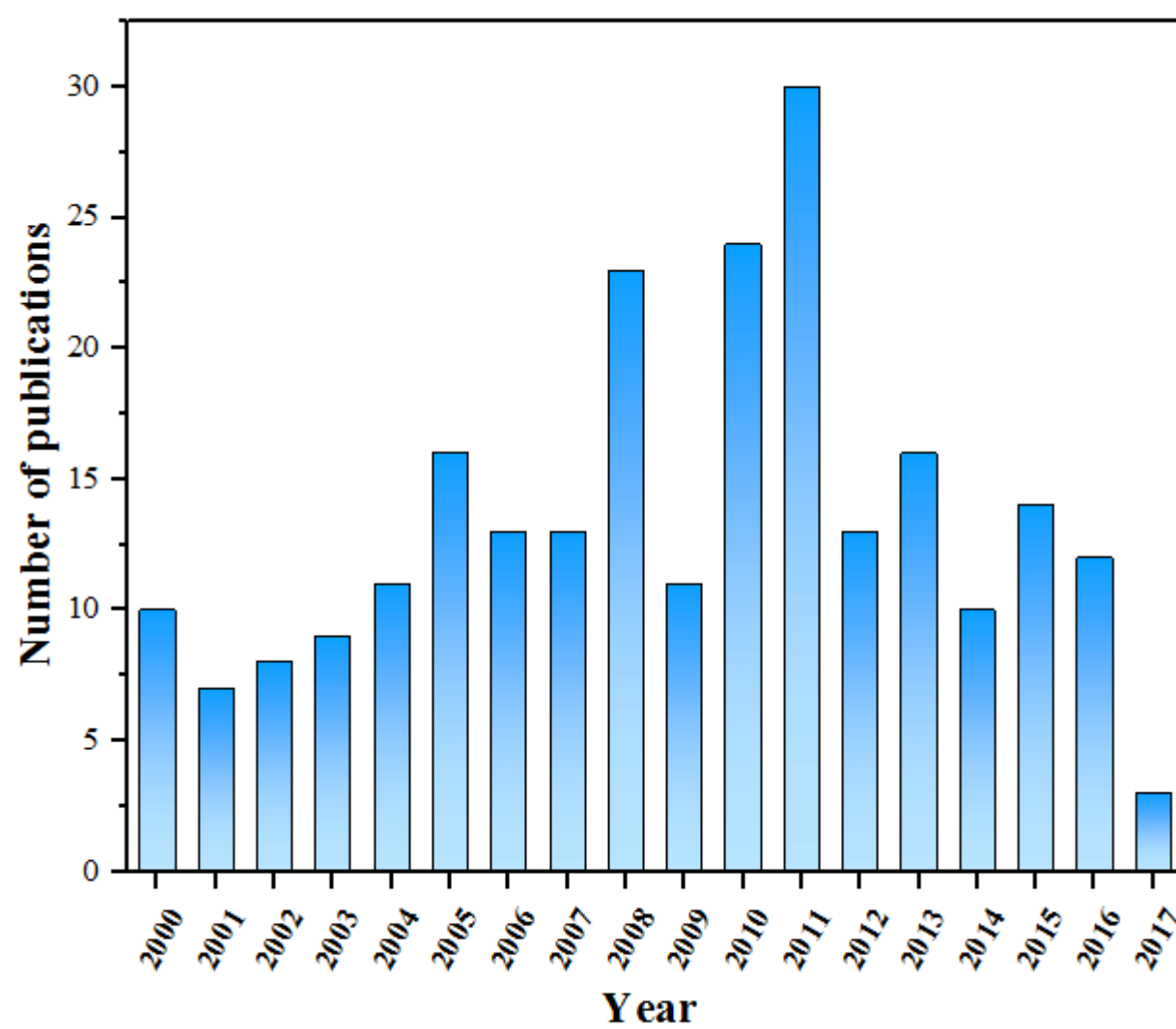
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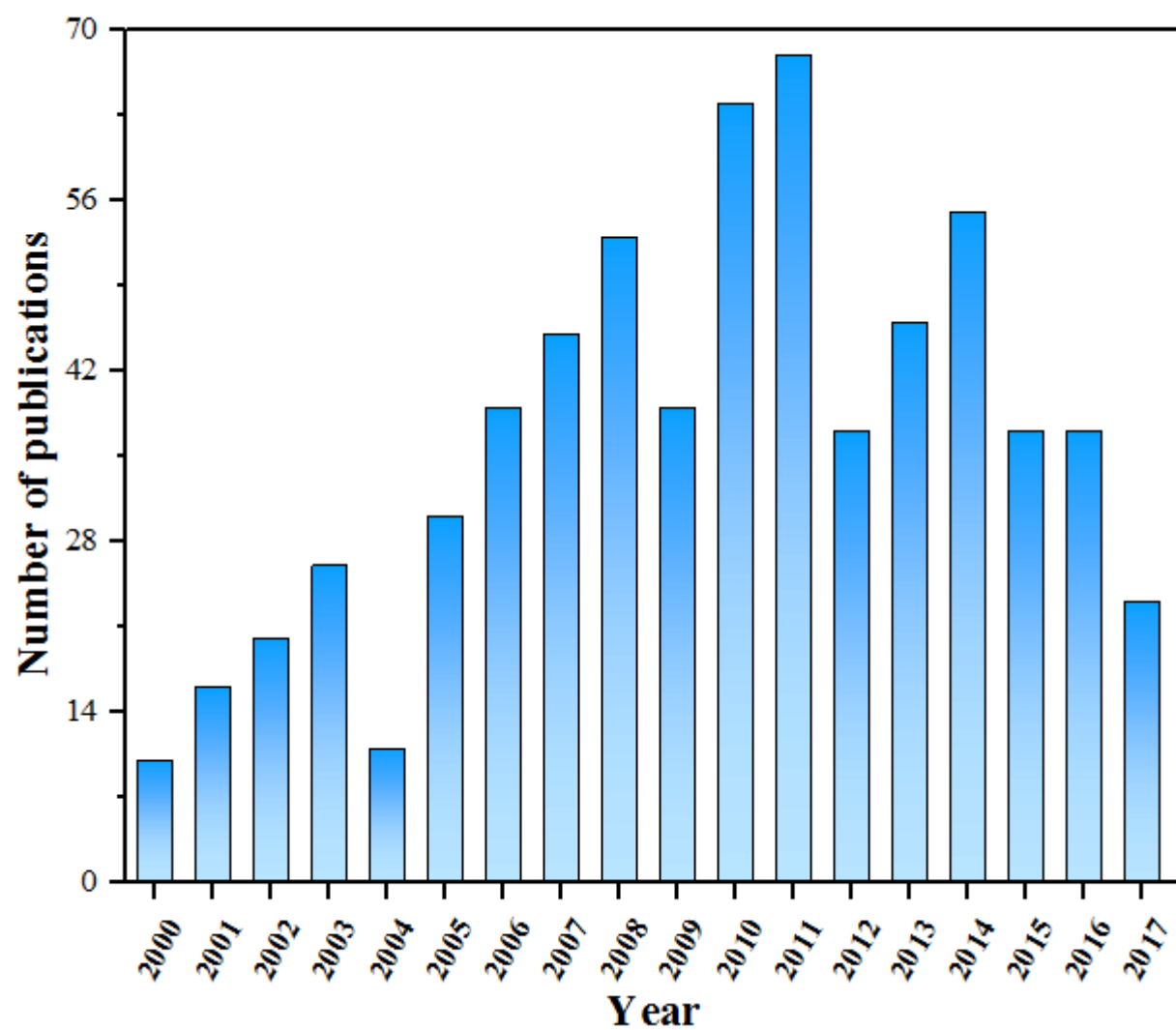
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**1 (a)**



1 (b)

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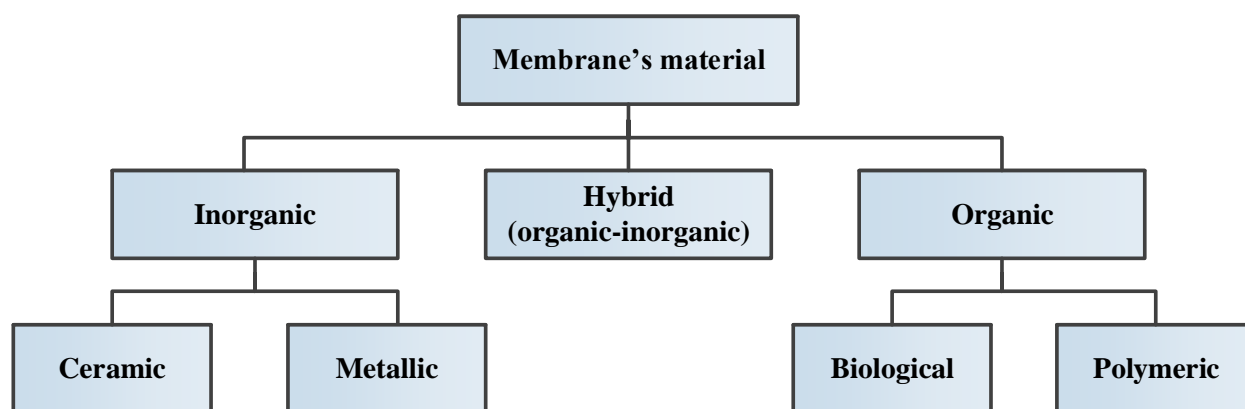


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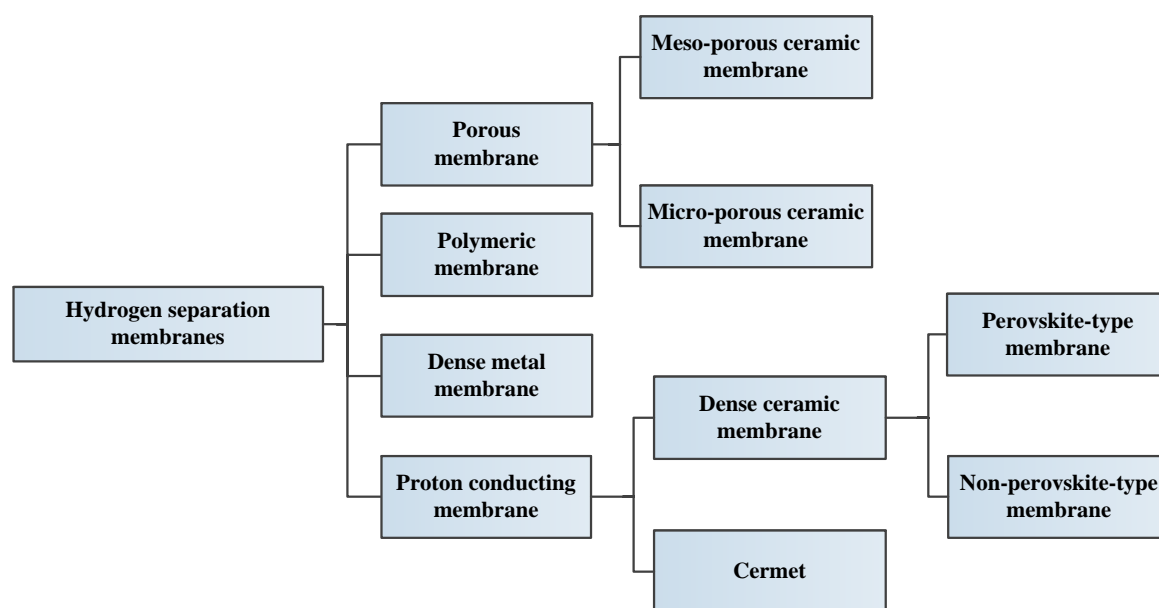


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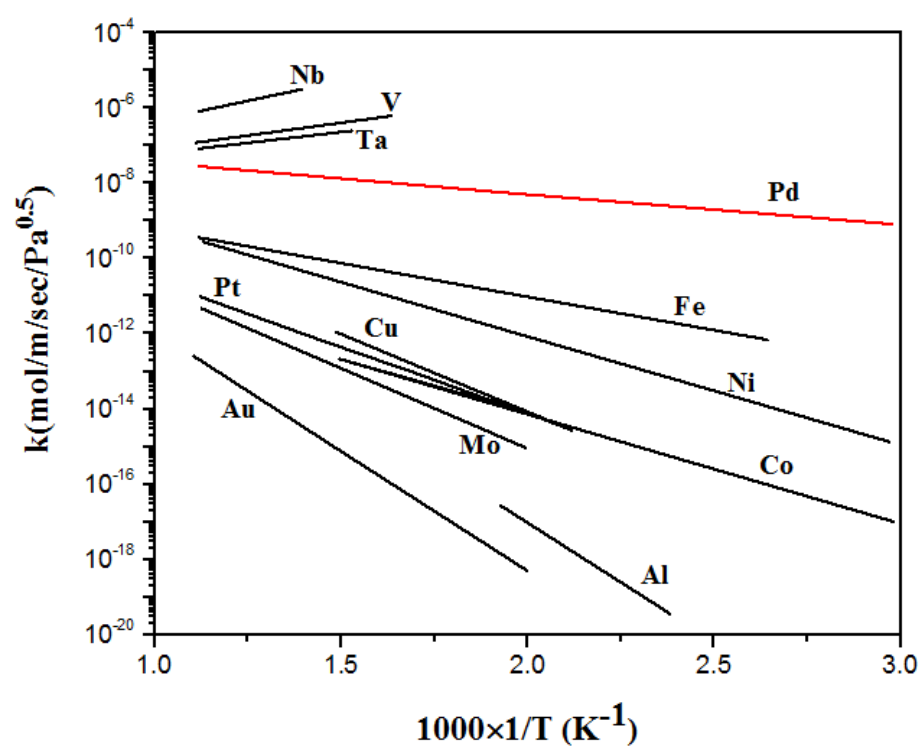


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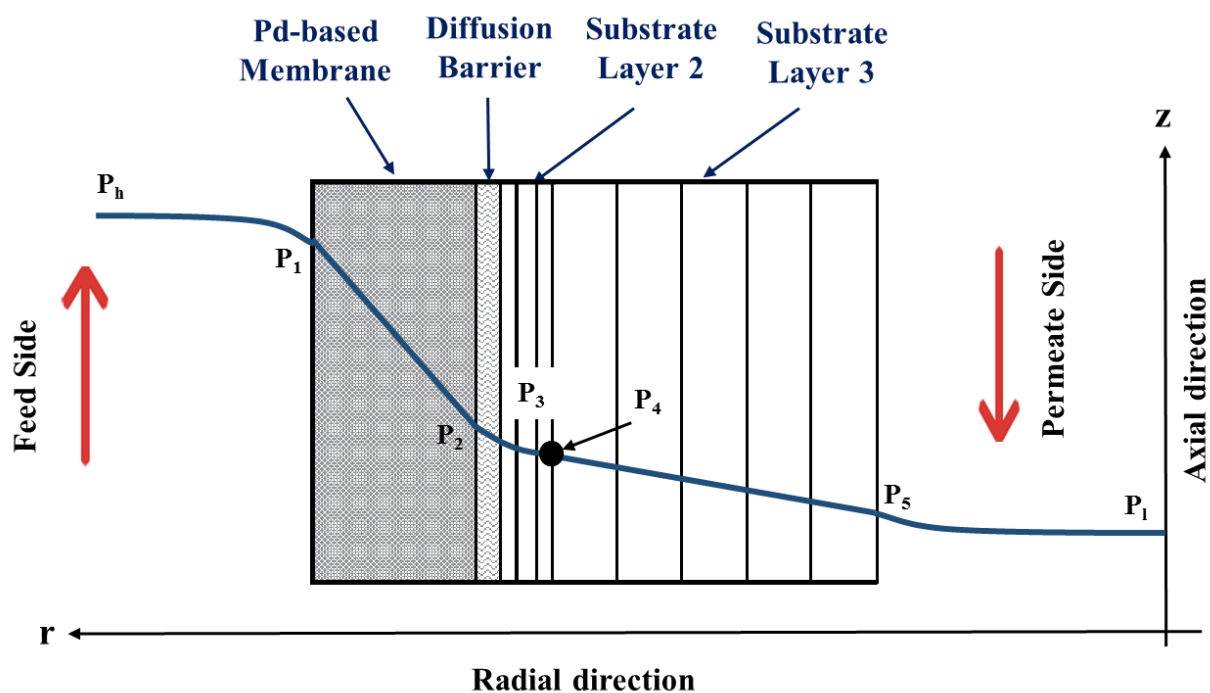


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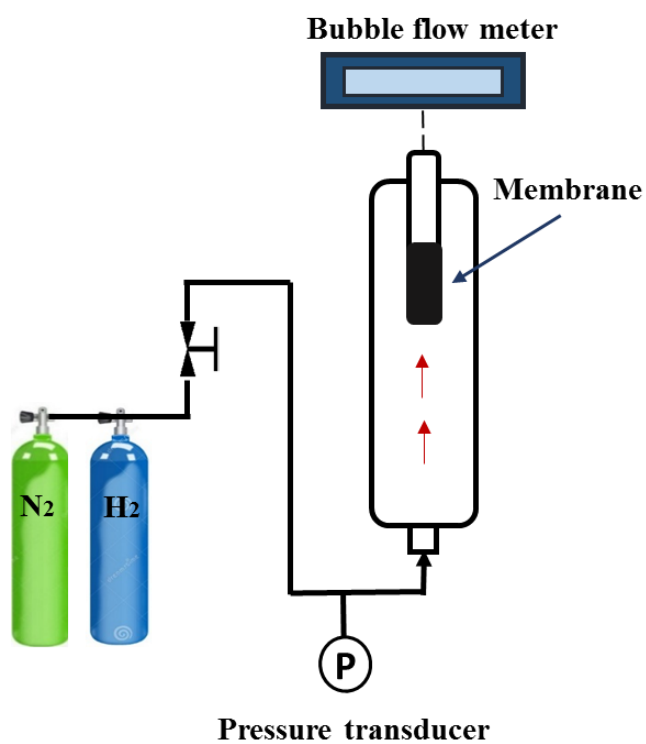


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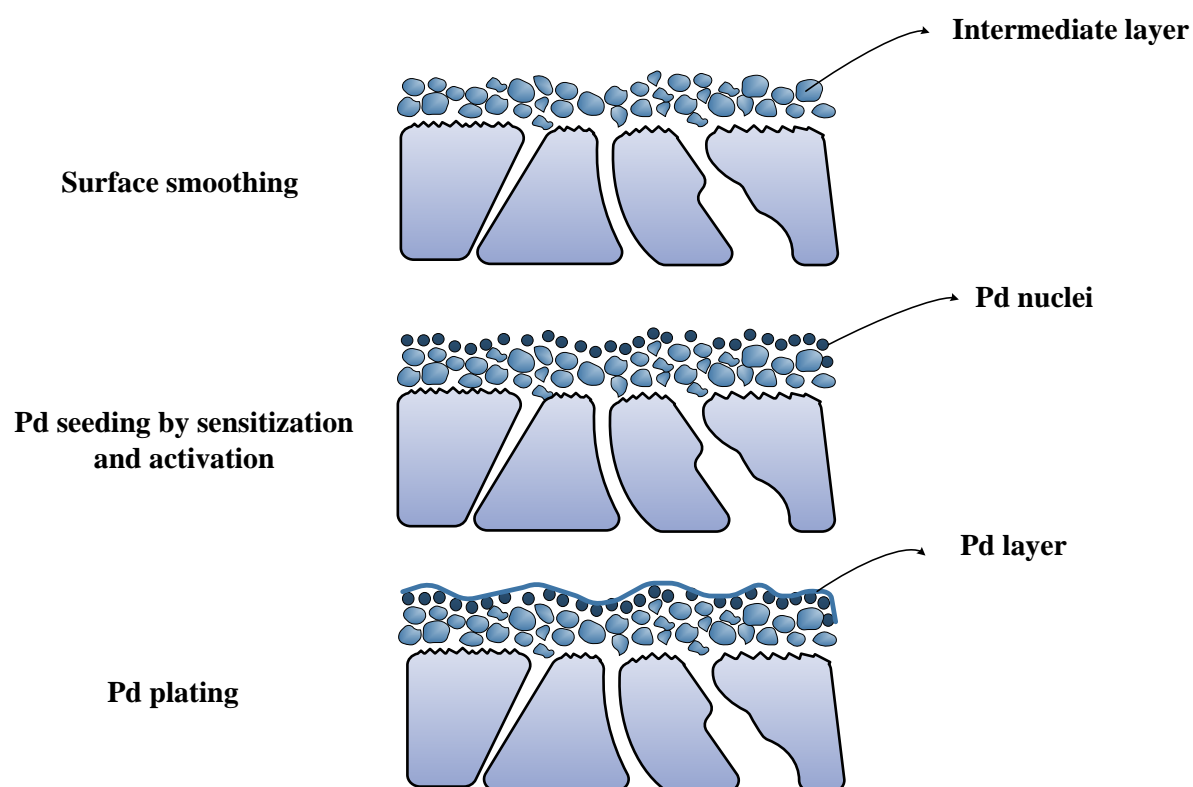


Figure 7

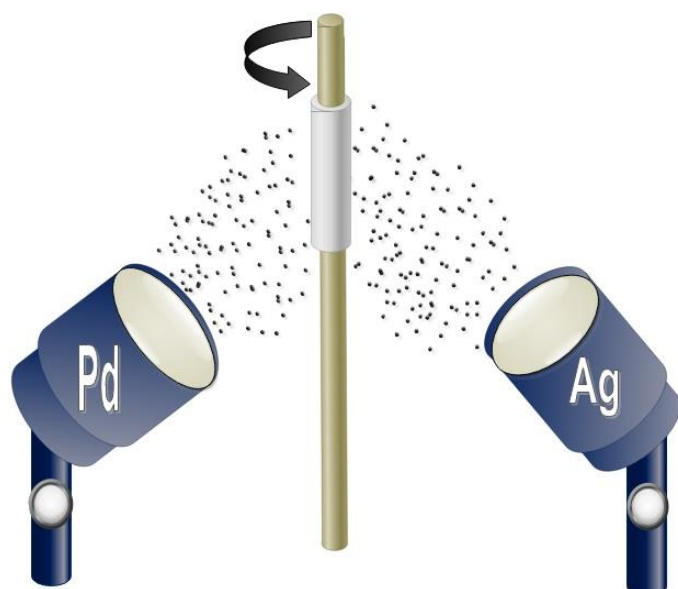
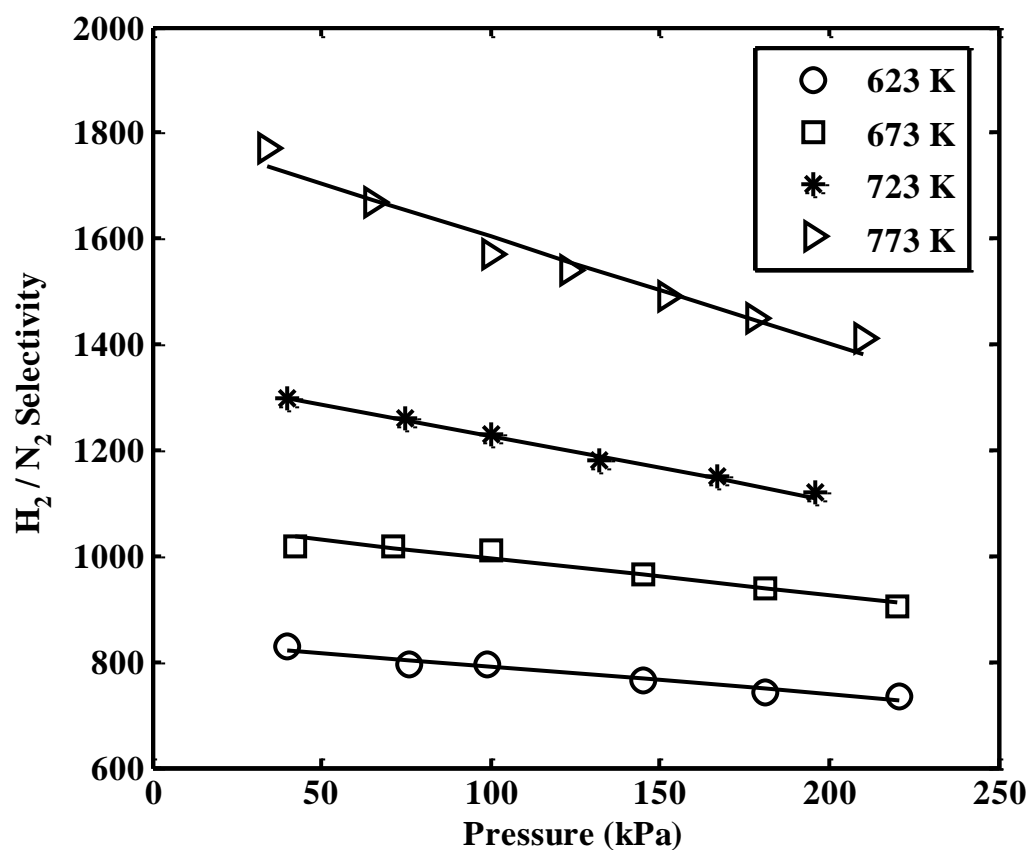
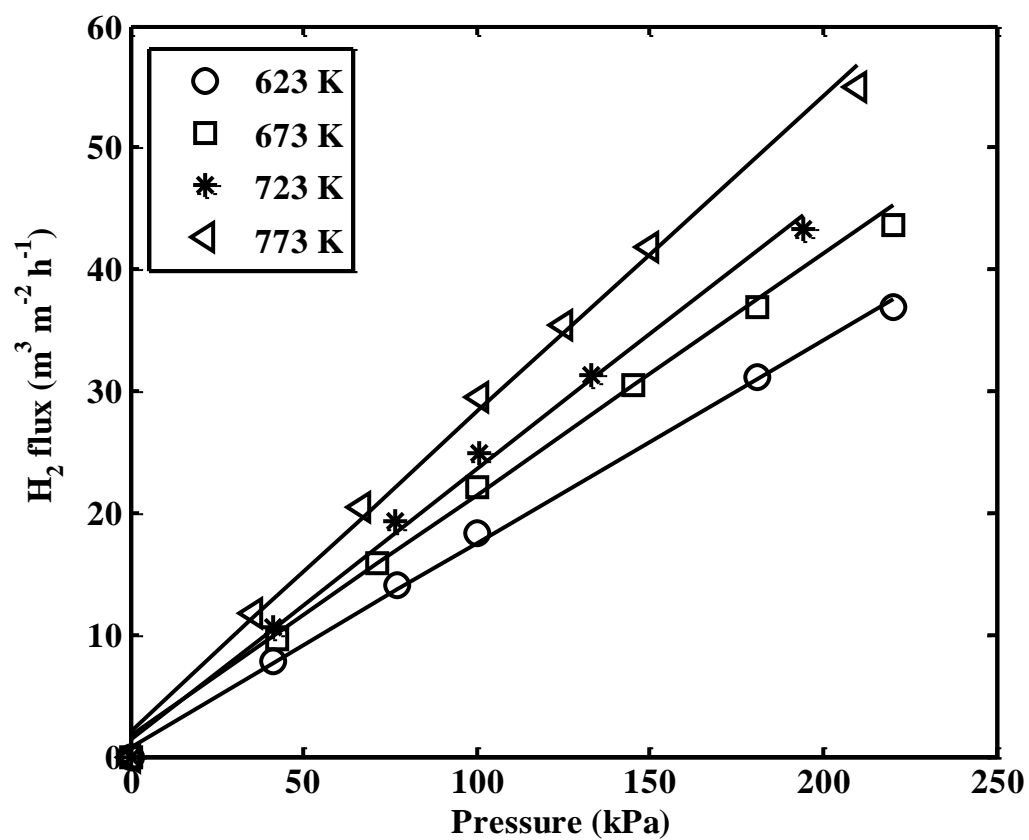


Figure 8



9 (a)



9 (b)

Figure 9

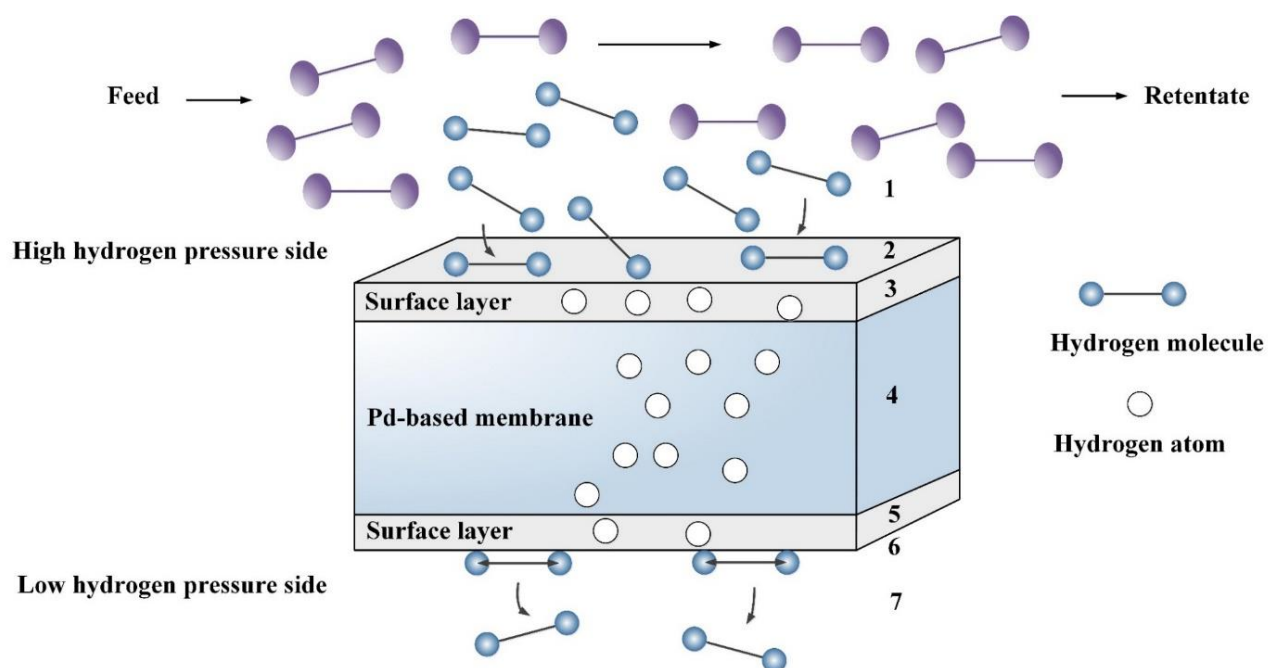


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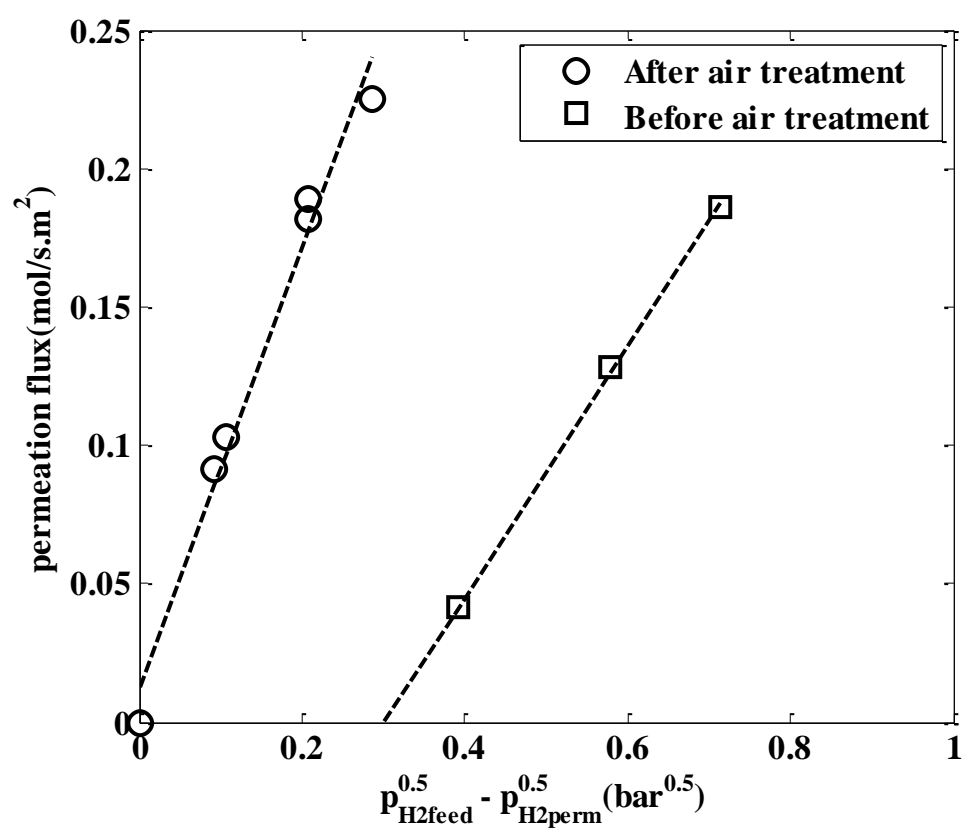


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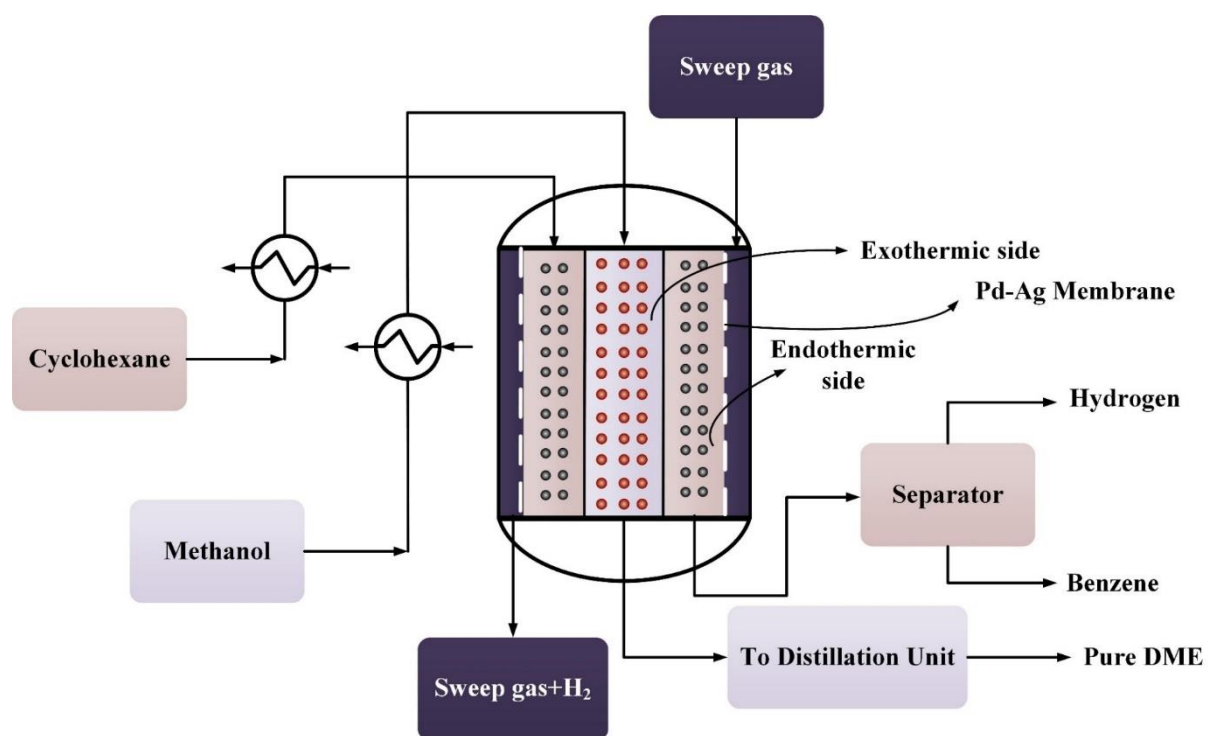


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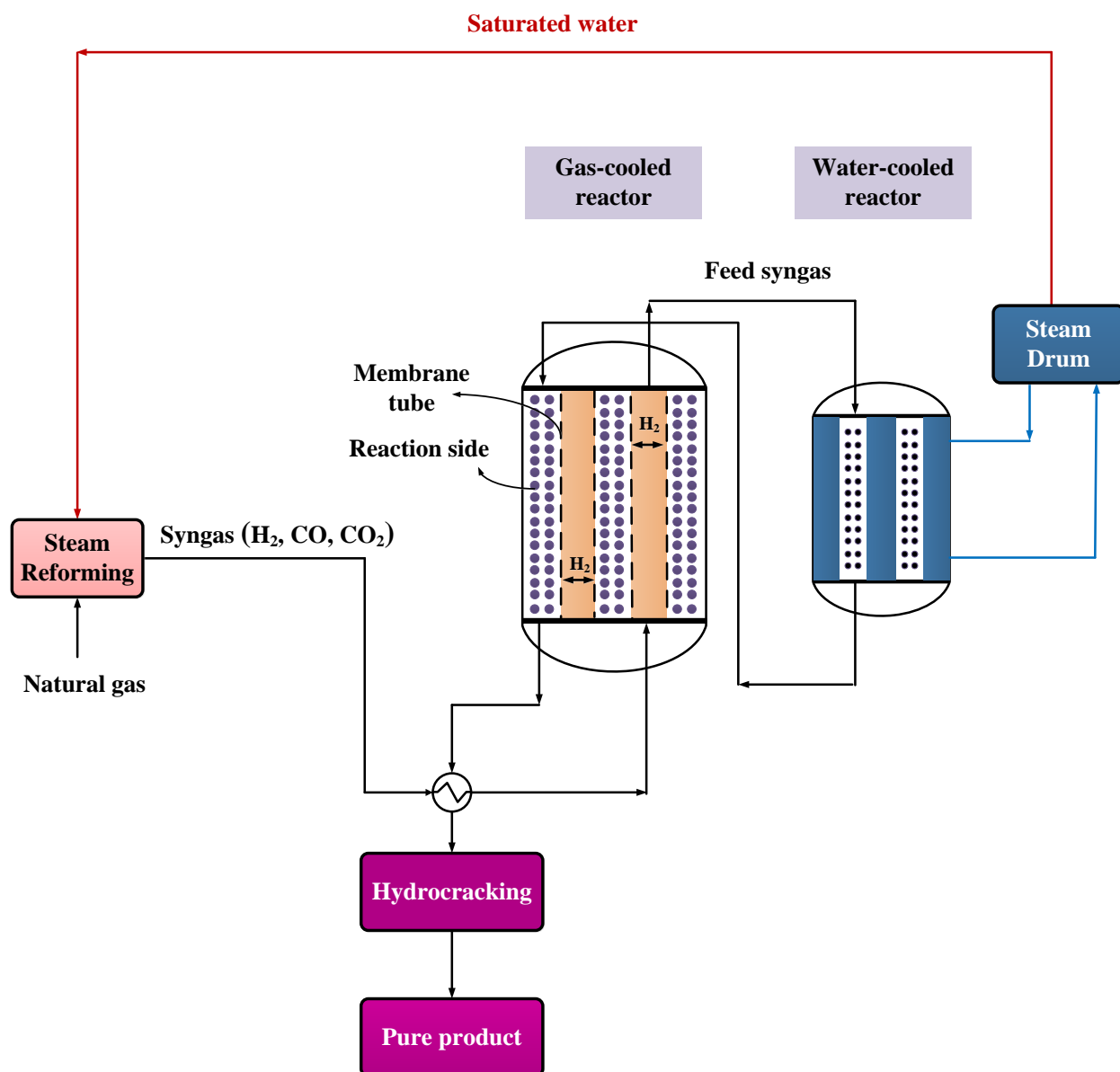
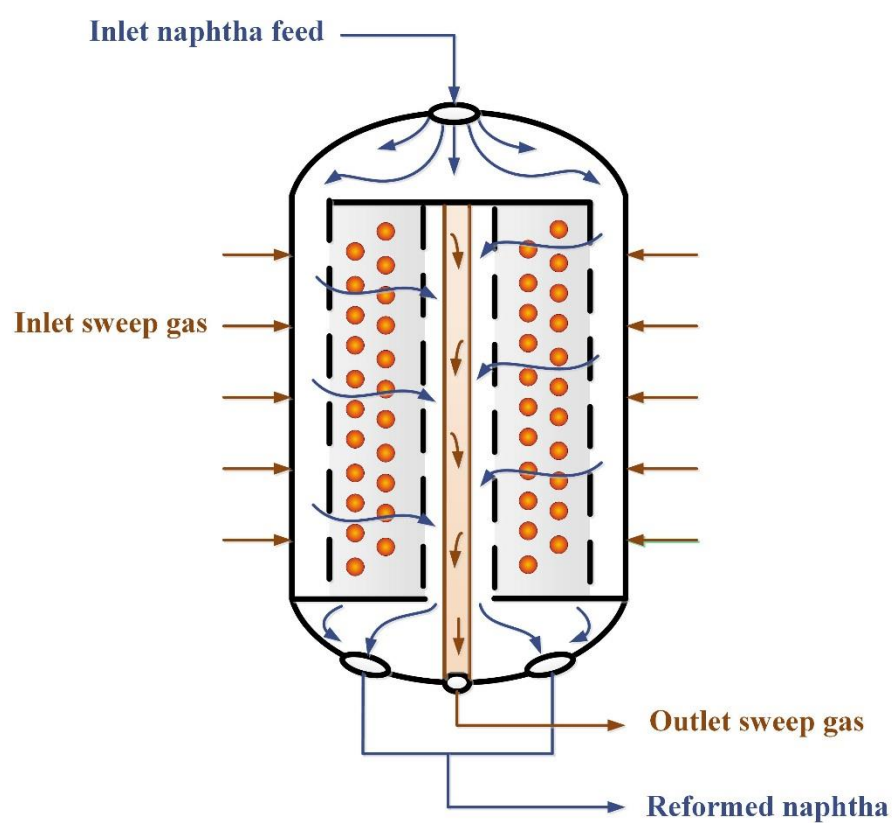
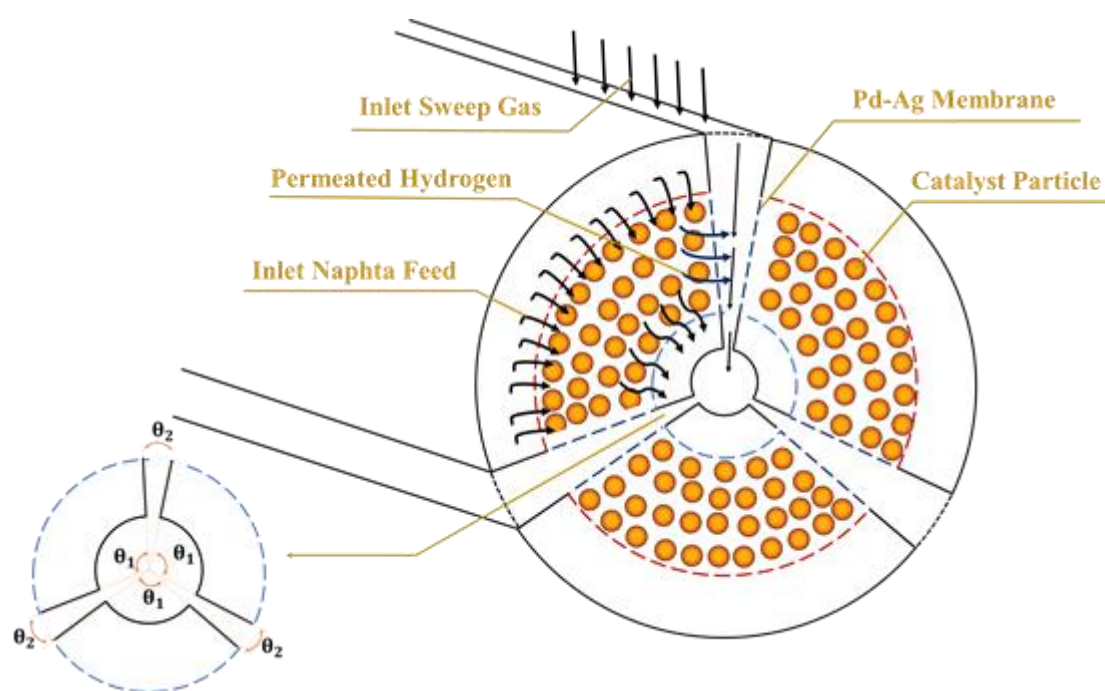


Figure 13

**14 (a)**



14 (b)

Figure 14

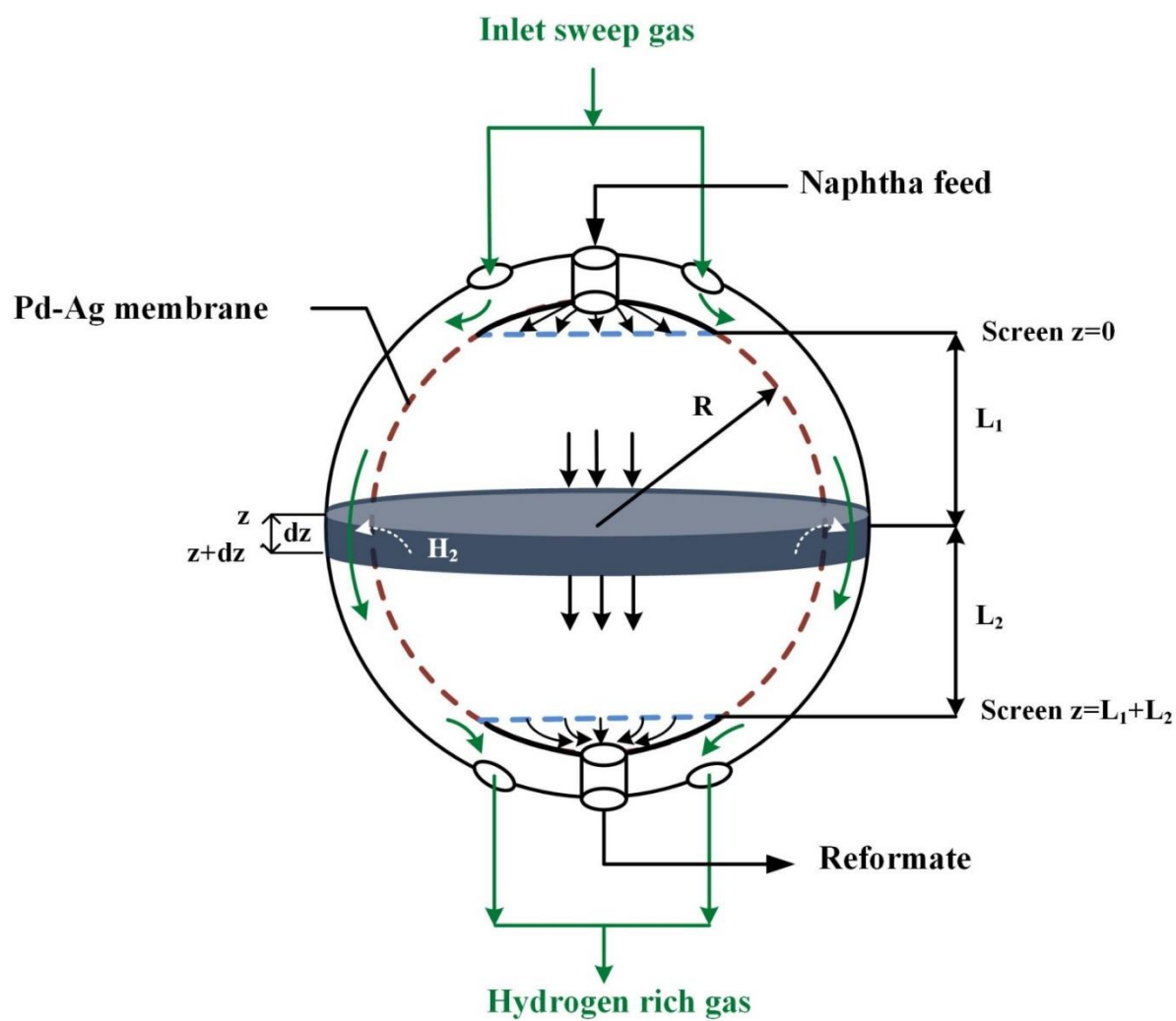
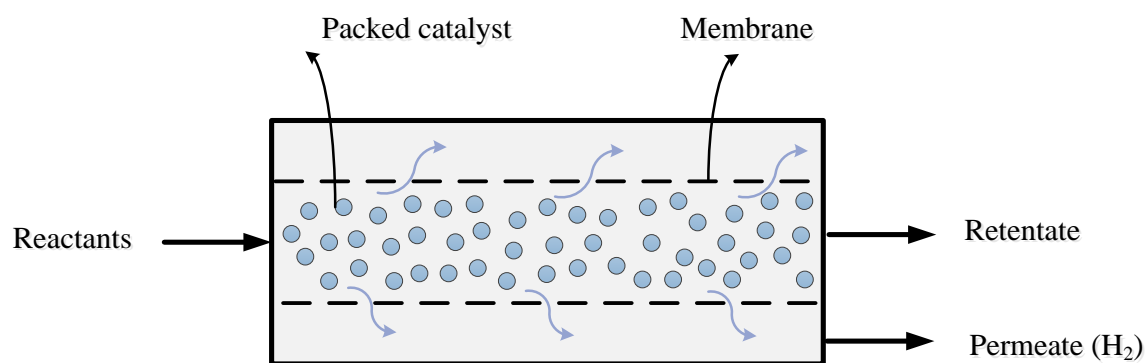
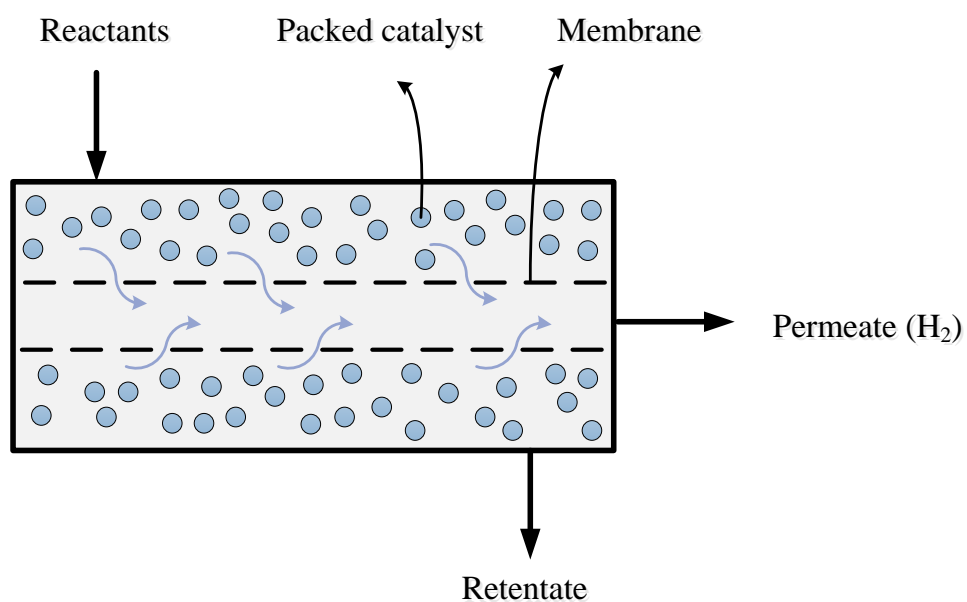


Figure 15



16 (a)



16 (b)

Figure 16

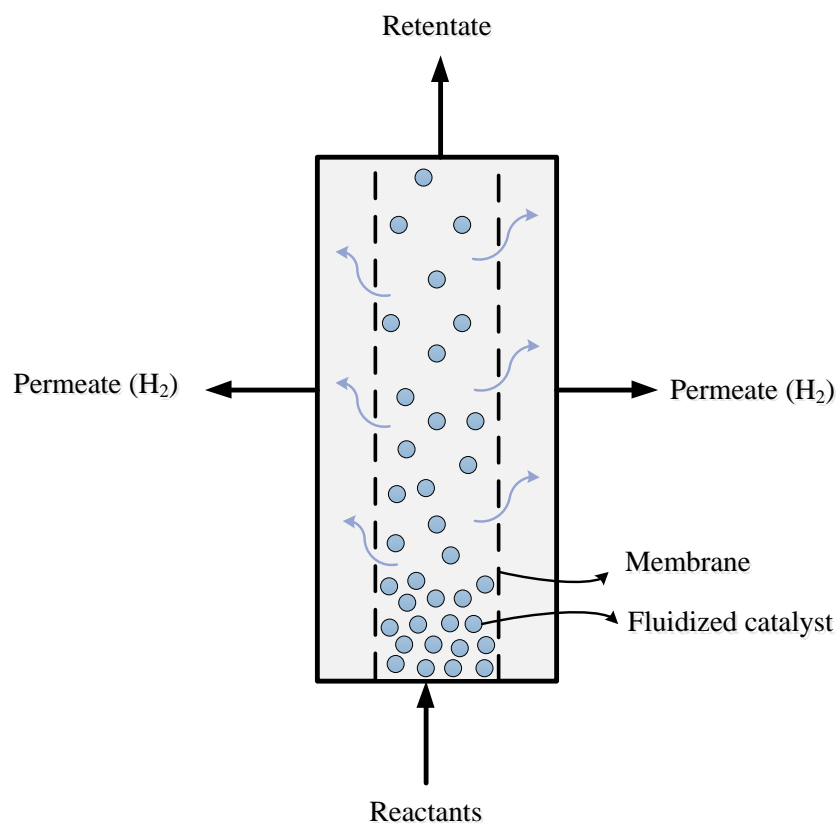


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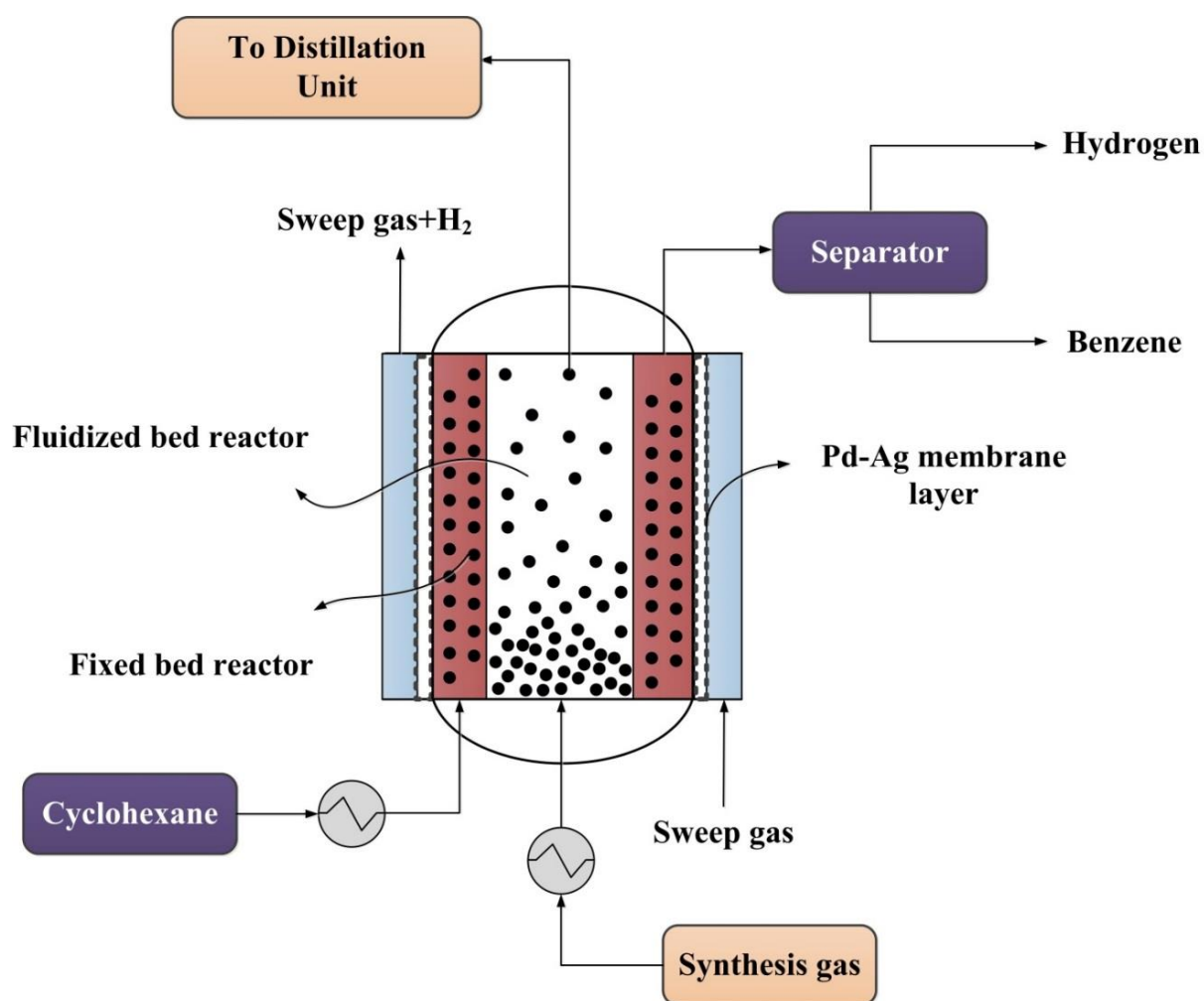


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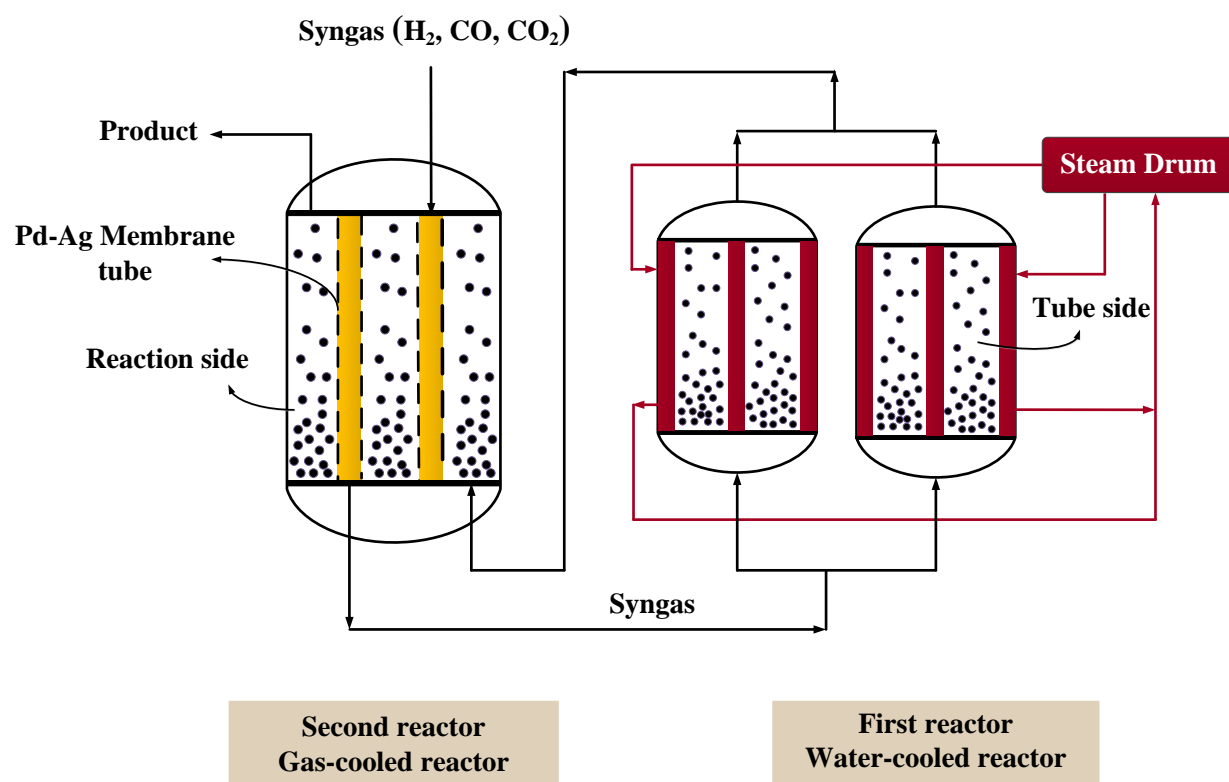


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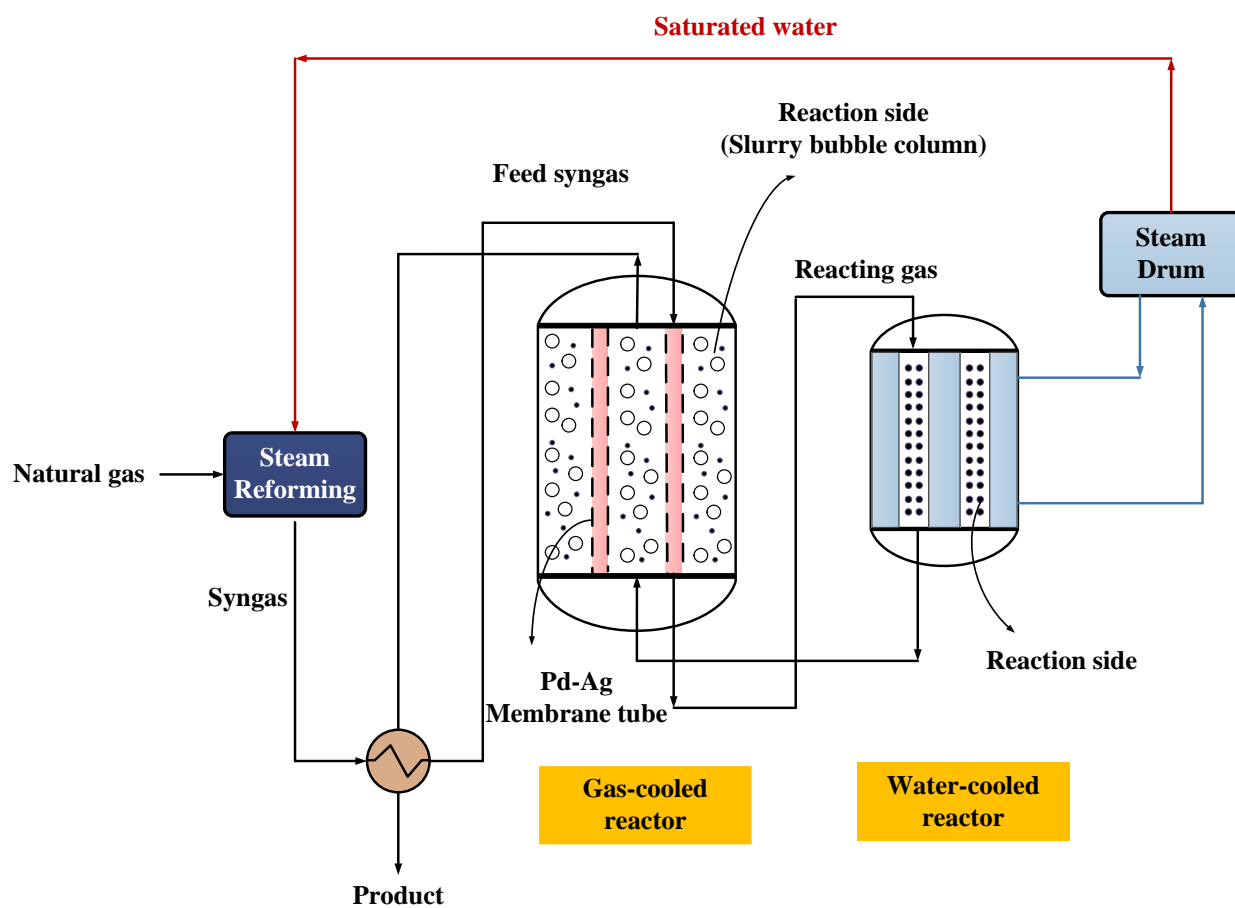


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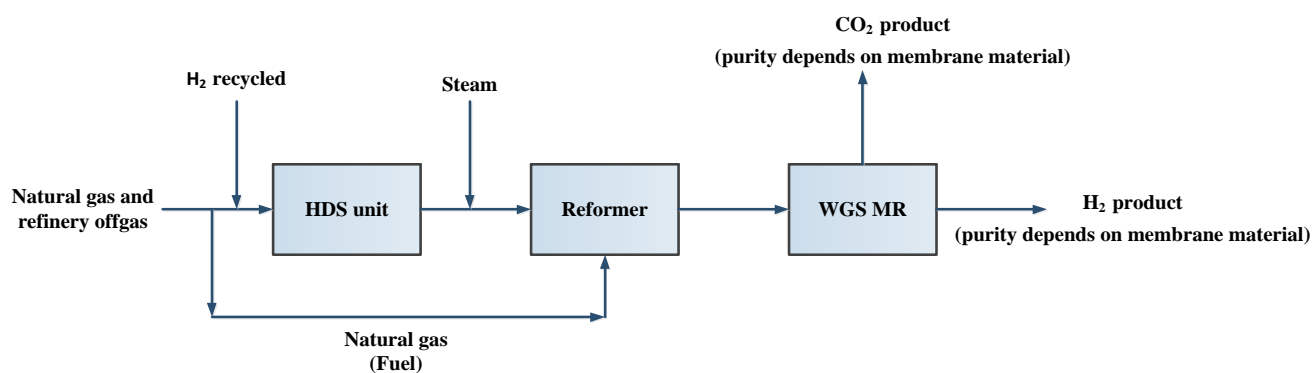


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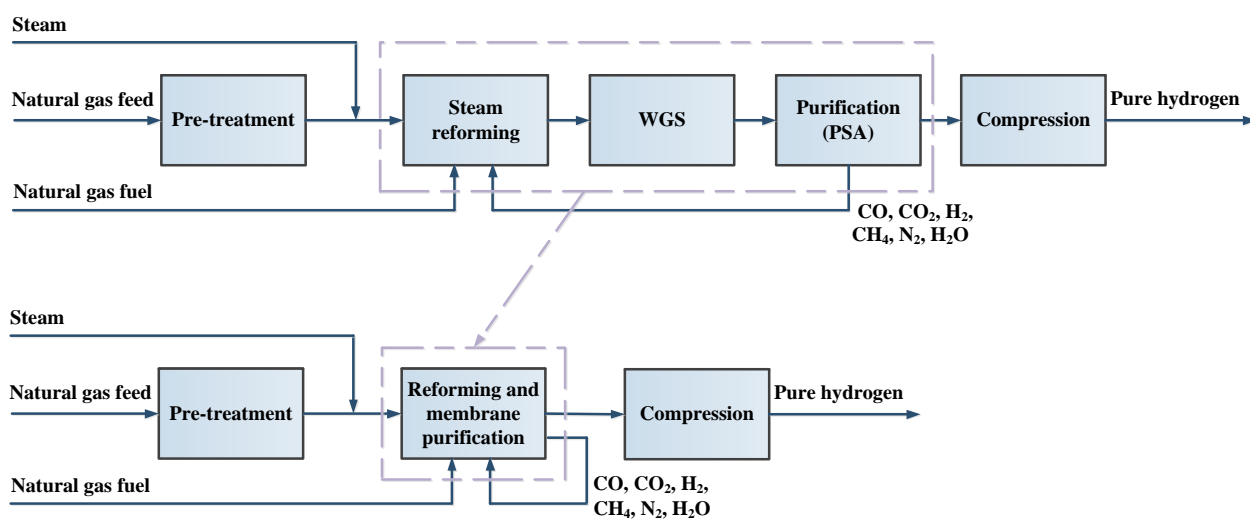


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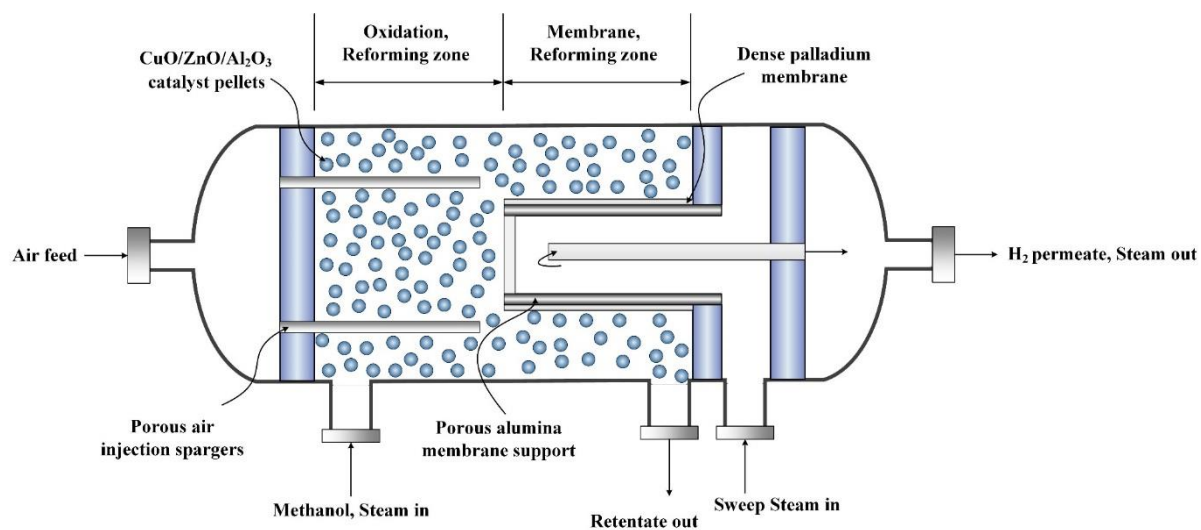


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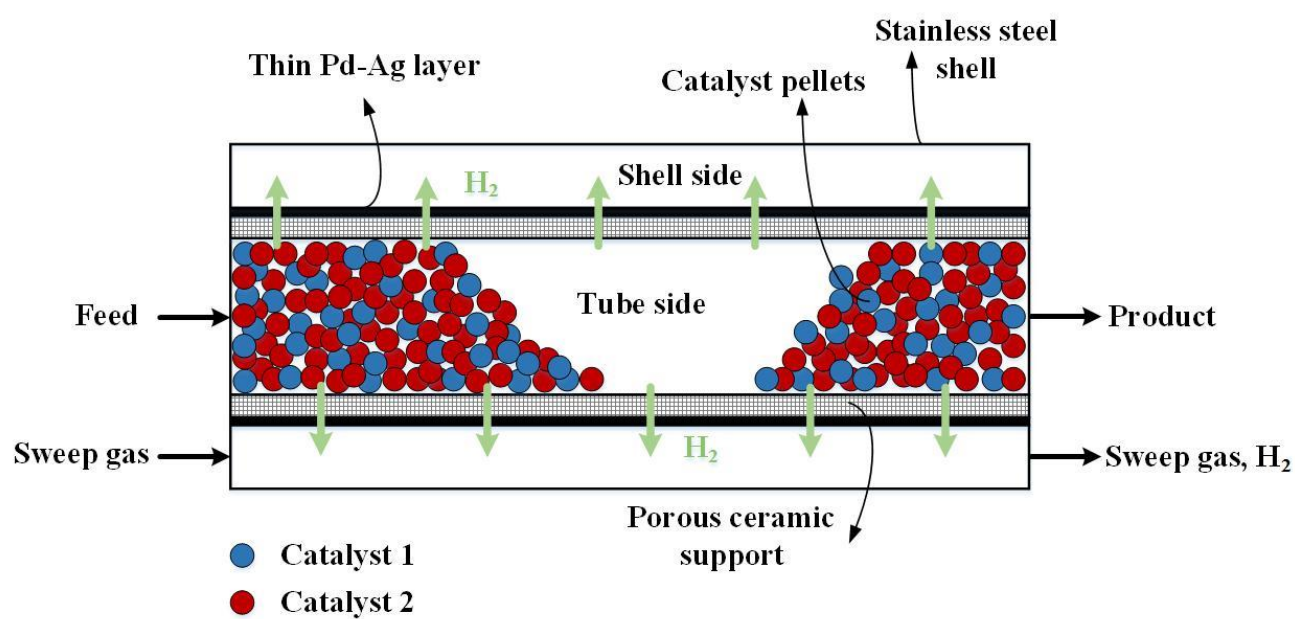


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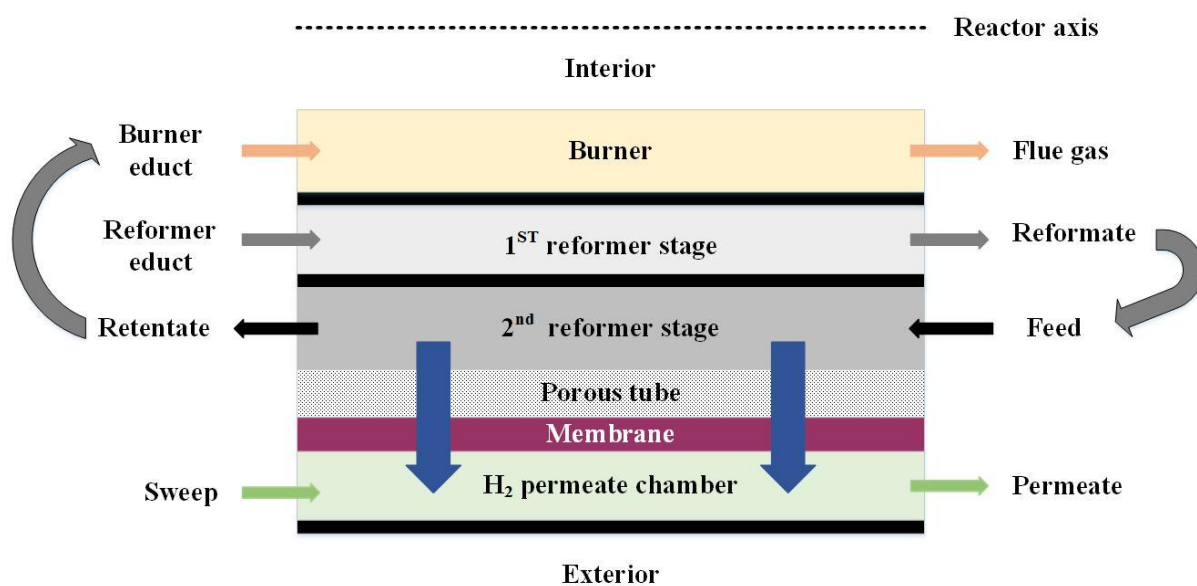


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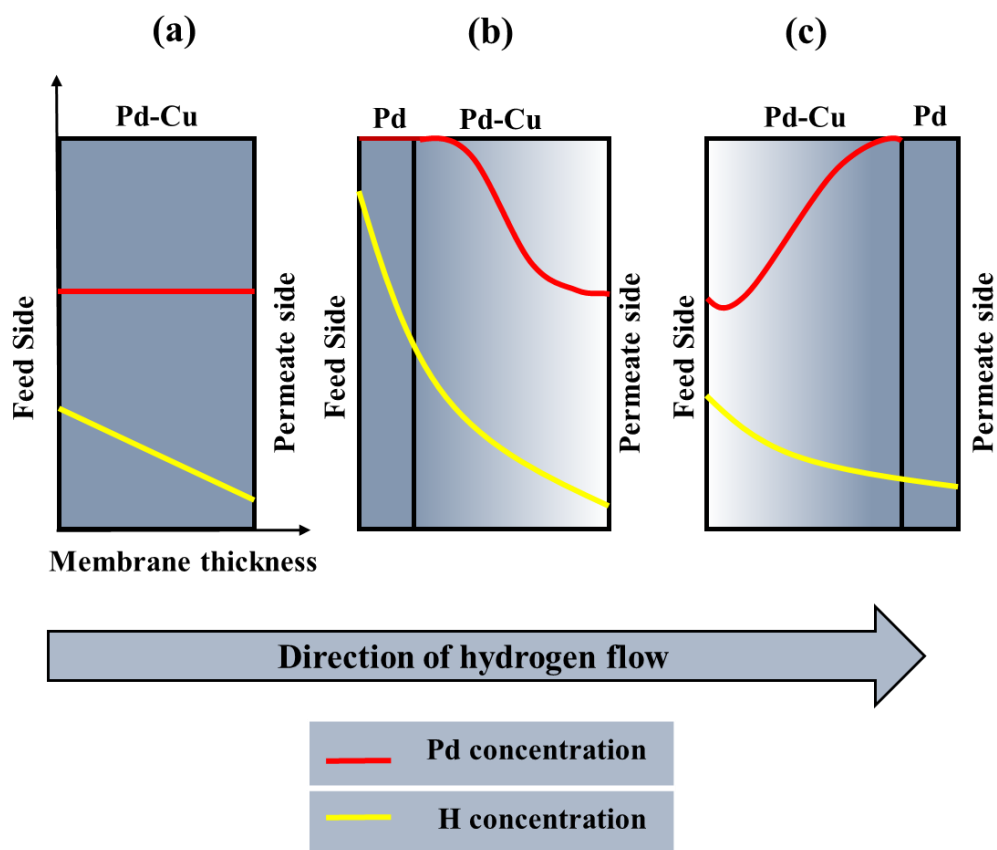


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Table 2: Some theoretical and experimental investigations on Pd-alloy membrane assisted in different types of reactor configurations

Table 1: Pd-based membranes efficiency for hydrogen separation

Membrane	Thickness (μm)	Temperature (K)	Driving force (MPa)	H ₂ flux ($\text{mol/m}^2 \text{ s}$)	H ₂ permeance ($\text{mol/s}\cdot\text{m}^2\cdot\text{Pa}$)	Selectivity coefficient	Ref
Pd/TiO ₂	13	648	10.8	0.16	$(1.6-6.4)\times 10^{-7}$	1000	[31]
Pd/MPSS	5	673	0.1	0.155	-	-	[6]
Pd/Al ₂ O ₃	7-15	673	0.1	0.086-0.134	-	-	[6]
Pd-CeO ₂ /MPSS	13	773	0.2	0.275	$9.67\times 10^{-4 \text{ a}}$	∞ (H ₂ /He)	[28]
Pd/HF	3-4	703	0.1	0.136	$(0.8-1)\times 10^{-6}$	1200-1500 (H ₂ /N ₂)	[36]
Pd/MPSS	10	753	0.1	0.089	-	Over 1000 (H ₂ /N ₂)	[37]
Pd/MPSS	19-20	773	0.101	0.015-0.030	7.027×10^{-6}	5000 (H ₂ /N ₂)	[38]
Pd/PG	13	773	0.202	0.189	-	-	[39]
Pd-Ag/PG	21.6	673	0.202	0.067	-	-	[39]
Pd/Al ₂ O ₃	0.5-1	623-723	0.1	0.05-0.1	$(0.5-1)\times 10^{-6}$	100-1000 (H ₂ /He)	[40]
Pd-Ag/MPSS	15	773	0.202	0.103	-	-	[41]
Pd-Cu/Al ₂ O ₃	3.5	623	0.1	0.056	4.27×10^{-4}	Over 7000 (H ₂ /N ₂)	[42]
Pd-Cu/Al ₂ O ₃	1.5	623	0.1	0.499	3.81×10^{-3}	93 (H ₂ /N ₂)	[42]
Pd-Ag	50	773	0.1	0.01	-	∞	[43]
Pd/MPSS	6	823	0.1	0.300	2×10^{-6}	∞ (H ₂ /Ar)	[44]
Pd-Ag/MPSS	4	773	0.1	0.280	2×10^{-6}	∞ (H ₂ /Ar)	[44]
Pd/ZrO ₂ /PSS	23	673	0.1	0.0734	$5.2\times 10^{-4 \text{ a}}$	320 (H ₂ /N ₂)	[45]
Pd/YSZ/PSS	28	723	0.3-0.4	0.01-0.06	$4.5\times 10^{-4 \text{ a}}$	∞ (H ₂ /N ₂)	[46]
Pd/SiO ₂ /PSS	6	773	0.5	0.133	2.7×10^{-6}	450 (H ₂ /N ₂)	[47]
Pd/Fe ₂ O ₃ /PSS	22	723	0.1	0.0853	$4.5\times 10^{-4 \text{ a}}$	∞ (H ₂ /N ₂)	[48]
Pd/NaAZ/PSS	19	723	0.5	0.0790	1.1×10^{-3}	608 (H ₂ /N ₂)	[49]
Pd/PSS	10	673	0.2	0.176	8.7×10^{-7}	11800 (H ₂ /N ₂)	[50]
Pd/Al ₂ O ₃	7	673	0.1	0.233	2.3×10^{-6}	7500 (H ₂ /N ₂)	[50]

Table 2: Some theoretical and experimental investigations on Pd-alloy membrane assisted in different types of reactor configurations

Membrane material	Thickness (μm)	Reactor type	Sweep gas	Feed	Reaction	Main Product	Temperature (k)	Ref
Pd-Au	5	CMR	-	methane	SRM	Hydrogen	>753	[184]
Pd-Ag	Variable	CMR	Nitrogen	propane and <i>n</i> -butane	Dehydrogenation	Hydrogen	Variable	[77]
Pd-Ru	5	CMR	-	methane	SRM	Hydrogen	853	[11]
Pd-Ag	50	MR	Steam	Ethanol	ethanol steam reforming (ESR)	Hydrogen	623	[185]
Pd	-	MR		Cyclohexane, methylcyclohexane,	Dehydrogenation	Hydrogen	573	[181]
Pd-Ag	-	FMR	Argon	Cyclohexane	Dehydrogenation	Benzene	503	[1]
Pd	13	MR	Argon	Dodecane	SR	Hydrogen	773	[2]
Pd-Ag	50	MR	-	Helium, Tritiated water	Gas detritiation	Hydrogen	573, 673	[186]
Pd	20	DI MR	-	Methanol	SR	Hydrogen	623	[144]
Pd-Ag	6	FR	Argon	Cyclohexane	Dehydrogenation	Benzene	503	[33]
Pd-Ag	70	MR	Nitrogen	CO, H ₂ O	WGS	Hydrogen	604-623	[36]
Pd-Ag	25	FB MR	-	Natural gas	MSR	Hydrogen	-	[91]
Pd-Ag	50	PB MR	Nitrogen	CO, H ₂ O, CO ₂ , H ₂	WGS	Hydrogen	473-573	[97]
Pd-Ag	6	CMR	-	Synthesis purge gas	Ammonia decomposition	NO _x	-	[98]
Pd-Ag	70	MR	-	CO, H ₂ O	WGS	Hydrogen	500-700	[99]
Pd-Ag	60	MR	-	CO, H ₂ O	WGS	Hydrogen	553-593	[100]
Pd	1	MR	-	Benzene	Hydroxylation	Phenol	Variable	[101]
Pd-Ag	60	MR	Nitrogen	Ethanol	OSR	Hydrogen	673, 723	[103]
Pd	7.5, 75	MR	-	CH ₄	SRM	Hydrogen	Variable	[104]
Pd	7.5, 75	MR	-	CO, H ₂ O	WGS	Hydrogen	Variable	[104]
Pd-Ag	50	MR	Argon	CO ₂ , CH ₄	CO ₂ reforming of methane	Hydrogen	520-570	[113]

Pd	-	CMR	-	Natural gas	SRM	Hydrogen	Variable	[162]
Pd-Ag	50	CMR	Nitrogen	Bio-Ethanol, Water	ESR	Hydrogen	673	[166, 167]
Pd-Ag	50, 60	MR	Nitrogen	Ethanol, Water	ESR	Hydrogen	673-723	[168]
Pd-Ru	254	MR	Nitrogen	Iso-butane	Dehydrogenation	Hydrogen	773	[183]
Pd-Ru	254	MR	Nitrogen	Propane	Dehydrogenation	Hydrogen	823	[183]
Pd-Ag	10	MR L	-	Synthesis gas	Methanol synthesis	Methanol	Variable	[187]
Pd-Ag	50	MT MR	Steam	Ethanol, Water	ESR	Hydrogen	633	[188]
Pd-Ag	20	MR	Nitrogen	Ethanol, Water	OSR	Hydrogen	593-723	[189]
Pd-Ag	Variable	MR	-	Synthesis gas	Methanol synthesis	Methanol	502	[190]
Pd-Ag	10	CMR	-	Urea wastewater	Ammonia decomposition	Hydrogen	-	[191]
Pd-Ag	60	MR	-	CO, H ₂ O	WGS	Hydrogen	533-593	[192]
Pd	3	MR	Steam	H ₂ , CO, CO ₂ and CH ₄	WGS	Hydrogen	573	[193]
Pd-Ag	10	FB MR	Syn gas	Syn gas	Dimethyl ether synthesis	Dimethyl ether	Variable	[194]
Pd-Ag	6	FM R	-	Ethane	Dehydrogenation	Ethylene	Variable	[195]
Pd	1600	MR	-	Methane	DR	Hydrogen	783	[196]
Pd-Ag	200	MR	-	cis-3-hexen-1-ol	Dehydrogenation	Hexanal	443-503	[197]
Pd-Ag	Variable	MR	-	CH ₄	SRM	Hydrogen	750	[198]
Pd-Ag	50-60	MT MR	Nitrogen	Ethanol, water	ESR	Hydrogen	963-1163	[199]
Pd	-	MR	Steam	Natural gas	SRM	Hydrogen	773	[200]
Pd	10	MR	Nitrogen	Ethylbenzene	Dehydrogenation	Styrene	923	[201]
Pd	50-150	MR	-	Synthesis gas	Methanol synthesis	Methanol	503	[202]
Pd	-	MR	-	Hydrogen Sulfide	Thermal decomposition	Hydrogen	973-1273	[203]
Pd-Ag	6	CMR	Nitrogen	Ethanol	Dehydrogenation	Ethylene	660	[35]
Pd-Ag	50	Flat-MR	Nitrogen	Methane	Methane decomposition	Higher alkanes	318, 373	[204]
Pd-Ag	50	MR	Nitrogen	Water, CO	WGS	Hydrogen	598-603	[205]

Pd	1	MR	Helium	Aromatic compounds	Direct hydroxylation	Phenol	423	[206]
Pd	4.5	MR	-	H ₂ O, liquid hydrocarbons	SR	Hydrogen	823	[207]
Pd-Ag	50	MR	Nitrogen	H ₂ O, CH ₃ OH	MeOHSR	Hydrogen	623-823	[208]
Pd-Ag	60	MR	-	CO, H ₂ O	WGS	Hydrogen	493-593	[209]
Pd-Cu	125	MT MR	Argon	CO, H ₂ O	WGS	Hydrogen	1173	[210]
Pd	200	MR	-	Cyclohexane, Methylcyclohexane	Dehydrogenation	Hydrogen	573	[211]
Pd	-	MR	-	Alkane	Dehydrogenation	Hydrogen	673	[212]
Pd-Ag	50	MR	-	Ethanol	ESR	Hydrogen	873	[213]
Pd	80-315	CM R	Nitrogen	Synthesis gas	Methanol synthesis	Hydrogen	443-500	[214]
Pd	1	PS MR	Nitrogen	Methane	SRM	Hydrogen	873	[215]
Pd-Ag	15	SS MR	-	Methane, H ₂ O	SRM	Hydrogen	943-1053	[216]
Pd-Ag	10	CM R	-	Naphtha	Naphtha reforming	Gasoline	777	[217]
Pd-Cu	50	MM R	Nitrogen	Benzene	Direct hydroxylation	Phenol	423-523	[218]
Pd-Ag	50	MR	Nitrogen	Ethanol	Partial oxidation	Hydrogen	723	[219]
Pd	4.5	FB MR	-	Ethanol	EAR	Hydrogen	973	[220]
Pd	-	CM R	-	Ammonia	Ammonia decomposition	Hydrogen	823	[221]
Pd-Ag	10	RFT MR	-	Naphtha	Naphtha reforming	Gasoline	777	[222]
Pd-Au	0.5-80	MR	-	CO, H ₂ O, CO ₂ , H ₂	WGS	Hydrogen	723	[223]
Pd	10	MR	Nitrogen	Ethylbenzene	Dehydrogenation	Styrene	833	[224]
Pd-Ag	800	MR	-	Synthesis gas	Methanol synthesis	Methanol	401	[225]
Pd	25	MR	-	Ethanol	ESR	Hydrogen	673	[226]
Pd	10	MR	-	CO, H ₂ O	WGS	Hydrogen	573	[227]
Pd-Ag	5	HF MR	Argon	CO, H ₂ O, Ar	WGS	Hydrogen	723	[228]