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Modeling of methane steam reforming reaction in tubular hydrogen permselective membrane reactor

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ABSTRACT

Over the years, producing hydrogen by methane steam reforming (MSR) process in membrane reactor founds high attractions. Hydrogen permselective Pd-Ag membrane shows the best performance for pure hydrogen production. In the present study, the modeling of natural gas steam reforming in the tubular Pd-Ag membrane reactor for producing CO-free hydrogen has been performed. The proposed model has been evaluated by some experimental data which obtained from a literature. The results confirm that the experimental data can be simulated by the proposed model with an acceptable accuracy. Effects of various operating parameters such as pressure, temperature, steam to methane ratio in the feed, membrane thickness as well as different flow configuration of reactants and sweep gas on the amount of methane conversion, hydrogen production and hydrogen-to-carbon monoxide ratio have been investigated and their optimum values have been determined. The novelty of the present study is investigating the effect all of the operational conditions on the process by simple mathematical modeling, which not to be considered in any previous study. Moreover only some qualitative studies about optimal operational conditions of MSR process have been done. Performed analyses confirm that increasing the steam-to-methane ratio in the feed, temperature as well as pressure of the reaction zone and reducing the thickness of membrane can increase the methane conversion and hydrogen production.

KEYWORDS

Pure hydrogen production;
Natural gas steam reforming;
Pd-Ag membrane reactor;
Hydrogen-permselective;
Optimum operation conditions.

INTRODUCTION

Nowadays, there are growing interests toward using pure hydrogen as a clean source of energy in scientific and industrial applications. Pure hydrogen is mainly used as the desulfurization agent in the petroleum, a raw material in chemical industries as well as a main source of feed for fuel cells[1]. Electrolysis of water, evaporation of coal and hydrocarbons reforming are some of the common process which often used for hydrogen production. Conventionally, in the industrial processes some of the hydrocarbon fuels convert into hydrogen, by partial oxidation, auto-thermal reforming and steam reforming.

Partial oxidation is an exothermic reaction in which incomplete combustion of a hydrocarbon fuel in presence of oxygen will be occurred. Zhu et al. show that even at low temperatures the reaction rate of the partial oxidation will be increased in presence of catalyst, such a process is so called catalytic partial oxidation[2].

In the auto-thermal reforming, methane, steam and oxygen is fed to the catalytic reactor. Steam reforming reaction consumes a part of produced energy in partial oxidation reaction, so amount of required energy is reduced relatively. Temperature of the auto-thermal reforming is lower than partial oxidation reaction and ratio of the hydrogen to carbon monoxide is higher[3].

In industrial scales, hydrogen is often produced by steam reforming of hydrocarbon such as methane or naphtha. In the natural gas steam reforming which is more important process, hot methane reacts with superheated steam in presence of catalyst. The main drawbacks of MSR are endothermic reaction and small ratio of the produced hydrogen to carbon monoxide[2].

In the recent years, enhanced demand to hydrogen production attracts more attention to steam reforming process and its improvement[4]. The economical analysis of various hydrogen production methods have done by Crabtree et al., they concluded that MSR is more economic than other industrial hydrogen production processes[5].

Although industrial hydrogen production often followed by a hydrogen separation process, a lot of researches have also been carried out to produce purified hydrogen using membrane technologies. Complete methane conversion to hydrogen and carbon dioxide (even at low temperatures) have been achieved using Pd membranes. Hydrogen permeation through the membrane shifts the equilibrium toward the higher methane conversion and yields higher monoxide-free hydrogen.

Iulianelli et al. have investigated H_2 production by low pressure MSR in a Pd-Ag membrane reactor over a Ni-based catalyst. They obtained higher methane conversion and hydrogen yield than a fixed bed reactor, which operated at the same conditions, i.e. temperature between 400 and 500°C and at relatively low pressure (1.0-3.0 bar). Using a sweep gas, they got 70% of high-purity hydrogen on total hydrogen produced[6].

In another related study Vasileiadis et al. investigated methane and methanol steam reforming in a membrane reactor for efficient hydrogen production by an experimental apparatus. They concluded that membrane reactor has higher performance than traditional reactor. They observed a same behaviour for both methane and methanol steam reforming[7].

Importance of the subject attracts scientist's efforts to develop some related mathematical modeling in this field. Among them Wang et al. developed a 3D two-fluid model to study hydrogen production by the sorption-enhanced steam methane reforming (SE-SMR) process in fluidized bed reactors. They concluded that very high production of hydrogen in SE-SMR could be obtained compared with the standard SMR process. They found a good agreement between their model and a related experiment[8].

Kyriakides et al. have simulated a low temperature MSR membrane reactor based on a 2D nonlinear and pseudo-homogeneous mathematical modelling. They concluded that in membrane reactor, methane conversion (60.24% at 10 atm) can reach similar values to that in a traditional reactor (61.21% at 10 atm and 700°C) at significantly lower temperatures (550°C)[9].

In the present paper, the modeling of MSR process in the tubular Pd-Ag membrane reactor has been performed. The proposed model has been evaluated using experimental data which obtained from literature. Obtained results confirm that the proposed model have excellent agreement with the experimental results. Methane conversion which represents the amount of hydrogen yield has been investigated under various operating conditions such as temperature and pressure of the reaction zone, thicknesses of membrane, flow configuration as well as natural gas-steam ratio in the entering feed. The effects of mentioned parameters on the produced hydrogen to carbon monoxide ratio have also been studied.

Although the MSR process in the membrane and traditional reactor have been widely studied experimentally as well as theoretically, but no important study can be found in the literatures which investigate the effect of all operational conditions. Moreover there isn't any significant study to find the operational conditions which maximize the amount of methane conversion, hydrogen production and hydrogen-to-carbon monoxide ratio. Hence in the present study the attention has been focused on these subjects.

MSR PROCESS IN THE MEMBRANE REACTOR

Hydrogen production by MSR process often is completed in three successive stages as follows:

1. Catalytic reforming of methane

This stage has been carried out at high temperature and pressure to produce syngas (Synthesis gas) which is a mixture of H_2 and CO. Reaction (1) represents the catalytic reforming of methane.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

$$\Delta H(298\,K) = 206\ kj/mol \qquad (1)$$

2. Catalytic reaction

During the second step carbon monoxide and steam react to produce H_2 and CO_2. This step of the reaction process is illustrated by Eq. (2) and (3). Reaction (2) is often called water-gas shift reaction.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

$$\Delta H(298\ K) = -41\,kj/mol \qquad (2)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$$

$$\Delta H(298\ K) = 165\,kj/mol \qquad (3)$$

3. Purification of hydrogen

Some technologies such as fuel cells need purified hydrogen to enhance their efficiency. The nature of the reaction implies that the reaction progress considerable at high temperature and more steam to methane ratio in the feed (about 3 to 4). Methane conversion about 80% could be reached at temperature above 850°C and 1 to 4 MPa pressure. In order to improve the resistance of equipments at high temperature and pressure, they should be made from some expensive and special materials, so the traditional MSR process is not economic.

MSR is endothermic reaction which needs high amount of energy to progress. This reaction often performed in the fixed bed tubular reactor while researcher's findings confirm that tubular membrane reactors have better performance and lead to more gentle operational conditions than traditional ones[6,10,11]. Effects of physical properties of membranes such as thickness and composition on the methane conversion and amount of hydrogen separation and production have been investigated by researchers[12,13].

Using a numerical study, Shigarov and Kirillov compared different types and operating modes of a tubular membrane reactor for SMR process. They investigated effects of some operating parameters and concluded that for a cylindrical membrane, the use of a catalytic bed based on waved bands of porous nickel instead of a granular bed of a commercial catalyst can theoretically increase the yield of hydrogen by 15–18%[14].

Tong and Matsumuta focus to the influence of catalyst activity and flow rate of reactants on the methane conversion and amount of hydrogen separation in the membrane reactor[15]. They state that by increasing the catalyst activity and permeation ability of membrane the separation of hydrogen and the yield will be improved.

Yu et al. derived the mathematical model of the MSR in the ceramic membrane reactor[16]. They investigate the effects of temperature, pressure and sweep gas flow rate on the methane conversion and hydrogen yield.

It is proved that rate of hydrogen production in the membrane reactor is higher than conventional reactors. Selecting appropriate membrane plays an important role in experimental and modeling studies, because it could produce higher amounts of purified hydrogen. Palladium based membranes are the most important membranes which have very excellent selectivity and permeation respect to hydrogen[17]. Hence carrying out MSR reaction in the Pd based membranes is quite better than other membranes and shows effective performance in the various operational conditions.

According to the Le Chatelier's principle, hydrogen permeation through a permselective membrane layer can change equilibrium conditions and moves the reaction toward the products, i.e., higher methane conversion[18].

Tsuru et al. carried out an experimental and modelling study on the process using bimodal catalytic membrane reactors at an isothermal and plug flow condition. They concluded that due to high driving force of hydrogen permeation, an increased performance for the production of hydrogen with an increased pressure was confirmed both by simulation and by experimentation[19].

Thus, by employing the membrane reactor, shift gas, hydrogen separation and purification operations can be done simultaneously in the single unit. Therefore the membrane reactor can reduce the total cost of the MSR process and improve economic conditions.

Although up to three decades ago, using membranes in the industrial processes was not common, but over the years, they are gradually employed in some industries such as oil and gas processes. One of the primary works in the MSR was performed in 1987 by Oertel et al; they studied hydrogen production in Pd membrane reactor with 100µm thickness and observed that the hydrogen production rate is very much[20]. The relatively high thickness of the used membrane decreases hydrogen permeation rate and so the reaction should be carried out at high temperature (700 to 800°C).

Scientists always try to adjust the reaction conditions and increase the rate of hydrogen production. Uemiya et al. produce higher amount of hydrogen using Pd membrane based on porous ceramic tubes reactor at lower temperatures. In their experiments the amount of hydrogen yield was increased by decreasing the pressure using the sweep gas[21,22].

Shu et al, using stainless steel tubes equipped with a Pd and Pd-Ag membrane, achieved 63% methane conversion in the MSR at operating temperature 500°C[4,23].

Nam and his colleagues reached to 80% methane conversion using Pd-Ruthenium membrane at 500°C temperature while traditional mode progress to 57% methane conversion at same operational condition[24].

The experimental study on steam reforming reaction in the Pd-stainless steel membrane reactor with 6 µm thickness has been done by Tong et al. The authors reached 0.26 mol/(m^2s) hydrogen flux at operating temperature about 500°C and about 100 Kpa pressure[25].

Gallucci et al, have done an experimental study using Pd-Ag membranes with 50µm thickness. In their study the effect of temperature and steam-to-methane ratio on the methane conversion was investigated[26]. In another study, Gallucci and colleagues studied effect of co-current and counter-current configuration of reactant and sweep gas on the methane conversion and hydrogen yield. The author's analyses confirm that the counter-current mode has better performance than co-current[27].

Marín et al. studied a MSR reactor by means of numerical simulations using a 2D model. They consider mass, energy and momentum balances in their analysis. The model was validated with experimental data, and the adequacy of a simplified 1D model to simulate the membrane reactor was evaluated and discussed in comparison to the 2D model. Then, the model was used to study the influence of the main operating variables (inlet temperature, pressure, space velocity, steam excess and sweep gas rate in the permeate side) on the reactor performance. Finally, the optimum operating conditions, corresponding to a maximum hydrogen permeation rate, were determined, and the behaviour of the optimized reactor is analysed in detail[28].

Assaf et al, proposed a mathematical model for isothermal MSR in Pd membrane reactor with 5-20 µm thickness. They stated that compared to the traditional reactor, the membrane reactor can increase methane conversion about 16% at different temperatures[29].

Hoang et al. derived a mathematical model for a traditional MSR process to obtain the optimum conditions for hydrogen production. They reported the steam-to-methane ratio 3 to 3.5 and temperature 1073 K as optimum operating conditions for producing highest amount of hydrogen[30].

Mathematical modeling

In order to investigate the effects of various operating variables on the MSR process and evaluate optimum operating conditions for maximizing methane conversion, a dual pipes reactor with hydrogen permselective membrane has been simulated. The modeling is done in both shell and tube of the membrane reactor at steady state, isothermal conditions and plug flow configuration. Figure 1 depicts a schematic of the reactor and location of the membrane. In this model the tube side of the reactor is reaction zone where the mixture of methane and steam enter it as the feed and reactions progress in the presence of AL_2O_3 catalyst. A Pd-Ag membrane is located between shell and tube sides of the reactor. Hydrogen permeates through the Pd-Ag membrane, so separating it from the reaction zone can result in increasing the methane conversion and hence promoting the hydrogen yield. Nitrogen as a sweep gas flows in the shell side of the reactor and carries the permeated hydrogen from shell zone. Xu and Froment[31] as well as Stephan and Willms[32] have a good study on the process and proposed some equations for reaction rates (Eqs. 4-6) for the MSR process reactions (Eqs.

1-3).

$$R_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}}\left[P_{CH_4}P_{H_2O} - \frac{P_{H_2}{}^3 P_{CO}}{K_1}\right]}{DEN^2} \quad (4)$$

$$R_2 = \frac{\frac{k_2}{P_{H_2}}\left[P_{CO}P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_2}\right]}{DEN^2} \quad (5)$$

$$R_3 = \frac{\frac{k_3}{P_{H_2}^{3.5}}\left[P_{CH_4}P_{H_2O}{}^2 - \frac{P_{H_2}{}^4 P_{CO_2}}{K_3}\right]}{DEN^2} \quad (6)$$

$$DEN = 1 + K_{CH_4}P_{CH_4} + K_{CO}P_{CO} + K_{H_2}P_{H_2} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}} \quad (7)$$

To calculate the reaction rate, it is necessary to evaluate partial pressure of reactants and products. The partial pressure of each component in the MSR process can be determined through following equations:

$$P_{CH_4} = F_{CH_4}\alpha \quad (8)$$

$$P_{H_2O} = F_{H_2O}\,\alpha \quad (9)$$

$$P_{H_2} = F_{H_2}\,\alpha \quad (10)$$

$$P_{CO} = F_{CO}\,\alpha \quad (11)$$

$$P_{CO_2} = F_{CO_2}\,\alpha \quad (12)$$

$$\alpha = \frac{P_T}{\left(F_{CH4} + F_{H2O} + F_{H2} + F_{CO} + F_{CO2}\right)} \quad (13)$$

TABLE 1 shows numerical values of adsorption equilibrium and reaction rate constants. Numerical values of the reaction equilibrium and membrane permeation constants are shown at the TABLE 2.

It should be noted that the mathematical modeling of the dual tubes membrane reactor is derived based on some assumptions which are listed below:

TABLE 1 : Values of reaction and adsorption constants[30]

Rate or Adsorption constant	Pre-exponential factor		Ea(j/mol)
	Value	Unit	
k_1	3.2573×10^{9}	mol. bar $^{0.5}$/$g_{cat.}$ s	209500
k_2	1954.8	mol.bar/g_{cat} . s	70200
k_3	7.7040×10^{6}	mol. bar $^{0.5}$/$g_{cat.}$ s	211500
K_{CO}	8.11×10^{-5}	bar $^{-1}$	-70230
K_{H2}	7.05×10^{-9}	bar $^{-1}$	-82550
K_{H2O}	1.68×10^{4}	-	85770
K_{CH4}	1.995×10^{-3}	bar $^{-1}$	-36650

TABLE 2 : Reaction equilibrium and Pd-Ag membrane permeation constants

Pre-exponential factor	Pre-exponential Factor		Ea/R
	Value	Unit	
K_1	5.754×10^{12}	bar ^{2}	11500 [30]
K_2	1.26×10^{-2}	-	-4600 [30]
K_3	7.24×10^{10}	bar ^{2}	21600 [30]
β	12.7503	mol/m.hr.bar $^{0.5}$	3507.33 [26]

1) Steady state condition: there is no radial gradient in temperature, pressure and velocity
2) Ideal gas law is governing
3) only hydrogen can permeate through Pd-Ag membrane
4) plug flow, no change occurs in the radial direction.

By the way, in the plug flow it is assumed that the conditions of fluid can change only along the axial direction of the reactor and no changes occur in the radial direction. Thus mass balance equation for different components has been written around a very small volumetric element (dv) which is equivalent to a longitudinal element (dz). Mass balance has been written around the dz element of the membrane reactor in isothermal condition for all of the components. The relevant element is shown in the Figure 1.

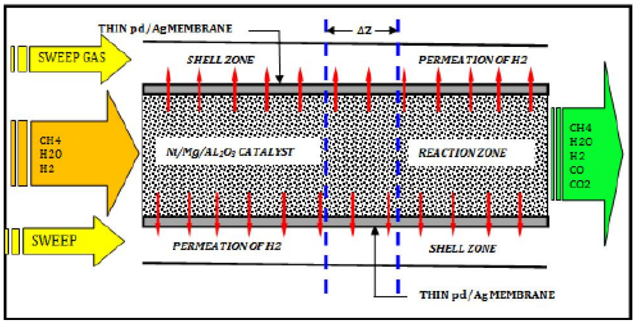

Figure 1 : Volumetric element for membrane reactor modelling

Applying the mass conservation law for the methane around the element of Figure 1 leads to Eq. (14). This equation expresses that how molar flow rate of methane changes along the reactor.

$$\frac{dF_{CH_4}}{dz} = -\pi\rho_c\left(r_m{}^2\right)\left(R_1 + R_3\right) \quad (14)$$

Changes in molar flow rate of the steam, H_2, CO and CO_2 in reaction zone and permeated hydrogen through the membrane have been presented using Eqs. 15-21.

$$\frac{dF_{H_2O}}{dz} = -\pi \rho_c \left(r_m^{\ 2}\right)\left(R_1 + R_2 + 2R_3\right) \tag{15}$$

$$\frac{dF_{CO}}{dz} = \pi \rho_c \left(r_m^{\ 2}\right)\left(R_1 - R_2\right) \tag{16}$$

$$\frac{dF_{CO2}}{dz} = \pi \rho_c \left(r_m^{\ 2}\right)\left(R_2 + R_3\right) \tag{17}$$

$$\frac{dF_{H_2}^{\ \ m}}{dz} = \pm \frac{2\pi r_m L\beta}{\delta}\left(P_{H_2}^{\ \ 0.5} - P_p^{\ 0.5}\right) \tag{18}$$

$$\frac{dF^{R}{}_{H_2}}{dz} = \pi \rho_c \left(r_m^{\ 2}\right)\left(3R_1 + R_2 + 4R_3\right) - \frac{dF_{H2}^{\ \ m}}{dz} \tag{19}$$

In the permeation side, the mass conservation equation is written only for hydrogen:

$$dF_{H_2}^{m} = \pm J_{H_2} \pi D\, dz \tag{20}$$

The minus and positive in above equation illustrate counter-current and co-current flow, respectively. Where:

$$J_{H_2} = \beta\left(\sqrt{P_{H_2}^{R}} - \sqrt{P_{H_2}^{m}}\right) \tag{21}$$

RESULTS AND DISCUSSION

As can be seen, the mathematical modeling of the mentioned membrane reactor is a set of ordinary differential and algebraic equations i.e., Eqs. 14-19. In order to comprehensive analysis of the MSR process in the membrane reactor, these coupling equations should be solved simultaneously.

The governing equations of the membrane reactor have been solved by fourth-order Runge-Kutta approach with the step size of 0.001. The selected value of the step size is worked out well for all of the performed analyses. By solving this system of equations, effects of different operating variables on the MSR process in the membrane reactor will be determined. The proposed model has been validated using the experimental results for Pd-Ag membrane reactor which has been reported by Gallucci et al[26].

Validate the proposed mathematical model

In this section, the performance of our proposed model has been evaluated over some experimental information associated to MSR process in the membrane reactor[26]. Gallucci et al. have conducted experimental study on the MSR process in the Pd-Ag membrane reactor. Composition of the feed stream and operating conditions of the employed membrane reactor in their work are listed in TABLE 3.

In order to evaluation the performance of the proposed model, the amounts of methane conversion in the membrane as well as traditional reactors (without any membrane) have been calculated by the proposed model and compared by experimental data of Gallucci et al[26].

TABLE 3 : Feed and sweep gas composition of the membrane reactor[26]

Feed condition	Value
CH_4 (mol %)	24.94
H_2O (mol %)	74.81
H_2 (mol %)	0.25
CO (mol %)	0
CO_2 (mol %)	0
Sweep gas (mol/min)	0.00217
Lumen pressure (bar)	1.22
Shell pressure (bar)	1.1

TABLE 4 shows the physical properties of the reactor, catalyst and membrane[26].

TABLE 4 : Physical conditions of the designed membrane reactor[26]

Parameter	Value	Unit
Reactor length	0.15	m
Catalyst density	2355.2	g/m^3
Inner diameter	1.02	cm
Outer diameter	2	cm
Membrane thickness	50	µm

The results of the proposed model (solid line) as well as experimental results of Gallucci et al (squared symbols) have been depicted in Figure 2 and their related numerical values are presented in TABLE 5. It is evident that there are very excellent agreement between the results of the proposed model and experimental information.

The presented errors in TABLE 5 have been calculated by Eq. (22). The error equation has been employed for calculating the relative errors between obtained value of our proposed model and the real value of experiment. The results confirm that the proposed model can simulate the behaviour of real membrane reactor with less than 10% which is an acceptable error from engineering point of view.

$$\mathbf{Error} = \left| \frac{X^{Calc.}_{CH4} - X^{Exp.}_{CH4}}{X^{Exp.}_{CH4}} \right| \qquad (22)$$

TABLE 5 : Validation the proposed model by the experimental study of Gallucci et al[26]

Reactor	Temperature	$x^{Exp.}_{CH4}$	$X^{Calc.}_{CH4}$	Error
Membrane Reactor	300	5	4.5	0.1
	350	11	10.6	0.036
	400	29	27.5	0.052
	450	42.7	44	0.029
Traditional Reactor	400	16	15.67	0.02
	450	26	24.25	0.067
	500	37	40.43	0.093

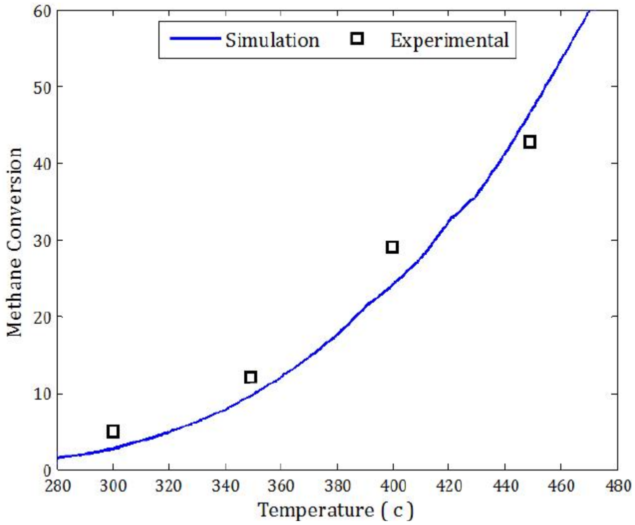

Figure 2 : Comparison of model and experimental results[26]

Effect of temperature

In order to investigate the effect of various operating conditions on the methane conversion, at first stage the effect of temperature is investigated and simulated results are presented in Figure 3. This figure shows methane conversion profiles along the reactor at various temperatures. As mentioned earlier, the methane steam reaction is an endothermic and equilibrium reaction, so according to Le Chatelier principle, increasing the temperature can move the reaction towards the heat consumption. Therefore, temperature has a positive effect on methane conversion and can lead to more methane consumption. So it can be concluded that the maximum methane conversion can be achieved at a maximum temperature which can be tolerated by the MSR process.

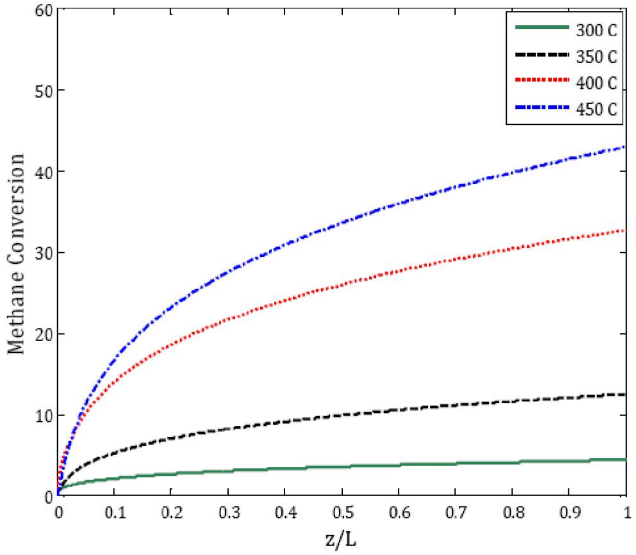

Figure 3 : Methane conversion profile in the membrane reactor at different temperatures

Effect of steam-to-methane ratio in the feed

This section considers effects of steam-to-methane ratio in the entering feed on the methane conversion and hydrogen-to-carbon monoxide ratio in the effluent stream. Figure 4 shows effect of steam-to-methane ratio on the methane conversion in the tabular membrane reactor. It is clear that increasing the steam-to-methane ratio can reach a higher methane conversion. By increasing the H_2O/CH_4 from 3 to 8.74 the methane conversion rises from 15% to 49%. The obtained results of the current investigation are same as experimental works of Gallucci et al[26]. They reported that the higher amount of steam to methane ratio in the feed, results

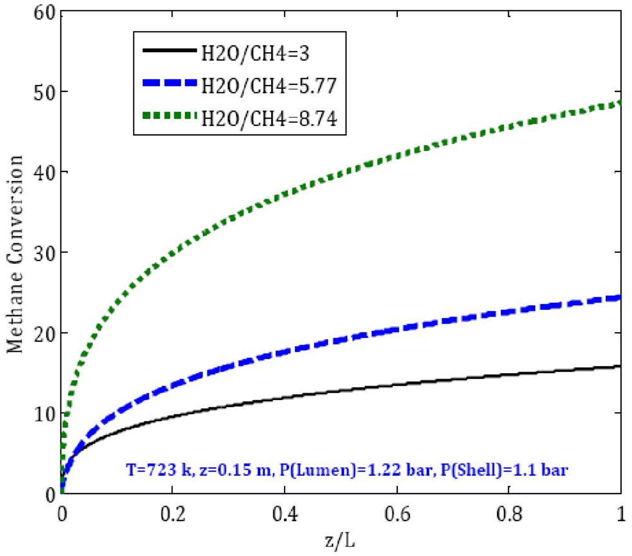

Figure 4 : Effect of H_2O/CH_4 ratio on the methane conversion

higher methane conversion and thus more hydrogen production.

Influence of entering steam-to-methane ratio has also been investigated on the ratio of the produced hydrogen-to-carbon monoxide. The latter ratio plays an important role in some industrial processes such as methanol synthesis which often use the products of the reforming unit. It is obvious that the higher amount of steam-to-methane can lead to higher hydrogen-to-carbon monoxide ratio. Figure 5 depicts the effect of steam-to-methane ratio on the amount of produced hydrogen-to-carbon monoxide.

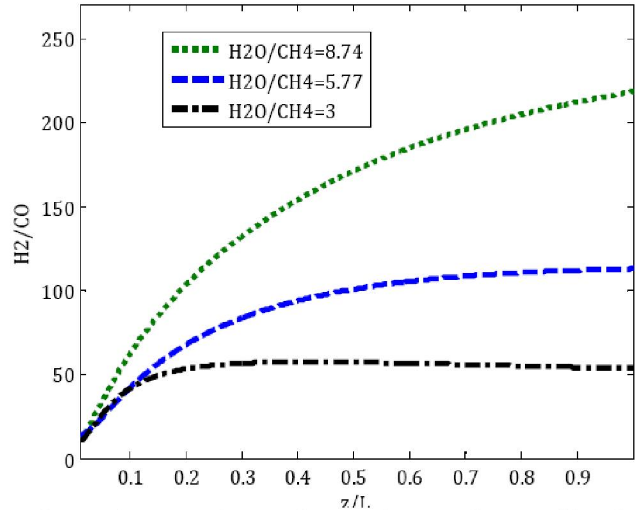

Figure 5 : Effects of H_2O/CH_4 ratio on the H2/CO ratio profile along the reactor

Effect of reaction zone pressure

Pressure changes in the reaction zone can effect on the methane reforming process. Profiles of methane conversion along the tubular membrane reactor at different pressures have been depicted in Figure 6. According to this figure, it is clear that increasing the reaction zone pressure can lead to higher methane conversion. Permeation of the produced hydrogen through the Pd-Ag membrane depends on its partial pressure in both sides of the membrane layer. Therefore, increasing the reaction side pressure has positive effects on the driving force for hydrogen permeation.

Whenever, the pressure of permeation side equals the pressure of tube side, driving force for hydrogen permeation approach to zero and methane conversion of membrane and traditional reactor become equal.

Effect of reaction zone pressure on the ratio of produced hydrogen-to-carbon monoxide is presented in Figure 7. It is clear that higher tube side pressure, can lead to higher amount of produced hydrogen-to- monoxide.

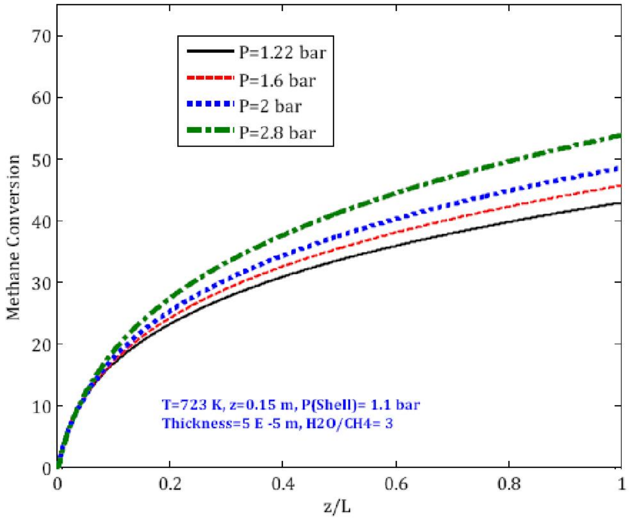

Figure 6 : Effect of the reaction zone pressure on the methane conversion profile

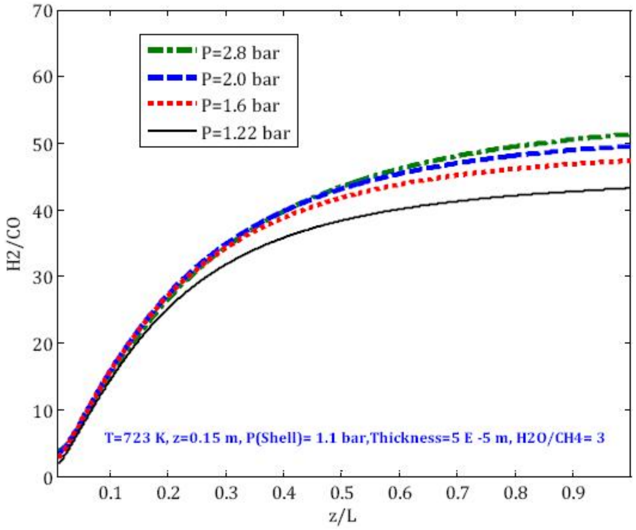

Figure 7 : Effect of reaction zone pressure on the produced H_2/CO ratio

Effect of membrane thickness

A permselective Pd based membrane is used to separate the produced hydrogen from the reaction zone and shift the equilibrium towards hydrogen production. Effect of membrane thickness on the methane conversion and produced hydrogen-to-carbon monoxide ratio is significant. The employed values of membrane thickness and other operating conditions have been presented in Figures 8 and 9. Figure 8 shows the effect of membrane thickness on the methane conversion.

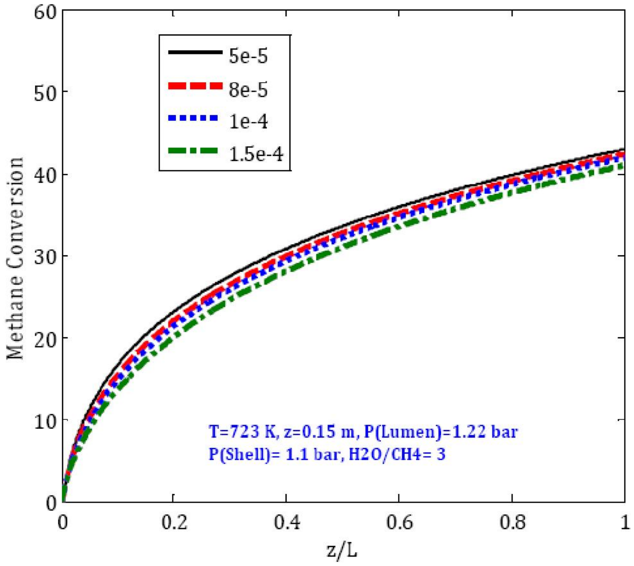

Figure 8 : Effect of membrane thickness on the methane conversion

It is known that reducing the thickness of hydrogen-permselective layer increases methane conversion beyond the equilibrium value. The latter issue can be explained in such way that, by increasing the thickness of membrane, the resistance against the hydrogen permeation through membrane layer rises while the hydrogen yields decrease. The lower membrane thickness can lead to higher methane conversion compared with thicker ones. As for Figue 9, it is quite obvious that the thickness of membrane has a minor effect on the ratio of produced hydrogen to carbon monoxide.

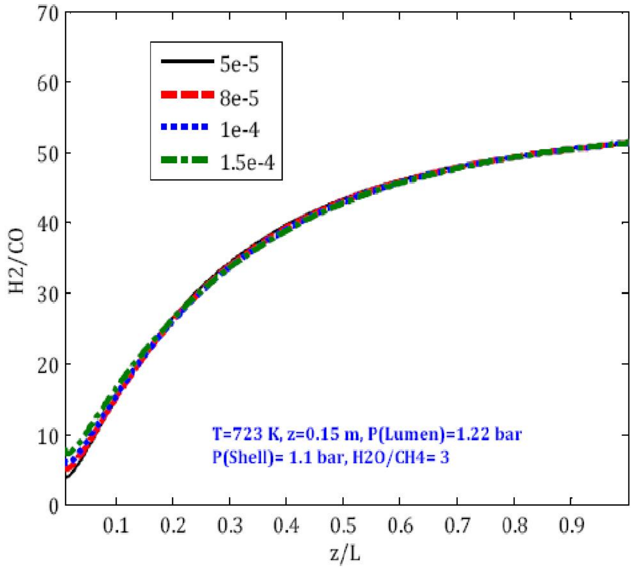

Figure 9 : Effect of membrane thickness on the ratio of produced H_2/CO

Effect of co and counter-current flow of reactants and sweep gas

By the way, in the present study, the effect of co-current and counter-current flow configuration of the reactants and sweep gas on methane conversion and amount of hydrogen yield have been investigated. The flow configuration of sweep gas and reactants has high effects on the driving force of hydrogen permeation through the Pd-Ag membrane. Flow configuration may change partial pressure profile of hydrogen in the both side of the membrane layer. It should be noticed that the hydrogen partial pressure has a direct effects on the methane conversion profile along the membrane reac-

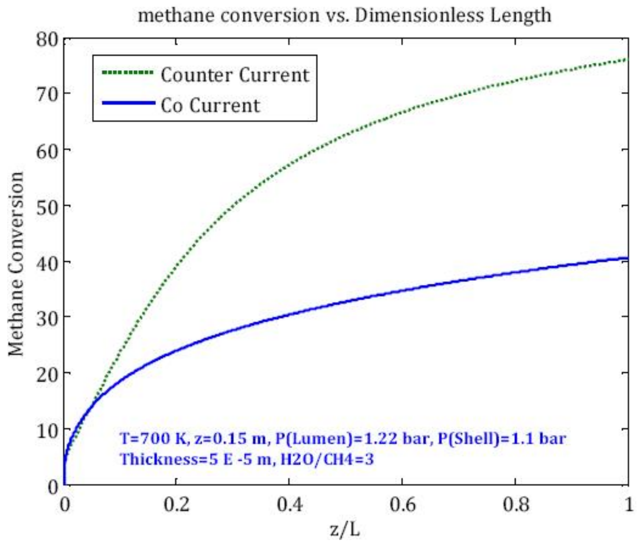

Figure 10 : Effect of co and counter-current flow configuration on the methane conversion

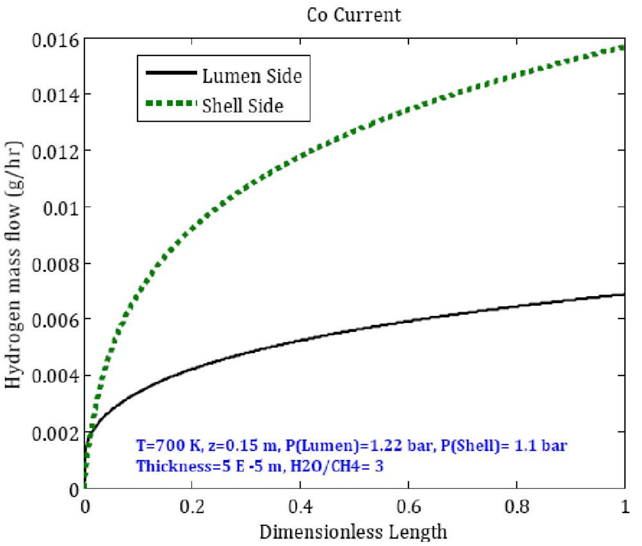

Figure 11 : Amount of hydrogen yield in the co-current flow of feed and sweep gas

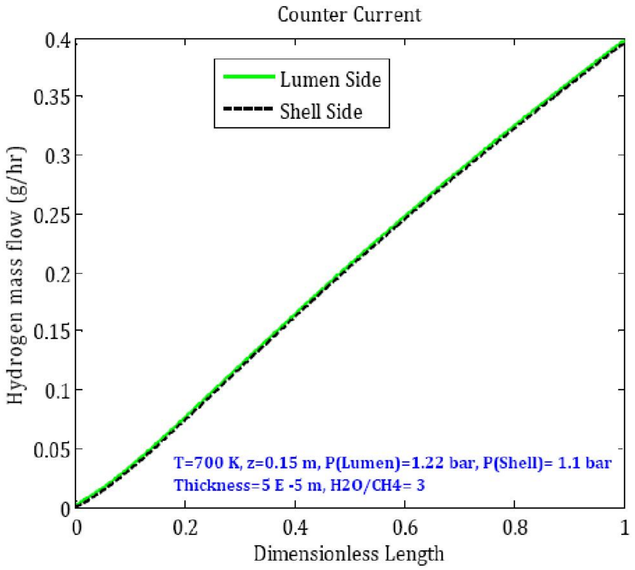

Figure 12 : Amount of hydrogen yield in the counter-current flow of feed and sweep gas

tor. Figure 10 introduces the profiles of methane conversion in the membrane reactor in co and counter-current flows. It is widely known that the higher driving force of co-current compared to the counter-current in the entrance of the reactor leads to increasing the hydrogen permeation, so methane conversion of co than counter-current configuration is higher. The driving force of the counter-current is more uniform than co-current mode which is large at the entrance and will be diminished afterward. This fact leads to higher methane conversion in the counter-current flow related to the co-current one as the distance from the reactor entrance is increased.

Figure 11 shows amount of hydrogen production from reaction zone (lumen side) as well as permeation zone (shell side) for co-current flow. The same figure has been presented for counter-current flow of sweep gas and reactants in Figure 12.

CONCLUSION

The aim of the present study is to model and simulate the behaviour of the MSR process in the novel tubular hydrogen permselective (Pd–Ag) membrane reactor. Effects of various operational and structural parameters such as reaction zone pressure, temperature, membrane thickness, entry steam-to-methane ratio as well as the flow configuration on the methane conversion, hydrogen yield and produced hydrogen-to-carbon monoxide ratio have been investigated. Moreover, comparing the experimental and modelling results has been performed and some investigation has been done for evaluating the value of operational conditions which maximize the amount of methane conversion. Optimization analysis confirms that increasing the ratio of steam-to-methane in the feed, temperature and pressure of the reaction zone and reducing the thickness of membrane can lead to the higher methane conversion and hydrogen production. Therefore the maximum sustainable temperature and pressure by process equipments, highest amount of steam-to-methane in the feed and the lowest thickness of membrane layer are found as optimal operational conditions. The obtained results justify that our proposed model have an acceptable agreement with those information which obtained experimentally.

NOMENCLATURE

R_i (i = 1, 2, 3): The rate of reaction i (mol/hr.gcat.); P_i (i = H_2O, CH_4, H_2, CO, CO_2) : Partial pressure of component i (bar); Ki (i = H2O, CH4, H2, CO): Adsorption coefficient of component i; Ki (i = 1, 2, 3): The equilibrium constant of reaction i; k_i (i = 1, 2, 3): The constant rate of reaction i; F_i: Molar flow rate of component i (mol/hr); Z: length of reactor (m); ρ_c : Catalyst particle density (gr/m^3); r_r : Inner radius of reactor (m); r_m : Radius of membrane (m); $F_{H2}{}^{m}$: Molar flow rate of permeated hydrogen through membrane (mol/hr); J_{H_2} : The flux of passing hydrogen through membrane (mol/m^2.hr); D: inner diameter of the reaction zone (m); X_{CH_4} : Methane conversion; β : Membrane permeability; δ : Membrane thickness (m).

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