

# Hydrogen Production: Overview of Technology Options and Membrane in Auto-Thermal Reforming Including Partial Oxidation and Steam Reforming

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**Abstract:** Hydrogen, a constituent in many chemical compounds in nature, is a key component for several chemical processes such as hydrogenation, hydrocracking, and hydrotreating, or even for fuel. On the other hand, Synthesis gas containing hydrogen, which is one of the most popular intermediate products are used in many industries. There are many ways for production of hydrogen such as reforming of hydrocarbons (e.g. natural gas), partial oxidation, autothermal reforming, membrane reactors, and thermal gasification of biomass and waste. In the world, more hydrogen is produced from natural gas. In this study, several methods of hydrogen production have been considered and all advantages and disadvantages of listed technologies have been expressed. Finally, according to these points optimum technology for hydrogen production has been proposed.

**Keywords:** Auto-thermal reforming, Hydrogen production, Membrane, partial oxidation, Steam reforming.

## 1. INTRODUCTION

Development of modern nation is highly depended on energy and it is an essential requirement for the development of the modern nation. Therefore, energy is a key consideration in discussions of sustainable development [1]. Growing attention on environmental problems such as the emissions of greenhouse gases is giving rise to consistent efforts for developing new and sustainable technologies [2]. Hydrogen is a potential non-carbon based energy system, which is best choice to replace fossil fuels. Hydrogen is considered as the alternative fuel as it can be generated from clean and green sources. However, presently very less percent of hydrogen is produced from renewable sources through water electrolysis while rest of it is still derived from fossil fuels [3, 4]. Hydrogen is future fuel and energy carrier; it is carbon free and hence environmentally friendly. Hydrogen is considered a clean and efficient energy carrier, since its combustion only produces water as by-product [1]. Since Hydrogen is source-independent so it is considered as a worldwide-accepted clean energy carrier [5] and has a high energy content per mass compared to petroleum (Table 1 [6]). Due to these advantages, H<sub>2</sub> can be used as energy sources for different appliances, such as hydrogen fuel cell vehicles and portable electronics. The reaction product is water, and there is no CO<sub>2</sub> emission. Although there are some nitrogen oxides produced during high temperature combustion, environmental pollutant can

be fully removed during low temperature utilization such as by fuel cells [7].

**Table 1: Energy Contents of Different Fuels [6]**

Fuel	Energy Content (MJ/kg)
Hydrogen	120
Liquefied natural gas	54.4
Propane	49.6
Aviation gasoline	46.8
Automotive gasoline	46.4
Automotive diesel	45.6
Ethanol	29.6
Methanol	19.7
Coke	27
Wood (dry)	16.2
Bagasse	9.6

Hydrogen is fast emerging as a clean energy source as an alternative to the existing fossil fuels, and truly, it is being considered as the energy currency of the future. In addition, pure hydrogen is required in the petrochemical industries as a feedstock for a wide range of products and also in the petroleum processing industries for preliminary hydro-processing of a wide range of feedstock [8]. Fuel cells, especially proton exchange membrane fuel cells (PEMFCs), are regarded as promising power sources for mobile and stationary applications in the future hydrogen energy epoch[9] and is a hot spot of research in recent years [10, 11]. Pure hydrogen, the ideal fuel for fuel cells,

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cannot easily be substituted by fossil fuels in short and medium-term because of the difficulties in producing, storing and transporting [12, 13]. Of course many applications for hydrogen can be named.

As told, hydrogen is widely used component. One of the most important is consumption in other processes.  $H_2$  is mostly used for the processing ("upgrading") of fossil fuels, and in the production of ammonia. The main consumers of  $H_2$  in the petrochemical plants include hydro de-alkylation, hydro desulfurization, and hydro-cracking.  $H_2$  is also used as a hydrogenating agent, particularly in increasing the level of saturation of unsaturated fats and oils (found in items such as margarine), and in the production of methanol. It is similarly the source of hydrogen in the production of hydrochloric acid.  $H_2$  is also used as reducing agent of metallic ores [14,15]. Many other reactions can be named that the hydrogen used in it [16-21]. Used as Coolant and Energy carrier [22] also used in semiconductor industry, biological reactions [23, 24], also safety and precautions [25] are other applications of hydrogen.

Traditionally, hydrogen is produced via steam reforming (SR) of hydrocarbons such as methane, naphtha oil or methanol/ethanol. But in industrial scale most of the hydrogen (more than 80%) is currently produced by SR of natural gas carried out in large multi-tubular fixed bed reactors. In small-scale applications, two other main alternatives are generally considered along with SR: partial oxidation (POX) reactions, with a significantly lower efficiency than SR, and auto-thermal reforming (ATR), where the POX (exothermic reaction) and SR (endothermic reaction) are carried out in the same reactor [26].

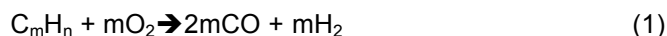
Many methods are used for hydrogen production. Metal-acid [27], Thermo chemical [28, 29], anaerobic corrosion [30], the serpentinization reaction [31], formation in transformers [32] and Xylose [33] are some of these methods. But POX and SR are conventional methods for hydrogen production. ATR is the other process that is very suitable for production of hydrogen that is a combination of POX and SR methods.

Each of these processes has advantages and disadvantages. Reformer downstream process is one of the problems that are in hydrogen production system. Purity of the hydrogen is one of the most important parameters that can be achieved by use of the membranes. In this study performance of the

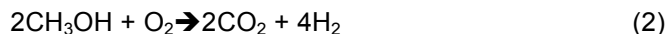
membranes in ATR (as optimal system of hydrogen production in commercial scale) are reviewed.

## 2. PARTIAL OXIDATION (POX)

Hydrocarbons are converted to hydrogen by partially oxidizing (POX) the hydrocarbon with oxygen as shown in Eq. 1 [34, 35]. As shown in Eq. 1 enthalpy of reaction is hydrocarbon dependent. For example if the feed is methanol, the enthalpy would be -193.2 kJ/mol (Eq. 2) which is the heat that is provided by the "controlled" combustion. It does not require a catalyst for operation usually, has minimal methane slip, and is more sulphur tolerant than the other processes. The process occurs at high temperatures with some soot formation and the  $H_2/CO$  ratio (1:1 to 2:1) is favored for the feeds to hydrocarbon synthesis reactors such as Fischer-Tropsch [35].



$\Delta H$  = hydrocarbon dependent, exothermic



$\Delta H = -193.2$  KJ/mol

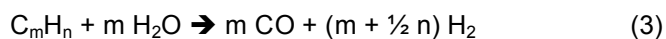
This process is a high exothermic reaction, and generally the operating temperature changes from 1100°C to 1200°C in order to prevent coking in the reactor [34]. As told, POX does not require a catalyst for operation usually; of course there are some studies that have examined the catalytic POX. POX has two types actually depending on the presence or absence of a catalyst: homogeneous POX or heterogeneous catalytic POX. Homogeneous POX is the reactions of fuels with the oxygen in air at high temperature and high pressure in the absence of any catalyst for producing syngas [36]. Higher sulphur tolerance, No heat source required, Compact system and Fast start-up are some advantages of POX. Low  $H_2/CO$  ratio, Highest temperature, Coke formation, Oxygen or air required and Too much heat production are disadvantages of this method [35].

## 3. STEAM REFORMING (SR)

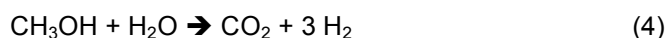
As it is mentioned, hydrogen is produced via SR of hydrocarbons such as methane, naphtha oil or methanol/ethanol in traditional way, as shown in Eq. 3. But on industrial scale SR of natural gas carried out in large multi-tubular fixed-bed reactors is currently used to produce most of the hydrogen (more than 80%) [35], [37]. Steam methane reforming (SMR), developed in

the 1930s, is considered as the most important and economic industrial process for the production of hydrogen [38, 39]. In order to produce pure hydrogen, the chemical processes are carried out in a number of reaction units (typically high temperature reformer, high and low temperature shift reactors) followed by separation units (mostly Pressure Swing Adsorption (PSA)) as shown in Figure 1. The large number of different process steps decreases the system efficiency and makes scale-down uneconomical [26].

The reforming process produces a gas stream composed primarily of hydrogen, carbon monoxide and carbon dioxide. Endothermic SR of hydrocarbons requires an external heat source. These processes are endothermic but amount of heat generated is dependent on the hydrocarbon raw materials. Reaction and amount of enthalpy for ethanol feed is shown in Eq. 3. SR does not require oxygen and produces the reformat with a high H<sub>2</sub>/CO ratio (3:1) which is beneficial for hydrogen production [35].



$\Delta H =$  hydrocarbon dependent, endothermic.



$\Delta H = +49 \text{ KJ/mol}$

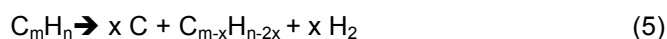
To supply the energy requirement process generally carried out at 700-900 °C and  $15-30 \times 10^5$  Pa, with nickel supported by alumina as the catalyst [40]. It is an approach with high hydrogen concentrations and higher system efficiencies, except the start-up time is typically long. The processing system tends to be heavy for SR and is more suitable for continuous operation under a steady state [34].

This technology is significantly limited by: (a) Thermodynamic equilibrium [41, 42] (b) Internal diffusion [39] (c) Carbon formation and catalyst deactivation [43, 44] (d) Heat transfer [45, 46] (e) Environmental pollution and CO<sub>2</sub> and NO<sub>x</sub> emission [47].

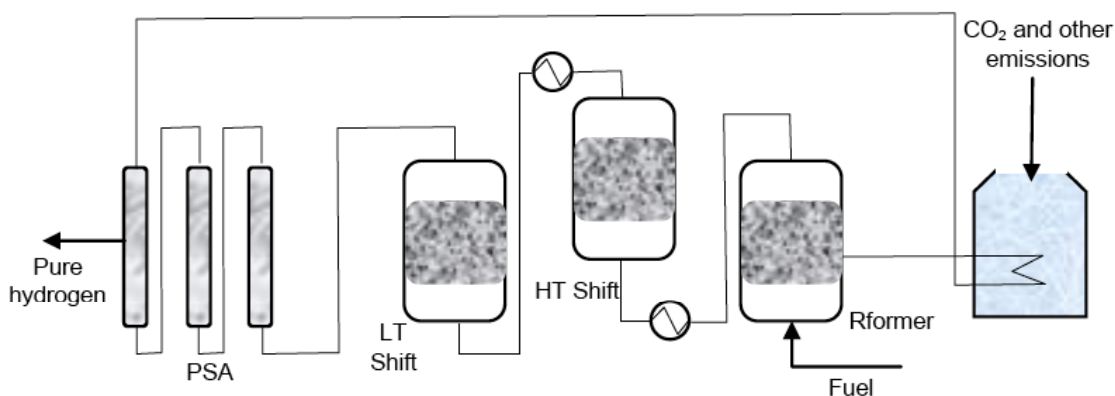
#### 4. SIDE REACTIONS OF HYDROGEN PRODUCTION

Several numbers of reactions may be occurred within the main reaction of producing the pure hydrogen or synthesis gas. For every reaction should be tried to achieve the minimum rate of producing undesired product with side reaction control. Coke formation (Eq. 5 to Eq. 7 [35]), WGS (Eq. 8 and Eq. 9 [35]) and CO oxidation (Eq. 10 and Eq. 11 [35]) are important side reaction in hydrogen production process. One of the most important effects of coke formation is production of carbon and obstruction of technologies that is the main problem for hydrogen production process. WGS is a reaction that can improve the conversion of feed to product and total process efficiency. Therefore Reverse Water Gas Shift (RWGS) can decrease main product (hydrogen). In addition CO oxidation is other side reaction that can effect on being exothermic or endothermic of course CO oxidation can change the composition of final product. So side reactions are important and must be controlled.

Carbon (coke) formation



$\Delta H =$  hydrocarbon dependent.



**Figure 1:** Conventional SR reaction scheme [26].

$$\Delta H = +172.4 \text{ KJ/mol}$$



Water gas shift



$$\Delta H = -41.1 \text{ KJ/mol}$$



CO oxidation



$$\Delta H = +283 \text{ KJ/mol}$$

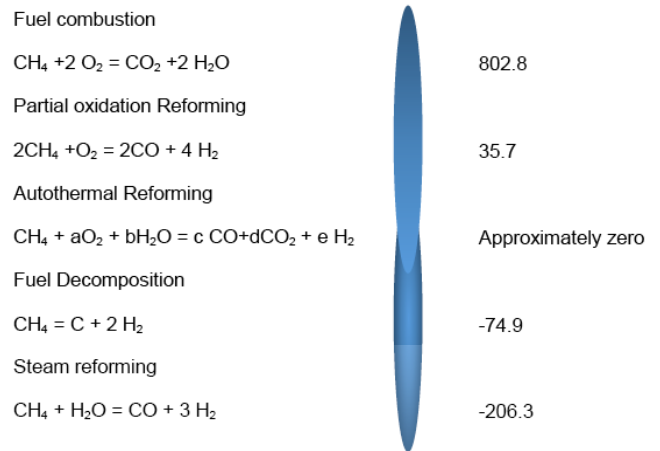


$$\Delta H = -242 \text{ KJ/mol}$$

Fuel processing requires modest temperatures (>180 °C for methanol, dimethyl ether, and other oxygenated hydrocarbons that can be readily activated, and >500 °C for most conventional hydrocarbons) and this temperatures can supply the Energy requirements for side reactions [35, 48].

## 5. AUTO-THERMAL REFORMING (ATR)

ATR combines POX and SR in a single process. The steam to carbon (S/C) ratio is the amount of H<sub>2</sub>O being added to the reaction relative to the amount of carbon in the fuel on a molar basis [49]. Combustion and POX reactions are exothermic or produce heat, while SR and fuel decomposition reactions are endothermic or consume heat. Typically, ATR reactions are considered to be thermally self-sustaining, and therefore, do not produce or consume external thermal energy as shown in Figure 2. Since both fuel decomposition and SR processes are endothermic, heat must be generated external to the reformer process. Catalysts are commonly used to enhance the



**Figure 2:** Reforming technologies spectrum [35].

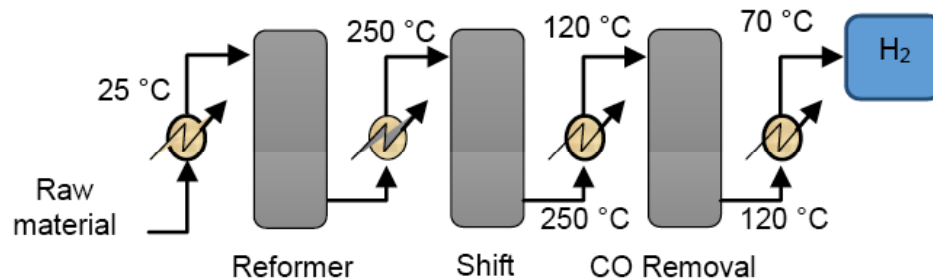
reaction rate of the reforming processes at lower temperatures [35, 49].

The performance of an ATR reactor is affected by the independent parameters such as inlet feed temperature, S/C, O<sub>2</sub>/C in feed, and pressure. Dependent parameters include reformat outlet temperature, conversion, and reactor heat loss [49]. A flow diagram of the basic process in ATR is presented in Figure 3 [50].

The ATR design features a burner, a combustion zone, and a catalyst bed in a refractory lined pressure vessel as shown in Figure 4 [51].

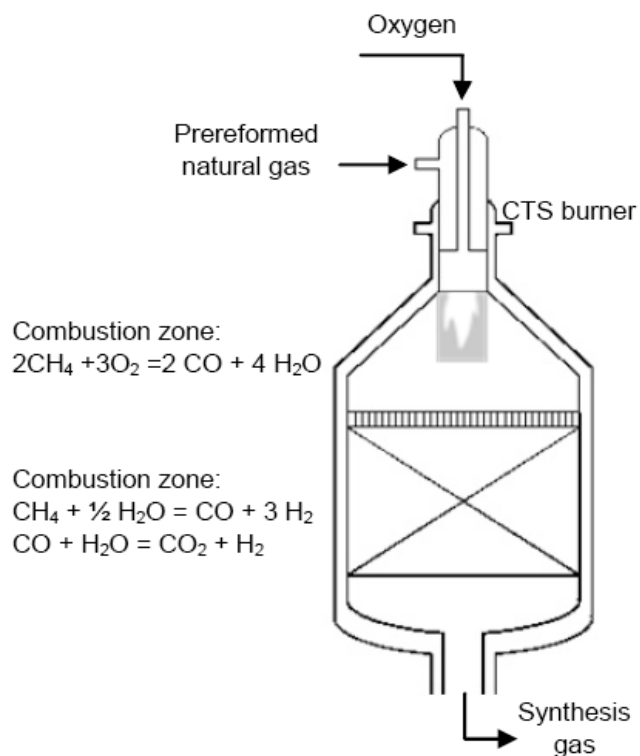
The burner provides mixing of the feed and the oxidant. The feed and oxygen react by sub-stoichiometric combustion in a turbulent diffusion flame in the combustion zone. The operation of the ATR is soot-free because the catalyst bed brings the SR and shift conversion reactions to equilibrium in the synthesis gas and destroys soot precursors, so that.

To ensure low pressure drop and compact reactor design, the catalyst loading is optimized with respect to activity and particle shape and size [51]. Although the



**Figure 3:** Flow diagram of ATR process [50].

results show that ATR operation can be achieved by using approximately 0.3 O<sub>2</sub>/CH<sub>4</sub> feed ratio, the interaction between the different parameters is quite complex [26].

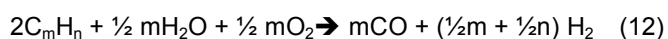


**Figure 4:** ATR reformer [51].

Zouhour Khila *et al.* [52] has done a comparative study on energetic and exergetic assessment of hydrogen production from bioethanol via SR, POX and ATR processes. It is noted that the mass balances show that the total required ethanol to generate 1 mol of hydrogen is 0.23 mol for the ATR, 0.24 mol for the POX and 0.25 mol for the Ethanol SR. For the ATR incoming energy, 82.5% is recovered in the useful product, hydrogen, whereas efficiencies are only 80.4% and 79.4% for the POX and ESR processes, respectively [52]. This results show that ATR process are well method with high performance for hydrogen production.

The main reaction that in ATR reformer is shown in Eq. 12. Enthalpy of this reaction is dependent on hydrocarbon type but is usually nearly zero for example if feed be methanol, amount of enthalpy will be zero [35].

ATR:



$\Delta H =$  hydrocarbon dependent, thermally neutral



$\Delta H = 0$

Water is a feed for steam reforming and air is required for partial oxidation system. Auto-thermal include SR zone and POX zone therefore water, air and fuel are feed for ATR process. Because of adding water this process named wet ATR. Using of carbon dioxide stead of water can change H<sub>2</sub>/CO in product (dry ATR).

The operating range of CO<sub>2</sub> conversion and syngas production in dry auto-thermal reforming is determined by Ming-Pin Lai *et al.* The equipment for this study includes a reformer unit, fuel feeding system, gas/liquid separation device, gas analyzing system and data acquisition system. A mass flow controller was used to determine the reactant feeding flow rate. Authors noted that in this process CO<sub>2</sub>/hydrocarbon is an important parameter that can change H<sub>2</sub> and CO percent in product [53].

Hot-spots [54], coke formation [55] and Fuel evaporation and mixing [56, 57] are major technical problems in an ATR reformer. The ATR reactor consists a thermal zone where POX happens, which generates heat to drive the SR reactions in a downstream catalytic zone. The temperature profile has a sharp rise to the peak in the POX zone and then a decrease due to the endothermic reactions to a relatively low and flat level in the SR zone. The non-uniform axial temperature distribution could cause the problem of so called "hot-spots". This problem is cause of technologies risk and can reduce the catalyst effect [34].

Coke is a high-molecular-weight polymer with low hydrogen content. Formation of coke on the catalyst surface is thought to occur in many instances by polymerization of aromatic compounds originally present or formed in reactions. Olefin and aromatic

Contents in diesel and jet fuels are precursors of coke formation [34].

Each of methods has advantages and disadvantages that for research and design process are important. A comparison of reforming technologies are noted in Table 2 [34, 35].

**Table 2: Comparison of Reforming Technologies [34,35]**

Technology	Advantages	Disadvantages
SR	Most extensive industrial experience Oxygen not required Lowest process temperature Best H <sub>2</sub> /CO ratio for H <sub>2</sub> production	Highest air emissions
ATR	Lower process temperature than POX Low methane slip	Limited Commercial experience Require air or oxygen
POX	Decreased desulfurization requirement Not catalyst require Low methane slip	Low H <sub>2</sub> / CO ratio Very high processing temperature Soot formation/ handling adds process complexity

The main drawbacks of conventional SR, POX and ATR conventional reactors are that all these reactions are equilibrium limited and (even in case of complete fuel conversion) produce a hydrogen rich gas mixture containing carbon oxides and other by-products. Consequently, in order to produce pure hydrogen, these chemical processes are carried out in a number of reaction units (typically high temperature reformer, high and low temperature shift reactors) followed by separation units (mostly pressure swing adsorption) [26]. A method for solving the purity of hydrogen in product is using of membrane technologies.

## 6. HYDROGEN SEPARATION MEMBRANES

Membrane is defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. The following characteristics should be in membranes for hydrogen separation [26]:

1. High selectivity towards hydrogen.
2. High flux.
3. Low cost.
4. High mechanical and chemical stability.

Hydrogen separation membranes may be classified into the following categories: polymeric membranes, porous membranes, dense metal membranes and proton conducting membranes. Comparison between the different membrane types for hydrogen separation is shown in Table 3. The perm-selectivity, the flux and the temperature range at which the membranes can be applied are the most important parameters when comparing membranes[36, 58].

Hydrogen separations from highly supercritical gases, such as methane, carbon monoxide, and nitrogen are easy to achieve by polymeric membranes, because of the extremely high diffusion coefficient of hydrogen relative to all other molecules except helium. Even though solubility factors are not favourable for hydrogen, the diffusion contribution dominates and

**Table 3: Comparison of Membrane Types for Hydrogen Separation [36], [58]**

Membrane type	Polymeric	Microporous Ceramic	Porous Carbon	Dense Metallic	Proton Conducting Dense Ceramic
Materials	Polymers: polyimide, cellulose acetate, polysulfone, etc.	Silica, alumina, zirconia, titania, zeolites, metal-organic frameworks (MOF)	Carbon	Palladium alloys	Perovskites
Temperature (°C)	<100	200–600	500–900	300–700	600–900
H <sub>2</sub> selectivity	Low	5–139	4–20	>1000	>1000
H <sub>2</sub> flux (10 <sup>-3</sup> mol m <sup>-2</sup> s <sup>-1</sup> ) at ΔP=1 bar	Low	60–300	10–200	60–300	6–80
Transport mechanism	Solution-diffusion	Molecular sieving	Surface diffusion, molecular sieving	Solution-diffusion	Solution-diffusion
Stability issues	Swelling, compaction, mechanical strength	-	-	-	-
Poisoning issues	HCl, SO <sub>x</sub> , CO	-	Strong adsorbing vapors, organics	H <sub>2</sub> S, HCl, CO	H <sub>2</sub> S
Cost	Low	Low	Low	Moderate	Low

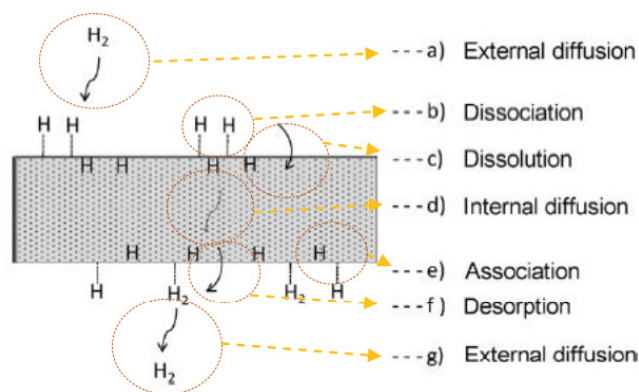
gives overall high selectivities. For example, the hydrogen/methane selectivity of some of the new rigid polyimide and polyaramide membranes is about 200 [59]. Hydrogen separation membranes may be classified into inorganic and polymeric membrane. Advantages and disadvantages of these membranes are shown in Table 4 [60].

Although polymeric membranes have been used for hydrogen separation in industries, particularly for low temperature applications for many years, the high temperature stability problem limits the applications of these membranes to membrane reactors for hydrogen production [59].

Operating via a solution-diffusion mechanism that intrinsically produces pure H<sub>2</sub> (suitable for direct use in a PEM fuel cell, for example), alloy membranes are also stable in the temperature range corresponding to a range of fossil fuel conversion reactions [61].

The mechanism of hydrogen permeation through palladium membranes has been studied extensively and it is well known that it generally follows a solution-diffusion mechanism. The steps involved in hydrogen transport from a high to a low pressure gas region are the following (Figure 5) (a) diffusion of molecular hydrogen to the surface of the palladium membrane, (b) reversible dissociative adsorption on the palladium surface, (c) dissolution of atomic hydrogen into the bulk metal, (d) diffusion of atomic hydrogen through the bulk metal, (e) association of hydrogen atom on the palladium surface, (f) desorption of molecular hydrogen from the surface, (g) diffusion of molecular hydrogen away from the surface [62].

Practical applications require high performance membranes possessing high permeation rates as well as good selectivity. However selectivity is normally



**Figure 5:** Solution diffusion mechanism of hydrogen permeation through a palladium membrane [65].

enhanced through the sacrifice of permeate, so it is essential to achieve a balance between these two properties for optimum performance. This can be obtained with membranes of low thickness, to maximize the flow of permeating molecules, and with minimum presence of cracks and pin-holes, to avoid nonselective e molecular diffusion. In addition, for use in practical equipment, the membranes must be mechanically strong and chemically resistant to poisons [63].

Inorganic silica membranes offer unique advantages for potential industrial applications, like high temperature hydrogen separation and simultaneous reaction and separation. They present high selectivity, and high stability at elevated temperatures and in chemically aggressive atmospheres, as well as low cost. The application of silica membranes in membrane reactors, using catalytically active or passive membranes has proved to be promising, since yields above equilibrium have been obtained by the continuous separation of the hydrogen product from the reaction system [64].

**Table 4: Comparison of Polymeric and Inorganic Membranes [60]**

Membrane	Advantages	Disadvantages	Current Status
Inorganic	Long term durability High thermal stability (>200 °C) Chemical stability in wide pH High structural integrity	Brittle (Pd) Expensive Some have low hydrothermal stability	Small scale applications Surface modifications to improve hydrothermal stability
Polymeric	Cheap Mass production (larger scale) Good quality control	Structurally weak, not stable, temp. limited Prone to denature & be contaminated (short life)	Wide applications in aqueous phase, and some gas separations

A. Lulianelli *et al.* studied the membrane that can be used for hydrogen separation from methanol SR. In Table 5, the most representative results in terms of conversion, hydrogen recovery and so on are reported about SMR reaction performed in membrane reactors [65].

## 7. MEMBRANE COMBINED WITH ATR

The development of a membrane ATR reactor is one of the solutions for the improvement of the conventional ATR process. By applying an H<sub>2</sub> membrane to an ATR reactor, pure hydrogen can be simultaneously produced as the conversion reaction proceeds and the process can be simplified. hydrogen can be simultaneously produced as the conversion reaction proceeds, and the process can be simplified [66]. Convectonal method for hydrogen production is

using of steam methane reforming unit. Downstream of reformer in this method is PSA technologies for purification of product. This technology is very complex and expensive therefore in many case using of this process is not cost effective (For example, the production of low value product).

M.L. Rodriguez *et al.* conducted a modelling of two dimensional membrane reactors for ATR of methane. In this study a two-dimensional, pseudo-homogeneous, steady-state model is proposed to represent the ATR of methane in a multitubular packed bed membrane reactor. In the present design, the inert membrane tubes are filled with catalyst particles. A stream of methane, steam and (optional) O<sub>2</sub> is fed by the tube side while a fraction of oxygen is distributed from the shell side through the tubular porous membrane (Figure 6) [67].

**Table 5: Some of the Most Representative Experimental Results About SMR Reaction in Membrane Reactors from the Open Literature**

Membrane	Membrane Preparation	H <sub>2</sub> /N <sub>2</sub> Selectivity	Catalyst	H <sub>2</sub> O/CH <sub>3</sub> OH	T [°C]	p [bar]	Conv. [%]	H <sub>2</sub> Recovery [%]	H <sub>2</sub> Permeate purity [%]
Pd-Ag (3.9mm layer)/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	ELP	Infinite	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	1/1	250	3	100	45	~ 100
Pd-Ag (20–25 mm layer)/PSS	ELP	-	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	1.2/1	240	10	36.1	18	-
Carbon molecular sieve	Pyrolysis	62 <sup>c</sup>	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	4.1	200	1	~95	~ 84	-
SiO <sub>2</sub> /g-Al <sub>2</sub> O <sub>3</sub> /Pt-SiO <sub>2</sub> /PSS	Soaking-rolling	-	Cu-Zn/based	1.3/1	230	-	100	9.1	-
Pd (20 mm layer)/PSS	ELP	4000	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	1.2/1	350	6	~95	97	99.7
Pd-Ag/TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	ELP	-	Ru-Al <sub>2</sub> O <sub>3</sub>	4.5/1	550	1.3	65	-	~72
SiO <sub>2</sub> /y-Al <sub>2</sub> O <sub>3</sub>	Soaking-rolling	~37	Cu-Zn/based	3/1	260	-	45	5	98
Carbon-supported	Pyrolysis	~5.5	CuO/Al <sub>2</sub> O <sub>3</sub> /ZnOMgO	3/1	250	2	55	-	~80
Carbon-supported	-	-	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	1.5/1	250	2	~99	-	97
Pd (20-25 mm layer)/PSS	ELP	Infinite	Cu-based	1.2/1	350	-	99	-	~100
Dense Pd-Ag (50mm thickness)	Cold-rolling	Infinite	CuO/Al <sub>2</sub> O <sub>3</sub> /ZnOMgO	3/1	300	3	-	80	~100
Dense Pd-Ru-In (200mm thickness)	-	Infinite	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	1.2/1	200	7	~90	~24	~100
Dense Pd-Cu (25mm thickness)	-	Infinite	Cu-Zn based	-	300	10	>90	~38	~100

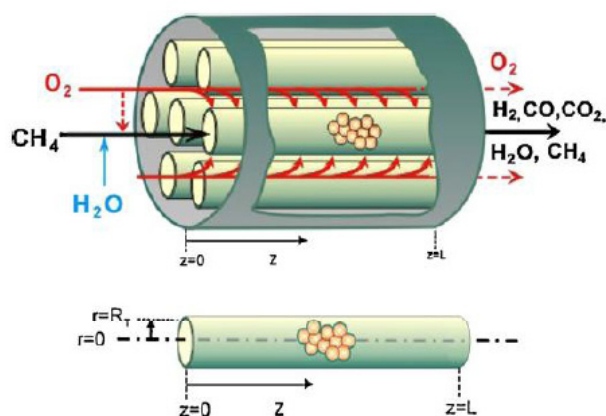
<sup>a</sup> [sccm/h/g-cat).

<sup>b</sup> WHSV.

<sup>c</sup> H<sub>2</sub>/Ar selectivity.

PSS = porous stainless steel





**Figure 6:** Schematic representation of the membrane reactor for ATR of methane [70].

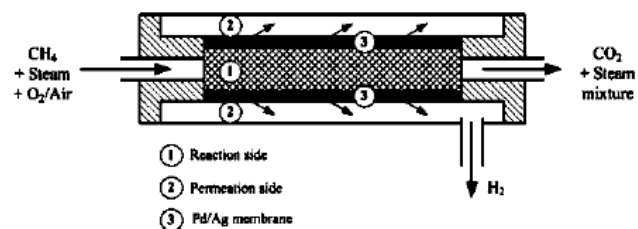
They noted that there are an important concern for ATR membrane that is concerning the mechanical stability of the membranes subjected to high temperatures and strong thermal gradients [67].

The Fluidized bed membrane reactors can be used for operating the auto-thermal reforming of hydrocarbons inside the membrane reactor. In fact the auto-thermal reforming in a packed bed membrane reactor is quite difficult due to the hot-spot at the reactor inlet which can melt down the membrane [26].

Zhongxiang Chen *et al*, do an experimental study about pure hydrogen production in a commercialized fluidized-bed membrane reactor with SMR and ATR catalysts. The operating performance of a bubbling fluidized-bed membrane reactor for generating hydrogen was investigated using Pd-Ag planar membranes and both a steam methane reforming

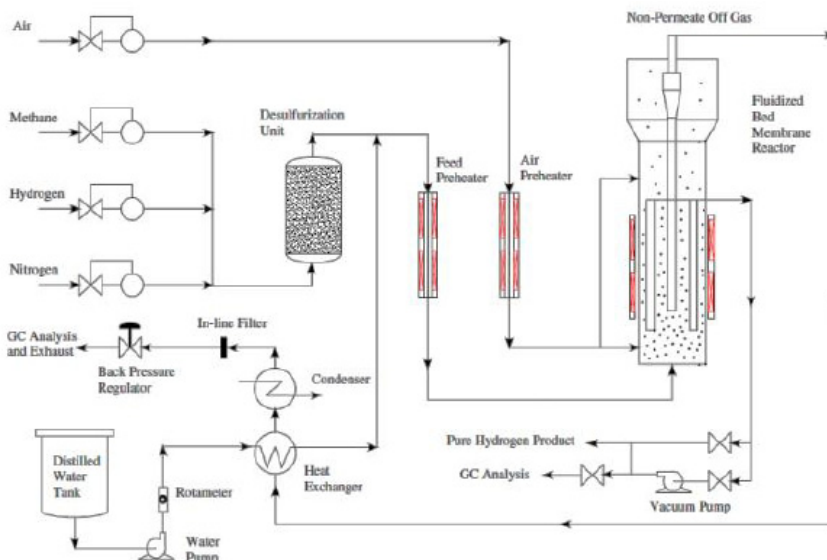
(SMR) catalyst and an auto-thermal reforming (ATR) catalyst. The reactor was mostly operated at 500-600°C and 1500-2600 KPa. A detailed parametric study showed improved overall membrane effectiveness factors and hydrogen permeation fluxes compared with previous tests. Hydrogen permeation fluxes were 4.8–12 Nm<sup>3</sup>/m<sup>2</sup> h for SMR catalyst operations and 9–18 Nm<sup>3</sup>/m<sup>2</sup> h for ATR catalyst operations, significantly higher than previous hydrogen permeation fluxes reported in the literature. The ATR catalyst led to better performance than the SMR catalyst. Some catalyst particles were lost during operation with both catalysts, while the catalyst activity was stable [40]. Schematic process flow diagram showing fluidized-bed membrane reactor and auxiliary components of this work is shown in Figure 7.

C. S. Patil studied packed bed membrane reactor for production of ultrapure hydrogen. The packed bed membrane reactor studied, consists of a tubular steel supported Pd-Ag membrane filled with a reforming catalyst, as schematically depicted in Figure 8 [68].



**Figure 8:** Schematic of the packed bed membrane reactor [68].

The conceptual feasibility of a Packed Bed Membrane Reactor for the autothermal reforming of



**Figure 7:** Schematic process flow diagram showing fluidized-bed membrane reactor and auxiliary components [71].

methane was investigated by a detailed numerical simulation study using a 2D reactor model, evaluating different modes of operation. It was shown that the use of a hydrogen perm selective membrane shifts the thermodynamic equilibrium constraints, enhances hydrogen production and decreases the CO concentration in the reactor exhaust. Contrary to the conventional packed bed reactors, higher reactor pressures increase the methane conversion and the total removal rate of hydrogen [68]. Therefore H<sub>2</sub> extraction can be achieved by using dead-end Pd membranes, and applying a vacuum on the permeate side.

A new membrane-assisted fluidized bed reactor is proposed where perovskite membranes are integrated in an oxidation section at the bottom and the Pd membranes in a reforming/shift section at the top (by Kuipers *et al.*) [68].

The reactor consists of two membrane-assisted fluidized bed sections: a POX bottom section and a SR/water gas shift top section. In this work a novel multifunctional reactor concept has been developed for the production of ultrapure H<sub>2</sub>. A high degree of process integration and process intensification is achieved by integrating perm selective Pd based metallic membranes for selective H<sub>2</sub> extraction (500–600 °C operating temperature) inside a fluidized bed reactor together with perm-selective dense perovskite membranes for selective O<sub>2</sub> addition (900–1000 °C operating temperature). Therefore author show that this reactor can produce pure hydrogen and high quality carbon dioxide and this reactors have many advantages Compared with convectional reactors [68].

The production of ultra-pure hydrogen via ATR of ethanol in a fluidized bed membrane reactor has been studied by Fausto Gallucci *et al.* [37]. It is possible to obtain overall ATR of ethanol while 100% of hydrogen can in principle be recovered at relatively high temperatures and at high reaction pressures due to simulation results based on a phenomenological model. At the same operating conditions, ethanol is completely converted, while the methane produced by the reaction is completely reformed to CO, CO<sub>2</sub> and H<sub>2</sub>.

Tony Boyd *et al* have been developed and tested a novel hydrogen reactor based on SR of natural gas. Pilot plant results carried out in a semi-industrial scale reactor will be presented. The reactor was operated up to 650°C and 14 bar. Pure hydrogen (99.999+%) was initially obtained from the reactor and an equilibrium shift was demonstrated [69]. But the ATR of methane in a packed bed membrane reactor is quite difficult due to

the hot-spot at the reactor inlet which can melt down the membrane. This problem is completely circumvented in fluidized bed membrane reactors. In this case both ATR and hydrogen recovery can be performed in a single reactor [26].

## CONCLUSION

There are various ways to produce hydrogen which partial oxidation, steam reforming and auto-thermal reforming are considered as industrial ones. According to advantages and disadvantages of each, auto-thermal reforming is considered as optimum one however difficulties during purity control of final product is one of the major disadvantages. Mentioned issue can be solved if membrane reactors are used. Due to researches have been done, it is notable that by using membranes, in addition to ultra-pure hydrogen production, reaction is improved in considered path and be more efficient. Pd membranes play critical role in researches, this kind of membrane is more selective and much more stable than hydrogen, that it is used in harsh auto-thermal processes as membrane reactors.

Membrane methods used for hydrogen production were studied by using auto-thermal. In this study, we found that this method can successfully be implemented in auto-thermal systems and technology in general will improve.

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