



## MODELING OF MEMBRANE REACTOR FOR METHANE STEAM REFORMING: AN ALTERNATIVE TO CONVENTIONAL REACTORS

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### KeyWords

Conventional methane reforming, hydrogen production, MATLAB simulation, membrane steam reforming, primary reforming, synthesis gas, tubular reactor

### ABSTRACT

Steam reforming which accounts for over 50% of hydrogen production is limited by thermal equilibrium. Frequent occurrences in conventional tubular steam reformer are sintering of catalysts, hot spots and hot-bands on tubes and low methane conversion. To overcome the equilibrium limitation of methane reforming, a membrane steam reformer is suggested whereby the production and separation of synthesis gas is consolidated in one system. In this study, 1-D steady state models were developed to predict the performance of methane steam reforming reaction in a membrane reactor. To evaluate the kinetics of membrane steam reforming of methane, the widely accepted Xu and Fromment equations were employed. MATLAB ODE23s solver which implements the 4th order Runge-Kutta algorithm was useful in obtaining solutions to the developed models. Effects of changing parameters such as inlet temperature, steam to gas ratio and membrane thickness, were investigated. Simulation studies carried out in this research revealed that performing reforming of methane in membrane type reactor can lead to 99% reactant conversion at moderate temperature (500-600 °C). Using input parameters of a conventional steam reformer (inlet temperature and pressure of 530°C /29bar respectively) resulted in a methane conversion and hydrogen yield of 73.6%/2.7 respectively. Model results showed a 21.6% increase of methane conversion in membrane reactor against a conventional steam reformer. The results were validated with [1] and deviations of 2% (methane conversion) and 9% (hydrogen yield) were recorded. Hydrogen yield reached 3.5 at an optimal temperature of 590 °C.

## 1. INTRODUCTION

Hydrogen, which is one of the most industrially produced gases, is useful in the synthesis of ammonia, Fischer-Tropsch process, and as fuel in perm-selective cell technology [2]. About 50% of hydrogen demand is met by steam reforming of natural gas in roof-fired conventional tubular reactors at 700-1000°C and 3-15bar [3, 4, 5]. The product of steam reforming is the hydrogen-rich synthesis gas (mainly H<sub>2</sub>, CO<sub>2</sub>, and CO). With hydrogen used for fuel-cells needing a higher purity specification, the major problem of producing hydrogen via steam reforming is the limitation of equilibrium conversion at very high temperatures [6, 7, 8]. Frequent catalyst tube ruptures, hotspots on tubes and failure of downstream process equipment are common occurrences in a hydrogen production plant. Syngas is purified in a water-gas shift converter, stripper/absorber system and methanation unit [9, 10]. The most popular means of purifying synthesis gas is pressure swing adsorption. This comes with the limitation of poor hydrogen recovery as almost 20% of H<sub>2</sub> is lost in the process [11]. Also available as a purification process are dense palladium membranes. Challenges associated with membranes are high membrane cost, instability at high temperature, and presence of sulphur compounds [11, 12]. The target of purification is to reduce the combined CO & CO<sub>2</sub> to 10 ppm maximum [13]. This is done to safeguard downstream compressing equipment and ammonia converter. The heat requirement for the endothermic process is supplied through down-firing burners placed side by side the tubes inside a furnace. A conventional steam reformer comprises hundreds of catalysts-loaded tubes [14] with burners for heat addition. Arranged in order of activity and selectivity, the catalysts for methane steam reforming are Ru, Rh, Ir, Pt [15]. Nickel catalysts are currently preferred due to cost and availability [16].

To overcome the problem associated with steam reforming in conventional tubular reactor, we can carry the reaction in a membrane reactor. This scheme offers the advantage of consolidating both reaction and separation processes in the same system. In a membrane steam reformer, palladium membranes are used since it is perm-selective to hydrogen. Hydrogen was found to be preferentially permeable through palladium membrane around 1863 [3, 17]. We classify membrane reactors into two areas to distinguish the type of catalysts used in the reaction process [18, 19, 20]. The advantage offered by membrane reactors comes from 'shift effect' [3]. As a result, the reforming reaction can be carried to completion without exerting excessively high temperature and pressure like it is done in conventional reactors. Reduced thickness leads to loss in H<sub>2</sub> perm selectivity and durability. Dense palladium membrane has been found susceptible to embrittlement owing to adsorbed hydrogen [11]. Israni *et al.* [21] suggest an optimal thickness of less than 14microns. This would lead to cost per material of about USD150/ft<sup>2</sup> (USD 1,614/m<sup>2</sup>).

Works on the commercialization of membrane reactors for generating high purity hydrogen are still developing. Anzelmo *et al.* [3] carried out a study to determine the performance of membrane reforming of methane. They found an equilibrium conversion of 64% at a temperature of 400°C. This conversion level is 57% more than is obtainable in a fixed bed reactor operated at the same temperature and pressure. Chen *et al.* [22] studied the effect of variation of sweep gas flow rate on membrane separation of hydrogen. They found that decreasing the size of membrane significantly improves hydrogen recovery yield. Changing the sweep gas flow had little to no impact if the membrane is 100% selective to hydrogen. Work on production of hydrogen from membrane reactor proposed the use of a 'Staged Membrane Reactor' because of the low resistance of membrane reactor to mechanical failure at high temperature [23]. In a more recent work by Anzelmo *et al.* [9], production of hydrogen from membrane steam reforming using natural gas added a step known as 'pre-reforming'. In the pre-reforming stage, the heavier hydrocarbons present in the feed gas were converted into methane, carbon oxides and hydrogen, leading to a higher energy recovery. Hence in this study, an alternative pathway for producing high purity hydrogen in a Membrane Reactor (MR) was provided. The aim of the research is to obtain model equations for predicting performance of a membrane steam reforming reactor used for hydrogen production.

## 2. MATERIALS AND METHODS

The membrane operation works independently of the steam reforming reaction. Therefore, we modeled the membrane reactor according to plug flow behavior. The steam reforming reactions in the membrane reactor are like those in conventional tubular reactors, the only difference being an additional side for permeation of hydrogen through palladium membrane to the separation side. The steam reforming reactions are given as [7, 24, 25, 26]:



### 2.1 MODEL DEVELOPMENT

The membrane reactor under study is modeled according to a conventional fixed bed reactor, assuming the membrane is not catalytic [18]. The model was developed assuming steady state operation, plug flow, selectivity of palladium membrane to only hydrogen,

1-dimensional flow and ideal gas behavior. To derive the models from the first principle, the law of conservation of mass was applied.

$$\left( \text{Rate of accum} \right) \left( \text{of component } i \right) = \left( \text{Rate of inflow} \right) \left( \text{of component } i \right) - \left( \text{Rate of outflow} \right) \left( \text{of component } i \right) + \left( \begin{array}{l} \text{Rate of gen.} \\ \text{or disappearance} \\ \text{of } i \text{ by chemical} \\ \text{reaction} \end{array} \right) \quad (4)$$

The membrane reactor section over which the material balance applies is shown in Figure 1.

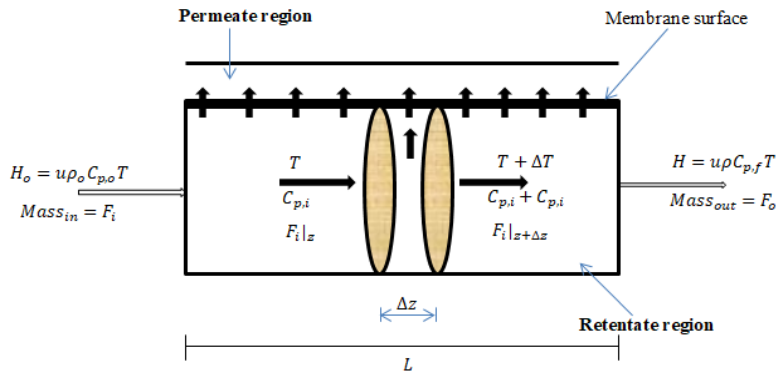


Figure 1 Sectional view of a Membrane Steam Reforming Reactor

The model equation can be written for the components taking part in the process as:

For Retentate side:

$$\frac{F_{CH_4}^0}{A} \frac{dX_{CH_4}}{dz} = -n_{CH_4} \rho_{cat} (\mathcal{R}_{CH_4}) \quad (5)$$

$$\frac{F_{CH_4}^0}{A} \frac{dX_{CO}}{dz} = n_{CO} \rho_{cat} (\mathcal{R}_{CO}) \quad (6)$$

$$\frac{F_{CH_4}^0}{A} \frac{dX_{CO_2}}{dz} = n_{CO_2} \rho_{cat} (\mathcal{R}_{CO_2}) \quad (7)$$

$$\frac{F_{CH_4}^0}{A} \frac{dX_{H_2O}}{dz} = -n_{H_2O} \rho_{cat} (\mathcal{R}_{H_2O}) \quad (8)$$

$$\frac{F_{CH_4}^0}{A} \frac{dX_{H_2}}{dz} = n_{H_2} \rho_{cat} (\mathcal{R}_{H_2}) - J_{H_2} \quad (9)$$

For the permeate region:

$$\frac{1}{A_m} \frac{dY_{H_2}}{dz} = J_{H_2} \quad (10)$$

According to [25] the dimensionless flow rates of the individual components taking part in the reaction can be expressed relative to the methane flow rate to obtain the conversion parameters of the components. In general, the conversion term can be written as:

$$X_i = \frac{F_i}{F_{CH_4}^0} \quad (11)$$

$$\frac{dY_{H_2}}{dz} = A_m \cdot \frac{p^0 \cdot \exp\left(\frac{-E_A}{RT}\right)}{\delta_m} \left( P_{H_2,rent}^{0.5} - P_{H_2,perm}^{0.5} \right) \quad (12)$$

### 2.3 KINETIC MODEL

The reaction kinetics for the process can be described by surface reaction mechanism prescribed by Langmuir and Hinshelwood

[25]. The individual rates of reaction of the species (CH<sub>4</sub>, H<sub>2</sub>O, CO, H<sub>2</sub>, CO<sub>2</sub>) are written as:

$$\mathcal{R}_{CH_4} = -(\mathcal{R}_1 + \mathcal{R}_3) \quad (13)$$

$$\mathcal{R}_{H_2O} = -(\mathcal{R}_1 + \mathcal{R}_2 + 2\mathcal{R}_3) \quad (14)$$

$$\mathcal{R}_{CO} = (\mathcal{R}_1 - \mathcal{R}_2) \quad (15)$$

$$\mathcal{R}_{H_2} = (3\mathcal{R}_1 + \mathcal{R}_2 + 4\mathcal{R}_3) \quad (16)$$

$$\mathcal{R}_{CO_2} = (\mathcal{R}_2 + \mathcal{R}_3) \quad (17)$$

Assuming surface mechanism as the rate determining-step as proposed by [25], [24], [27] and [28], the reaction rates can be expressed as

$$\mathcal{R}_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{KEQ_1})}{\left(1 + K_{CH_4} P_{CH_4} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + \frac{K_{H_2O} P_{H_2O}}{K_{H_2} P_{H_2}}\right)^2} \quad (18)$$

The term in the denominator of equation 18 can be shortened as

$$\phi_{mem} = 1 + K_{CH_4} P_{CH_4} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + \frac{K_{H_2O} P_{H_2O}}{K_{H_2} P_{H_2}} \quad (19)$$

Similarly, the rate expressions for reactions (2) and (3) are given as:

$$\mathcal{R}_2 = \frac{\frac{k_2}{P_{H_2}}(P_{CO} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}}{KEQ_2})}{\phi_{mem}^2} \quad (20)$$

$$\mathcal{R}_3 = \frac{\frac{k_3}{P_{H_2}^{3.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}^4}{KEQ_3})}{\phi_{mem}^2} \quad (21)$$

The rate equations of the individual species participating in the reforming reaction are

$$\mathcal{R}_{CH_4} = \frac{\frac{k_1}{P_{H_2}^{2.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{KEQ_1})}{\phi_{mem}^2} + \frac{\frac{k_3}{P_{H_2}^{3.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}^4}{KEQ_3})}{\phi_{mem}^2} \quad (22)$$

$$\mathcal{R}_{H_2O} = \frac{\frac{k_1}{P_{H_2}^{2.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{KEQ_1})}{\phi_{mem}^2} + \frac{\frac{k_2}{P_{H_2}}(P_{CO} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}}{KEQ_2})}{\phi_{mem}^2} + \left( \frac{\frac{k_3}{P_{H_2}^{3.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}^4}{KEQ_3})}{\phi_{mem}^2} \right)_1 \quad (23)$$

$$\mathcal{R}_{CO} = \left( \frac{\frac{k_1}{P_{H_2}^{2.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{KEQ_1})}{\phi_{mem}^2} - \frac{\frac{k_2}{P_{H_2}}(P_{CO} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}}{KEQ_2})}{\phi_{mem}^2} \right) \quad (24)$$

$$\mathcal{R}_{H_2} = \frac{1}{\phi_{mem}^2} \left( 3 \left( \frac{k_1}{P_{H_2}^{2.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{KEQ_1}) \right) + \frac{k_2}{P_{H_2}}(P_{CO} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}}{KEQ_2}) + 4 \left( \frac{k_3}{P_{H_2}^{3.5}}(P_{CH_4} \cdot P_{H_2O} - \frac{P_{CO_2} \cdot P_{H_2}^4}{KEQ_3}) \right) \right)$$

## 2.4 DETERMINATION OF PARAMETERS

The kinetic terms in the rate expression of Xu and Froment used in the models are summarized in Table 1. The rate constant can be calculated by fixing the data in the table into the Arrhenius equation.

$$k = k_0 e^{\frac{-E_a}{RT}} \quad (26)$$

Table 1 Kinetic & Adsorption Parameters [25, 29]

Kinetic parameter	Pre-exponential factor	$E_a$ (J/mol)
$k_1$	4.2248e15 (mol atm <sup>0.5</sup> /g h)	240.1
$k_2$	1.955e6 (mol/g h)	67.13
$k_3$	1.0202e15 (mol atm <sup>0.5</sup> /g h)	243.9
$K_{CH_4}$	6.65e-4 (atm <sup>-1</sup> )	- 38280
$K_{H_2O}$	1.77e05	88680
$K_{H_2}$	6.12e-9 (atm <sup>-1</sup> )	-82900
$K_{CO}$	8.23e-5 (atm <sup>-1</sup> )	- 70650
$\beta$ (H <sub>2</sub> flux)	2.889e-1 (m <sup>3</sup> /m h atm <sup>0.5</sup> )	12540

Table 2 Data for Calculating Equilibrium Constant [25, 29]

Parameter	Pre-exponential factor	Delta H
KEQ1	7.846e12 (atm <sup>2</sup> )	220200
KEQ2	1.412e-2	-37720
KEQ3	1.11e11 (atm <sup>2</sup> )	182400

## 2.4 PARTIAL PRESSURE DETERMINATION

The equation used to express partial pressures in terms of conversion is widely available in literatures [7, 25, 30, 31]. The general expression for partial pressure is

$$P_i = \left( \frac{F_i^{in} \mp F_i^{generated/consumed}}{F_{total}} \right) x P_t \quad (27)$$

Where  $F_{total}$  is total molar flow;  $F_i^{in}$  is the molar flow of component  $i$  in the feed;  $F_i^{generated/consumed}$  is the amount of  $i$  generated or depleted from chemical reaction;  $P_t$  total pressure of the mixture. A summary of partial pressure expressions is given in Table 3.

Table 3 Summary of Partial Pressure Expression

Parameter	Expression
$P_{CH_4}$	$\left(\frac{1 - X_{CH_4}}{\theta}\right)$
$P_{H_2O}$	$\left(\frac{\phi_{H_2O} - X_{CH_4} - X_{CO_2}}{\theta}\right)$
$P_{CO}$	$\left(\frac{\phi_{CO} + X_{CH_4} - X_{CO_2}}{\theta}\right)$
$P_{CO_2}$	$\left(\frac{\phi_{CO_2} + X_{CO_2}}{\theta}\right)$
$P_{H_2}$	$\left(\frac{1 + 3X_{CH_4} - X_{CO_2} - \frac{F_{H_2}}{F_{CH_{4,o}}}}{\theta}\right)$
$\theta$	$\left(\frac{1 + \phi_{H_2} + \phi_{CO_2} + \phi_{CO} + \phi_{H_2O} - Y_{H_2}}{P_t}\right)$
$\phi_i$	$\frac{F_{i,o}}{F_{CH_{4,o}}}$

## 2.4 ENERGY BALANCE

The energy balance is performed over an elemental portion of the reactor as shown in Figure 1, by applying the principle of conservation of energy.

$$\left[ \begin{array}{c} \text{Rate of accum} \\ \text{of heat} \\ \text{within the system} \end{array} \right] = \left[ \begin{array}{c} \text{Rate of inflow} \\ \text{of heat} \\ \text{into the reactor} \end{array} \right] - \left[ \begin{array}{c} \text{Rate of} \\ \text{outflow} \\ \text{of heat out} \\ \text{of the reactor} \end{array} \right] + \left[ \begin{array}{c} \text{Rate of} \\ \text{heat} \\ \text{generation or} \\ \text{depletion} \\ \text{by chemical} \\ \text{reaction} \end{array} \right] - \left[ \begin{array}{c} \text{Rate of heat} \\ \text{flux} \\ \text{thru the} \\ \text{membrane} \end{array} \right] \quad (28)$$

Substitution of the individual terms in equation (28) as appeared in Figure 1 yields the following energy balance model

$$\frac{dT}{dz} = \frac{(-\Delta H_{R,i})(R_i)}{\rho_i c_{p,i} u} + \frac{U_{mem} \pi D_m (T_{mem} - T)}{\rho_i c_{p,i} u} \quad (29)$$

## 2.5 SPECIFIC HEAT CAPACITY OF REACTING COMPONENTS

The value of specific heat capacity is calculated as a function of the mole fractions of the reacting components and expressed as polynomial function [30]. The specific heat capacity written as a function of temperature and composition is given as:

$$C_{p,mix} = \sum_{i=1}^n (y_i C_{p,i}) \quad (30)$$

$$C_{p,i} = a_{i,o} + b_{i,o} T + c_{i,o} T^2 + d_{i,o} T^3 + e_{i,o} T^4 \quad (31)$$

The coefficients for calculating the specific heat capacity is in Table 4.

Table 4 Heat Capacity Coefficients for Reacting Components [30]

S/No	Specie	$a_{i,o}$	$b_{i,o}$	$c_{i,o}$	$d_{i,o}$	$e_{i,o}$
1	$CH_4$	403.584	9.057	-1.443E-2	1.581E-5	-6.343E-9
2	$H_2O$	1563.077	1.604	-2.933E-3	3.216E-6	-1.157E-9
3	$CO$	968.390	0.449	-1.152E-3	1.657E-6	-7.346E-10
4	$H_2$	13602.45	3.402	-3.358E-3	-3.908E-7	1.705E-9
5	$CO_2$	429.929	1.874	-1.949E-3	1.297E-6	-3.999E-10

The governing equation used in evaluating the individual component's enthalpies is [32, 33]:

$$\Delta H_{R,i} = \sum H_i^0(298) + \int_{T_{mem}}^T (C_{p,i} dT) \quad (32)$$

The overall heat transfer coefficient is modelled by equation in [33] as

$$U = \frac{2\pi L k_q (Temp - T)}{\ln(R_{out}/R_2)} + 2\pi R_{out} L \sigma (Temp^4 - T^4) \quad (33)$$

The values of enthalpies for obtaining heat of formation are given in Table 5.

Table 5 Enthalpies of Reforming Reaction [33]

Parameter	Value $\left[\frac{KJ}{mol}\right]$
$H_1^0(298)$	206
$H_2^0(298)$	41
$H_3^0(298)$	165

## 2.6 BOUNDARY AND INITIAL CONDITIONS

In solving the model equations for predicting the performance of the membrane reformer, the following boundary conditions were adopted:

$$\frac{dX_i}{dz} \Big|_{z=0} = 0 \quad (34)$$

$$\frac{dY_j}{dz} \Big|_{z=0} = 0 \quad (35)$$

$$\frac{dT}{dz} \Big|_{z=0} = 530^\circ C. \quad (36)$$

In equation 34,  $i$  mean  $CH_4, CO_2$  while  $j$  in equation 35 is  $H_2$ .

## 2.7 OPERATIONAL/MODEL DATA

The input data that used to solve the model were obtained from Notore Chemical Industries PLC and relevant literatures.

Table 6 Reactor Parameters [25]

Parameter	Value
Total Pressure (atm)	29.0
Catalyst density (gcat/m <sup>3</sup> )	2355.2
Reactor length (m)	20.0
Tube internal radius (m)	0.1016
Tube external radius (m)	0.1322
Membrane radius (m)	0.0203

### 3. DISCUSSION OF MODEL RESULTS

The graphical analysis of the results obtained from the solution of the model equations of the membrane reactor under study is presented in this section of the work.

#### 3.1.1 TEMPERATURE PROGRESSION ALONG THE REACTOR

Figure 2 shows the temperature progression of the reformed gases along the membrane reactor length.

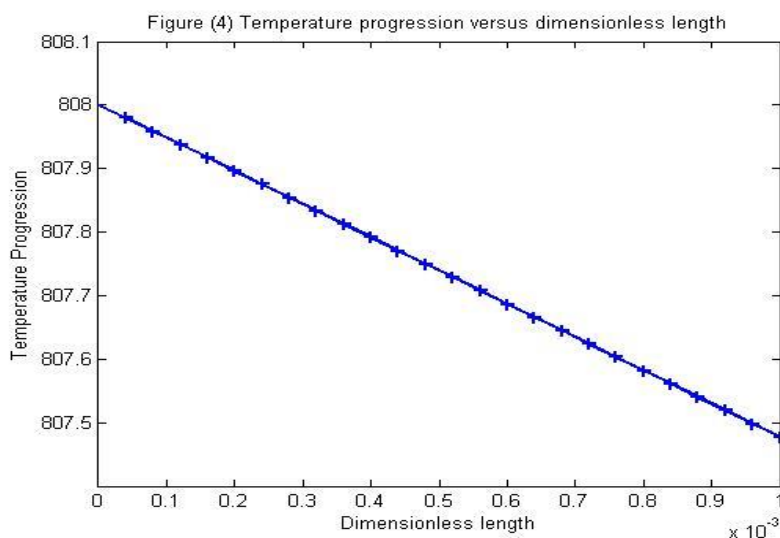


Figure 2 Temperature Progressions [K] along Reactor Length

Figure 2 shows the temperature profile along the length of the reactor. As shown on the curve, temperature drops progressively across the reactor length, which is characteristic of an endothermic reaction. As shown in Figure 2, reforming of methane is possible at 530 °C (803 K) inlet temperature in a membrane reactor without raising temperature to as high as 850 °C (1123 K) as done in tubular reactors. Therefore, performing methane steam reforming in a membrane reactor allows for operation at lower temperature hence preventing deactivation and sintering of catalysts [1].

#### 3.1.2 FRACTIONAL CONVERSION OF METHANE ALONG THE REACTOR

Figure 3 shows the fractional conversion of methane (the limiting reactant) along the reactor length.



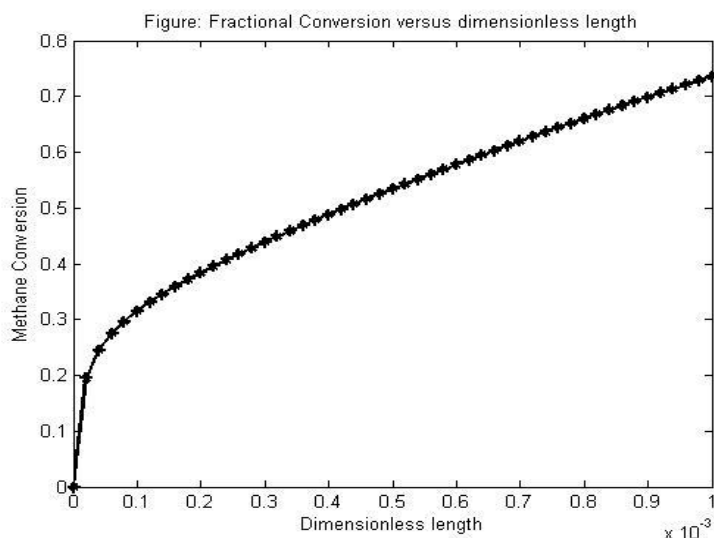


Figure 3 Methane Fractional Conversion along the Membrane Reactor

The rate at which methane is used up to generate hydrogen and carbon mono/di- oxides is shown in Figure 3. The fractional conversion of methane was obtained using plant inlet temperature of 530 °C, 29 bar reactor pressure with a membrane thickness of 6 microns. As shown on the curve the conversion of methane progressively increases along the membrane reactor. A maximum of 73.6% was obtained at 530 °C. This high conversion at the moderate temperature is possible as removal of produced hydrogen through the membrane shifts equilibrium to more formation of hydrogen.

### 3.1.3 COMPONENT YIELD ANALYSIS

The yield of respective components along the dimensionless reactor length is shown in Figure 4.

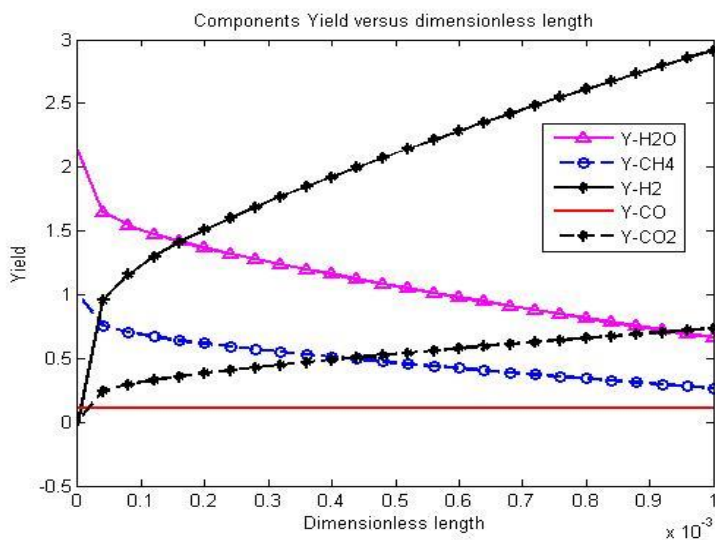


Figure 4 Components Yield along the Membrane Reactor

The uptrend of hydrogen confirms that a high yield of hydrogen is achievable in a membrane reactor of up to 3.4. Similarly, yield of methane and steam drop progressively, confirming they are being used up to form hydrogen and carbon dioxide.

### 3.2 SIMULATION STUDIES

Figure 5 shows the effect different inlet temperatures have on yield and conversion.

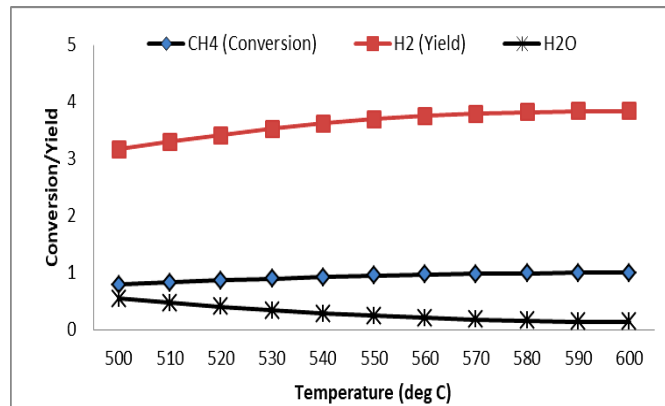


Figure 5 Effect of Temperature on Conversion/Yield

Figure 5 shows the effect different inlet temperatures have on yield and conversion. The result was obtained by simulating between temperature ranges of 500-600 °C while keeping all other parameters constant. As shown in Figure 5, increasing inlet temperature also increases methane conversion and hydrogen yield. A conversion of 99% was obtained at inlet temperature of 590 (C). Conversely, increasing the steam inlet temperature reduces the residual steam in the reactor exit. This shows that the steam in the feed gas is being converted to hydrogen.

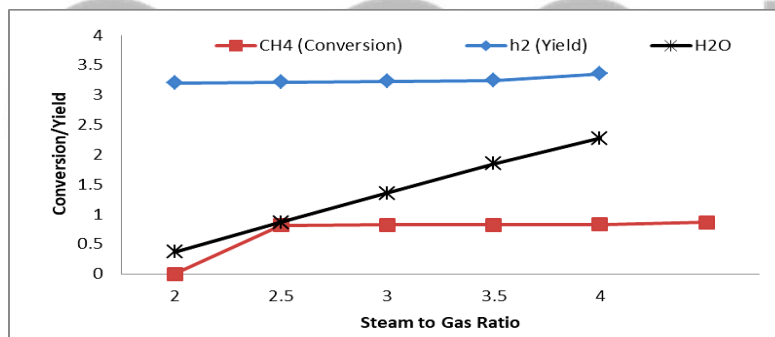


Figure 6 Effect of Steam to Gas Ratio on Conversion/Yield

Figure 6 implies that steam content in the reactor exit increases as the steam to gas ratio is raised from 2 to 4. A methane conversion of 86% and hydrogen yield of 3.35 were obtained at maximum steam-to-gas ratio of 4.0.

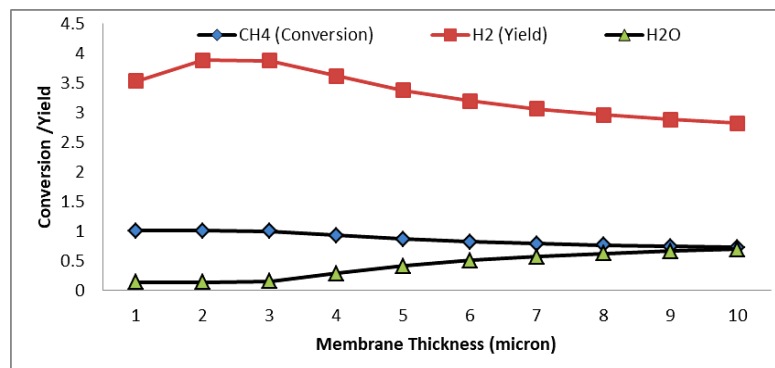


Figure 7 Effect of Membrane Thickness on Conversion/Yield

Figure 7 confirms that reducing the membrane size favors methane conversion and hydrogen yield. Between membrane thicknesses of 2-3 microns, a 100 % methane conversion was attained in the reactor. Conversely, the residual steam exiting the reactor increases as thickness of membrane increases.

### 3.3 MODEL VALIDATION

The model from this work was validated with results of similar works from literatures. Table 7 shows the comparison of methane conversion and hydrogen yield results obtained by [1] against the models using similar operating parameters. At an operating temperature and pressure of 550°C and 25bar, a deviation of 2% on methane conversion was obtained. Similarly, a maximum deviation of 9.3% hydrogen yield was obtained. In table 8, the conversions of methane and hydrogen yield of the membrane model are compared to that from plant. There was a 21% increase in the membrane reactor against that in a conventional tubular reactor operating under the same inlet temperature and pressure.

Table 7 Comparison of [1] Results against Model

parameter	Conversion/Yield		Deviation
	Literature (Membrane)	Model (Membrane)	
CH <sub>4</sub>	99.00%	97.18%	2%
H <sub>2</sub>	3.2	3.5	9.3%
Temperature	550	550	0%
S/C	2.5	2.5	0%
Pressure	25	25	0%

Table 8 Comparison of Plant Data and Model

Parameter	Conversion/Yield		Change (%)
	Plant (conventional) (Tubular)	Model (Membrane)	
CH <sub>4</sub>	60.50%	73.60%	21.65289
H <sub>2</sub>	0.954	2.7612	189.434
Temp. (°C)	530	530	-

### CONCLUSION

This research focused on predicting the performance of a membrane reactor as an alternative to conventional tubular reactor for carrying out the steam reforming of natural gas. The governing equations comprise 5 ordinary differential equations for describing conversion of reaction components along the reactor. A 6th equation for describing temperature progression was obtained from energy balance. The widely used reaction rate of Xu and Fromment was applied to describe the reaction kinetics of methane steam reforming. A MATLAB program was written to solve the models by using input parameters from plant (conventional reactor). It was discovered that conversion of methane in a membrane reactor is higher than that in a conventional reactor by 21.6 %. We compared the models with plant data using the same inlet temperature of 530 °C. A methane conversion of 60.5% (plant) against 73% (model) respectively was obtained. Using membrane reforming reactor will significantly reduce system and reaction temperature to between 500 – 600 °C compared to a conventional tubular reactor operating temperature of 700-1000 °C, while maintaining a higher product yield. Optimization of the membrane reactor used for steam reforming showed the possibility of 99.9% conversion of the limiting reactant (methane) at around 590°C.

## NOMENCLATURE

$A_t$	Reactor tube area [m <sup>2</sup> ]
$A_m$	Effective membrane area [m <sup>2</sup> ]
$C_{p,i}$	Specific heat capacity [ $\frac{kJ}{kg K}$ ]
$D_m$	Diameter of membrane [m]
$E_a$	Activation energy [J/mol]
$F_i$	Molar flow of component $i$ [ $\frac{kmol}{hr}$ ]
$F_i^{in}$	Initial molar flow of $i$ [ $\frac{kmol}{hr}$ ]
$F_i^o$	Initial molar flow of $i$ [ $\frac{kmol}{hr}$ ]
$F_{total}$	Total molar flow [ $\frac{kmol}{hr}$ ]
$H_0$	Flow of enthalpy into the reactor [ $\frac{kJol}{hr}$ ]
$H_f$	Flow of enthalpy out of the reactor [ $\frac{kJol}{hr}$ ]
$i$	Reaction components $CH_4, CO, CO_2, H_2O, H_2$
$J_{H_2}$	Hydrogen molar flux [kJol/m <sup>2</sup> h]
$k_1$	Reaction (R <sub>1</sub> ) rate constant [kmol atm <sup>0.5</sup> /kgcat h]
$k_2$	Reaction (R <sub>2</sub> ) rate constant [kmol atm <sup>-1</sup> /kgcat h]
$k_3$	Reaction (R <sub>3</sub> ) rate constant [kmol atm <sup>0.5</sup> /kgcat h]
$k_o$	Pre-exponential factor
$K_i$	Adsorption constant of chemical species $i = CH_4, CO, CO_2, H_2O, H_2$ [atm <sup>-1</sup> ]
$KEQ_i$	Equilibrium constant ( $i = 1, 2, 3$ ) [atm <sup>2</sup> ]
KWH	Kilowatt Hour
$L$	Reactor length [m]
$M_i$	Molecular weight [kg/kmol]
$N_i$	Mole of component $i$ [kmol]
$P_{eH_2}$	Hydrogen Permeance
$P_{H_2,retentate}$	Partial pressure of hydrogen in the retentate side [atm]
$P_{H_2,permeate}$	Partial pressure of hydrogen in the permeate side [atm]
$P_i$	Partial pressure of component $i$ [atm]
$P^o$	Operating pressure [atm]
$R$	Gas constant [ $\frac{Jol}{mol.K}$ ]
$R_{out}$	Outer tube radius [m]
$S$	Entropy [J/molK]
SCFH	Standard cubic feet per hour
$t$	Time [sec]
$T$	Absolute temperature [K]
$T_{mem}$	Temperature of surface [K]
$u$	Superficial velocity [m/sec]
$U_{mem}$	Overall heat transfer coefficient [W/m <sup>2</sup> K]
USD	United States Dollar
$X_i$	Fractional conversion of component $i$
$Y_i$	Mole fraction
$Y_{H_2}$	Hydrogen yield per mole of feed
$Z$	Space coordinates [m]
$\delta_m$	Membrane thickness [m]
$\sigma$	Stefan Boltzmann's constant [W/m <sup>2</sup> K <sup>4</sup> ]
$\Delta H_{298}$	Heat of reaction [ $\frac{kJol}{mol}$ ]
$\Delta z$	Differential length [m]
$-\Delta G_i$	Gibb's free energy [Jmol <sup>-1</sup> K <sup>-1</sup> ]
$n_i$	Stoichiometric ratio

$\rho_{cat}$	Catalyst density $\left[\frac{kg}{m^3}\right]$
$\rho_t$	Density of mixture $\left[\frac{kg}{m^3}\right]$
$\mathcal{R}_i$	Rate of reaction of for reactions 1,2,3 [kmol/kgcat.h]

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