

THE EFFECT OF DIFFERENT OPERATION CONDITIONS ON THE RATIO OF CO TO H₂ PRODUCED IN STEAM REFORMING PROCESS

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Abstract

Steam reforming of natural gas or naphtha using Nickel-Alumina catalyst is the most important process in the production of synthesis gas (H₂ + CO₂) and pure hydrogen. Synthesis gas is a very valuable raw material for the production of various chemicals such as hydrogen, methanol, and ethylene glycol. In this research, by modeling of a steam reforming reactor and using experimental data and solving the equations with the MATLAB software package, the effect of different operational conditions such as the ratio of steam to methane, temperature and pressure of inlet feed to the reactor have been investigated on the rate of produced CO and H₂ along the reactor. The results obtained from the simulation are in agreement with the data extracted from industrial units. The rate of production of CO and H₂ increases with increasing temperature along the reactor due to the endothermic nature of production reactions. Moreover, it was observed that with increasing pressure, according to Le Chatelier's principle, the trend of production reactions tend to the left-hand side and reduction of the rate of products. Hence the rate of produced CO and H₂ has been decreased.

Keywords: Steam Reforming Process, Heterogeneous Model, Reactor Model, Steam to Methane Ratio.

1. Introduction

Steam reforming of natural gas is an economical method of producing synthesis gas and generating hydrogen. Natural gas and its conversion to value-added products are of great importance. In this regard, the use of syngas is of great importance in the gas conversion industry. Various chemicals are produced by using syngas along with other related processes. The application of the Fischer-Tropsch synthesis process is to produce heavy hydrocarbons by using natural gas and production of syngas. With respect to increasing oil price and worldwide approach towards producing clean fuels, the Fischer-Tropsch process is justifiable and has attracted many investors. Syngas is a valuable raw material for the production of various chemicals such as methanol synthesis, Fischer-Tropsch synthesis, oxo synthesis, and iron ore regeneration, production of heavy alcohols, esters, ketones and variety of hydrocarbons. Some of these reactions are presented in Table 1 [1-2]:

The Syngas was originally produced from a mixture of coke, air and water vapor and was regarded but one of the most common and economical techniques to convert hydrocarbons since 1930. Within the hydrocarbons, the only production of light hydrocarbons is commercially economic. Production of natural gas, propane, and butane are of great importance, respectively. Nowadays, by using special catalysts, naphtha is regarded as feed. Low price and vast gas reserves, more purity of products, and less formation of coke on the surface of catalyst are the main reasons for natural gas conversion in syngas production. The process of conversion of natural gas is based on the catalytic reaction of hydrocarbon with the aid of a

reforming agent at high temperature. This reforming agent can be water vapor, carbon dioxide, oxygen, and or a mixture of them. The combination percentage of produced syngas depends on the type of hydrocarbon, reforming agent and its amount, operational condition, and the type of catalyst.

Table 1. Syngas consumption applications

Row	Process	Reactions
1	Methanol synthesis	$CO + 2H_2 \rightarrow CH_3OH$
2	Ethylene glycol synthesis	$2CO + 3H_2 \rightarrow HOCH_2CH_2OH$
3	Oxo synthesis	$CH_3CH \equiv CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO \rightleftharpoons \rightleftharpoons \rightleftharpoons, CH_3CH(CH_3)CHO$
4	Fischer-Tropsch synthesis	$8CO + 16H_2 \rightarrow C_8H_{16} + 8H_2O$
5	Iron Ore regeneration	$Fe_2O_3 + 1.5(H_2 + CO) \rightarrow 2Fe + 1.5(H_2O + CO_2)$ $Fe_3O_4 + 2(H_2 + CO) \rightarrow 3Fe + 2(H_2O + CO_2)$

The natural gas conversion process is mostly used to produce syngas with a small ratio of H₂/CO [4]. Major operational variables for this process are the ratios of H₂O/CH₄ and CO₂/CH₄ and temperature and pressure, and the major methane consumption reactions in this process are in the form of reactions (I) and (II) shown in Table 2 [5]. It is to be mentioned that the reactions above can be added and rewrite the reactions as (III) or (IV). Reaction (IV) is called dry reforming reaction.

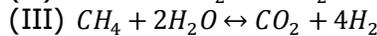
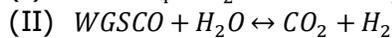
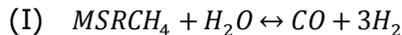
Table 2. Methane reaction in the vapor reforming process

No.	Reactions	ΔH_{298}^0 (KJ/mol)
I	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206.1
II	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41.15
III	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	+165.0
IV	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	+247.3

In this research, a one-dimensional heterogeneous model has been used to simulate a reactor of steam reforming unit and model equations solved by MATLAB software with ode 15s command. The simulation results are in agreement with the data extracted from industrial units.

2. Reactions and materials

Three main reactions of the process are as follows:



The experiments were carried out in the presence of Nickel/Alumina (Ni/Al₂O₃) at more than 500°C and pressure of approximately 30 bar and around 400 parallel tubes with an inside diameter of 10 cm and a length of 10 to 12 meters.

Froment *et al.* [9] introduced three reaction equations regarding three steam reforming process of methane (MSR):

1. The rate of transformation of methane to carbon monoxide

$$r_1 = \frac{\frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1} \right)}{(DEN)^2} \tag{1}$$

2. The rate of transformation of carbon monoxide to carbon dioxide

$$r_2 = \frac{\frac{k_2}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2} \right)}{(DEN)^2} \tag{2}$$

3. The rate of transformation of methane to carbon dioxide

$$r_3 = \frac{\frac{k_3}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_3} \right)}{(DEN)^2} \quad (3)$$

$$DEN = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + \left(\frac{K_{H_2O} p_{H_2O}}{p_{H_2}} \right) \quad (4)$$

The rate of formation of CO and CO₂ and also CH₄ consumption is equal to:

$$R_{CO} = r_1 - r_2 \quad (5)$$

$$R_{CO_2} = r_2 + r_3 \quad (6)$$

$$R_{CH_4} = r_1 + r_3 \quad (7)$$

The constants used in rate equations are obtained by the relations from reference [7]. As stated above, the reactor consists of many parallel tubes with the inside diameter of 10 cm and length of 11 m placed inside the furnace chamber that radiation and convection play the main roles in the heat transfer process.

3. Modeling of steam reforming reactor

In order to model the steam reforming reactor, the assumptions are Steady-state conditions, One-dimensional heterogenic model, Plug flow reactor (with respect to the ratio of length to diameter).

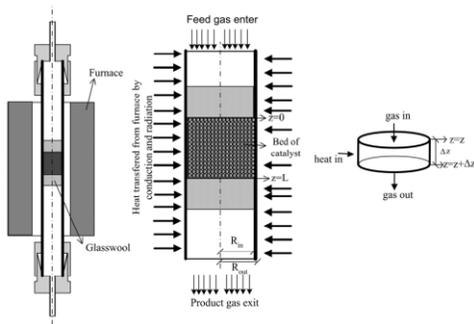


Figure 1 A cross-section of a fixed bed reactor for the transformation of methane to steam

All tubes are considered identical, and only one tube out of 450 is considered for modeling, Heat flux is constant from furnace side along the reactor, Ideal gas flow, Diffusion phenomena is ignored at all reactor directions, Coke formation is ignored. Figure 1 shows a cross-section of a fixed bed tubular reactor for which mass transfer equations, heat transfer, and momentum considered for an element are written for the distance between Z and Z + ΔZ.

Mass transfer equations can be written as follows:

$$\frac{dX_{CH_4}}{dz} = A_C \cdot \frac{\rho_b \cdot \eta_{CH_4} \cdot R_{CH_4}}{F_{CH_4}^0} \quad (8)$$

$$\frac{dX_{CO_2}}{dz} = A_C \cdot \frac{\rho_b \cdot \eta_{CO_2} \cdot R_{CO_2}}{F_{CH_4}^0} \quad (9)$$

Heat transfer equation can be written as follows:

$$\frac{dT}{dz} = \frac{1}{G_{mass} \cdot C_{p,overall}} \cdot \left(\frac{4HF}{d_i} + \rho_b \sum_{i=1}^3 (-\Delta H_i) \eta_i r_i \right) \quad (10)$$

Momentum equation:

$$\frac{dP}{dz} = - \frac{1.75 G_S (1-\epsilon)}{\phi_s D_p \epsilon^3 \rho_g} \quad (11)$$

And finally boundary layer condition:

At Z=0: X_{CH₄} = 0, X_{CO₂} = 0, P = P_{IN}, T = T_{IN}

Calculation of partial pressure of fractions in any reactor height (z): With assumption of the preliminary information:

Steam/CH₄ molar feed ratio=3.358; H₂/CH₄ molar feed ratio=0.122;

CO₂/CH₄ molar feed ratio=0.056; N₂/CH₄ molar feed ratio=0.164

To calculate partial pressure of fractions following equations are used:

$$\delta = \frac{1 + \theta_{H_2O} + \theta_{CO} + \theta_{CO_2} + \theta_{H_2}}{P_T}$$

$$\theta_j = \frac{F_j^0}{F_{CH_4}^0}, j: CH_4, CO_2, H_2O, CO, H_2, P_T = total\ pressure \quad (12)$$

With the above definitions, the partial pressure of fractions is calculated through the following relationships:

$$P_{CH_4} = (1 - X_{CH_4})/\delta \tag{13}$$

$$P_{H_2O} = (\theta_{H_2O} - X_{CH_4} - X_{CO_2})/\delta \tag{14}$$

$$P_{CO} = (X_{CH_4} - X_{CO_2})/\delta \tag{15}$$

$$P_{CO_2} = (\theta_{CO_2} + X_{CO_2})/\delta \tag{16}$$

$$P_{H_2} = (\theta_{H_2} + 3 \cdot X_{CH_4} - X_{CO_2})/\delta \tag{17}$$

$$P_{CO_2} = \theta_{N_2}/\delta \tag{18}$$

Having obtained partial pressure, partial molar, and partial mass of fractions can be calculated at any height.

$$y_j = P_j/p_T, x_j = (y_j * MW_j * totalmolarflowrate) / (totalmassflowrate) \tag{19}$$

In the above relationships, at any (z), total molar flow rate, methane transformation, and carbon dioxide production percentages are obtained by mass equilibrium equations, and the total pressure is obtained through momentum equation. Total mass flow rate is constant and can be used from usual assumptions. The reactions heat at base temperature (298 °K) is given as follows [9]:

$$\Delta_r H_{298k, reaction1}^0 = 206310 J \cdot mol^{-1} \quad \Delta_r H_{298k, reaction2}^0 = -41200 kJ \cdot mol^{-1}$$

$$\Delta_r H_{298k, reaction3}^0 = 165110 kJ \cdot mol^{-1}$$

As is observed, the inlet pressure and temperature are 29 bar and 793.15K. By using HYSYS software, the inlet gas and steam flow rate are obtained as: total mass flow rate=447.6 kg/hr.

The catalyst specifications are: $D_p = 0.0173$ m, (pellet equivalent diameter); ϵ = Catalyst bed void fraction = 0.6; $\rho_b = 1362$ kg cat./m³r (catalyst bed density); $\rho_s = 2355.2$ kg cat./m³s (solid catalyst density); $\phi_s = 0.6563$ (pellet sphericity).

By using MATLAB functions, the four differential equations (mass balance, energy, and momentum) have been solved. The differential equations of this model are stiff type, and therefore ode15s order used to solve it.

4. Results and discussion

4.1. The effect of inlet steam to methane ratio (S/C)

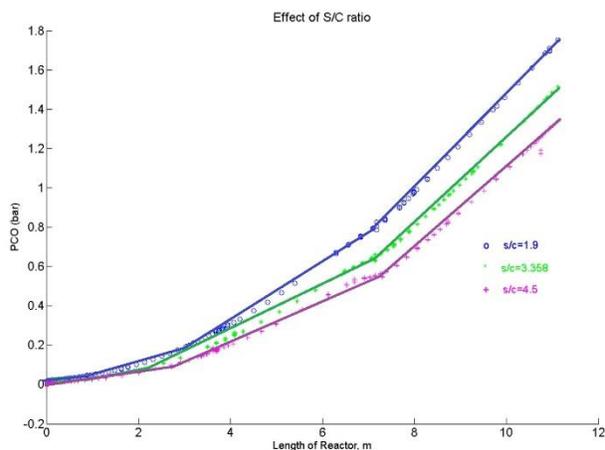


Figure 2 The investigation of the effect of steam to methane ratio on the partial pressure of CO along the reactor

The ratio of steam to methane is one of the most important parameters affecting the MSR process. With respect to constant inlet gas flow rate, the change in the ratio of steam to methane is the change in steam flow rate.

Figure 2 shows the effect of the ratio of steam to methane on the partial pressure of produced CO along the reactor. For three ratios S/C= 2.9, 3.358, and 4.5.

With increasing height, the partial pressure of CO will increase in the first reaction due to production, but with increasing steam to methane ratio, the partial pressure of carbon monoxide decreases.

4.2. The effect of inlet feed temperature:

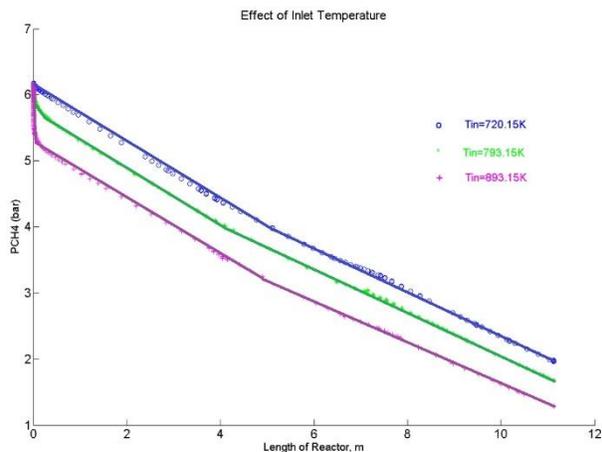


Figure 3. The investigation of the effect of inlet temperature on the partial pressure of CH₄ along the reactor

Moreover, with increasing reactor height, the partial pressure of CO₂ increases due to advances of reactions 2 and 3. Meanwhile, with increasing inlet temperature, due to the endothermic nature of the dominant reaction in CO₂ production, the partial pressure decreases. Due to a higher concentration of methane, the increasing slope of partial pressure in the beginning 6 meters of the reactor is higher, and in the end sections, the amount of methane for transformation to CO₂ is very low.

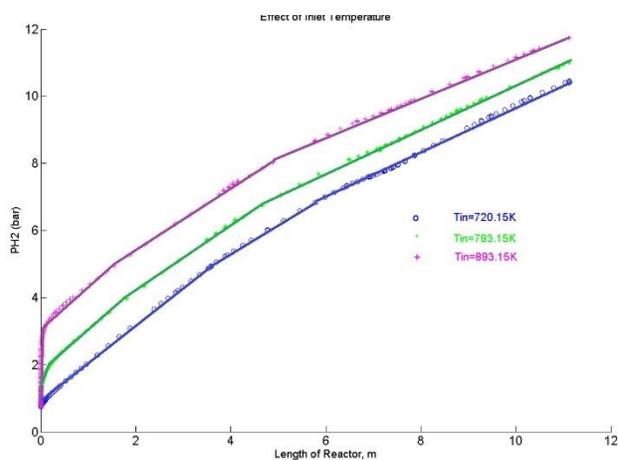


Figure 4. The investigation of the effect of inlet temperature on the partial pressure of H₂ along the reactor

4.3. The effect of inlet pressure

Total inlet pressure used in the simulation is 29 bars that have been considered as reference. Products distribution and process parameters are drawn at two pressures about 10 bars higher and lower.

Figure 5 shows the effect of inlet pressure on methane molar fraction along the reactor. For three inlet pressure P_{in} = 20, 29, and 39 bar:

The primary inlet temperature used in the simulation is 793.15 °K (52 °C) that is considered as reference. For comparison of production distribution, two curves have been drawn at two temperatures around 100 °C higher and lower. Figure 3 shows the effect of inlet temperature on the partial pressure of produced CH₄ along the reactor. For three inlet temperature T_{in} = 720.15, 793.15, and 893.15°C.

The trends of reduction in the partial pressure of methane along the reactor are similar at all three inlet temperatures. Meanwhile, with increasing temperature, due to the endothermic nature of reactions 1 and 3 in methane transformation, the partial pressure of methane decreases.

Figure 4 shows the effect of inlet temperature on the partial pressure of produced H₂ along the reactor. For three inlet temperature T_{in} = 720.15, 793.15, and 893.15°C.

As is observed, with increasing reactor height, the partial pressure of H₂ increases due to advances of reactions 2 and 3. Meanwhile, with increasing inlet temperature, due to the endothermic nature of the dominant reaction in H₂ production, the partial pressure decreases. Also, with increasing reactor height, the partial pressure of CO will increase due to advances of reactions 1 and 3. Furthermore, with increasing inlet temperature, due to the endothermic nature of the dominant reaction in CO production, the partial pressure decreases.

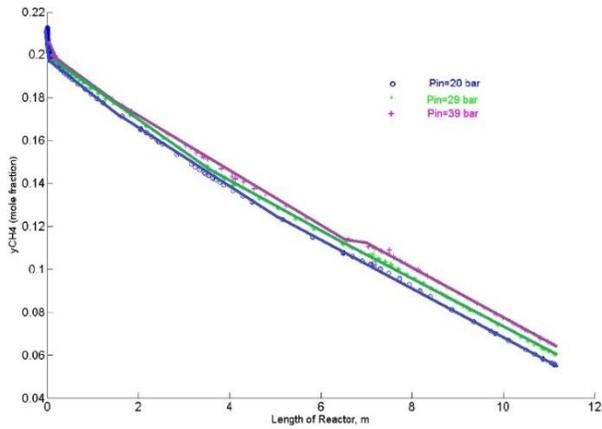


Figure 5. The investigation of the effect of pressure on methane fraction along the reactor

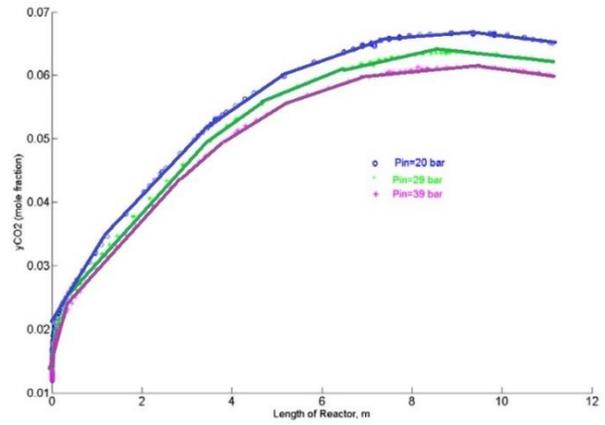


Figure 6. The investigation of the effect of inlet pressure on CO₂ molar fraction along the reactor

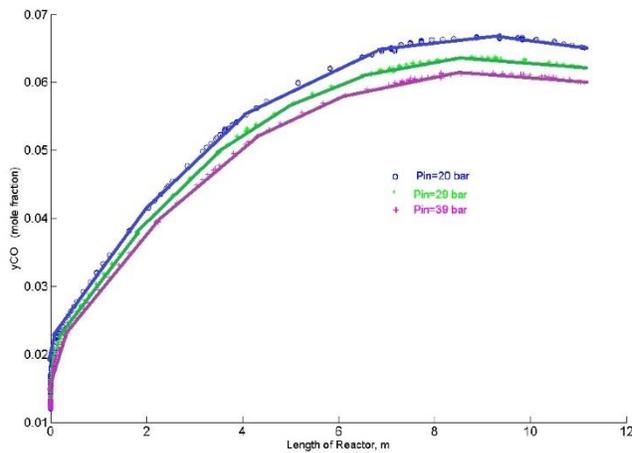


Figure 7. The investigation of the effect of inlet pressure on CO molar fraction along the reactor

The results show that along with the reactor, methane molar fraction decrease due to methane consumption. Meanwhile, the increase or decrease of 10 bars in the inlet pressure, has a negligible effect on methane transformation due to equal stoichiometry of both sides of reactions and the curves do not change much. Therefore, since pressure increase in equilibrium reactions lead to tending the reactions towards fewer moles, reactions tend to the left-hand side, and as a result, less methane is transformed.

(The higher pressure curve is at a higher level). Figure 6, 7 and 8 show the effect of inlet pressure on CO₂, CO and H₂ molar fraction of produced H₂ along the reactor. For three inlet pressure $P_{in} = 20, 29,$ and 39 bar:

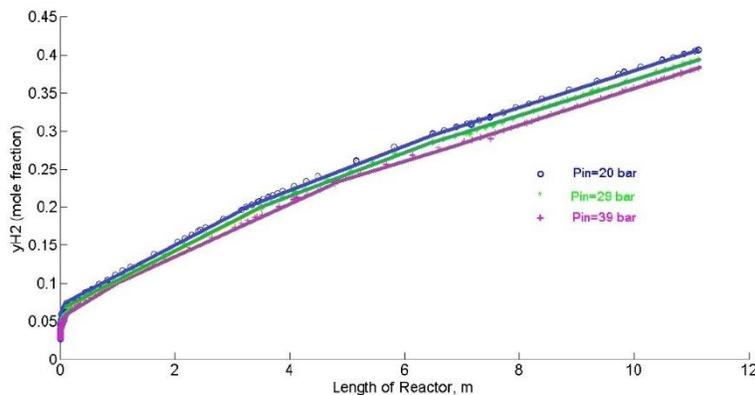


Figure 8. The investigation of the effect of inlet pressure on H₂ molar fraction along the reactor

Along the reactor, the molar fractions of CO, CO₂, and H₂ increase because of the production of CO, CO₂, and H₂. As described earlier, pressure increase works in favor of products transformation to reactants (left-hand side of equilibrium reactions) and therefore decreases.

5. Conclusion

In this research, a one-dimensional heterogeneous model has been used to simulate a reactor of steam reforming unit and model equations solved by MATLAB software with ode 15s command. As it can be observed from the results, along the reactor, the rate of CO and H₂ have been increased due to production reactions, but with increasing the ratio of steam to methane, the rate of CO and H₂ have been decreased due to the reduction of methane as reacting fraction. On the other hand, the rate of production of CO and H₂ increases with increasing temperature along the reactor due to the endothermic nature of production reactions.

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