

Modeling and Simulation of Methanation Catalytic Reactor in Ammonia Plant

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Abstract: The methanation reactor in the state company of fertilizers south region in Basrah is modeled and simulated. The one-dimension heterogeneous catalytic reaction model is predicated. The mole fraction, temperature, and pressure profiles are predicted by using a such model. Also, the profile of the effectiveness factor of the reactions are evaluated and it is reported that it decrease with the length of reactor. The results of simulated model show a good compatibility with the available industrial data.

keywords: Methanation, Modeling, Simulation, heterogeneous.

1. INTRODUCTION

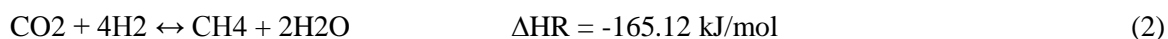
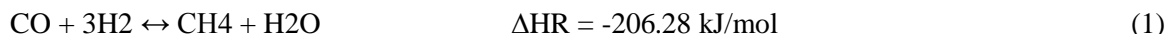
Methanation reactor plays an important role in ammonia production units. It is placed after the removal carbon dioxide section. Also, it has an important role in fulfils the process of oxides of the carbon to methane conversion.

Methanation synthesis is one of the process stages which are a catalytic exothermal in temperature range between 473 and 673 K and pressure from 20 to 70 bar. The syngas produced (H₂ and CO) enters a methanation reactor with high feed H₂/CO ratio ≥ 3 where it is converted into CH₄. This methane can be used to produce synthesis gas as recycle stream to steam reforming section [1-6].

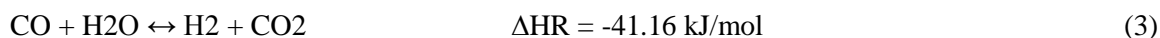
Methanation reactions are the reverse methane steam reforming reactions, which generally carried out over nickel catalysts. Therefore, nickel was investigated as an effective catalyst for oxides carbon methanation [5].

The industrial production of ammonia is usually performed by using an iron catalyst, which may be strongly poisoned by oxygen compounds. Therefore, it is important to remove the residual carbon monoxide and carbon dioxide from the synthesis gas. This is done by methanation reactions, performed by a nickel catalyst upstream the main reactor.

The principle of catalytic synthetic production of methane from oxides of the carbon and hydrogen was discovered such as are the main methanation reactions [2] [3]:



Both reactions are very exothermic and involve a decreasing in the number of moles. However, The reaction called Water Gas Shift (WGS) occurs simultaneously whenever active catalysts are used:



In the present study, the composition of gases, temperature, pressure, and the profiles of the effectiveness factor have been predicated with a one-dimensional heterogeneous catalytic reaction model of methanation reactor which located in state company of fertilizers south region in Basrah

2. MODELING OF METHANATION REACTOR

The following assumptions are taken into account for modeling the industrial methanation reactor.

1. Steady state operation

2. Ideal gas behavior
3. Adiabatic operation
4. Concentration and temperature gradients in radial direction are ignored.

2.1. Kinetic of Reactions

The equations of kinetics rate for steam methane reforming reaction, water gas shift, and carbon dioxide reforming reactions are adopted from Xu and Froment [7].

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

$$R_2 = \frac{k_2}{P_{H_2}} \left[P_{CO} \times P_{H_2O} - \left(\frac{P_{H_2} \times P_{CO_2}}{K_{e,2}} \right) \right] \times \frac{1}{DEN^2}$$

$$R_3 = \frac{k_3}{P_{H_2}^{3.5}} \left[P_{CH_4} \times P_{H_2O}^2 - \left(\frac{P_{H_2}^4 \times P_{CO_2}}{K_{e,3}} \right) \right] \times \frac{1}{DEN^2}$$

Where

$$DEN = 1 + K_{ad,CO} \times P_{CO} + K_{ad,H_2} \times P_{H_2} + K_{ad,CH_4} \times P_{CH_4} + K_{ad,H_2O} \times P_{H_2O} / P_{H_2}$$

For methanation

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

$$R_2 = \frac{k_2}{P_{H_2}} \left[P_{CO} \times P_{H_2O} - \left(\frac{P_{H_2} \times P_{CO_2}}{K_{e,2}} \right) \right] \times \frac{1}{DEN^2}$$

$$R_3 = \frac{k_3}{P_{H_2}^{3.5}} \left[P_{CH_4} \times P_{H_2O}^2 - \left(\frac{P_{H_2}^4 \times P_{CO_2}}{K_{e,3}} \right) \right] \times \frac{1}{DEN^2}$$

The reaction rate constant can be evaluated by using Arrhenius equation as follows :

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

The equilibrium constants can be expressed by using the following equations [8]:

$$K_{e,1} = \text{EXP} \left(\frac{-26830}{T} + 30.114 \right)$$

$$K_{e,2} = \text{EXP} \left(\frac{4400}{T} - 4.036 \right)$$

$$K_{e,3} = K_{e,1} \cdot K_{e,2}$$

2.2. Mass, Energy and Momentum Balance Equations

The rate of consumption or formation of individual gas species based on reactions in equations (1) to (3) is determined by summation up the reaction rates of those species in the three reactions [8 and 9]:

$$\frac{\partial F_{(CH_4)}}{\partial l} = -\rho_C (1 - \varepsilon_B) A (\eta_1 \cdot R_1 + \eta_3 \cdot R_3)$$

$$\frac{\partial F_{(CO)}}{\partial l} = \rho_c(1 - \varepsilon_B)A.(\eta_1.R_1 - \eta_2.R_2)$$

$$\frac{\partial F_{(CO_2)}}{\partial l} = \rho_c(1 - \varepsilon_B)A.(\eta_2.R_2 + \eta_3.R_3)$$

For methanation

$$\frac{\partial F_{(CH_4)}}{\partial l} = \rho_c(1 - \varepsilon_B)A.(\eta_1.R_1 + \eta_3.R_3)$$

$$\frac{\partial F_{(CO)}}{\partial l} = -\rho_c(1 - \varepsilon_B)A.(\eta_1.R_1 + \eta_2.R_2)$$

$$\frac{\partial F_{(CO_2)}}{\partial l} = \rho_c(1 - \varepsilon_B)A.(\eta_2.R_2 - \eta_3.R_3)$$

The equation of energy balance can be derived as follows [8, 9 and 10]:

$$F_g C_{P,g} \cdot \frac{\partial T}{\partial l} = \sum_{k=1}^3 (-\Delta H_{r,k}^\circ) \cdot \eta_k \cdot R_k \cdot \rho_c (1 - \varepsilon_B) \cdot A$$

Pressure drop with the axial direction in the fixed bed is described by the Ergun equation [10]:

$$\frac{\partial P}{\partial l} = -\left(\left(\frac{150(1 - \varepsilon_B)^2 \cdot \mu_g \cdot u_g}{\varepsilon_B^3 \cdot D_s^2} \right) + \left(\frac{1.75(1 - \varepsilon_B) \rho_g \cdot u_g^2}{\varepsilon_B^3 \cdot D_s} \right) \right)$$

3. EFFECTIVENESS FACTOR ANALYSIS

The actual reaction rate is affected by the molecular diffusion into the micro pore which is inside the catalyst in the heterogeneous reaction. Therefore, to measure how much the reaction rate is lowered because of the resistance to pore diffusion, the effectiveness factor can be defined as follows [10]:

$$\eta = \frac{\text{actual mean reaction rate within pore}}{\text{rate if not slowed by pore diffusion}}$$

or

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

Thiele modulus φ can be defined as the ratio of reaction rate to the diffusion rate. If the catalyst pellet is sphere, the Thiele modulus can be defined by previous studies as follows [11,12]:

$$\varphi_k = \frac{D_s}{6} \sqrt{\frac{k_{vk} \cdot \rho_b \cdot (1 + k_{e,k})}{k_{e,k} \cdot D_{e,k}}}$$

The effective diffusion coefficient is expressed by the bellow equation:

$$D_{e,k} = \frac{1}{\frac{1}{D_{kn,i}} + \frac{1}{D_{i,mix}}}$$

4. RESULTS AND DISCUSSION

Figure (1) shows the profile of mole fraction of each component with the length of the reactor. The mole fraction of methane and water are rapidly increased until 1 m of the length of the reactor. Then above 1m, it is slightly increased because the mole fraction of CO reduced to reach zero at 0.27 m of the length of the reactor.

The mole fraction of CO₂ reduced with the length of the reactor because it is consumed by reaction 2.

Figure 2 shows the temperature of the bulk of gases increases with length of the reactor because of the exothermic behavior of three reactions.

The pressure of gases is dropped with the axial distance of reactor ($\Delta p=0.21$ bar) because of the friction between particles of gases, particles of gases with pellets of catalyst, and with wall of the reactor as shown in figure 3.

Figure 4 shows the effectiveness factor increases in the beginning of the reactor because of high concentration of reactants. After that, the effectiveness factor decreases because the concentration of CO reduces to zero and the reaction number 1 and 2 are reversed.

The simulation results and reactor data are compared as shown in table 1. A very good agreement between actual and theoretical results where the relative error is found less than 2%

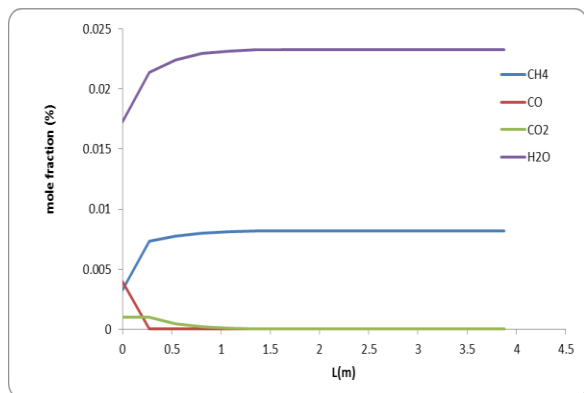


Fig1. The profile of mole fractions of gases with the length of the reactor

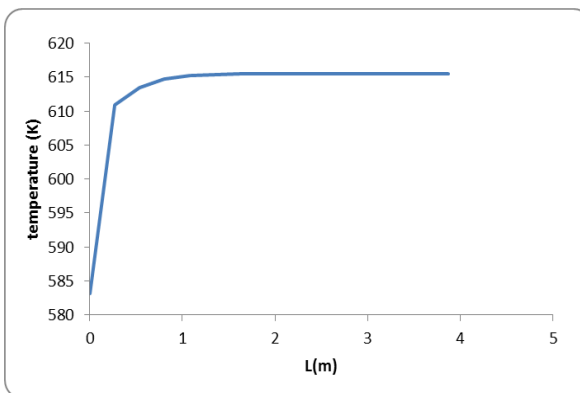


Fig2. The profile of the temperature of gases with the length of the reactor

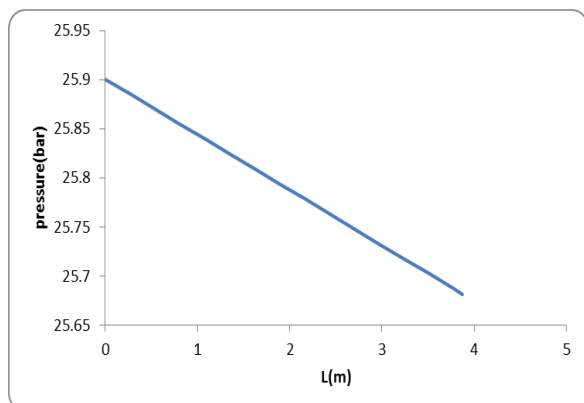


Fig3. The profile of pressure of gases with the length of reactor

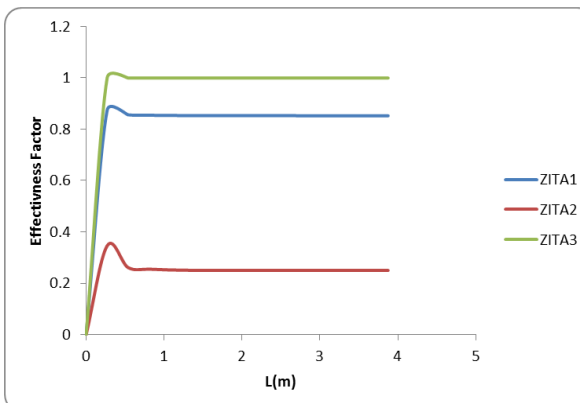


Fig4. The profile of Effectiveness factor with the length of reactor

Table1. The actual and theoretical results for methanation reactor

Component	Input flow rate (kmol/h)		Output flow rate (kmol/h)	
	actual	theoretical	actual	theoretical
CH ₄	16.7977	41.85341396	42.586	41.85341396
H ₂ O	89.0564	119.1721082	110	119.1721082
H ₂	3786.8	3706.572864	3704.32	3706.572864
CO	20.68	0	0	0
CO ₂	5.06	5.7464E-06	0	5.7464E-06
N ₂	1236.49	1236.49	1236.49	1236.49
Ar	14.71	14.71	14.71	14.71

5. CONCLUSIONS

The simulation results show a good agreement with actual data of methanation reactor. Methane and steam are rapidly increased at the beginning of the reactor while flow rate of carbon monoxide and carbon dioxide reduces to reach zero. The temperature of gases is increased with the reactor length and the pressure is dropped to 0.21 bar. The effectiveness factor reduces with the axial distance of the reactor. This simulation model shows a high reliability for the design of an industrial methanation reactor.

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