# Dynamic Simulation of the Steam Reforming of Methane for the Production of Hydrogen in a Catalytic Fixed Bed Membrane Reactor

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This paper presents an one-dimensional isothermal modelling for a CFBMR ($H_2$ permeable). The work has been developed to simulate the SRM to produce $H_2$. The dynamic simulation for molar flow rates of $H_2$ was analyzed in the permeation side and shell side zones at different temperatures at the exit of the proposed system. The model has allowed the validation for the conversion of $CH_4$ by comparing of optimized values. Additionally, the molar flow rates for chemical species ($CH_4$, $H_2O$, $H_2$, $CO$ and $CO_2$) were analyzed along of the CFBMR (shell side) at t = 14 s, a comparison between permeation side and shell side for $H_2$ and the molar flow rates of $H_2$ in the permeation side and shell side zones at different temperatures.

## 1. Introduction

Hydrogen is widely used as an important chemical feedstock and it is also regarded as a promising future clean fuel. Currently, many chemical, petrochemical and petroleum refining industries and well perceived as a pollution-free primary energy carrier for future transportation fuel as well as electricity generation. The steam reforming of methane (SRM) is the primary hydrogen production route on industrial scale. Methane ($CH_4$) is the main component of conventional natural gas (NG) which can also be obtained from associated gas, stranded NG and shale gas. It was previously determined that three reactions are predominant (Xu and Froment, 1989), the (SRM), water gas shift (WGS) and overall steam reforming of methane (OSRM).
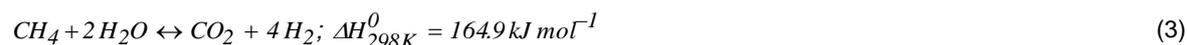
- Reaction of the SRM;

$$CH_4 + H_2O \leftrightarrow CO + 3H_2; \; \Delta H^0_{298K} = 205.8 \, kJ \, mol^{-1} \tag{1}$$

- Reaction of the WGS;

$$CO + H_2O \leftrightarrow CO_2 + H_2; \; \Delta H^0_{298K} = -41.1 \, kJ \, mol^{-1} \tag{2}$$

- Reaction of the OSRM.

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2; \; \Delta H^0_{298K} = 164.9 \, kJ \, mol^{-1} \tag{3}$$

The steam reforming process of methane (SRPM) for the hydrogen production can be studied using various reactor configurations such as fixed be reactors, fluidized bed reactors and membrane reactors (fixed bed membrane reactors or fluidized bed membrane reactors). The use of a permeable membrane reactor offers the potential for a compact unit in combining both the reaction and separation in a simple unit. Several studies have been carried out over SRPM for separating $H_2$ from a reaction mixture using Pd-based membrane reactors (Marín et al., 2012; Sadooghi and Rauch, 2013). The most of these researches have been experimentally and numerically investigated to produce $H_2$ at high temperature. The main focus of the

experimental studies was to develop the robust catalysts which are resistant for carbon deposition. While the numerical works have been reported to simulate the hydrogen production using Pd-based membrane and robust catalysts, respectively.

The catalytic fixed bed membrane reactors (CFBMRs) can significantly improve the production of thermodynamically limited reactions. Hydrogen-selective membranes permit hydrogen produced by reactions to escape under the influence of the difference in the hydrogen partial pressures to the permeate side where an inert gas such as nitrogen can be used to purge hydrogen. This type reactor is promising for thermodynamically limited reactions such as steam reforming. In this CFBMRs, the effect of the intraphase transport by considering diffusion inside the catalyst pellets on both sides of the coupled CFBMR. The Fickian diffusion model has been used for the reactants for assuming the diffusion process through a stagnant bulk phase with the diffusivities of components in the reacting mixture along the radial direction inside catalyst pellets.

The commercial hydrogen separation by metallic membranes is mainly focused on palladium alloys. Palladium (Pd) membranes have been proposed for application in hydrogen separation for many years due to their exclusive selectivity for hydrogen. Pd is known to be highly soluble for hydrogen and it can tolerate hydrocarbon containing streams. Pd-based membranes also put forward the possibility of hydrogen separation at high temperature aiming at combining a separation process with a chemical reaction in one unit. Membrane application in the chemical, petrochemical and petroleum industries for separation and reaction processes were recently reviewed.

The objective of this study is to theoretically investigate the SRM to produce $H_2$ (permeation side and shell side) in the CFBMR at different temperatures at the exit of the system in study.

## 2. Kinetic mechanism

The kinetic models treat the mechanism, rates of chemical reactions and the resulting concentrations of species at some point in time and space of a CFBMR. These models are generally related to specific processes, providing important considerations for relating to the mechanisms of reactions and ways to increase the rate of a reaction or process. The process discussed here has involved the main reactions of SRM. In normal operation, the reaction (1) is the SRM, the reaction (2) shows water-gas shift and the reaction (3) presents the overall SRM. Reactions (1)-(3) are reversible (equilibrium). Thermodynamically, reactions (1) and (3) are strongly endothermic. On the other hand, the reaction (2) is exothermic. Components of reactions (1), (2) and (3) are defined like methane ($CH_4$), water ($H_2O$), carbon monoxide (CO), hydrogen ($H_2$) and carbon dioxide ($CO_2$). The stoichiometric coefficients of components were presented in Table 1.

*Table 1: Stoichiometric coefficients $\sigma_{ij}$ for components of reactions*

| Reactions | $CH_4$ | $H_2O$ | CO | $H_2$ | $CO_2$ |
|-----------|--------|--------|-----|-------|--------|
| 1 | -1 | -1 | +1 | +3 | 0 |
| 2 | 0 | -1 | -1 | +1 | +1 |
| 3 | -1 | -2 | 0 | +4 | +1 |

### 2.1 Mathematical modelling on intrinsic kinetic process

The kinetic mathematical model applied here considers only three homogeneous reactions (1), (2) and (3) according to Langmuir-Hinshelwood concept (Xu and Froment, 1989).

$$R_{SRM} = \frac{k_{SRM}}{P_{H_2}^{2.5}} \frac{\left( P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{SRM}} \right)}{(DEN)^2} ; \quad R_{WGS} = \frac{k_{WGS}}{P_{H_2}} \frac{\left( P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{WGS}} \right)}{(DEN)^2} \tag{4}$$

$$R_{OSRM} = \frac{k_{OSRM}}{P_{H_2}^{3.5}} \frac{\left( P_{CH_4} P_{H_2O}^2 \frac{P_{H_2}^4 P_{CO_2}}{K_{OSRM}} \right)}{(DEN)^2} ; \quad DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + \frac{K_{H_2O} P_{H_2O}}{P_{H_2}} \tag{5}$$

Where $R_j$ (j = SRM, WGS and OSRM; DEN is denominator in Eq(4) and (5)) are the rates of reactions (1)-(3). The reaction rate coefficients ($k_j$, j = SRM, WGS and OSRM) and the adsorption constants of gases ( $K_{CH_4}$ ,

$K_{H_2O}$, $K_{H_2}$ and $K_{CO}$) have an Arrhenius type dependence with temperature. On the other hand, $P_i$ (i = $CH_4$, $H_2O$, CO, $H_2$ and $CO_2$) are the partial pressures of the respective components within the catalyst and DEN is a dimensionless parameter. The Arrhenius expressions for the reaction rate coefficients, adsorption constants for the components $CH_4$, $H_2O$, $H_2$ and CO and the equilibrium constants are listed in Table 2.

*Table 2: Kinetic, adsorption and equilibrium parameters for the reactions involved in steam reforming process of methane (Xu and Froment, 1989)*

| Parameters of Eqs(4) to (5) | Units |
|---|---|
| **Rate coefficients** | |
| $k_{SRM} = 9.490 \times 10^{16} \, exp\left(-\dfrac{28.879\,K}{T_s}\right)$; $k_{OSRM} = 2.290 \times 10^{16} \, exp\left(-\dfrac{29.336\,K}{T_s}\right)$ | $kmol\,kP_a^{0.5}\,kg^{-1}\,h^{-1}$ |
| $k_{WGS} = 4.390 \times 10^{4} \, exp\left(-\dfrac{80743\,K}{T_s}\right)$ | $kmol\,kP_a^{-1}\,kg^{-1}\,h^{-1}$ |
| **Adsorption coefficient constants** | |
| $K_{CH_4} = 6.650 \times 10^{-4} \, exp\left(\dfrac{46042.0\,K}{T_s}\right)$; $K_{H_2O} = 1.770 \times 10^{3} \, exp\left(-\dfrac{106663.5\,K}{T_s}\right)$ | $kP_a^{-1}$ |
| $K_{H_2} = 6.120 \times 10^{-11} \, exp\left(\dfrac{9971.13\,K}{T_s}\right)$; $K_{CO} = 8.230 \times 10^{-7} \, exp\left(\dfrac{8497.71\,K}{T_s}\right)$ | $kP_a^{-1}$ |
| **Equilibrium constants** | |
| $K_{SRM} = 1026676 \, exp\left(-\dfrac{26.830\,K}{T_s} + 30.11\right)$; $K_{WGS} = exp\left(\dfrac{4400\,K}{T_s} - 4.063\right)$ | $kP_a^{2}$ |
| $K_{OSRM} = \left\{1026676 \, exp\left(-\dfrac{26.830\,K}{T_s} + 30.11\right) exp\left(\dfrac{4400\,K}{T_s} - 4.063\right)\right\}$ | $kP_a^{2}$ |

The net rates for each component (consumption and formation) type of reactions (1), (2) and (3) have been obtained by using the following equation (Oliveira and Silva, 2012).

$$r_i = \sum_{j=1}^{n} \sigma_{ij} R_j \tag{6}$$

Where $r_i$ are the net rates of that species (i) in reactions ($R_j$), $\sigma_{ij}$ are the stoichiometric coefficients of species and $R_j$ are the reaction (1), (2) and (3) rates.

Effectiveness factors $\eta_i$ are used to account for the intraparticle transport limitation. Thus, the Eq(6) was rewritten as given below.

$$r_i = \sum_{j=1}^{n} \eta_j \sigma_{ij} R_j \tag{7}$$

The Eq. (7) can be used to obtain $r_{CH4}$, $r_{H2O}$, $r_{H2}$, $r_{CO}$ and $r_{CO2}$. The details of these net rates have given by Oliveira and Silva, (2013).

## 3. Mathematical modelling

A conceptual schematic of the integrated CFBMR was developed to investigate the SRM according to the Figure 1. The inner is the tube is the supported membrane and the outer one is the non-permeable shell. The catalyst (Ni/γ-Al$_2$O$_3$) is packed in the shell side where the reactants (methane and steam) are introduced. The sweep gas (nitrogen or steam) is fed into the tube side in the co-current flow mode. In this system, three reforming reactions occur in the non-permeable shell by producing light gases ($H_2$, CO and $CO_2$).

The mathematical modelling and computer simulation for the CFBMR are in continuous development aiming to improve the knowledge of the phenomenological processes for this simple unit (combining both the reaction and separation). According to its applications, the CFBMRs are applied in the chemical, petrochemical and oil refining industries. For this work, an one-dimensional mathematical model without axial dispersion taking into account diffusional limitations in the solid porous network was developed. This model has been projected like

isothermal dynamic pseudo-homogeneous model. The mass balance equations are given by the following partial differential equation system.
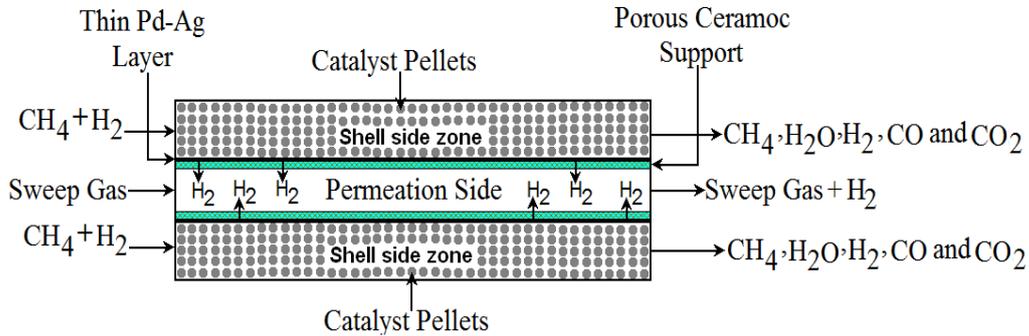


*Figure 1:* Schematic representation of the CFBMR for the SRM

### 3.1 Balance equations for the shell side zone

The differential balances of the molar flow rates ($F_i$) for the model components i ( i = $CH_4$, $H_2O$, $H_2$, CO and $CO_2$) in the reaction side (shell side) are given as follows.

$$\frac{u_s}{g}\frac{\partial F_i}{\partial t} + \frac{4\tau Q_g}{4 d_{shell}^2}\frac{\partial F_i}{\partial z} = \pi R_{Shell}^2 \rho_s L(1-\varepsilon_b)\sum_{j=1}^{3}\sum_{i=1}^{5}\eta_j \sigma_{ij} r_i - 2\pi R_{Shell} J_i^s \; ; \; when\, i \neq H_2, \, thus \, J_{i \neq H_2}^s = 0 \qquad (8)$$

- The initial and boundary conditions for the Equation (8) are given as:

$$F_i\big|_{t=0} = F_{i,0} \; ; \; for\,all\,z \, ; F_i\big|_{t=0} = F_{i,0} \; for \; reactants \; and \; F_i\big|_{t=0} = 0 \; for \; products \qquad (9)$$

$$F_i\big|_{z=0^+} = F_{i,Ent.} \; ; \; for\,t \geq 0 \, ; \; \frac{\partial F_i}{\partial z}\bigg|_{z=L} = 0 \; ; \; for\,t \geq 0 \qquad (10)$$

### 3.2 Balance equation for the permeation side zone

The mass balance equation for the molar flow rate ($F_{H2}$) of $H_2$ in the permeation side zone (inner tube of CFBMR) is written as follows:

$$\frac{u_s}{g}\frac{\partial F_{H_2}}{\partial t} + \frac{4\tau Q_g}{4 d_{inner\,tube}^2}\frac{\partial F_{H_2}}{\partial z} = 1.0061 x 10^{-12} \, exp\left(-\frac{767.38}{T}\right)\left(\frac{A}{\delta}\right)\left[\left(P_{H_2}^s\right)^{0.5} - \left(P_{H_2}^t\right)^{0.5}\right] \qquad (11)$$

- The initial and boundary conditions for the Eq(11) are given as:

$$F_{H_2}\big|_{t=0} = 0 \; ; \; for\,all\,z \; ; \; F_{H_2}\big|_{z=0^+} = F_{H_2,Ent.} \; ; \; for\,t \geq 0 \, ; \; \frac{\partial F_{H_2}}{\partial z}\bigg|_{z=L} = 0 \; ; \; for\,t \geq 0 \qquad (12)$$

## 4. Solution of the model equations using the technique of the Laplace transform

The Laplace transform methodology was applied for changing the set of the partial differential equations (PDFs) into a set of ordinary differential equations (EDOs) (Silva and Oliveira, 2013). Then, the new set of EDOs has been integrated by a subroutine based on the Runge-Kutta Gill with automatic step size and double precision to ensure accuracy (Oliveira and Silva, 2013).

## 5. Results and discussion

The mathematical modelling was developed to analyze the molar flow rates of chemical species ($CH_4$, $H_2O$, $H_2$, CO and $CO_2$) on the shell side zone as well as the molar flow rate of $H_2$ into the permeation side zone. The proposed model for this work has been used to relate the evolution of the molar flow rates over space (z)

along the CFBMR (shell side zone and permeation side zone). For this simulation, the computational code was fed with parameters shown in Table 3.

*Table 3: Parameters for the modelling involved in steam reforming of methane*

| Categories | Properties | Numerical values | References |
|---|---|---|---|
| Operating conditions | Shell side feed inlet temp., $T_{in,ss}$(K) | 800 | Ji et al., (2003) |
| | Per. side feed inlet temp., $T_{in,ps}$(K) | 800 | Ji et al., (2003) |
| | Shell side pressure $P_{ss}$, (bar) | 14 | Ji et al., (2003) |
| | Permeation side pressure, (bar) | 14 | Ji et al., (2003) |
| Feed composition | Inlet flow rate of $CH_4$, $F_{CH4}$ (kmol s$^{-1}$) | $2.5 \times 10^{-6}$ | Ji et al., (2003) |
| | Inlet flow rate of $H_2O$, $F_{H2O}$ (kmol s$^{-1}$) | $3.5 \times 10^{-6}$ | Ji et al., (2003) |
| | Inlet flow rate of $H_2$, $F_{H2}$ (kmol s$^{-1}$) | 0 | Ji et al., (2003) |
| | Inlet flow rate of CO, $F_{CO}$ (kmol s$^{-1}$) | 0 | Ji et al., (2003) |
| | Inlet flow rate of $CO_2$, $F_{CO2}$ (kmol s$^{-1}$) | 0 | Ji et al., (2003) |
| | $CH_4/H_2O$ ratio | 0.667 | Ji et al., (2003) |
| | Inlet partial pres. of $CH_4$, $p_{CH4}$ (bar) | 5.46 | Pantoleontos et al.,(2012) |
| | Inlet partial pres. of $H_2O$, $p_{H2O}$ (bar) | 18.34 | Pantoleontos et al.,(2012) |
| | Inlet partial pres. of $H_2$, $p_{H2}$ (bar) | 0.68 | Pantoleontos et al.,(2012) |
| | Inlet partial pres. of CO, $p_{co}$ (bar) | 0.00 | Pantoleontos et al.,(2012) |
| | Inlet partial pres. of $CO_2$, $p_{CO2}$ (bar) | 0.31 | Pantoleontos et al.,(2012) |
| Gas solid | Porosity of catalyst bed, $\varepsilon_b$ (dimen.) | 0.43 | Ji et al., (2003) |
| | Catalyst density, $\rho_B$ (kg m$^{-3}$) | 2,100 | Ji et al., (2003) |
| | Effect. Factors ($\eta_i$) for Eqs. 1, 2, 3 | 0.07, 0.07 and 0.57 | Xu and Froment, (1989) |
| | Shell side radius, $R_{shell}$ (m) | $3.00 \times 10^{-3}$ | Ji et al., (2003) |
| | Thickness of dense membrane, $\delta$ (m) | $5.0 \times 10^{-5}$ | Ji et al., (2003) |
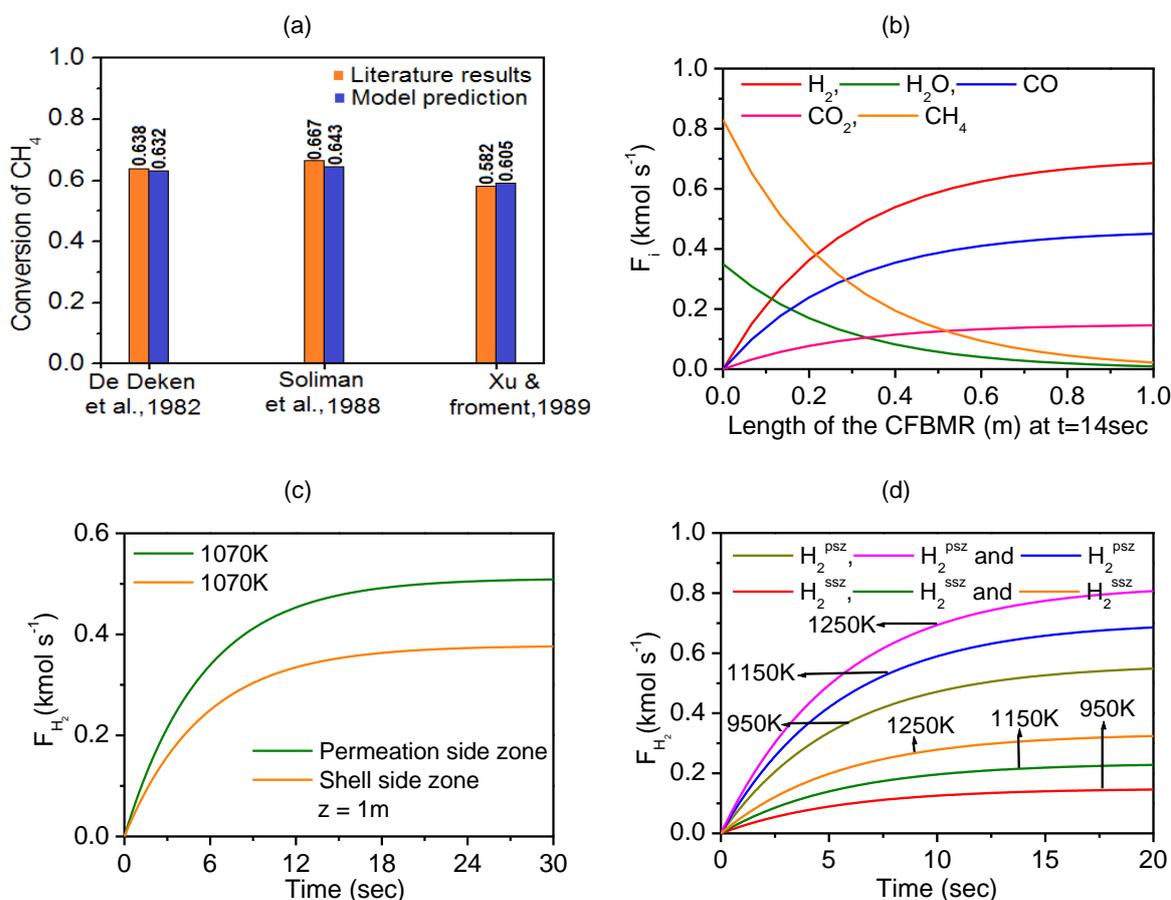
*Figure 2: (a) Validation of the model, (b) Profiles of chemical species (CH₄, H₂O, H₂, CO and CO₂) along the CFBMR, (c) Evolutions of molar flow rates in the permeation side and shell side zones and (d) Evolutions of molar flow rates in the permeation side and shell side zones at different temperatures*

Figure 2(a) shows a validation before simulating the CFBMR, the main program which is used to simulate the conventional CFBMR has been checked with data of the literature. The simulation results for conversion of $CH_4$ and data for different authors were validated by comparison. Figure 2(b) reports the profiles of $CH_4$, $H_2O$, $H_2$, CO and $CO_2$ versus the space variable along the CFBMR (shell side zone). Figure 2(c) shows the evolution of the molar flow rates in the permeation side and shell side zones versus the time variable at the exit. Figure 2(d) presents the evolutions of the molar flow rates of $H_2$ at different temperatures (1,250K, 1,150K and 950K) in the permeation side and shell side zones.

## 6. Conclusions

Conducted in the context of reform of the line of chemical components, this research will resort numerical methodology in order to carry out the development process in isothermal catalytic membrane reactor dynamics of fixed bed. In conditions allowed for this research, the method of Runge-Kutta Gill was used to predict the model components ($CH_4$, $H_2O$, $H_2$, CO and $CO_2$). The development of computer code to process and analyze the behavior of the variables in this research allowed the lead the following conclusions:
- The validation confirmed by comparing which the results of this research and the results obtained by different authors are good agreement;
- Consumption and production have shown the profiles of chemical species ($CH_4$, $H_2O$, $H_2$, CO and $CO_2$) along the CFBMR;
- The molar flow rates of $H_2$ at 1,070K shown an evolution with the time. Once, The amount of $H_2$ is most in the permeation side zone than in the shell side zone;
- The molar flow rates of $H_2$ at different temperatures (1,250K, 1,150K and 950K) have shown an evolution with the time. Once, the amount of $H_2$ is most in the permeation side zone than in the shell side zone.

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