SIMULATION STUDY OF METHANE AUTOTHERMAL REFORMING FOR HYDROGEN PRODUCTION

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ABSTRACT

Hydrogen production from an autothermal system is mathematically investigated using one-dimensional steady state fixed bed model. A series of simulation is analyzed at different operating parameters which are inlet temperature, operating pressure and steam to methane feed ratio at a fixed oxygen to methane ratio. The results revealed that an excess steam restricted hydrogen production by lowering the bed temperature which is important to drive endothermic steam reforming. An increase of reactor pressure after 3 atm slightly affected methane conversion and this could be beneficial in membrane reactor system. Higher inlet temperatures also showed an increase in hydrogen production but as far as catalyst constraint is concern, it has to be wisely control. The result showed that a maximum fraction of H_2-CO can be achieved at operating pressure of 3 atm, a feed temperature of 850 K and water to methane ratio of 3.

1. INTRODUCTION

In year to come, hydrogen has become a widely used feedstock in chemical, petroleum industries and petrochemical fields. In addition, hydrogen is expected to be an energy sources since it offer several environmental and economic advantages compare to other fuels (Jamal and Wyszynski, 1994; Rosen, 1991).

The hydrogen production from methane can be obtained from a number of principle processes. (Hickman and Schimdt, 1992) have demonstrated that the direct partial oxidation of methane to synthesis gas is a promising alternative to steam reforming. Surprisingly high selectivity of hydrogen and carbon monoxide and more than 80% conversion of methane on Pt monoliths occur at temperature 1373 K and at very short contact times between 10^{-4} and 10^{-2} s achieved. Partial oxidation needs external cooling in general.

Steam reforming of methane shows highest hydrogen production efficiencies (Ersoz et. al, 2003). However, the required of large heat input due to highly endothermic reaction is considered as a major drawback for automotive application. The reaction usually carried out at a temperature of 773-1173 K generated using an external furnace.

Methane steam reforming conversion is usually around 78%, limited by the thermodynamic equilibrium.

In recently proposed reaction system, the endothermic heat and part of steam required for steam reforming are balance with the heat produced by methane oxidation in the presence of two different catalysts (Ma & Trimm, 1996; Ma, Trimm and Jiang, 1996), Pt / Al_2O_3 for oxidation and Ni/MgO-Al$_2$O$_3$ for reforming catalyst. The system is at best performance when the catalysts were physically mixed (Ma and Trimm, 1996). Since the system is coupled of highly exothermic oxidation and highly endothermic reforming reaction the heat integration is very important for optimum condition (Ahmet et. al, 2002) plus the product distribution is largely influenced by the inlet feed ratio and inlet temperature.

The objective of this work is a computational effort to predict the system behavior under several operating condition. For this, a series of reactor simulation were performed at a different operating condition considering water to methane inlet ratio, inlet temperature, and operating pressure using one dimensional adiabatic fixed bed model.

1.1. Reaction system consideration

ATR system is a combination of exothermic partial oxidation and endothermic steam reforming in the presence of catalysts that drive both of reactions. ATR using methane as fuel required start up initiation or heat supply to the system because of low activity of methane before becomes self-operated. It may be supplied by external heating (Rostrup-Nielson, 1984) or by combusting part of the fuel (Twigg, 1989). The key feature of the system is that no external energy source required.

The reaction system is an adiabatic fixed bed reactor in which both Pt/Al$_2$O$_3$ and Ni/MgO-Al$_2$O$_3$ are mixed together in a one bed system. The oxidation reaction is very fast catalyzed by Pt based catalyst while steam reforming running on Ni based catalyst. In this simulation it is assumed that all of the four reactions occur simultaneously the fact that the catalyst for oxidation and reforming is mixed together for improved mass and heat transfer (Ahmet et. al, 2001)

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \text{(TOX)}$$
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \text{(SR1)}$$
$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \text{(SR2)}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{(WGS)}$$

1.2. Reaction Kinetics

The three main reactions were considered in the ATR system was methane oxidation, steam reforming and water gas shift reaction. Kinetics for every reaction is taken from (Trimm and Lamm, 1980) for oxidation, steam reforming and water gas shift from (Xu and Froment, 1989). Noted that the kinetics of reforming and water gas shift display a negative order in hydrogen partial pressure that could resulted infinity at a zero of hydrogen partial pressure. The former author conducted the experiment in the presence of hydrogen to avoid reoxidation of Nickel catalyst by steam. To avoid this, the simulations were conducted by introducing a very small amount of hydrogen in the feed (1×10^{-8} kmol/hr).

Table 1. Reaction Kinetics

reaction	Rate of reaction	Catalyst	References
TOX	$$-r = \dfrac{k_1 p_{CH_4} p_{O_2}}{\left(1 + K^{ox}_{CH_4} p_{CH_4} + K^{ox}_{O_2} p_{O_2}\right)^2} + \dfrac{k_2 p_{CH_4} p_{O_2}}{\left(1 + K^{ox}_{CH_4} p_{CH_4} + K^{ox}_{O_2} p_{O_2}\right)}$$	Pt/Al_2O_3	Trimm and Lamm (1980)
SR1	$$-r = \dfrac{k/p^{2.5}_{H_2}\left(p_{CH_4} p_{H_2O} - p^3_{H_2} p_{CO}/K_{eq}\right)}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O}/p_{H_2}\right)}$$	Ni/MgO-Al_2O_3	Xu and Froment (1989)
SR2	$$-r = \dfrac{k/p^{3.5}_{H_2}\left(p_{CH_4} p^2_{H_2O} - p^4_{H_2} p_{CO_2}/K_{eq}\right)}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O}/p_{H_2}\right)}$$	Ni/MgO-Al_2O_3	Xu and Froment (1989)
WGS	$$-r = \dfrac{k/p_{H_2}\left(p_{CO} p_{H_2O} - p_{H_2} p_{CO_2}/K_{eq}\right)}{\left(1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} p_{H_2O}/p_{H_2}\right)}$$	Ni/MgO-Al_2O_3	Xu and Froment (1989)

2. MATHEMATICAL MODEL

An adiabatic one-dimensional fixed bed model was used in the simulation. Concentration and temperature gradient is assumed occur only in the axial direction. The only transport mechanism operating in the axial direction is the overall flow itself and is considered to be plug flow type. In order to avoid having to integrate the continuity equation inside the pellet in each increment, the constant terms of effectiveness factor were introduced that represent the intraparticle diffusion limitation (De Groote and Froment, 1996). The effect of pressure drop also incorporated into the model. The simulation is based on the following set of differential equations.

Component balances

$$\frac{dF_{CH4}}{dz} = -A\rho_b(\eta_1 r_1 + \eta_2 r_2 + \eta_4 r_4)$$

$$\frac{dF_{O2}}{dz} = -A\rho_b(2\eta_1 r_1)$$

$$\frac{dF_{H2O}}{dz} = -A\rho_b(\eta_2 r_2 + \eta_3 r_3 + 2\eta_4 r_4 - \eta_1 r_1)$$

$$\frac{dF_{CO}}{dz} = A\rho_b(\eta_2 r_2 - \eta_3 r_3)$$

$$\frac{dF_{CO2}}{dz} = A\rho_b(\eta_1 r_1 + \eta_3 r_3 + \eta_4 r_4)$$

$$\frac{dF_{H2}}{dz} = A\rho_b(3\eta_2 r_2 + \eta_3 r_3 + 4\eta_4 r_4)$$

Energy balances

$$\frac{dT}{dz} = \frac{A\rho_b \sum_j \eta_j r_j (-\Delta H_j)}{\sum_i F_i Cp_i}$$

Pressure drop (Ergun equation)

$$\frac{dP}{dz} = -\frac{G}{\rho g_c D_p}\left(\frac{1-\theta}{\theta^3}\right)\left(\frac{150(1-\theta)}{D_p} + 1.75G\right)$$

The above sets of ordinary differential equation were solved simultaneously using Matlab m-files simulation.

3. RESULT AND DISCUSSION

The simulation was carried on at different inlet temperature in range of 800-950 K at different H_2O/CH_4 ratio. Figure 6 showed the maximum temperature achieved in the reactor is less than 1100 K when the inlet temperature increased from 800 to 900 K, temperature above than 1100 K occur when feed at 950 K and at a low H_2O/CH_4 ratio. Since the molar flow rate of methane and O_2/CH_4 ratio is constant for all run, any increased of initial steam flow rate lower the maximum bed temperature, it can be concluded that steam facilitate heat transfer in the beds and acts as coolant that controls the bed temperature. This can verify the range of inlet temperature that could be considered to control the temperature constraint inside the reactor.

The simulation also conducted at zero steam inlet to see how the kinetic responded to temperature profiles across the axial bed, figure 1 showed that an initially increased of temperature profile resulted from high methane oxidation rate that control the reaction pathway. However, this effect was not dominant as the temperature started to decrease indicating the endothermic steam reforming reaction started to occur. However the endothermic rate is weak due to low fraction of steam produced from the methane oxidation were less sufficient to drive steam reforming. Finally, the temperature increased very sharp due to strong oxidation reaction to an equilibrium temperature.
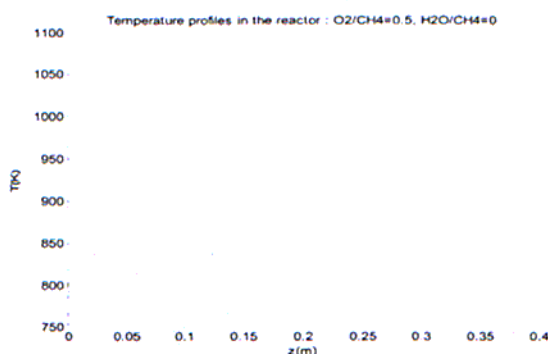
Temperature profiles in the reactor : O2/CH4=0.5, H2O/CH4=0

Figure 1. Temperature profiles vs. axial reactor coordinate without steam addition

However, different results were observed when steam was added to the feed. Figure 2 showed an initially decreased due to the prevailing endothermic reforming reaction that controls the reaction pathway. The temperature then reaches a minimum value and started to increase consecutively towards equilibrium value. The reforming rate at the reactor inlet is considerably higher than methane oxidation rate. As a result, initial temperature decrease and started to increase because of the high heat production from the oxidation and water gas shift reaction.

Temperature profiles in the reactor : O2/CH4=0.5, H2O/CH4=1.5
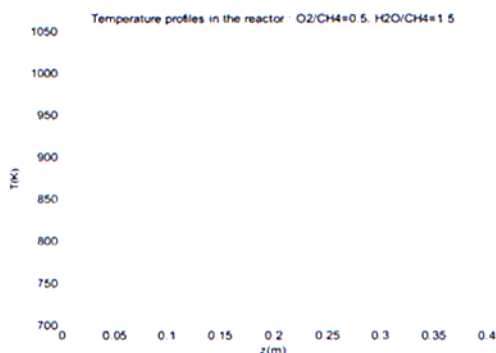
Figure 2. Temperature profiles vs. axial reactor coordinate

In the gas phase packed bed system, pressure drop is one of the important parameter since the concentration of species is related to total pressure. However, pressure drop can be assumed negligible if the diameter particle is very small. This was checked by incorporating pressure drop effect to the model, and the averaged is 0.004 atm was observed.

The simulation also conducted at a different operating pressure, figure 3 showed the effect of operating pressure to the maximum methane conversion achieved in the reactor. It can be concluded that ATR is favored at low operating pressure and the predicted maximum conversion can be achieved at operating pressure of 3 atm, any increased of the system pressure resulted a slightly decreased in methane conversion.
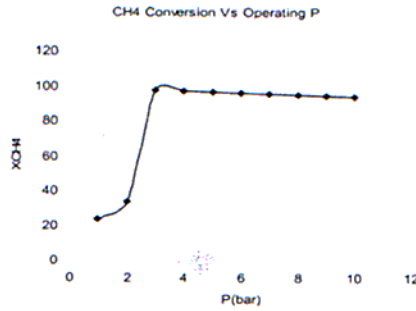
Figure 3. Methane conversion Vs. operating pressure at Tin = 850 K, $H_2O/CH_4=3$

Fig 4 and 5 show a $Y_{H_2} - Y_{CO}$ fraction and methane conversion versus inlet H_2O/CH_4 ratio at a different inlet temperature. It is observed that $Y_{H_2} - Y_{CO}$ fraction is maximized at low H_2O/CH_4 ratio and continuing to decrease depending on inlet temperature. It seem that excess steam inhibit steam reforming reaction resulted a low $Y_{H_2} - Y_{CO}$ fraction. The maximum $Y_{H_2} - Y_{CO}$ fraction is predicted at H_2O/CH_4 of 3 when inlet temperature of 850 K was introduced. A different profiles were observed at high inlet temperature Tin>850 K, the predicted $Y_{H_2} - Y_{CO}$ fraction almost constant when H_2O/CH_4 ratio increased, at Tin 900 K, the fraction were slightly decrease at H_2O/CH_4 ratio of 4.5 and becoming high at H_2O/CH_4 ratio of 5, this probably due to lower performance of the kinetics expression at high temperature since the corresponding author obtained the kinetic at relatively low temperature 773<T< 848 K (de Smet et.al, 2001).
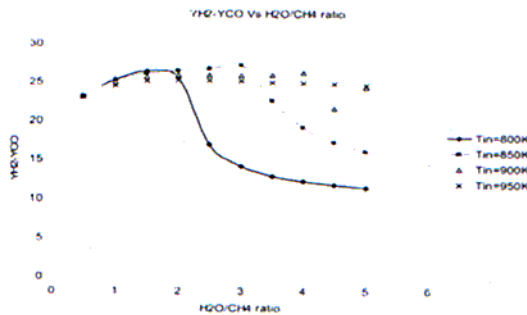

Figure 4. $Y_{H_2} - Y_{CO}$ fraction vs. H_2O/CH_4 ratio at a different inlet temperature

Methane conversion shows a similar profile to the $Y_{H_2} - Y_{CO}$ fraction. Methane is almost completely consumed at high temperature inlet condition in which accelerates the reaction rate. At Tin=800 K, the maximum conversion of 96% achieved at H2O/CH4 of 1.5 and further decrease to 35% at H_2O/CH_4 of 2.5, any increase of steam beyond this value showed a relatively constant of methane conversion attained. At Tin=850 K showed a shifted of conversion where a maximum value is predicted at H_2O/CH_4 of 2.5 and   start   to   decrease   consecutively.
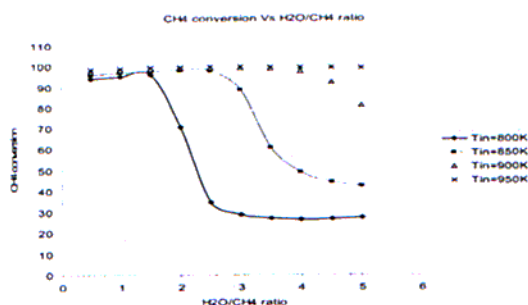
Figure 5. Methane conversion vs. H_2O/CH_4 ratio at a different inlet temperature

A slightly different in conversion compared to $Y_{H_2} - Y_{CO}$ fraction at H_2O/CH_4 of 3 where conversion was dropped to 88% but high $Y_{H_2} - Y_{CO}$ fraction were achieved at this point. The conversion drop due to relatively low equilibrium temperature achieved in the reactor approximately 900 K compared to equilibrium temperature at H_2O/CH_4 of 2.5 (figure 6). The more steam is predicted to favor the equilibrium water gas shift reaction that convert more CO to H_2. Figure 7 and 8 showed the product equilibrium profiles along the reactor length, it can be concluded that more steam will drive the water gas shift reaction to equilibrium. However, the H_2 production amount from water gas shift reaction is low compared to reforming reaction, thus the H_2 production is dominated by reforming reaction as more steam is added to the system the lower equilibrium temperature will be, furthermore at fixed O2/CH4 ratio the heat from methane oxidation were not sufficient enough to meet the steam addition in order to drive endothermic reforming reaction, finally less H_2 is observed.
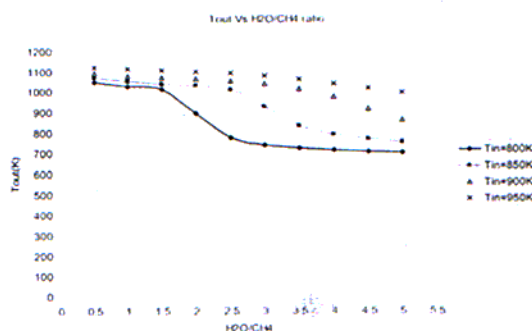

Figure 6. Temperature out vs. H_2O/CH_4 ratio at a different inlet temperature

In addition, steam also can be seen to affect the product equilibrium distribution along the reactor length. The figure 7 and 8 below indicate the shift of product distribution to the end of the reactor according to steam input. Figure 7 showed the equilibrium condition can be achieved at 0.2m of the reactor length and moved toward the end of the reactor at high H_2O/CH_4 ratio. At a certain extent, the system is unable to reach its equilibrium and a requirement of longer reactor length is necessary. Since this system involved a reversible reaction, it is clearly to say that, reaching equilibrium condition is essential for maximum H_2 hydrogen production performances.

The above discussion however not clearly state the CO content since the simulated system only consider a single ATR reactor system and CO content is still in a high amount in term of PPM measurement. The requirement of CO reduction unit is essential for the fuel cell application to treat the CO to the level value which the PEMFC can tolerate. However, CO production from the simulated system show a decreasing behavior when more steam is added to the system (figure 7 and 8). This can be explained by WGS reaction which is favored at low temperature corresponding to high steam input.
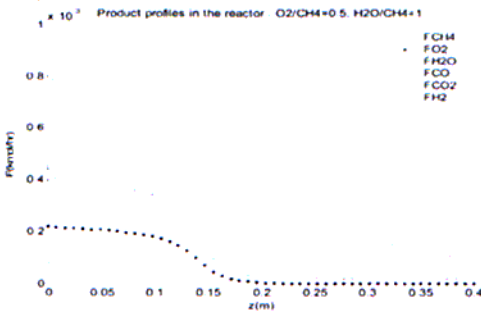

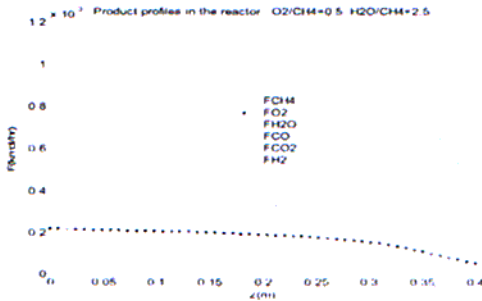**Figure 7.** Product distribution Vs. reactor axial coordinate

Figure 8. Product distribution vs. reactor axial coordinate

4. CONCLUSION

Autothermal reforming system for hydrogen production is mathematically investigated by a series of simulation. A steady state, one-dimensional adiabatic fixed bed model was used to predict the system behavior. The model accounted intraparticle diffusion limitation by introducing constant effectiveness factor to avoid numerical complexity. The increase of H_2O/CH_4 ratio after a certain value consequently decreases of methane conversion and $Y_{H_2} - Y_{CO}$ fraction. Even though, higher inlet temperature will facilitate hydrogen production but the system can suffer from a nearly explosive operating condition that becoming as a major drawback. The CO content however is not a major discussion here since the application of ATR in membrane reactor system will be considered in future that eliminated the used of CO reduction unit. The resulted obtained in this simulation will be as a preliminary data and very helpful in simulating the membrane reactor system. Finally, the hydrogen production is predicted to favor at operating pressure of 3 and inlet temperature of 800 to 900 K as long as catalyst deactivation is concern.

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