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An On-Board Pure H₂ Supply System Based on A Membrane Reactor for A Fuel Cell Vehicle: A Theoretical Study

Payam Parvasi ^{1,*}, Seyyed Mohammad Jokar ¹, Angelo Basile ² and Adolfo Iulianelli ^{2,*}

¹ Department of Chemical, Petroleum and Gas Engineering, Shiraz University of Technology, Shiraz 71345, Iran; jokar@sutech.ac.ir

² Institute on Membrane Technology of the Italian National Research Council (CNR-ITM), Via Pietro Bucci, Cubo 17/C, 87036 Rende (CS), Italy; a.basile@itm.cnr.it

* Correspondence: parvasi@sutech.ac.ir (P.P.); a.iulianelli@itm.cnr.it (A.I.)

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Abstract: In this novel conceptual fuel cell vehicle (FCV), an on-board CH₄ steam reforming (MSR) membrane reformer (MR) is considered to generate pure H₂ for supplying a Fuel Cell (FC) system, as an alternative to the conventional automobile engines. Two on-board tanks are forecast to store CH₄ and water, useful for feeding both a combustion chamber (designed to provide the heat required by the system) and a multi tubes Pd-Ag MR useful to generate pure H₂ via methane steam reforming (MSR) reaction. The pure H₂ stream is hence supplied to the FC. The flue gas stream coming out from the combustion chamber is used to preheat the MR feed stream by two heat exchangers and one evaporator. Then, this theoretical work demonstrates by a 1-D model the feasibility of the MR based system in order to generate 5 kg/day of pure H₂ required by the FC system for cruising a vehicle for around 500 km. The calculated CH₄ and water consumptions were 50 and 70 kg, respectively, per 1 kg of pure H₂. The on-board MR based FCV presents lower CO₂ emission rates than a conventional gasoline-powered vehicle, also resulting in a more environmentally friendly solution.

Keywords: fuel cell vehicle; hydrogen; on-board Pd-Ag membrane reformer; methane steam reforming reaction

1. Introduction

Nowadays, fuel cell vehicles (FCVs) supplied by pure H₂ are considered as a viable alternative to the internal combustion engine (ICE) powered vehicles [1]. In a H₂ powered FCV, H₂ reacts with O₂ to generate power that is further transformed into mechanical energy, Figure 1.

Figure 1. Conceptual scheme of a fuel cell vehicle (FCV) provided by a H₂ pressurized tank [2].

Proton exchange membrane fuel cells (PEMFCs) are the most used fuel cells typology in transportation applications [1,2]. They are commonly supplied by pure H_2 , provided from an external source and stored in a pressurized tank [2]. With respect to the common ICE powered vehicles, a FCV presents several advantages including silent operations, lower temperature, rapid start-up, lower leakage and corrosion concerns, and lower greenhouse gases (GHGs) emission [3]. Typically, about 4–7 kg of pure H_2 are stored in a FCV by means of pressurized tanks [1,2]. In particular, 4 kg of H_2 enables a FCV driving-range autonomy without refueling for around 320 km [1].

Nevertheless, some open issues still remain regarding the adoption of FCVs implementing an on-board H_2 production or a H_2 storage system, both presenting drawbacks needing further development prior to be proposed at larger scale [4]. In this regard, the U.S. Department of Energy (DOE) first established, and it is still under development, the on-board H_2 storage program [5], also to introduce new methods to meet the needs of the customers. Another important aspect of research is related to low energy-density of H_2 , which is responsible for its difficult storage in a car. Indeed, too large or too heavy H_2 pressurized tanks would be required to ensure an adequate driving-range as currently guaranteed by the conventional ICEs vehicles [4]. Consequently, the on-board H_2 generation via fuel reforming processors seems to be a quite attractive option, particularly if MSR reformers are used to generate H_2 , because this solution could exploit the CH_4 pipeline infrastructure still existing for CH_4 fueled ICE vehicles, even though further complexity would be added to the system and an increase of the costs as well. The former issues were analyzed in deep by Ma and Spataru [4]. Different studies in literature address the development of on-board H_2 generation systems using different kind of fuels such as methanol, ethanol, and other hydrocarbons. Boettner and Moran [6] and Wu et al. [7] worked on the on-board FCVs development, implementing methanol fuel processors for H_2 generation, and they demonstrated the economic advantage of this solution in terms of capital cost with respect to FCVs adopting a direct H_2 supplying by tank. Purnima and Jayanti [8] simulated the on-board reforming of ethanol for a FC powered vehicle, also coupling a methane reformer to provide the heat of ethanol reforming reaction. They demonstrated that an overall efficiency of a bit less than 50% could be reached by the proposed system. Zhang et al. [9] analyzed the use of dimethyl ether (DME) as a fuel for on-board reformer in a PEM fuel cell system. They proved that the DME reformer could supply acceptable hydrogen for a FCV [9]. An on-board n-heptane fuel processor system was simulated for driving a 2–3 kW FCV by Karakaya and Avcı [10], coupling a methane combustor also for supplying the required heat for n-heptane steam reforming. Darwish et al. [11] investigated the feasibility of hydrogen generation in a 50 kW FCV by on-board naphtha reforming process. They founded that a 70 L fuel tank should be required to guarantee 5 h of continuous driving time due to a consume of 14 L/h of naphtha in the reformer. Myers et al. [12] pointed out how MSR represents an efficient process for H_2 generation for FCVs supplying, highlighting the following advantages: (1) N_2 dilution effect could be ignored and, consequently, the highest H_2 generation may be attained by MSR reaction among the other H_2 generation methods (autothermal reforming and partial oxidation); (2) the high temperature of the output gas stream could provide the heat inputs required, (3) no need to compress air to the system because the reaction pressure could be achieved by pumping the reactants; (4) the CH_4 price is consistently lower than that of other fuels.

To the aforementioned examples, a consistent number of research studies was dedicated in the last decade to find alternative solutions to the conventional reformers under the purpose of pursuing the principles of Process Intensification Strategy (PIS) [13]. In this regard, the role of membrane engineering in the application of PIS in the fuel reforming was largely studied, demonstrating several advantages over the conventional technologies [14–21]. In the field of H_2 generation, many studies were dedicated to the conversion of CH_4 into pure H_2 via reforming reactions in membrane reformers (MRs), highlighting the operational and economic benefits over the conventional reformers [16–18,22–25]. In particular, metallic membranes were largely studied in MR applications, with palladium and its alloys resulting the dominant materials for preparing inorganic membranes due to the high solubility and permeability of H_2 through them [19,20,26–31].

The H_2 produced in a fully H_2 perm-selective Pd-based MR is hence directly useful for a PEMFC supply without needing any additional H_2 purification stage. This constitutes the superiority of an on-board Pd-based MR adoption over an on-board conventional reformer, which would require further H_2 purification stage processes to purify the reformed H_2 -rich stream in order to meet the strict purity requirements of a PEMFC (CO content below 10 ppm).

The H_2 transport through a dense palladium or palladium-alloy film occurs in six stages under a driving force (from a high to a low pressure gas region): (a) diffusion of molecular H_2 at the Pd membrane surface, (b) reversible dissociative adsorption on the Pd surface, (c) dissolution of atomic H into the bulk metal, (d) diffusion of atomic H through the bulk metal, (e) association of H atom on the Pd surface, (f) desorption of molecular H_2 from the surface, (g) diffusion of molecular H_2 away from the surface [20].

Hence, the H_2 permeation through Pd-based membranes is generally described by the Sieverts–Fick law (1):

$$J_{H_2} = \frac{Q(p_{hps}^{0.5} - p_{lps}^{0.5})}{\delta} \quad (1)$$

where, J_{H_2} represents the H_2 permeating flux, Q the H_2 permeability, δ the thickness of the palladium/palladium alloy film, p_{hps} and p_{lps} are the H_2 partial pressures on the high pressure (feed) and low pressure (permeate) sides, respectively, while “0.5” is the Sieverts pressure exponent, representing the bulk diffusion controlling step of the H_2 permeation mechanism [21].

Several applications are noticed in literature regarding the application of Pd-based MRs to carry out MSR reaction for generating pure H_2 to be directly supplied to PEMFCs (with standard requirements of highly H_2 concentrated streams showing CO concentration below 10 ppm) [5,8,16,18,19], reaching high CH_4 conversions generally at lower temperatures than the equivalent conventional reformers [17,32] due to the selective permeation of H_2 through the membrane that is responsible for the shift of MSR reaction towards the products, enhancing both the conversion and H_2 yield [16,22–25]. Although a large body of literature on MRs for H_2 for generation may be noticed, to our best knowledge there are no applications of FCVs adopting MRs on-board. This choice would result more convenient also than a solid oxide electrolysis cell (SOEC) utilization for generating pure hydrogen. Indeed, the former shows as main issue (still unsolved) the high degradation under a longer operation, which would result as a limit for ensuring stable and long vehicle cruising. The SOEC degradation may occur in cell components such as hydrogen/air electrodes and electrolytes due to structural, electrochemical, and thermal modifications in the components, which in turn would affect the SOEC performance.

The novelty of this work consists of the modeling of an on-board Pd-Ag based multi-tubes MR used for generating 5 kg/day of pure H_2 from MSR reaction to be supplied to a FCV (in this case, a pure CH_4 feed stream was assumed without sulphur based odorants as-on the contrary-normally present in the already existing CH_4 refueling stations). As the diffusion could be neglected in angular direction at low pressures [26,27], a 1-D model was adopted to evaluate macroscopically the size, the efficiency, and the hydrogen generation performance of the proposed on-board membrane-based fuel processor as a viable option for the FCVs development.

2. On-Board Processor Description

Figure 2 shows the schematic diagram of the proposed Pd-Ag MR on-board to produce pure H_2 from MSR reaction for a FCV application.

Two separate tanks are embedded to provide water and CH_4 for the system. MSR reaction is carried out in a multi-tubes MR packed with a Ni-based catalyst, adopting tubular unsupported Pd-Ag membranes, 50 μm thick. The heat required for carrying out the MSR reaction is supplied by burning a portion of the CH_4 in a combustion chamber, placed before the MR. The combustion chamber produces high temperature flue gas, giving the possibility of generating steam and hot combustion air by flue

gas heat exchanging with water and air in heat exchangers and evaporators. The produced steam and hot air are used in the MR.

Figure 2. The proposed system for pure hydrogen producing in an on-board engine.

3. Mathematical Modeling

This theoretical study evaluates the feasibility of the proposed on-board MR and the entire FCV system, which is modeled at steady state and non-isothermal conditions.

3.1. Combustion Chamber Mass and Energy Balances

The differential volume element of thickness Δz for the combustion chamber is shown in Figure 3.

Figure 3. An elemental volume of the combustion chamber.

The combustion process is assumed complete. The mass and energy balances are written for an adiabatic reactor.

$$\frac{dF_i}{dz} = \sum_j \eta r_j \rho_B \quad i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}_2, \text{O}_2 \quad (2)$$

$$\frac{dT_{\text{combustion}}}{dz} = \frac{r_{\text{combustion}}(-\Delta H_f) \eta \rho_B A_C - \sum_{i=1}^4 C p_i \frac{dF_i}{dz} (T_{\text{combustion}} - T_{\text{ref}})}{\sum_{i=1}^4 C p_i F_i} \quad (3)$$

where F_i is the molar flow rate of component i , η is catalyst effectiveness factor, r_j is rate of reaction of component j , ρ_B is the bed density, $T_{\text{combustion}}$ is the combustion chamber temperature, ΔH_f is the enthalpy change of combustion reaction and A_C is the cross area of the chamber. The boundary conditions of combustion chamber are as following:

$$z = 0 ; F_i = F_{i \text{ feed1}}, T_{\text{combustion}} = T_{\text{feed1}} \quad (4)$$

where $F_{i \text{ feed1}}$ and T_{feed1} are the molar flow rate of component i and the temperature of the combustion chamber feed.

3.2. Reformer Mass and Energy Balances

The Pd-Ag MR packed with a Ni-based catalyst is modeled on the basis of an elemental volume of the MR, as shown in Figure 4.

Figure 4. An elemental volume of the membrane reformer (MR) during MSR reaction process.

It may be schematized in three zones: reaction side, membrane side, and heating media (flue gas zone).

3.2.1. Reaction Side

The reaction side mass balance is written according to Equation (2).

Equation (5) shows the expression to calculate the H_2 permeation flux (J_{H_2}):

$$J_{H_2} = \frac{Q_{Pd-Ag}}{\delta} (p_{H_2}^r)^{0.5} - (p_{H_2}^m)^{0.5} \quad (5)$$

In this equation, $p_{H_2}^r$ and $p_{H_2}^m$ are H_2 partial pressures in the reaction and membrane sides, respectively. Furthermore, δ and Q_{Pd-Ag} are the Pd-Ag membrane thickness and H_2 permeability, respectively.

For the dense Pd-Ag membrane Q_{Pd} is determined by [28], assuming also its full H_2 perm-selectivity:

$$Q_{Pd-Ag} = \frac{p_0}{\delta} \exp\left(-\frac{E_0}{RT}\right) \quad (6)$$

where p_0 is the pre-exponential factor ($6.82 \times 10^{-5} \frac{\text{mol}}{\text{m}^2 \text{s} \sqrt{\text{bar}}}$) and E_0 is the apparent activation energy (13,412 J/mol). R is the universal gas constant, and T is the bulk temperature.

By considering the poisoning effect of possible byproducts formed during MSR reaction such as CO or CO_2 on the H_2 permeability of the dense Pd-Ag membrane, the following equations developed by Perez et al. [28] were considered:

$$J_{\frac{H_2}{CO \text{ or } CO_2}} = J_{H_2} \times J_{H_2}^* \quad (7)$$

$$J_{H_2}^* = \left(1 - \alpha \frac{K_i \bar{p}_i}{1 + K \bar{p}_i}\right) \quad (8)$$

In Equations (7) and (8), $J_{\frac{H_2}{CO \text{ or } CO_2}}$ and $j_{H_2}^*$ are the H_2 permeation flux in the presence of CO or CO_2 and the normalized flux of H_2 , respectively. α is a dimensionless parameter depending only on

the temperature (it accounts for additional effects of the adsorbed gas), K_i the adsorption equilibrium constant (Pa^{-1}), and $\bar{p}_i$ average partial pressure (Pa) of species i . Table 1 shows the quantities of α and K_i at different temperatures. At $T > 400^\circ\text{C}$, the CO effect on H_2 permeability is not comparable with the CO_2 one and, at $T > 450^\circ\text{C}$, also the CO_2 effect results to be negligible [28].

Table 1. The α and K_i parameters of Equation (9) taken from Perez et al. [28].

$T\ (^{\circ}\text{C})$	CO		CO ₂	
	α	K_i	α	K_i
450	0.12	1×10^{-4}	0.62	4.93×10^{-6}
400	0.20	1.03×10^{-4}	0.77	6.30×10^{-6}
300	0.77	1.34×10^{-4}	0.80	1.17×10^{-5}
250	0.78	3.35×10^{-4}	0.90	1.50×10^{-5}

By considering the Equations from (5) to (8), the H_2 flow rate in the reaction side could be calculated by the following equation:

$$\frac{dF_{\text{H}_2}^r}{dz} = \sum_{j=1} \eta r_j \rho_b + \frac{Q_{Pd} \cdot 2\pi \cdot (r_0 + \delta)}{\delta} \left(1 - \alpha \frac{k_i \bar{p}_i}{1 + k_i \bar{p}_i}\right) (p_{\text{H}_2}^{r, 0.5} - p_{\text{H}_2}^m, 0.5) \quad (9)$$

The energy balance of the reaction side could be written as follows:

$$\frac{dT_{\text{reac}}}{dz} = \frac{\eta \rho_B \sum_{j=1}^4 r_j (-\Delta H_{f,j}) A_C - \sum_{i=1}^6 C p_i \frac{dF_i}{dz} (T - T_{\text{ref}}) + \pi D_{\text{so}} U_{\text{shell}} (T_{\text{flue gas}} - T_{\text{reac}})}{\sum_{i=1}^6 C p_i F_i} \quad (10)$$

where T_{reac} is the reaction side temperature, $\Delta H_{f,j}$ is the enthalpy change of reaction i , A_s is the cross area of reaction side, and D_{so} is the external diameter of the reaction side.

The following boundary conditions should be applied:

$$z = 0; F_i = F_{i, \text{feed}}, T_{\text{reac}} = T_{\text{heat-exchanger-exit}} \quad (11)$$

3.2.2. Membrane Side

The membrane side mass balance is:

$$\frac{dF_{\text{H}_2}^m}{dz} = \frac{Q_{Pd} \cdot 2\pi \cdot (r_0 + \delta)}{\delta} \left(1 - \alpha \frac{k_i \bar{p}_i}{1 + k_i \bar{p}_i}\right) (p_{\text{H}_2}^m, 0.5 - p_{\text{H}_2}^r, 0.5) \quad (12)$$

The boundary conditions for the membrane side are as follows:

$$z = 0; F_{\text{H}_2} = F_{\text{H}_2, \text{sweep}} \quad (13)$$

3.2.3. Flue Gas Side

The energy balance of the flue gas could be written as follows:

$$\frac{dT_{\text{flue gas}}}{dz} = \frac{\pi D_{\text{so}} U_{\text{shell}} (T_{\text{reac}} - T_{\text{flue gas}})}{\dot{m}_{\text{flue gas}} C_{P_{\text{flue gas}}}} \quad (14)$$

where $T_{flue\ gas}$ is the temperature of heating media. The following boundary condition should be applied:

$$z = 0 ; T_{flue} = T_{combustion_exit} \quad (15)$$

The overall heat transfer coefficient is given by the following correlation:

$$\frac{1}{U_{shell}} = \frac{1}{h_i} + \frac{A_i \ln\left(\frac{D_o}{D_i}\right)}{2\pi L K_w} + \frac{A_i}{A_o} \frac{1}{h_o} \quad (16)$$

where h_i and h_o are the heat transfer coefficients obtained by the following correlation [33]:

$$\frac{h}{C_p \rho \mu} \left(\frac{C_p \mu}{K} \right)^{2/3} = \frac{0.458}{\varepsilon} \left(\frac{\rho V d}{\mu} \right)^{-0.407} \quad (17)$$

where, in the above equation, V is velocity of gas and the other parameters are those of bulk gas phase.

3.3. Reaction Kinetics

Considering the Westbrook and Dryer (WD) global one step mechanism, the following reaction could be considered for the combustion chamber [34]:

Equation (19) addresses the concerning reaction rate for CH_4 combustion [34]:

$$R_{combustion} = 2.118726 \times 10^{11} e^{\frac{-35000}{RT}} [CH_4]^{0.2} [O_2]^{1.3} \text{ (units in cm, s, cal, and mol)} \quad (19)$$

CH_4 conversion takes place in the MR via the steam reforming reaction over a Ni based catalyst.

The corresponding reaction rate equations are as follows [31,32]:

$$R_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}} \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_1} \right)}{\left(1 + K_{CH_4} P_{CH_4} + K_{H_2} P_{H_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O} / P_{H_2} \right)^2} \quad (23)$$

$$R_2 = \frac{\frac{k_2}{P_{H_2}^{3.5}} \left(P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_2} \right)}{\left(1 + K_{CH_4} P_{CH_4} + K_{H_2} P_{H_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O} / P_{H_2} \right)^2} \quad (24)$$

$$R_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}} \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_1} \right)}{\left(1 + K_{CH_4} P_{CH_4} + K_{H_2} P_{H_2} + K_{CO} P_{CO} + K_{H_2O} P_{H_2O} / P_{H_2} \right)^2} \quad (25)$$

The catalyst effectiveness factors for R_1 , R_2 , and R_3 are 0.01, 0.01, and 0.3, respectively, (taken from [32]). They were considered constant due to the short length of the reaction tubes (50 cm). Thermodynamic and rate constants for Equations (23)–(25) over Ni-based catalysts are given in Table 2, where reactions rates are in $\text{mol.kg}^{-1}.\text{s}^{-1}$, and the various partial pressures in bar.

Table 2. Thermodynamic and rate constants for Equations (23)–(25) are taken from Xu and Froment [32].

$k_1 = 1.8 \times 10^{-6} \exp\left(\frac{240,100}{R}\left(\frac{1}{648} - \frac{1}{T}\right)\right)$	$\left(\frac{\text{kmol.bar}^{0.5}}{\text{kgcat.h}}\right)$	(26)
$k_2 = 2.2 \times 10^{-5} \exp\left(\frac{243,900}{R}\left(\frac{1}{648} - \frac{1}{T}\right)\right)$	$\left(\frac{\text{kmol.bar}^{0.5}}{\text{kgcat.h}}\right)$	(27)
$k_3 = 7.6 \exp\left(\frac{67,100}{R}\left(\frac{1}{648} - \frac{1}{T}\right)\right)$	$\left(\frac{\text{kmol.bar}^{-1}}{\text{kgcat.h}}\right)$	(28)
$K_i = \exp\left(-\frac{\Delta G_{rxn_i}^\circ}{RT}\right)$	$i = 1, 2 \text{ and } 3$	(29)
$K_{CH_4} = 1.8 \times 10^{-1} \exp\left(\frac{-38,300}{R}\left(\frac{1}{823} - \frac{1}{T}\right)\right)$		(30)
$K_{H_2} = 2.9 \times 10^{-2} \exp\left(\frac{-82,900}{R}\left(\frac{1}{648} - \frac{1}{T}\right)\right)$		(31)
$K_{CO} = 40.9 \exp\left(\frac{-70,700}{R}\left(\frac{1}{648} - \frac{1}{T}\right)\right)$		(32)
$K_{H_2O} = 0.4 \exp\left(\frac{88,700}{R}\left(\frac{1}{823} - \frac{1}{T}\right)\right)$		(33)

3.4. Heat Exchangers and Evaporator Modeling

As shown in Figure 2, two heat exchangers and an evaporator are designed for preheating the CH_4 , water, and air on their way to the membrane processor. They are placed before the combustion chamber and MR. The general energy balance equations for these two exchangers are:

$$(F_C C_{P_C} T_C)_0 - (F_C C_{P_C} T_C)_L + Q_{HEX} = 0 \quad (34)$$

$$(F_C C_{P_C} T_C)_0 - (F_C C_{P_C} T_C)_L + Q_{HEX} = 0 \quad (35)$$

where C_{P_C} and C_{P_H} are heat capacities of cold and hot streams in heat exchangers. T , F , and Q_{HEX} are the temperature, flow, and heat transfer rate, respectively. The general energy balance equations for evaporators are:

$$(F_H C_{P_H} T_H)_L - (F_H C_{P_H} T_H)_0 - Q_{evap.} = 0 \quad (36)$$

$$\dot{m}_{water} H_{liquid} - \dot{m}_{water} H_{vapor} + Q_{evap.} = 0 \quad (37)$$

where $Q_{evap.}$ is the heat transfer rate in the evaporator.

4. Numerical Solution

Figure 5 shows the flowchart of the program developed for modeling the proposed on-board processor.

Figure 5. The flowchart of the program for solving the on-board MSR processor model.

As shown, at first the initial guesses are declared. The guessing parameters are:

1. The combustion chamber inlet temperature ($T_{c,in}$),
2. The reformer reaction side inlet temperature ($T_{r,in}$),
3. The combustion chamber feed composition and flowrate.

The modeling codes were written by MATLAB 2016a software. The modified Rosenbrock method (ode23s) was used to solve the set of stiff ordinary differential equations (ODEs). A total of 100 nodes were considered for numerical solution of ODEs [35].

5. Results and Discussion

In this section, the developed model is used to investigate the loop's performance and the impact of various parameters on it. Table 3 shows the specifications of the Toyota Mirai FCV, in which it is reported a H_2 tank capacity of 5 kg, a H_2 consumption in a combined cycle cruising equal to 0.76 kg H_2 /100 km, and the total cruising range for this car equal to 500 km [36].

Table 3. The specifications for Toyota Mirai FCV [36].

Parameter	Value
Maximum output	155 hp
H_2 consumption (combined cycle)	0.76 kg H_2 /100 km
Cruising range	500 km
H_2 tank capacity	5 kg

The proposed system could be hence replaced with the proposed innovative on-board H_2 production system (Figure 6). It should be mentioned that the methane consumption is proportional to FCV speed. Therefore, a fuel injection system should be applied to set the amount of methane injected to the on-board processor.

Figure 6. The replacement of the on-board MR combined to a H_2 storage tank on a FCV [36].

The operating and geometrical parameters of the on-board processor model are listed in Table 4. The parameters were chosen to give a reasonable fuel processor geometry for a five-passenger,

mid-size sedan (Toyota Mirai). The membrane tubes thickness of 50 μm was chosen due to the higher permeability and lower manufacturing cost than thicker dense and unsupported membranes present in the market [30,37].

Table 4. The operating and geometric parameters of the on-board processor.

Parameter	Value
Tube length in pure hydrogen producer (cm)	50
Tube length in combustion chamber (cm)	10
Cross area of the tubes (cm^2)	5.4
Number of tubes	25
Pressure of methane and steam in pure H_2 producer inlet (bar)	10
Temperature of methane in pure H_2 producer inlet ($^\circ\text{C}$)	500
Pressure of methane and steam in combustion chamber inlet (bar)	1
Temperature of methane in combustion chamber inlet ($^\circ\text{C}$)	25
Outer reaction side diameter in pure H_2 producer	1"
Outer shell side diameter in pure H_2 producer (cm)	3
Catalytic bed density (kg/m^3)	780
Outer tube side diameter in combustion chamber (cm)	0.5
Membrane thickness (μm)	50

5.1. The Processor Performance

The methane conversion and H_2 recovery were calculated with the following equations:

$$X_{\text{CH}_4} = \frac{F_{\text{CH}_4}^{\text{feed}} - F_{\text{CH}_4}^{\text{product}}}{F_{\text{CH}_4}^{\text{feed}}} \times 100 \quad (38)$$

$$\text{H}_2\text{recovery} = \frac{F_{\text{H}_2}^{\text{membrane side}}}{F_{\text{H}_2}^{\text{membrane side}} + F_{\text{H}_2}^{\text{reaction side}}} \times 100 \quad (39)$$

The developed MR model was validated in our previous work [37]. The required feed flow rates (CH_4 , water, and air) for the system are summarized in Table 5.

Table 5. Feed flow rates for the proposed on-board MR.

Material	Consumption Value (kg/kg pure H_2)
Methane	50
Water	70
Air	435

Figure 7 shows CH_4 conversion and pure H_2 production rate versus the reformer length. Complete CH_4 conversion is achieved in the MR outlet stream with a pure H_2 production a bit higher than 5 kg/day as in the target of the FCV requirements.

Figure 8 reports the simulation related to CO_2 and pure H_2 productions along the CH_4 consumption. Considering that the Environmental Protection Agency (EPA) report (2018) [38] sets the average CO_2 emission for a five-passenger car equal to around 253 g/km (126.5 kg for a cruising range of 500 km), the simulation of the MR of Figure 8 shows that the maximum CO_2 production is below this requirement in the outlet stream coming out from the MR, making the MR process theoretically feasible under the aforementioned limitations.

Figure 7. Methane conversion and pure hydrogen production rate of the MR, Pd-Ag membrane thickness = 50 μm , water to methane ratio = 2.5, inlet temperature = 500 $^{\circ}\text{C}$, and inlet pressure = 10 bar.

Figure 8. CO_2 and pure H_2 productions versus CH_4 consumption for Pd-Ag membrane thickness = 50 μm and water to methane ratio = 2.5, inlet temperature = 500 $^{\circ}\text{C}$, and inlet pressure = 10 bar.

In addition, taking into account that the feed of CH_4 depends on the vehicle's H_2 consumption, CH_4 consumption is highly depleted for a FCV presenting lower engine power. Steam to CH_4 mole ratio is a significant parameter affecting MSR process efficiency. This ratio ranges from 2 to 3 for industrial steam methane reformers [22].

5.2. The Processor Flexibility

Figure 9 shows the effect of feed ratio on pure H_2 production rate. As shown in the simulation, the H_2 production increases as the steam to CH_4 mole ratio increases, even though values higher than 4 do not affect significantly the H_2 production rate, meanwhile overcoming 5 kg/day as requested by the FCV target. On the contrary, the H_2 recovery decreases as a consequence of a steam/ CH_4 ratio increase. Indeed, at higher steam/ CH_4 ratio the amount of steam in excess lowers the H_2 partial pressure in the reaction side, globally determining a lower H_2 permeation driving force, which involves a lower amount of H_2 collected in the permeate side.

Figure 9. Pure H₂ production rate and hydrogen recovery ratio versus water to methane ratio, Pd-Ag membrane thickness = 50 μ m, inlet temperature = 500 $^{\circ}$ C, and inlet pressure = 10 bar.

The simulations of Figure 10 show the effect of an increase of pressure on the H₂ production rate and H₂ recovery. In both cases, a higher pressure favors an increase of production rate and the recovery. This because a higher pressure determines a larger H₂ permeation driving force, which enhances CH₄ conversion due to an improved “shift effect” on the reaction system, with consequent larger H₂ production. For the same reason, more H₂ is collected in the permeate stream and the recovery is consequently improved. Nevertheless, unsupported Pd-based membranes suffer relatively high pressure due to structural limits. Therefore, realistically, an operating pressure with unsupported Pd-based membranes should not overcome 5–6 bar.

Figure 10. Pure H₂ production rate and hydrogen recovery versus MR pressure, Pd-Ag membrane thickness = 50 μ m, water to methane ratio = 2.5, and inlet temperature = 500 $^{\circ}$ C.

A technical solution for this issue was found by Basile et al. [39], who increased the permeate pressure to respect a total pressure difference across the membrane not higher than 5 bar. Nevertheless, the H₂ permeation driving force depends on the H₂ partial pressure difference and not on the total pressure difference; high H₂ recovery was, then, achieved without structural problems for the dense unsupported Pd-Ag membrane.

However, fuel cell systems for vehicle applications are much more complex than stationary systems because of the need to accommodate load-following transients, identifying this requirement as a fundamental challenge of on-board fuel reforming [40]. In this regard, transient performance for the MRs used in on-board FCVs applications result to be still an open issue, particularly at the shut-down and restart phases. Larger experimental tests will be required for solving the aforementioned problems, which were out of the scopes of this work.

6. Conclusions

H₂ storage in FCVs represents one of the most challenging issues in this field. This theoretical work studied the feasibility of implementing a novel on-board MR able to produce pure H₂ on demand from MSR reaction. CH₄ and water were preheated by waste flue gas and reacted within a synthesis loop equipped with a Pd-Ag MR. The results showed that the system was able to produce 5 kg/day of pure H₂, which is suitable for a FCV cruising range of 500 km. A total of 50 kg of CH₄ and 70 kg of water were needed as feeding reactants to generate 1 kg of pure H₂.

The effects of various parameters such as CH₄ consumption rate, water to methane ratio, and operating pressure on the processor performance were investigated. The model showed that large pure H₂ production rates were reached by the Pd-Ag MR at both higher steam to CH₄ ratio and operating pressure.

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Nomenclature

A_c	Cross area of reaction side (m)
C_{pi}	Specific heat of component i (J kmol ⁻¹ K ⁻¹)
D_{So}	External diameter of reaction side (m)
E_0	Activation energy of membrane
F_i	Molar flow rate of component i
$\Delta G_{rxn_i}^\circ$	Standard Gibbs free energy change of reaction i
$\Delta H_{f,i}$	Enthalpy change of reaction i
k_i	Reaction rate constant
K_i	Adsorption equilibrium constant
P_i	Partial pressure of component i (bar)
r_0	Membrane tube radius (m)
Q_{Pd}	Hydrogen permeability
r_j	Rate of reaction of component j (kmol m ⁻³ s ⁻¹)
R	Universal gas constant (J kmol ⁻¹ K ⁻¹)
$T_{combustion}$	Reaction side temperature (K)
T_{react}	Reaction side temperature (K)
T_{shell}	Temperature of heating stream (K)
U_{shell}	Overall heat transfer coefficient (W m ⁻¹ s ⁻¹)
X_{CH_4}	Methane conversion
X_{CO_2}	Carbon dioxide conversion
z	Axial direction
δ	Membrane thickness
η	Catalyst effectiveness factor

ρ_B	Bed density (kg m^{-3})
DME	Dimethyl ether
DOE	Department of energy
FCV	Fuel cell vehicle
GHG	Greenhouse gases
ICE	Internal combustion engine
MR	Membrane reformer
MSR	Methane steam reforming
ODE	Ordinary differential equations
PEMFC	Proton exchange membrane fuel cell
PIS	Process intensification strategy

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