

Kinetic Based Simulation of Methane Steam Reforming and Water Gas Shift for Hydrogen Production Using Aspen Plus

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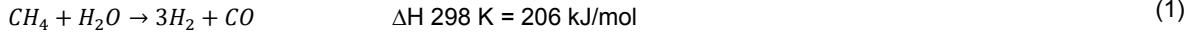
This paper presents the kinetic-based simulation of methane steam reforming (MSR) from natural gas and water gas shift (WGS) reaction for hydrogen production. It is found that most simulations of these reactions were either done as balance or equilibrium based. Although it provides simplicity, such approach has limitations, especially for sensitivity analysis, control and optimisation. In order to improve and optimise the reactor performance, kinetic-based simulation is necessary. The kinetic data for MSR and WGS reactions were obtained from literature. The simulation was performed in Aspen Plus using RPLUG model blocks with rearranged Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model. The results of the simulation show good agreement with results found in the literature. Apart from that, sensitivity analysis was carried out to observe the effect of several parameters such as temperature, pressure, catalyst weight and ratio feed to the reactor performance.

1. Introduction

Hydrogen is recognised as a capable energy carrier in the future. Hydrogen energy has the potential to become energy resource and can reduce the dependency on fossil fuel in the future. The product of hydrogen combustion is mainly water with less amount of nitrogen oxide or sulphur oxide. Hydrogen combustion has high energy content, approximately 143 MJ/kg lower heating value (LHV), triple to that of petroleum (Chu et al., 2015). In 2002, 48 % of hydrogen is produced from natural gas, 30 % from heavy oil and naphtha, 18 % from coal and 4 % from electrolysis (Logan, 2004). Methane steam reforming (MSR) is one of the important processes in the production of hydrogen and syngas. MSR is comprehensively used and is a matured technology in hydrogen production industries, but it has a high carbon product released at almost 7 kg CO₂/kg H₂. A commonly MSR system consists of four sequential units, namely desulfuriser, reformer, shift reactor and separation units (Soltani et al., 2014). Desulfuriser can be removed if the natural gas feed is pure methane. Shift reactor involves a WGS reaction in which carbon monoxide react with steam to produce carbon dioxide and hydrogen gas (Choi and Stenger, 2003). The purpose of water gas shift (WGS) on the other hand, is to reduce the carbon monoxide production and optimise the production of hydrogen (Antzara et al., 2014). Mostly in previous study simulation of these reactions were based on stoichiometry or equilibrium model (Boyano et al., 2012). Although it provides simplicity, the results obtained are very limited as such could not offer insights on the process characteristics. There is a need to simulate the reactions using kinetic-based model which particularly useful for reactor sizing, costing, sensitivity analysis as well as control and optimisation. In this study, our objective is to simulate MSR and WGS reactions using kinetic expression model in RPLUG reactor block with LHHW reaction model in Aspen Plus. The kinetic data for both reactions were based on literature for performance and validation purposes and therefore could predict the performance of the reactor at high accuracy with low maximum relative error (Er-rbib and Bouallou, 2014). Apart from that, sensitivity analysis will be carried out to provide insights on the process characteristics.

2. Reaction Kinetics for Methane Steam Reforming (MSR) and Water Gas Shift (WGS)

Hydrogen production via MSR involves reaction between methane with steam to produce hydrogen and carbon monoxide in a catalytic fixed-bed reactor with a molar ratio CH₄ and H₂O of 1 : 3 based on the following reaction formula:



For fast reaction, Ni-based catalyst supported on alumina is commonly used in industry (Fernandes and Soares, 2006). The rate expression for the MSR reaction, R_{MSR} based on Langmuir-Hinshelwood (LHHW) reaction mechanism on Nickel catalyst is as follows:

$$R_{MSR} = \frac{\frac{k_1}{P_{H_2}^{2.5}} [P_{CH_4} P_{CO} - \frac{P_{H_2}^3 P_{CO}}{K_1}]}{DEN^2} \quad (2)$$

$$\text{Where } DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + \frac{K_{H_2O} P_{H_2O}}{P_{H_2}}$$

k_1 and K_1 are the rate constant and equilibrium constant for MSR. P_i and K_i are the partial pressure and adsorption equilibrium constant of component i . The rate expression above cannot be used directly in Aspen Plus as the general equation for LHHW used the following equations:

$$R = \frac{(\text{kinetic factor})(\text{driving force})}{\text{adsorption term}} \quad (3)$$

Where,

$$\text{kinetic factor} = k \left(\frac{T}{T_0} \right)^n e^{-\left(\frac{E}{R} \right) \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (4)$$

$$\text{driving force} = K_1 \prod_{i=1}^N C_i^\alpha - K_2 \prod_{j=1}^N C_j^\beta \quad (5)$$

$$\text{adsorption term} = \left[\sum_{i=1}^M K_1 \left(\prod_{j=1}^N C_j^M \right) \right]^m \quad (6)$$

In Aspen Plus, the pre-exponential constant, adsorption constant used the following equation:

$$K = A \exp\left(\frac{B}{T}\right) T^C \exp(DT) \quad (7)$$

The equation does not fit Eq(3) and need to be rearranged. Using natural logarithm (Ln) and some rearrangements, the newly rearranged equation is shown below:

$$R_{MSR} = \frac{k_1 K_1 \left[K_1 \frac{P_{CH_4} P_{CO}}{P_{H_2}^{2.5}} - P_{H_2}^{0.5} P_{CO} \right]}{DEN^2} \quad (8)$$

The kinetic coefficient and equilibrium constant in Eq(8) are shown in Table 1. The modelling parameters can now describe in Aspen Plus using RPLUG block based on LHHW kinetics model. Note that, hydrogen was added in the feed stream to avoid division by zero in Eq(8).

The WGS reaction is normally used after reforming or gasification process to reduce carbon monoxide and increase hydrogen yield. The reaction formula is shown in Eq(9). It is a reversible and exothermic reaction and involves two reactors in series, namely high temperature and low temperature, which operated at 400 °C and 210 °C (Amadeo and Laborde, 1995). Iron-based catalyst and the copper-based catalyst is commonly used in industry for this reaction (Amadeo and Laborde, 1995).



The kinetic model for reaction in Eq(9) is based on a LHHW reaction mechanism. The rate reaction, RWGS is given by:

$$R_{WGS} = \frac{k_0 P_{CO} P_{H_2O} (1 - \beta)}{(1 + K_1 P_{CO} + K_2 P_{H_2O} + K_3 P_{CO_2} + K_4 P_{H_2})^2} \quad (10)$$

Where,

$$\beta = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O} K_e} \quad (11)$$

k_o and K_e are the rate and equilibrium constant for WGS reaction. The kinetic coefficient and equilibrium constants in Eq(10) are shown in Table 1. As for MSR, the rate expression above need to be rearranged to fit Aspen Plus RPLUG block based on LHHW kinetics model input requirements as shown below:

$$R2 = \frac{k_o(P_{co}P_{h2o} - \frac{P_{co2}P_{H2}}{K_e})}{(1 + K1P_{co} + K2P_{H2O} + K3P_{co2} + K4P_{H2})^2} \quad (12)$$

Table 1: Kinetic parameter for methane steam reforming and water gas shift

MSR (Singh et al., 2014)				WGS(Amadeo and Laborde, 1995)			
Parameter	Pre-exponential factor	Ea or ΔH (J/mol)	Ln K	Parameter	Ea or ΔH (J/mol)	Ea or ΔH (J/mol)	Ln K
k1	4.2248×10^{15} (mol atm ^{0.5} /g h)	240,100		ko	0.92 (mmol/g s atm ²)	4,080	
K1	7.846×10^{12} (atm ²)	220,200	29.69	K1	2.21	-910	0.79
K _{CH4}	6.65×10^{-4} (atm ⁻¹)	-38,280	-7.31	K2	0.4	-1,420	-0.92
K _{H2O}	1.77×10^5 (atm ⁻¹)	88,680	12.08	K3	0.0047	-24,720	-5.36
K _{H2}	6.12×10^{-5} (atm ⁻¹)	-82,900	-9.70	K4	0.052	-14,400	-2.96
K _{CO}	8.23×10^{-5} (atm ⁻¹)	-70,650	-9.41				

3. Process Simulation and Modelling

The hydrogen production process was modelled in Aspen Plus V8.6. The components involved were water, methane, carbon dioxide, carbon monoxide and hydrogen. The thermodynamic method used is RKSMHV2 based on the Redlich-Kwong-Soave equation of state with modified Huron-Vidal mixing rules (Er-rbib and Bouallou, 2014). This model is suitable for non-polar and polar compounds in combinations with light gases (Technology, July 2010). Figure 1 shows the process flowsheet. At this stage, the recycle stream is not considered. The feed stream to the MSR reactor was natural gas and steam. The natural gas does not contain hydrogen sulphide and carbon dioxide. Both of these streams were mixed in MIX-01 before heated up to 700 °C. The diameter of the MSR reactor was 0.2 m and the length was 10 m. The output streams from the heater were then introduced to the MSR reactor using RPLUG model block which operated isothermally. The output stream from the MSR reactor were then fed to a WSG reactor at 400 °C which operated adiabatically with a pressure of 1 bar. The WSG reactor was modelled using RPLUG model block. RPLUG is a rigorous model for plug flow reactors which assumes perfect mixing in the radial direction and it can model for three-phase reactors. The WGS reactor diameter was 5 m and the length was 0.3 m. Both reactors involved single reaction and the side reaction is neglected.

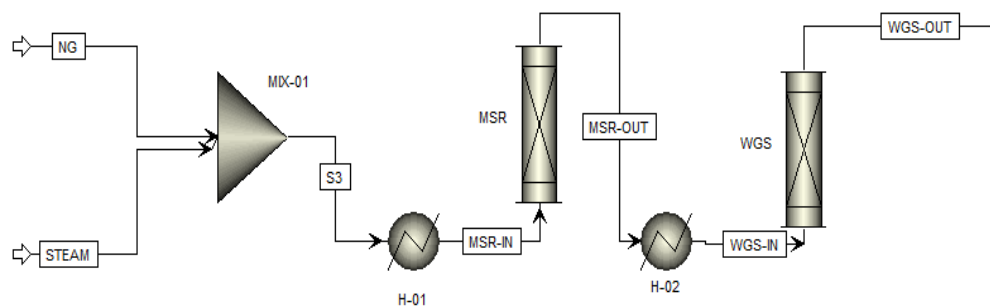


Figure 1: Aspen Plus process flow diagram for MSR and WGS reaction

4. Model Validation

The modelling approach in this work is validated with the same operating conditions from previous experiment by Singh et al. (2014) for MSR and Amadeo and Laborde (1995) for WGS. In the work by Singh et al. (2014), it can be seen in Figure 2(a) that the conversion of methane for conventional reactor increased rapidly at the first meter of the reactor length. After that, the conversion started to resolve. The same trend is found in the simulation work as shown in Figure 2(b). It was found that the highest error was at 1 m with 11.71 % while the smallest error is at 2 m with 0.53 %. Overall the mean error is 3.27 % as such it can be concluded that the

modelling approach for MSR is valid. The same approach is considered for WGS modelling. Figure 3(a) shows the experimental results by Amadeo and Laborde (1995). It shows the relationship between the partial pressure of feed water into the reactor with the conversion of carbon monoxide. The RPLUG block model was set to have the same design parameters as in the experimental work which includes the operating condition, catalyst specification and component flow rate. The hydrogen feed is 0.003604 L/s and carbon monoxide flow rate is 0.000983 L/s. The result from the simulation shows an agreement with the experimental data which indicate that with increased partial pressure of water the conversion of carbon monoxide to carbon dioxide will also increase. It can be concluded that the modelling approach for WGS reaction is valid.

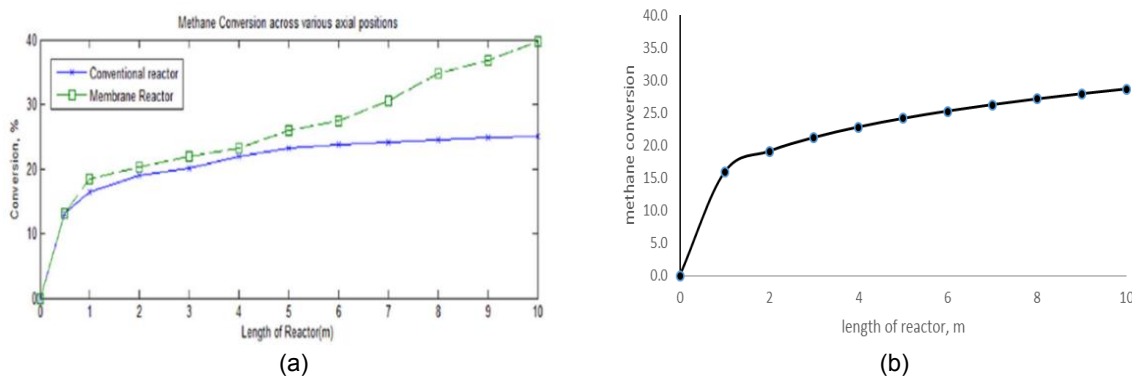


Figure 2: The conversion of MSR (a) from (Singh et al., 2014) (b) from simulation using Aspen Plus.

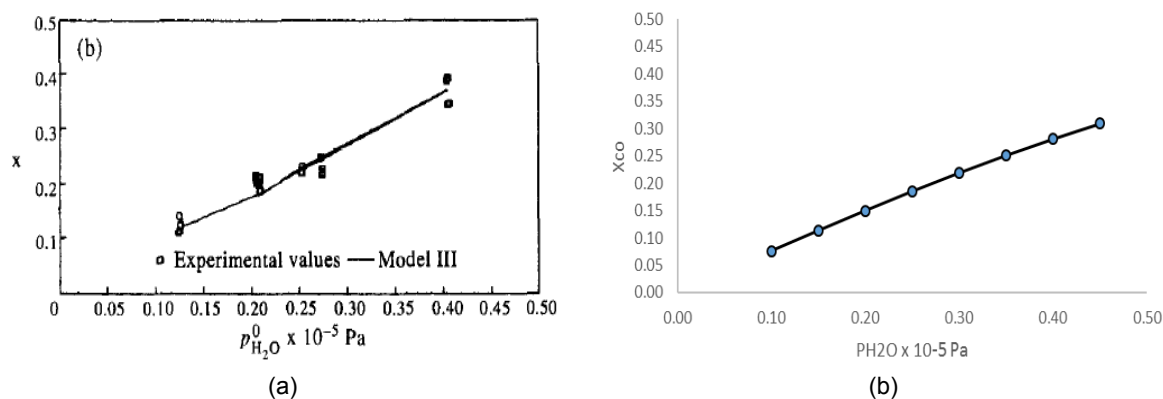


Figure 3: Carbon monoxide conversion with partial pressure (a) from (Amadeo and Laborde 1995) (b) from simulation

5. Sensitivity Analysis

Sensitivity analysis of the reactor performance was done by changing several operation variables, namely catalyst weight, reactor temperature and pressure and steam-to-methane feed ratio into the reactor. During sensitivity analysis, the manipulated variables were varied while the other design parameters remain unchanged. Figure 4 shows the result of the sensitivity analysis. In Figure 4(a), it can be seen that with increased catalyst weight in the reformer, the hydrogen flow rate also increased especially at the first 100 kg. However, at 300 kg the hydrogen flow rate starts to become constant. The same increment is observed for the shift reactor as the increment in catalyst weight increase the carbon dioxide flow rate. The rapid increment is observed at the first 50 kg before the carbon dioxide flow rate started to be constant. At this point, almost all carbon monoxide had been converted to carbon dioxide.

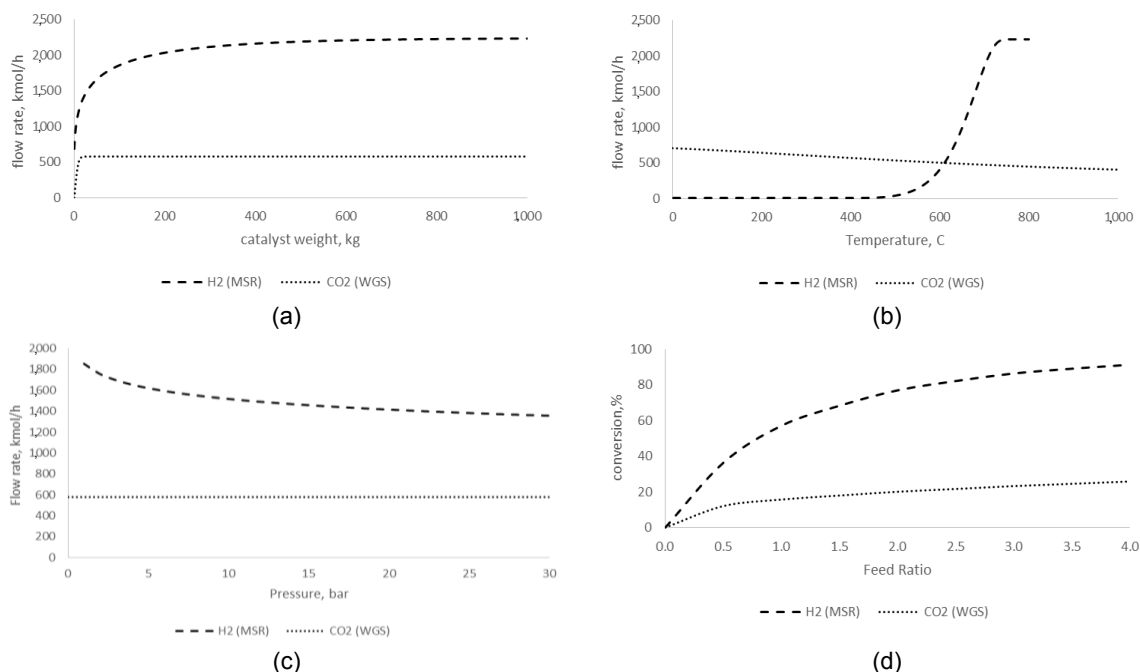


Figure 4: Sensitivity analysis on MSR and WGS (a) weight catalyst (b) temperature feed to reactor (c) pressure feed to the reactor (d) ratio feed for water steam and methane.

As shown in Figure 4 (b) is the response of the hydrogen molar flow rate to reactor temperature increment. For the reformer, hydrogen started to produce at 500 °C and increased drastically until 700 °C. After that, hydrogen flow rate started to become constant. At this point, all the methane had been converted into hydrogen. This trend shows that for MSR reaction, the hydrogen produced depends on a certain range, which is 500 °C to 700 °C in this case. For WGS reaction, it is found that as the feed temperature increased, there was a drop in the carbon dioxide molar flow rate. This is because the equilibrium constant decreases with an increase in temperatures thus lower down the conversion of carbon monoxide at the higher temperature. Figure 4 (c) shows the effect of pressure on hydrogen flow rate. For MSR, it is found that when the pressure is increased, the hydrogen molar flow rate shows the inverse response. The highest hydrogen produced is at 1 bar. For WGS, the result shows that the effect of pressure to carbon dioxide molar flow rate is insignificant. Figure 4 (d) shows the effect of hydrogen flow rate towards change in steam to methane feed ratio. When the steam feed flow rate is increased, the percentage of methane conversion also increased. This shows that the feed ratio is important to ensure the reaction is pushed to the right side thus increase hydrogen flow rate. For WGS reaction, it is found that the conversion of carbon monoxide is higher when the steam ratio is increased. From the figure conversion of 90 % can be achieved when the ratio steam to carbon monoxide is four.

6. Conclusion

This study successfully model and simulate kinetic based MSR and WGS reaction using modified LHHW model in Aspen Plus. Both reaction model have been validated and show very good agreement with existing experimental data. Upon validation, the sensitivity analysis was conducted. It is found that for both reactions, catalyst weight, reactor temperature and steam : methane feed ratio greatly affect the reactor performance production. However, pressure seems to have low effect to these reactions. The successful modelling and simulation of the kinetic-based hydrogen production set an important basis in our work. Further significance analysis can be done which include work on optimisation, operability and controllability study and sustainability assessment.

Acknowledgement

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