

# Study Of Molar Flow, Mole Fraction, Partial Pressure Variation In Process Of Pure Hydrogen Production In Multichannel Membrane Reactor

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**Abstract**—Hydrogen has a high energy as a fuel but the machine that burns hydrogen does not produce any pollution. Steam methane reforming (SMR) is a reaction that is used in industrial scale for producing hydrogen. So it is necessary to perform endothermic reactions at high temperature so that reaction is favorable thermodynamically. SMR reaction in an MCMR reactor in addition to adjusting the reaction conditions reduces the economic costs due to combining the separation, reaction and heat transfer units in a single vessel. Thus, the one-dimensional modeling of the reactor is done in STEADY-STATE and non-isothermal conditions to assess the professional conditions of the process while the catalyst in this type of reactor is considered as coated on the channel walls and thus the heat transfer is only through the walls.

**Keywords**— *Hydrogen, Membrane Reactor, Steam methane reforming*

## I. INTRODUCTION

The rapid development of the industrial and transport sectors and improved living standards has led to an increase in global energy consumption. Today the energy systems are mainly based on crude oil, natural gas and coal. All of these sources of energy are nonrenewable while the use of these energy sources increases the concentration of greenhouse gases (such as CO<sub>2</sub>) and global temperature rise.

In recent years, hydrogen as an alternative to fossil fuels has been focused. Hydrogen has the highest energy content among the fuels but it has the lowest normal pressure for gas in terms of volume. Hydrogen can save energy and it is a carbon-free energy carrier. Hydrogen is the most abundant element in the universe and when it is used in a fuel cell or an internal combustion engine, its product is a pollution-free energy and water as a byproduct. The use of fuel cells is developing in the automobile industry and to produce energy in power plants.

An advantage of hydrogen as an energy source is its flexibility. While fossil fuels are limited to specific geographic areas, hydrogen production is possible in

almost any location because hydrogen can be produced from fossil and non-fossil fuels.

Today, 95% of produced hydrogen is through 95% the most important part of which is produced by reforming methane [4].

The most important method of producing syngas is steam methane reforming (SMR). The SMR process can be designed such that the main purpose of which is to produce hydrogen. In this case the produced syngas a large amount of hydrogen [5].

There are various methods for separating hydrogen from syngas the most important of which includes:

- Amine absorption (removing CO<sub>2</sub>)
- Pressure swing adsorption (PSA)
- Cryogenic distillation
- Membrane separation

In general, steam methane reforming (SMR) is a reaction which requires high energy consumption and because the reactions are endothermic and the need for proper reforming percentage the gas should be provided with enough energy so that the reaction would move towards equilibrium. The analyses conducted by researchers have shown that if the process is carried out in a membrane reactor, the required operating conditions such as temperature and pressure are adjusted for the reaction and hydrogen can be removed from the system selectively and the production reactions' thermodynamic equilibrium is converted to production which leads to achieve high conversion percentage even at lower operation temperature.

Yu-Ming Lin et al have modeled and studied the impact of removing hydrogen from the palladium membrane based on methane conversion in the SMR process experimentally the results of which suggest that the use of palladium membranes leads to achieving the conversion percentage of higher than 80% [6].

Genyin Ye et al have modeled hydrogen production in a fluidized bed membrane reactor in ASPEN PLUS

Software and it is observed that removing hydrogen in the location leads to the equilibrium shift [7].

One-dimensional SMR process modeling is done for hydrogen production in PBR and MR reactors in STEADY STATE and ISOTHERMAL conditions by Jean-François ROUX and compared with each other the results of which indicate that the existence of a membrane in the process modifies the reaction conditions and leads to the achievement of higher conversion rates and finally accessing the methane conversion to 95% at a pressure of 16 bar and the temperature of 600°C [8].

Fausto Gallucci et al have studied the impact of using a sweep gas on methane conversion the results of which indicates that using a sweep gas such as

steam in an MR reactor that could be easily separated from hydrogen increases methane conversion at lower temperatures because this reduces the hydrogen concentration in the membrane and shifts equilibrium to higher methane conversion [9].

The basic concept of multi-channel membrane reactor is used for dehydrogenation. The multi-channel membrane reactor with palladium membrane is proposed for water-gas shift reaction. Multi-channel membrane reactors are usually described as a plate, wall and micro-channels to produce hydrogen with high efficiency. The use of these reactors is followed by reducing the economic costs.

The main idea of these reactors is to follow the condensing heat exchanger's design. The cold channels in which the endothermic reforming reaction is ongoing are located in the vicinity of the warm channels in which exothermic reaction takes place.

The catalyst usually coats the channel walls. The multi-channel reactor increases heat transfer surface and the hydrogen production level compared to the reactor volume.

Increased scale in these reactors is possible by repeating the pattern of the mentioned channels while the reaction physics and hydrodynamics remain as before.

Accordingly A. Vigneault et al have performed the 2D modeling of a multi-channel membrane reactor under steady state in both isothermal and non-isothermal for producing hydrogen by SMR process in MATLAB environment [5].

In this study, one-dimensional modeling of SMR process modeling is done for hydrogen production in packed bed Multichannel Membrane Reactor in STEADY STATE and ISOTHERMAL conditions. In this modeling MCC channel is located in the vicinity of SMR channel to provide the required heat. Flow regime is considered as expanded laminar to facilitate solving the momentum equations and also this current is considered as co-current to reduce the temperature changes. The catalyst in the process SMR process is alumina based nickel. The catalyst has coated the

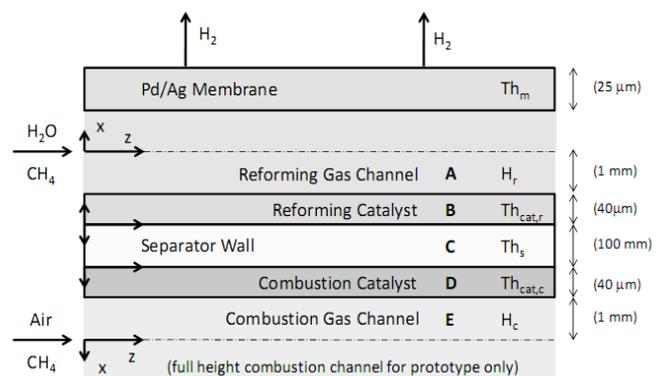
channel walls. In this model, each channel includes a gas phase and catalyst layer. Also in this modeling steam is used as a sweep gas to modulate reaction conditions and increase the methane conversion. In this parameters such as changes in molar flow of the reactants and products along the reactor length and the changes partial pressure of the reactants and products compared to the conversion percentage are studied in the reforming channel.

Flow regime is considered as expanded laminar to facilitate solving the momentum equations and also this current is considered as co-current to reduce the temperature changes.

The catalyst in the process of burning methane is palladium and alumina based nickel in SMR. In both

channels the catalyst has coated the channel wall. In this modeling there two channels that each channel includes a gas phase and is a catalyst layer.

Figure 1- Schematic of 1-D Model, including base case



dimensions, not to Scale.

(Subscripts: Pd/Ag membrane m; SMR channel r; catalyst layer

Cat; separator wall s; MCC channel c.)

Basic assumptions considered for modeling the mentioned process are as follows:

Basic modeling assumptions

1. Gas behavior is assumed as ideal
2. The process is assumed as adiabatic and there is no heat loss in the environment
3. Coke formation is ignored
4. Pressure drop is ignored
5. Fourier's law is applied for the thermal conductivity

Fick's law is applied for infiltration

## I. MODELING

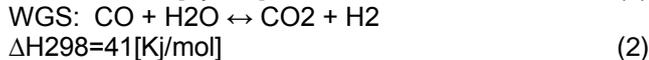
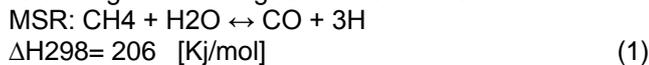
A. Accordingly mathematical 2D modeling of SMR process to produce hydrogen in a packed bed multi-channel membrane reactor under the STEADY STATE and ISOTHERMAL conditions are investigated. To

solve the modeling, differential equations including mass equilibrium, energy equilibrium for the reactant, reaction kinetics and physical properties are written and obtained by the simultaneous solution of equations the concentration and temperature distribution in the reactor was obtained. Flow regime Flow regime is considered as expanded laminar to facilitate solving the momentum equations. The common differential models by the relevant boundary conditions are solved in MATLAB and the flow and mole fraction of each material is obtained based on the reactant and product components as well as changes in temperature in the reactor. Based on the rate equations for reactions the raw material including methane and steam are used along the reactor and their value is reduced.

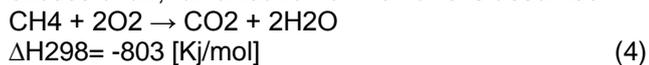
To validate the model and ensure the accuracy of results the results were compared with existing experimental data. The effective operating parameters include the temperature of the input feed to the reactor, steam ratio and reactor length the effect of which was analyzed on methane conversion and the results were reported. Here the equations, boundary conditions and the materials for MCMR one-dimensional modeling will be presented and the schematic of the process is presented in Figure 3.

### B. Kinetics

For the reforming catalyst, methane steam reforming and water-gas-shift reactions are:



For the combustion catalyst, given the stoichiometric excess of air, full oxidation of methane is assumed.



### A. Physical Properties

- Diffusivity

For gas mixtures, it is assumed:

$$D_{i,mix} = \phi_{ij} \quad (5)$$

- Heat Capacity

The heat capacity relationship for a single component  $CP_i$  as a function of temperature  $T$ , neglecting pressure effect, was determined (Sandler, 1999) as:

$$C_{pi} = A_i + B_i T + C_i T^2 + D_i T^3 \quad (6)$$

- Thermal Conductivity

For the thermal conductivity in the gas channels, we neglected the effect of pressure and used the following relation (Bird et al., 2002) for  $K_{mix}$  of a gas mixture:

$$k_{mix} \sum_i^n \frac{y_i k_i}{\sum_j y_j \phi_{ij}} \quad (7)$$

- Viscosity

The viscosity of the mixture was estimated (Bird et al., 2002) from:

$$\mu_{mix} \sum_i \frac{y_i \mu_i}{\sum_j y_j \phi_{ij}} \quad (8)$$

$$\mu_i = \mu_i^{ref} \left( \frac{T}{T^{ref}} \right)^\beta \quad (9)$$

### B. Component Material and Energy Balance Equations

Based on the assumption of ideal gases, we write:

$$c = \frac{P}{R_g T} \quad (10)$$

$$P_i = y_i P \quad (11)$$

### C. Velocity Profiles

Assuming fully developed laminar flow in the gas channel, the velocity profile in the axial direction  $V_z$  is assumed to follow the two-dimensional relation (Bird et al., 2002):

$$v_z = 1.5 v_{ave,z} \left( 1 - \left( \frac{x}{H_k} \right)^2 \right) \quad (12)$$

Were integrated:

$$\int_{-H_k}^{H_k \text{ or } 0} c v_z dx \Big|_{z=0} - \int_{-H_k}^{H_k \text{ or } 0} c v_z dx \Big|_{z} + \int_0^z Th_{cat,k} \sum_i R_i dx dz + \int_0^z J_{H_2,m} dz = 0 \quad (13)$$

Here  $Th_{cat,k}$  is the catalyst layer thickness.  $R_i$  is the rate of production of component defined as:

$$R_i = \sum_j \sigma_{ij} r_j \quad (14)$$

The rate of reaction  $R_i$  is defined in section A.  $\sigma_{ij}$  is the stoichiometric coefficient of component  $i$  for reaction  $j$ .  $J_{H_2,m}$  is the molar flux of hydrogen through the membrane, defined based on Sievert's law:

$$J_{H_2,m} = -\Omega_m \frac{A_m}{Th_m} \exp\left(\frac{-E_m}{R_g T_m}\right) (\sqrt{P_{H_2,r}} - \sqrt{P_{H_2,m}}) \quad (15)$$

### D. Component Material and Energy Balance Equations

The general equation of continuity at steady state for a component  $i$  in a mixture (adapted from Bird et al. (2002)) is:

$$-(\nabla \cdot c_i v^{\rightarrow}) - (\nabla \cdot J_i^{\rightarrow}) + R_i = 0 \quad (16)$$

From Fick's law of diffusion:

$$J_i^{\rightarrow} = -D_{i,mix} \nabla c_i \quad (17)$$

We developed the general energy balance equation elsewhere:

$$\nabla T \cdot \sum_i (C_{pi} c_i v^{\rightarrow}) + \nabla T \cdot \sum_i (C_{pi} J_i^{\rightarrow}) + \nabla \cdot q^{\rightarrow} + \sum_j \Delta H_{ix} r_j = 0 \quad (18)$$

There are four heat transfer/generation terms in Eq. (18), representing in order: (1) transfer by convection, (2) transfer by diffusion, (3) transfer by

conduction, and (4) heat generation due to reactions. Assuming Fourier's law of conduction, we write  $q^{\rightarrow}$  as:

$$q^{\rightarrow} = -k_{mix}\nabla T \quad (19)$$

To use MATLAB built-in functions, it was necessary to reduce the order of the differential equations to one for both concentration and temperature. To overcome this limitation, we used first order transformations in the transverse direction:

$$c_i = c_{1i} \quad (20)$$

$$\frac{\partial c_i}{\partial x} = c_{2i} \quad (21)$$

$$T = T_1 \quad (22)$$

$$\frac{\partial T_1}{\partial x} = T_2 \quad (23)$$

From this point on,  $C_i$  is referred to as  $C_{1i}$ , and  $T$  becomes  $T_1$ . Backward difference discretization was applied in the axial direction for any dependent parameter  $u$ :

$$\frac{\partial u_b}{\partial z} = \frac{1}{\Delta z_{b-1}}(u_b - u_{b-1}) \quad (24)$$

#### E. Gas Phase Material balance $b \neq 1$

$$\frac{dc_{2i}}{dx} = \frac{1}{D_{i,mix,b}}(v_{z,b} \frac{1}{\Delta z_{b-1}}(c_{1i,b} - c_{1i,b-1}) + c_{1i,b} \frac{1}{\Delta z_{b-1}}(v_{z,b} - v_{z,b-1})) \quad (25)$$

#### Energy balance $b \neq 1$

$$\frac{dT_{2,b}}{dx} = \frac{1}{k_{mix,b}} \left\{ \frac{1}{\Delta z_{b-1}}(T_{1,b} - T_{1,b-1}) \sum_i (C_{Pi,b} c_{1i,b} v_{z,b}) - T_{2,b} \sum_i (C_{Pi,b} D_{i,mix,b} c_{2i,b}) \right\} \quad (26)$$

#### F. Catalyst Layer

##### Material balance $b \neq 1$

$$\frac{Dc_{2i,cat kb}}{DX} = \frac{1}{D_{i,eff,b}}(-R_{i,b}) \quad (27)$$

##### Energy balance $b \neq 1$

$$\frac{dT_{2cat kb}}{dx} = \frac{1}{k_{cat kb}} \left\{ (-T_{2cat kb}) \sum_i (C_{Pi cat kb} D_{i,eff,b} c_{2i,cat kb}) + \sum_j \Delta H_{rx,j} r_{j,b} \right\} \quad (28)$$

#### G. Separator wall

Assuming Neglecting heat conduction in the axial direction will be

$$\frac{dT_{2,s,b}}{dx} = 0 \quad (29)$$

$$\frac{dT_{2,s,b}}{dx} = 0 \quad (30)$$

#### H. Nickel-Based Catalyst Kinetics

Nickel-Based Catalyst Kinetics For a Ni-based catalyst, a study by Elnashaie et al. (1990) showed that the general rate equation based on Langmuir-Hinshelwood-Hougen-Watson approach, developed by Xu and Froment (1989) describes most accurately

the kinetics for a wide range of conditions. The reforming catalyst used was Ni 15.2 wt%/MGAL<sub>2</sub>O<sub>4</sub>. The rate equations per mass,  $r_j'$ , for the three reactions are:

$$r_1' = \frac{\frac{k_1}{P_{H_2}^{2.5}}(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{e,1}})}{DEN^2} \quad \left[ \frac{kmol}{kg_{cat}h} \right] \quad (31)$$

$$r_2' = \frac{\frac{k_2}{P_{H_2}}(P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{e,2}})}{DEN^2} \quad \left[ \frac{kmol}{kg_{cat}h} \right] \quad (32)$$

$$r_3' = \frac{\frac{k_3}{P_{H_2}^{3.5}}(P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{e,3}})}{DEN^2} \quad \left[ \frac{kmol}{kg_{cat}h} \right] \quad (33)$$

$$DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + P_{H_2O} K_{H_2O} / P_{H_2} \quad (34)$$

$$K_{e,1} = \exp\left(\frac{-26830}{T} + 30.114\right) \quad [bar^2] \quad (35)$$

$$K_{e,2} = \exp\left(\frac{4400}{T} - 4.036\right) \quad [-] \quad (36)$$

$$K_{e,3} = \exp\left(\frac{-22430}{T} + 26.078\right) \quad [bar^2] \quad (37)$$

$$K_i = A_i \exp\left(\frac{-\Delta H_{sorp,i} * 1000}{R_g T}\right) \quad (38)$$

$$k_j = A_j \exp\left(\frac{-E_j * 1000}{R_g T}\right) \quad (39)$$

## II. BOUNDARY CONDITIONS

With the same assumptions listed earlier, performing energy and mass balances across interfaces, the continuity principle, and feed conditions at the inlets (subscript o), the boundary conditions are obtained.

#### A. Gas Phase

Gas channel - inlet conditions ( $z = 0$  and  $b = 1$ ) at the entrance of the reactor, the temperature  $T_1$  is assumed constant at the feed condition:

$$T_{1,b=1} = T_{1,0} \quad (40)$$

$$T_{2,b=1} = 0 \quad (41)$$

#### B. Gas channel - catalyst interface

$$\sum_i J_{i,x,k} H_{i,x} \Big|_{x=-H_k} = \sum_i J_{i,x,catk} * H_{i,cat,k} \Big|_{x=-\tau H_{cat,k}} \quad (42)$$

$$T_{2,k,b} \Big|_{x=-H_k} = \frac{k_{cat,k,b} T_{2,catk}}{k_{mix,b}} \quad (43)$$

#### C. Gas channel - membrane interface

$$T_{2,r} \Big|_{x=H_r} = 0 \quad (44)$$

#### D. Catalyst Layer

$$\frac{dT_{1,catk,b}}{dx} = T_{2cat kb} \quad (45)$$

E. Catalyst layer - inlet conditions

$$T_{1cat,k,b=1} = T_{1,k,b=2} \quad (46)$$

F. Catalyst - gas channel interface

$$T_{1cat,k} \Big|_{x=Th_{cat,k}} = T_{1,k} \Big|_{x=-H_k} \quad (47)$$

G. Separator Wall

At the entrance of the reactor, we assume no gradient in the separator wall in the axial direction, therefore:

1. Separator wall - inlet conditions:

$$T_{1,s,b=1} = T_{1,s,b=2} \quad (48)$$

2. Reforming catalyst interface:

$$T_{1,s,b} \Big|_{x=0} = T_{1,cat,r,b} \Big|_{x=0} \quad (49)$$

3. Combustion catalyst interface:

$$T_{1,s,b} \Big|_{x=Th} = T_{1,cat,r,b} \Big|_{x=0} \quad (50)$$

H.

III. RESULTS

To study the effect of different variables on the SMR process and determine the optimal conditions to maximize the percentage of methane conversion, multi-channel membrane reactors are modeled by the law of conservation of mass, the reaction rate equations, and adsorption and membrane infiltration. The mathematical modeling of this system leads to equations by the solution of which it is possible to make a comprehensive analysis of the effect of various variables on the process. Modeling is done in the steady state and Plug flow. Modeling is done in the STEADY-STATE and non- isothermal conditions.

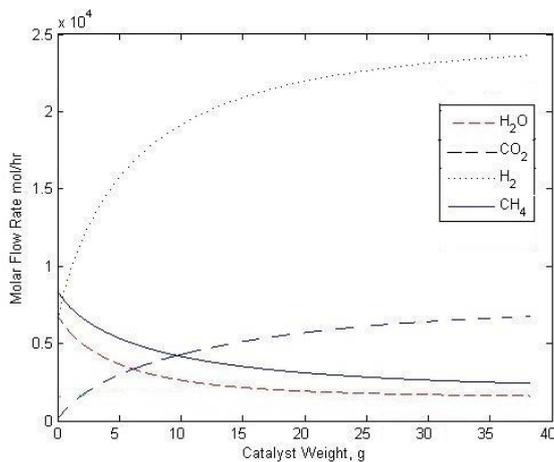


Figure 3: Changes in the molar flow of reactants and products based on the consumed catalyst

Figure 3 presents the molar flow of the products compared to the consumed catalyst in grams. It can be observed that the hydrogen molar flow has been 0.6 moles per second at the beginning of the reaction when the catalyst content was 0 because the hydrogen production is increased at the beginning of the reaction

due to the concentration of hydrogen production reactant and as the concentration of hydrogen production reactant reduces the use of catalyst retains the rate of methane conversion to hydrogen which would not have been possible without the presence of a catalyst.

Figure 4 presents changes in mole fraction of the products and raw materials along the reactor in the presence of membrane. It can be understood from this chart that the mole fraction of hydrogen in the first reactor has increased significantly is less than 5 cm and then it has a downward trend while the mole fraction of carbon dioxide has increased constantly during the process. As a part of carbon monoxide mole fraction is consumed in the reaction and produces hydrogen, it is less than 0.05 moles. The mole fraction of methane in the reactor has a downward trend due to consumption and conversion into hydrogen.

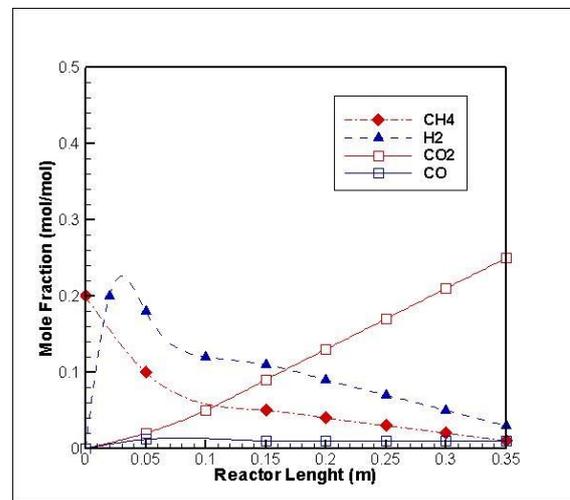


Figure 4: Changes in the mole fraction of reactants and products along the reactor in the presence of membrane

Figure 5 presents the partial pressure of the reactants and products compared to the conversion percentage and by increasing the products' conversion their partial pressure is increased because the number of moles of each component increases relative to the total materials in the channel and thus by consuming the reactants their partial pressure is reduced.

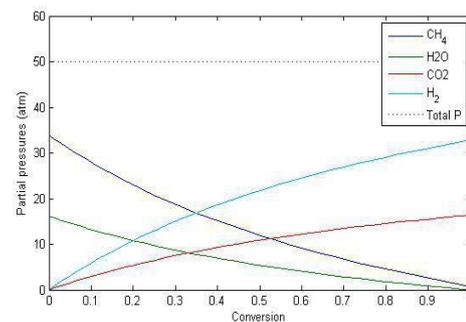


Figure 5: The changes in partial pressure of reactants and products to the conversion rate.

### CONCLUSION

Membrane reactor has a simpler process than the old model which is applied in several stages without the use of membrane. In the membrane reactor the produced hydrogen is recovered by infiltration through the membrane at the same time of the reaction. Simultaneous hydrogen recovery reduces hydrogen concentration in the reactor substantially and thus provides the conditions for reaction and in fact the membrane prevents the reaction from reaching the equilibrium and increases methane conversion percentage significantly by hydrogen recovery through infiltration. In this type of reactor carbon monoxide production is negligible which increases efficiency. Temperature reduction along the reactor is due to reforming reaction which is an endothermic reaction. Initial mole fraction of the raw materials is reduced along the reactor which is due to their consumption.

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