



## MODELING AND SIMULATION OF STEAM METHANE REFORMING (SMR) PROCESS FOR THE PRODUCTION OF HYDROGEN

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### Abstract

*Kinetic rate for steam methane reforming (SMR) over a nickel based catalyst was studied over desirable reaction conditions. A one-dimensional heterogeneous model was developed with variation along the axial direction, for a fixed bed catalytic reactor. The model was simulated on a MATLAB model builder, and the Effects of some process variables such as temperature, pressure and mass flowrate across the bed on the yield of hydrogen was investigated. High temperature (approximately 1130K) and low pressure, between (40.25 to 39.45 bar), favors the conversion of H<sub>2</sub> and CO between 0 – 1.25m of the reactor length and thereafter stabilizes. The drop in pressure was attributed to frictional losses between the particle of gases, catalyst pellets and walls of the reformer. The model was validated by comparing the conversion of CH<sub>4</sub> and CO<sub>2</sub> from the process data and the model. The conversions are close fall within the ranges of 0.3-0.4 and 0.78-0.87 for H<sub>2</sub> and CH<sub>4</sub> respectively as predicted by literatures.*

**Keywords;** Modeling, Steam Methane Reforming, Hydrogen Production

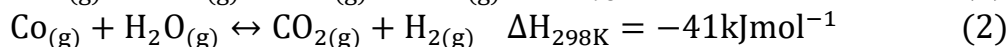
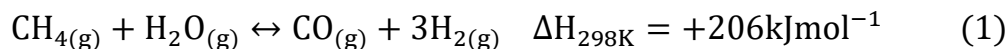
### Introduction:

Due to climate change, emission of greenhouse gases coupled with the depletion of fossil reserve and the needs to meet the food demand for the growing world population has redirected the interest of many researchers in the recent time (Neha and Vineet, 2015). Hydrogen, as an alternative, has gained interest in last two decades. Unlike coal, gas, or oils, hydrogen is not a primary energy source but must first be produced using energy from other source. Hydrogen can be produced from diverse resources, both renewable (hydro, wind, wave, solar,

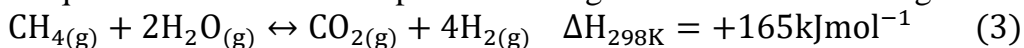
biomass and geothermal) and non-renewable (coal, natural gas, and nuclear) Edward *et al.*,(2007).

Hydrogen is produced by a number of ways such as electrolysis, Steam Methane Reforming (SMR), auto CO<sub>2</sub> methane reforming and partial oxidation reforming. Among all of these processes, SMR process is the cheapest and is used commercially to meet the hydrogen demands worldwide (Steinberg and Cheng (1989)). The steam reformer is very important process equipment, used in the production of ammonia, via the production of hydrogen. The Hydrogen requirement is met by, catalytically reacting a mixture of steam and methane (due to its high hydrogen contents and low capital cost compared to other hydrocarbon) at an elevated temperature to form a mixture of Hydrogen and oxides of Carbon.

Amongst all the available processes steam methane reforming (SMR) is the most established and commonly used process to produce syngas on a large scale. SMR contributes Over 50% of the world's H<sub>2</sub> production. The conventional SMR process used in industries consists of two main steps: in the first step endothermic SMR reaction (reaction) takes place at a high temperature (~800 to 1000 °C) and medium pressure (at 20 to 35 atm) and in the second step, the exothermic water gas shift (WGS) reaction (reaction) runs at a lower temperature (~200 to 400 °C) and medium pressure (10 to 15 atm).



This two-step process of SMR enhances the H<sub>2</sub> production by shifting the reaction (1) in the forward direction at a high temperature followed by reaction (2) at a lower temperature. The overall SMR process is endothermic in nature and requires additional heat to proceed. The global SMR reaction is given as;



The conventional steam methane reformer consists of a furnace that contains tubes in it, with catalyst loaded in these tubes to speed up the rate of the reaction (1). Many efforts have been made in the past to develop the most suitable catalyst for this process. SMR is faced with some problems which includes; low methane conversion due to reversibility, coke formation, catalyst deactivation, heat transfer issues, and diffusion limitations (Armor 1999, Alkattib, A and Boumaza M. 2014). Several attempts have been made to model and simulate the SMR using model based (Alkattib, A and Boumaza M. 2014, Amro *et al.*, 2015, Mahmud *et al.*, 2016) and artificial neural network (Nugrohol

*et al.*, 2009). Nugrohol *et al.*, 2009 developed a model based on artificial neural network and fuzzy logic. Their model was successful but limited due to the Gaussian and static assumptions which are not true for process data. In this study, the model as developed by Rand and Jassim, 2015, which is based on the works of Froment and Xu 1989, will be adopted.

Xu and Froment presented the most widely used kinetic model for SMR. In their model they considered carbon dioxide ( $\text{CO}_2$ ) as a non-adsorbing gas on the surface of the catalyst and the reaction kinetics depend upon the partial pressure of the steam.

The objective of this study is to carry out the modeling and simulation of a primary reformer. The kinetics of the SMR process will be developed over a Nickel-based catalyst supported by  $\alpha\text{-Al}_2\text{O}_3$ . These kinetics will be implemented in a 1-dimensional ideal plug flow heterogeneous model of the process in an industrial-scale adiabatic fixed bed reactor.

## General Methodology

### Equipment and Materials

The schematic diagram of the set-up is shown in figure 1.

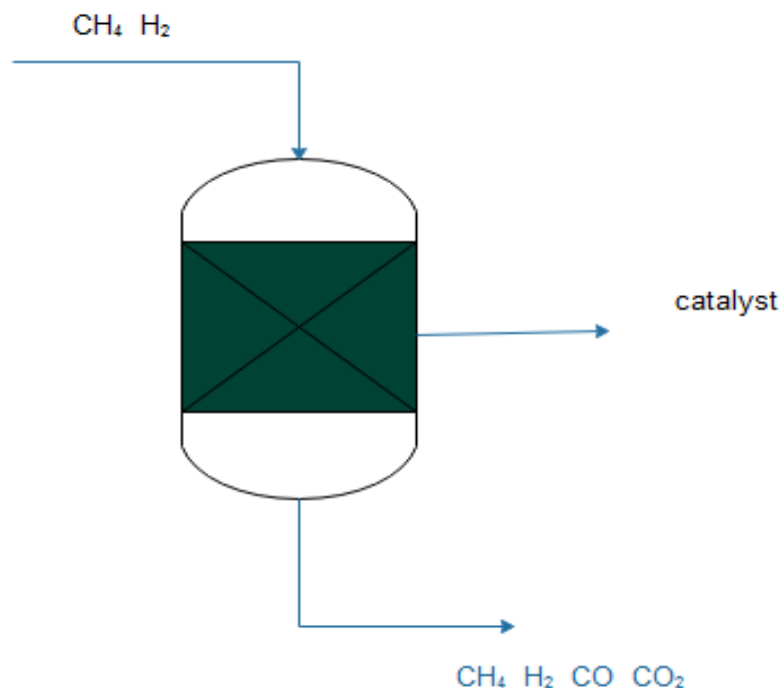


Fig1; An experimental setup for Steam Methane reforming Process

**In this model; the following assumptions are made:**

- Operation is adiabatic in nature
- Ideal gas law is applicable
- Concentration and temperature gradients along the radial direction are negligible. So, only one-dimensional variation in concentration and temperature i.e. in the axial direction is considered.
- No temperature gradient is considered in the catalyst particles
- Porosity of the bed is constant

The Mathematical model is composed of mass and energy balance equations both in the gas and solid phase. The mass, energy and momentum balance equations are given.

$$\frac{dF_i}{dw} = -R_i \quad \text{Eq.1}$$

However, the catalyst weight is expressed as;

$$w = zA\rho_{cat}(1 - \varepsilon_B) \quad \text{Eq.2}$$

Substituting for w in Eq.1,

$$\frac{dF_i}{d(zA\rho_{cat}(1-\varepsilon_B))} = -R_i \quad \text{Eq.3}$$

The cross sectional area, A,  $\rho_{cat}$  and  $(1 - \varepsilon)$  are constant since the fluid properties do not vary over the cross-section of the reactor. Therefore,

$$\frac{dF_i}{dz} = -R_i A \rho_{cat} (1 - \varepsilon_B) \quad \text{Eq.4}$$

The rates of reaction of the three reactions are expressed as  $R_1$ ,  $R_2$  and  $R_3$  for reaction (1), (2), and (3) respectively.

Mole Balance for  $\text{CH}_4$ :

$$\frac{dF_{\text{CH}_4}}{dz} = A\rho_{cat}(1 - \varepsilon_B)(-R_1\eta_1 + -R_2\eta_2) \quad \text{Eq.5}$$

Mole Balance for  $\text{H}_2\text{O}$ :

$$\frac{dF_{\text{H}_2\text{O}}}{dz} = A\rho_{cat}(1 - \varepsilon_B)(-R_1\eta_1 + -R_2\eta_2 + -2R_3\eta_3) \quad \text{Eq.6}$$

Mole Balance for  $\text{H}_2$ :

$$\frac{dF_{\text{H}_2}}{dz} = A\rho_{cat}(1 - \varepsilon_B)(3R_1\eta_1 + R_2\eta_2 + 4R_3\eta_3) \quad \text{Eq.7}$$

Mole Balance for  $\text{CO}_2$ :

$$\frac{dF_{\text{CO}_2}}{dz} = A\rho_{cat}(1 - \varepsilon_B)(R_2\eta_2 + R_3\eta_3) \quad \text{Eq.8}$$

Mole Balance for  $\text{CO}$ :

$$\frac{dF_{CO}}{dz} = A\rho_{cat}(1 - \varepsilon_B)(R_1\eta_1 + -R_2\eta_2) \quad \text{Eq.9}$$

Equation 5 to 9 represents the material balance model for the primary reformer. The energy balance across the reactor is has been derived as change in the temperature throughout the reactor length as reported by several authors (Khorsand and Deghan, 2007; Rand and Jassim, 2015; Abdulrazzaq *et al.*, 2015).

$$F_i C_{p_i} \frac{dT}{dz} = \sum_{k=1}^3 A\rho_{cat}\eta_k R_k(1 - \varepsilon_B)(-\Delta H^{\circ}_{R,k}) + \pi dq \quad \text{Eq.10}$$

The energy balance due to temperature gradient is as expressed in Eq.11

$$\frac{dT}{dz} = \frac{\sum_{k=1}^3 A\rho_{cat}\eta_k R_k(1 - \varepsilon_B)(-\Delta H^{\circ}_{R,k}) + \pi dq}{\sum F_i C_{p_i}} \quad \text{Eq.11}$$

For material flow through cylindrical catalyst packed bed, the pressure drop across the bed length can be estimated by the Ergun equation derived by Bird *et al.*, (1960). The pressure drop expression across the reactor bed is give as Eq.12

$$\frac{dP}{dz} = - \left[ \frac{150(1 - \varepsilon_B)^2 \mu u}{\varepsilon_B^3 d_p^2} + \frac{1.75(1 - \varepsilon_B) \rho u^2}{\varepsilon_B^3 d_p} \right] \quad \text{Eq.12}$$

The rate equations of the kinetics rate for primary reformer reactions (steam methane reforming reaction, water gas shift, and carbon dioxide reforming reactions) are adopted from Xu and Froment (1989).

$$R_1 = \frac{k_1}{P_{H_2}^{2.5}} \left[ P_{CH_4} \times P_{H_2O} - \left( \frac{P_{H_2}^3 \times P_{CO}}{K_{e1}} \right) \right] \times \frac{1}{DEN^2}$$

$$R_1 = \frac{k_2}{P_{H_2}} \left[ P_{CO} \times P_{H_2O} - \left( \frac{P_{H_2} \times P_{CO_2}}{K_{e2}} \right) \right] \times \frac{1}{DEN^2}$$

$$R_3 = \frac{k_3}{P_{H_2}^{3.5}} \left[ P_{CH_4} \times P_{H_2O}^2 - \left( \frac{P_{H_2}^4 \times P_{CO_2}}{K_{e3}} \right) \right] \times \frac{1}{DEN^2}$$

where

$$DEN = 1 + K_{ad.co} \times P_{CO} + K_{ad.H_2} \times P_{H_2} + K_{ad.CH_4} \times P_{CH_4} + K_{ad.H_2O} \times \frac{P_{H_2O}}{P_{H_2}}$$

The reaction rate constants are evaluated according to the Arrhenius equation

$$K_k = A_k \times \text{EXP} \left( \frac{-E_k}{R_g T} \right)$$

$$k_1 = 4.225 \times 10^{15} \text{EXP} \left( \frac{-240100}{RT} \right)$$

$$k_2 = 1.995 \times 10^6 \text{EXP} \left( \frac{-67130}{RT} \right)$$

$$k_3 = 1.02 \times 10^{15} \text{EXP} \left( \frac{-243900}{RT} \right)$$

$$K_{\text{adH}_2\text{O}} = 1.77 \times 10^5 \text{EXP} \left( \frac{-88680}{RT} \right)$$

The equilibrium constants are evaluated according to the expressions

$$K_{e1} = \text{EXP} \left( \frac{-26830}{T} + 30.114 \right)$$

$$K_{e2} = \text{EXP} \left( \frac{440}{T} - 4.036 \right)$$

$$K_{e3} = K_{e1} \cdot K_{e2}$$

The adsorption coefficients are evaluated according to the expressions below. The kinetic constants were obtained for nickel catalyst grains 0.18 – 0.25 mm in size (Xu and Froment, 1989; Kagyrmanova *et al.*, 2006)

$$K_{\text{adCO}} = 8.23 \times 10^{-5} \text{EXP} \left( \frac{70650}{RT} \right)$$

$$K_{\text{adH}_2} = 6.12 \times 10^{-9} \text{EXP} \left( \frac{82900}{RT} \right)$$

$$K_{\text{adCH}_4} = 6.65 \times 10^{-4} \text{EXP} \left( \frac{3828}{RT} \right)$$

$$K_{\text{adH}_2\text{O}} = 1.77 \times 10^5 \text{EXP} \left( \frac{-88680}{RT} \right)$$

For an industrial size primary reformer reactor, the effectiveness factor needs to be considered in order to apply the kinetic equation to the industrial reformer model. The effectiveness factor can be estimated either by empirical relation and diffusion-reaction model approach using the Thiele Modulus (Xu and Froment, 1989).

$$\eta_k = \frac{1}{\varphi} \left( \frac{1}{\tanh(3\varphi)} - \frac{1}{3\varphi} \right)$$

Where;

$$\varphi_k = \frac{d_p}{6} \sqrt{\frac{k_{v,k} \rho_{\text{cat}} (1 + K_{e,k})}{K_{e,k} D_{e,k}}}$$

$$D_{e,k} = \frac{\varepsilon_p}{\tau} \left( \frac{D_{\text{kn},i} \times D_{\text{imix}}}{D_{\text{kn},i} + D_{\text{imix}}} \right)$$

$$K_{v,1} = k_1 0.08314 \left( \frac{T}{p^{1.5}} \right)$$

$$K_{v,2} = k_2 0.08314 T$$

$$K_{v,3} = k_3 0.08314 \left( \frac{T}{p^{1.5}} \right)$$

The model equations 5 to 12 were simulated using MATLAB application package, to evaluate the variation of conversion, consumption and formation rate, temperature and pressured drop across the bed length.

**Table 1:** Feed condition and reactor parameters from Dangote data sheet and literature

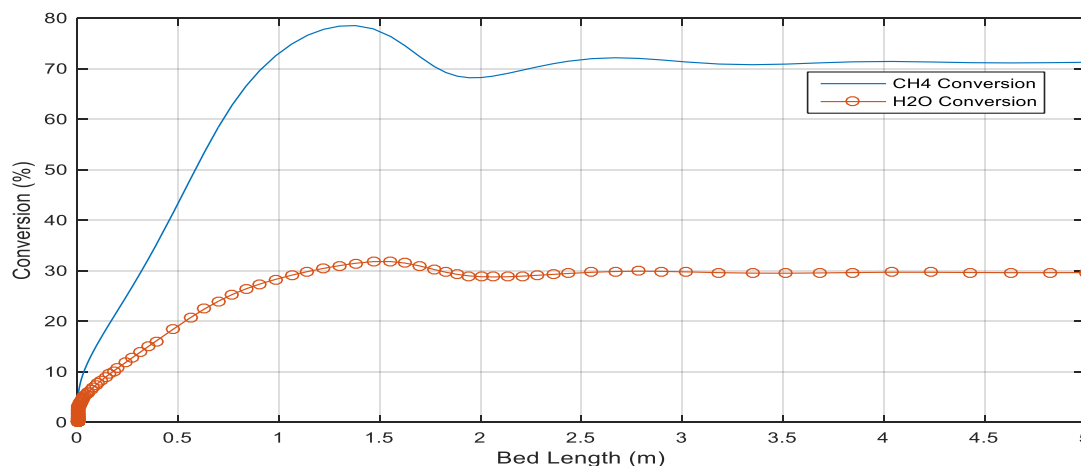
Parameters	Value
<b>Temperature [°C]</b>	517.1871
<b>Pressure [kPa]</b>	4023.9858
<b>Molar Flow [kmol/hr]</b>	156925.26
<b>Mass Density [kg/m<sup>3</sup>]</b>	11.3316
<b>Catalyst Density [kg/m<sup>3</sup>]</b>	970
<b>Fluid Viscosity, [kg.sec/m<sup>2</sup>]</b>	2.418x10 <sup>-6</sup>
<b>Bed Void Fraction</b>	0.50
<b>Catalyst Particle Diameter [mm]</b>	0.25
<b>Bed Area [m<sup>2</sup>]</b>	15
<b>Heat Added to Reactor [kJ/hr]</b>	7490132338.3649
<b>Bed length [m]</b>	5.0
<b>Initial Flow rate of CH<sub>4</sub> [kmol/hr]</b>	30846.5551
<b>Initial Flow rate of H<sub>2</sub>O [kmol/hr]</b>	119169.371
<b>Initial Flow rate of H<sub>2</sub> [kmol/hr]</b>	1540.4400
<b>Initial Flow rate of CO [kmol/hr]</b>	0.0076
<b>Initial Flow rate of CO<sub>2</sub> [kmol/hr]</b>	1902.8964
<b>Initial Temperature [K]</b>	790.4800
<b>Initial Pressure [bar]</b>	40.2400

## Results and Discussions.

The feed and operating condition of the primary reformer was taken from the Dangote data sheet, while the parameters are obtained from literatures (see table 1).

Figure 2 shows the percentage conversion for methane and steam. The conversion rate for both  $\text{CH}_4$  and  $\text{H}_2\text{O}$  increased steadily from length 0 – 1.25m of the reactor length at a temperature of approximately 1130K and then stabilizes. This increase could be as a result of high catalyst activity at the beginning. The conversion rate can also be affected by change in temperature or pressure. At constant pressure, Increased in temperature will favor the endothermic while increasing pressure favors the side with the equilibrium (i.e. Chaterlier’s principles). Beyond the peak point (at 1.4m of the reactor length) a slight decrease in  $\text{CH}_4$  conversion was observed, this could be attributed to decrease in reactant and/or reduction in catalyst activity (due to coking, CO) as the reaction proceeds with an increase in  $\text{H}_2$  yield.

Figure 4 shows the pressure profile across the bed length of the primary reformer. The pressure varies from 40.25 to 39.45 bar at the inlet and the exit respectively. The drop in pressure is as a result of frictional losses between the particle of gases, catalyst pellets and walls of the reformer. Pressure drop is an important parameter in a reformer. Low pressure drop is a desirable characteristic of a Particular catalyst shape, because of a lower mechanical energy loss.



**Figure 2:** Conversion of reactants across bed length



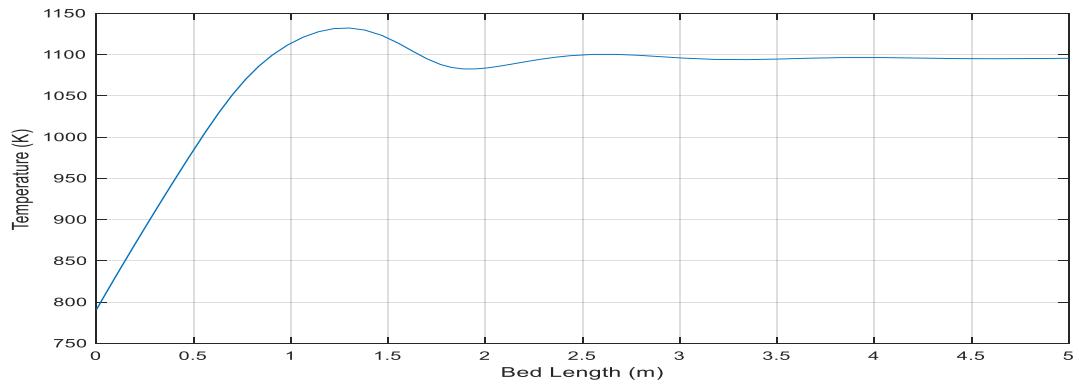


Figure 3: Temperature profile across bed length

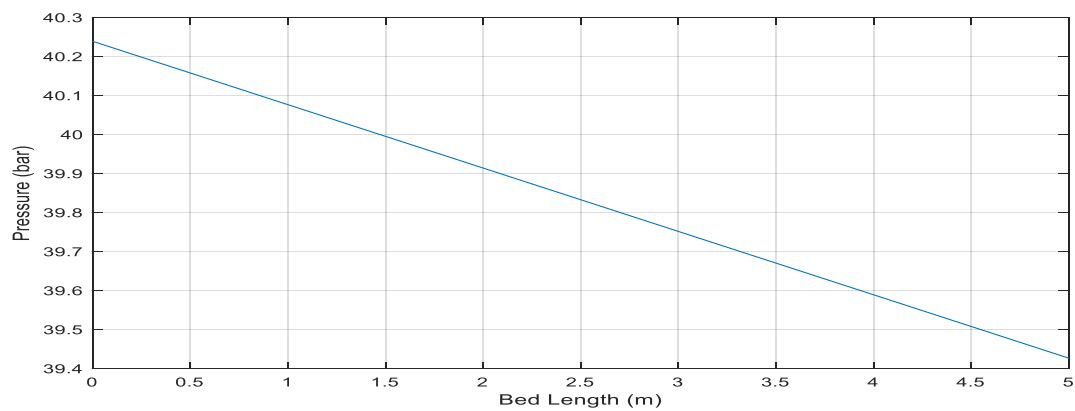


Figure 4: Pressure profile across bed length

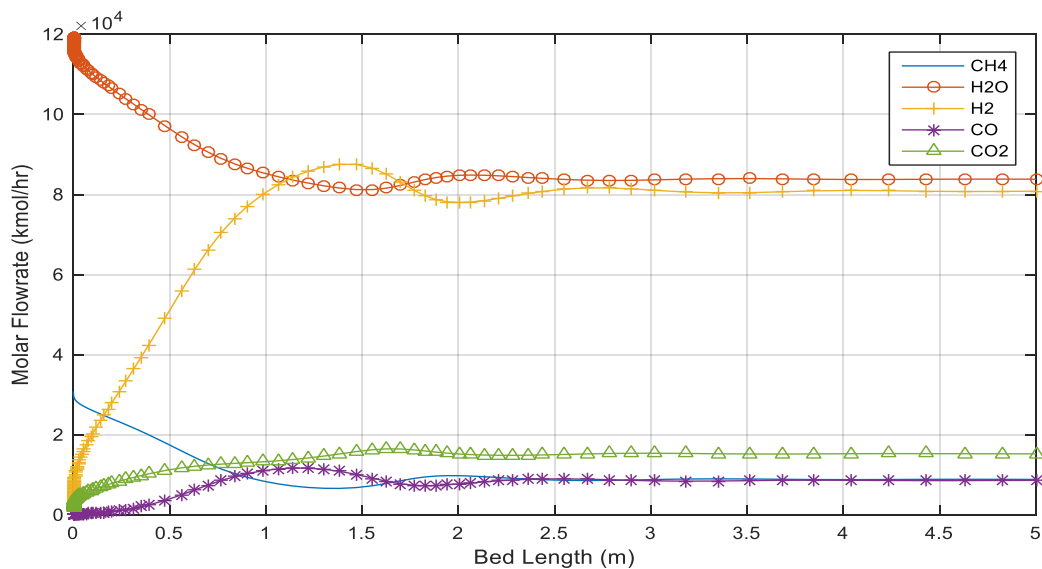


Figure 5: Molar flow rate of components across bed length

Figure 5 shows the component distribution across the bed length of the reformer. Mass balances of the five components were carried out using one dimensional heterogeneous modeling for fixed bed reactor. As expected, H<sub>2</sub> is produced at the expense of steam and methane. As shown in figure 5, the CO level was low throughout the length of the reactor, because the shift reaction goes to equilibrium easily as reported by Khomenko *et al.* However, the CO<sub>2</sub> fraction would not increase further over 11 meters, because the WGS reaction is exothermic, while the hydrogen content increases further because the methane steam reforming action is endothermic. It is also evident that CO is more than CO<sub>2</sub> at the reactor exit, which is the result of the WGS reaction being reversed at high temperature due to its exothermic nature.

The model was validated by comparing the result from the process plant with that predicted by the model. The model predicted a maximum conversion of about 0.8 and 0.32 for CH<sub>4</sub> and CO<sub>2</sub> compared to 0.86 and 0.31 for plant data respectively. The conversions are close and fall within the ranges of 0.3-0.4 for H<sub>2</sub>O and 0.78-0.87 for CH<sub>4</sub> as predicted by Mahmud *et al.*, 2016 and Hae-Guet *et al.*, 2019.

## Conclusion

The kinetic model for steam methane reforming process was successfully modelled and simulated for a fixed-bed reactor using a MATLAB model builder. The Model describes the behavior of all components (H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>) involved in the synthesis of hydrogen for the ammonia production process. The effects of process variables such as temperature, pressure and mass flowrate across the bed length on the yield of hydrogen was investigated. At temperature approximately 1130K and pressure between 40.25 to 39.45 bar, the conversion of H<sub>2</sub> and CO was favored and thereafter stabilizes. The model was validated by comparing the conversion rate of CH<sub>4</sub> and CO<sub>2</sub> from the process data and the model. The values are close and fall within the ranges of 0.3-0.4 and 0.78-0.87 for H<sub>2</sub> and CH<sub>4</sub> respectively as predicted by literatures.

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