Study of chemical reactions effect on the design and the performance of an industrial secondary reformer reactor in the fertilizers plants

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Abstract: This paper will discuss and analyze the effect of chemical reactions number on the design and performance of the industrial secondary reformer reactor. The secondary reformer reactor is a large-scale unit in the Ammonia production plants. The secondary reformer reactor operation is adjusted to achieve the required stoichiometric ratio of Nitrogen and Hydrogen necessary for ammonia production. The Carbon Dioxide Reforming reaction equation in the catalyst bed of secondary reformer reactor has been investigated for two models A and B. The comparative study between the two models is carried out relative to the same operation conditions. The two models have been checked successfully against data available in the industrial secondary reformer reactor in the State Company of Fertilizers South Region in the Basra/Iraq. The theoretical results of model A are closer to the industrial plant data than model B.

Key words: Fertilizers and Ammonia Plants, modeling and simulation, Autothermal Reformer reactor, steam reforming reactions, catalysis, Hydrogen production.

1. Introduction

The Ammonia plant is characterized with high temperatures, pressures and content of explosion gases such as (natural gases and Hydrogen). The secondary reformer in Ammonia plant is a process in which partially converted process gases from a tubular steam reformer by the internal combustion and the catalyst reforming. The secondary reformer reactor is used to produce a final synthesis gas having hydrogen to nitrogen mole ratio of 3 to 1. In the secondary reformer reactor, the process gases is mixed with compressed air that has been preheated to about 550°C. The combustion of the oxygen in the air produces high temperature in this area which, using to reforming of methane, while the nitrogen is required for the eventful synthesis of ammonia product. The Reformat gases leaving the secondary reformer is then cooled to 350°C in a waste heat boiler, where the operation conditions of this reactor are listed in (A.A.AL-Dhfeery and A.A.Jassem, 2012). The overall heat of reactions will be endothermic in catalyst bed, and external heat is necessary. This heat is provided from exothermal reactions in combustion zone, when the reaction is exothermal it takes place in adiabatic reactors. The temperature is obtained by introducing air, which also provides the nitrogen for ammonia synthesis. Secondary Reformer is product a mixture of hydrogen, nitrogen, carbon monoxide, carbon dioxide, steam, and very low methane content as shown in figure 1. The present search aims to compare between the two models (A) and (B) at the same operation conditions to show the effect of Carbon Dioxide Reforming reaction equation on the design and the performance of the secondary reformer reactor relative to Basra Fertilizers Plant, the originality of the work lies in this proposal. While, Each model was discussed by various researchers alone to study the operation conditions, redesign or
evaluated the performance of secondary reformer reactor. Some researchers such as Ali AL-Dhfeery and Ala’a Jassem, Akbar Zamanian et.al, J.Pina and D.O.Borio, S.Vaccaro et.al, and D.L.Hoang et.al were used the Model (A). Whereas, Model (B) was used by Some of other such as Kayvan Khorsand and Khadijeh Deghan, K.Vakhshouri and M.Hashemi, Yong Ho Yu , and Yong Ho Yu and Mihail H.Sosna. Modeling and simulation of the catalytic reforming reactions of methane over nickel catalyst (Ni/MgAl₂O₄) RKS-2 in the secondary reformer reactor are studied for two Models A and B to investigate the effecting of chemical reactions number on the design and the performance of reactor.

Figure 1: layout of the components distribution around the industrial secondary reformer reactor streams in Basra Fertilizer Plant, where the \( F_{\text{Tot}} \) is the total molar flowrate of combustion chamber (Kmol/hr)

2. Mathematical model

In most ammonia plants, the secondary reformer reactor consists of a refractory-lined pressure vessel with a burner, combustion chamber and catalyst bed as follows:

2.1 The combustion chamber model

In the combustion chamber, no kinetics was considered. The oxidation reactions in this zone were assumed to take place instantaneously, and all oxygen reacted, and hence no need for a catalyst. The atomic material and energy balances can calculated as shown in A.A.AL-Dhfeery and A.A.Jassem, (2012). The chemical reactions of combustion chamber can be assumed as

\[
\begin{align*}
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} \quad \Delta H_r^\circ = -242 \text{ KJ/mol} \\
\text{CH}_4 + \frac{3}{2} \text{O}_2 & \rightarrow \text{CO} + 2\text{H}_2\text{O} \quad \Delta H_r^\circ = -519.760 \text{ KJ/mol}
\end{align*}
\]
2.2 Catalyst bed model

In this study, the catalyst bed, is investigated the model of fixed bed reactor based on the reactions kinetics of Froment & Xu. Anyway, two models have been examined in this section (catalyst bed) to explain the effecting of the Carbon Dioxide Reforming reaction equation on the design and performance of the catalyst bed of industrial secondary reformer reactor.

where, the first model (A) deals with three chemical reactions as follows

\[
\begin{align*}
CH_4 + H_2O &\leftrightarrow CO + 3H_2 \quad \text{(Steam Methane Reforming)} \\
CO + H_2O &\leftrightarrow CO_2 + H_2 \quad \text{(Water Gas Shift)} \\
CH_4 + 2H_2O &\leftrightarrow CO_2 + 4H_2 \quad \text{(Carbon Dioxide Reforming)}
\end{align*}
\]

While, the second model (B) deals with two chemical reactions inside the catalyst bed of the secondary reformer as follows

\[
\begin{align*}
CH_4 + H_2O &\leftrightarrow CO + 3H_2 \quad \text{(Steam Methane Reforming)} \\
CO + H_2O &\leftrightarrow CO_2 + H_2 \quad \text{(Water Gas Shift)}
\end{align*}
\]

The reactions kinetic of two models on a Ni/MgAl₂O₄ catalyst are based on a Langmuir–Hinshelwood reactions mechanism by Froment and Xu which, the reactions rates expressions can be described by the following equations

For Steam Methane Reforming reaction (S.M.R)

\[
R_1 = \frac{k_1}{P_H^{2.5} \cdot DEN^2} \left[ P_{CH_4} \cdot P_{H_2O} - \left( P_{H_2}^{3} \cdot P_{CO} / K_{e,1} \right) \right] \quad (8)
\]

Rate of reaction for Water Gas Shift reaction (W.G.S):

\[
R_2 = \frac{k_2}{P_H^{2.2} \cdot DEN^2} \left[ P_{CO} \cdot P_{H_2O} - \left( P_{H_2} \cdot P_{CO2} / K_{e,2} \right) \right] \quad (9)
\]

And, the reaction rate for Carbon Dioxide Reforming reaction (C.D.R):

\[
R_3 = \frac{k_3}{P_H^{3.5} \cdot DEN^2} \left[ P_{CH_4} \cdot P_{H_2O}^{2} - \left( P_{H_2}^{4} \cdot P_{CO2} / K_{e,3} \right) \right] \quad (10)
\]

where the \( R_k \) is the rate of reaction for reaction \( k \) (Kmol/Kg\textsubscript{cat}.hr), the \( k_k \) is the constant of reaction rate for reaction \( k \) (According to Arrhenius constant), the \( K_{e,k} \) is the equilibrium constant for reaction \( k \) (bar⁻²) (except reaction number 2 dimensionless unit), the DEN is the denominator in the expressions for the reaction rates (Dimensionless unit), the \( P \) is the pressure of gases (Bar).

where, Denominator (DEN) is defined by the following equation

\[
DEN = 1 + K_{ad-CO} \times P_{CO} + K_{ad-H_2} \times P_{H_2} + K_{ad-CH_4} \times P_{CH_4} + K_{ad-H_2O} \times P_{H_2O} / P_H \quad (11)
\]

where the \( K_{ad,i} \) is the adsorption coefficient of i-component (According to unit of \( A_{ad,i} \)).
The adsorption coefficients can be expressed by using the following equation as noted by Vant’ Hoff equation:

\[ K_{ad,i} = A_{ad,i} \times EXP \left( \frac{-\Delta H_{ad,i}}{R_g T} \right) \]  \hspace{1cm} (12)

Where the \( A_{ad,i} \) is the pre-exponential factor for adsorption of i-component (Bar\(^{-1}\)) except steam (Dimensionless unit), the \( \Delta H_{ad,i} \) is the adsorption enthalpy for i-component (KJ/mol), the \( R_g \) is the universal gas constant (8.314\times10^{-3}) (KJ/mol.K), the \( T \) is the temperature (K). The pre-exponential factors for adsorption and the adsorption enthalpies are quoted from Froment and Bischoff in table 1.

The equilibrium constants can be evaluated by using the following equations:

\[ K_{c,1} = EXP \left( \frac{-26830}{T} + 30.114 \right) \]  \hspace{1cm} (13)

\[ K_{c,2} = EXP \left( \frac{44000}{T} - 4.036 \right) \]  \hspace{1cm} (14)

\[ K_{c,3} = K_{c,1} \times K_{c,2} \]  \hspace{1cm} (15)

Also, the reaction rate constant can be estimated using the following equation as noted by Arrhenius:

\[ k_k = A_k \times EXP \left( \frac{-E_k}{R_g T} \right) \]  \hspace{1cm} (16)

Where the \( A_k \) is the arrhenius constant for reaction k (According to chemical reaction equation k), the \( E_k \) is the activation energy for the reaction k (KJ/mol). The Arrhenius constants and the activation energies are also quoted from Froment and Bischoff in table 1.

**Table 1: The kinetic parameters of S.M.R, W.G.S, C.D.R reactions**

<table>
<thead>
<tr>
<th>Arrhenius Expression</th>
<th>Parameter</th>
<th>Arrhenius constants ( A_k ) (kmol/kg(_c).hr)</th>
<th>Activation Energies ( E_k ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.M.R</td>
<td>4.2248E+15 (Bar(^{0.5}))</td>
<td>240.1</td>
<td></td>
</tr>
<tr>
<td>W.G.S</td>
<td>1.955E+06 (Bar(^{-1}))</td>
<td>67.13</td>
<td></td>
</tr>
<tr>
<td>C.D.R</td>
<td>1.0202E+15 (Bar(^{0.5}))</td>
<td>243.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Van't Hoff Expression</th>
<th>Parameter</th>
<th>Pre-Exponential Factor ( A_{ad,i} )</th>
<th>Adsorption enthalpy ( \Delta H_{ad,i} ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>6.65 E-04 (Bar(^{1}))</td>
<td>-38.28</td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>1.77 E+05 (-)</td>
<td>88.68</td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>6.12 E-09 (Bar(^{1}))</td>
<td>-82.9</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>8.23 E-05 (Bar(^{1}))</td>
<td>-70.65</td>
<td></td>
</tr>
</tbody>
</table>

The mass balance for i-component and heat balance in an axial direction based on an adiabatic one-dimensional heterogeneous catalytic reaction model.
2.2.1 Model A

The changes for each component along the reactor length can be calculated by the following equations

\[
\frac{\partial F_{(i)} / \partial \ell}{\partial t} = -\rho_c (1 - \varepsilon_b) A (\eta_1, R_1 + \eta_2, R_2)
\]

(17)

\[
\frac{\partial F_{(H_2O)} / \partial \ell}{\partial t} = -\rho_c (1 - \varepsilon_b) A (\eta_1, R_1 + \eta_2, R_2 + 2\eta_3, R_3)
\]

(18)

\[
\frac{\partial F_{(H_2)} / \partial \ell}{\partial t} = \rho_c (1 - \varepsilon_b) A (3\eta_1, R_1 + \eta_2, R_2 + 4\eta_3, R_3)
\]

(19)

\[
\frac{\partial F_{(CO)} / \partial \ell}{\partial t} = \rho_c (1 - \varepsilon_b) A (\eta_1, R_1 - \eta_2, R_2)
\]

(20)

\[
\frac{\partial F_{(CO_2)} / \partial \ell}{\partial t} = \rho_c (1 - \varepsilon_b) A (\eta_2, R_2 + \eta_3, R_3)
\]

(21)

where the \( F_i \) is the molar flowrate of i-component (Kmol/hr), the \( \ell \) is the axial coordinates (m), the \( \rho_c \) is the density of catalyst (kg/cm\(^3\)), the \( \varepsilon_b \) is the porosity of packed bed (m\(^3\_void/m\(^3\)), the \( \eta_k \) is the reaction effectiveness factor for reaction k (dimensionless unit), the \( A \) is the cross section area (m\(^2\)).

The change of temperature along the reactor length can be described as follows:

\[
\frac{\partial T_s}{\partial \ell} = \frac{\rho_c (1 - \varepsilon_b) A (\eta_1, R_1, (-\Delta H_{r,1}^f) + \eta_2, R_2, (-\Delta H_{r,2}^f) + \eta_3, R_3, (-\Delta H_{r,3}^f))}{F_{CH_4} C_{P,CH_4} + F_{H_2O} C_{P,H_2O} + F_{H_2} C_{P,H_2} + F_{CO} C_{P,CO} + F_{CO_2} C_{P,CO_2} + F_{N_2} C_{P,N_2} + F_{Ar} C_{P,Ar}}
\]

(22)

where the \( \Delta H_{r,ik}^f \) is the standard heat of reaction k (KJ/mol), the \( C_p \) is the specific heat capacity (KJ/kg.K).

The change of catalyst surface temperature along the reactor length can be found as follows [9]:

\[
T_s = T_s^0 + \left[ \frac{\rho_c (1 - \varepsilon_b) (\eta_1, R_1, (-\Delta H_{r,1}^f) + \eta_2, R_2, (-\Delta H_{r,2}^f) + \eta_3, R_3, (\Delta H_{r,3}^f))}{6, (1 - \varepsilon_b) h} \right]
\]

(23)

Where the \( T_s^0 \) is the temperature of catalyst surface(K), the \( h \) is the heat transfer coefficient (KJ/m\(^2\)K.hr) \( h = (\text{Nu.K}) / D_s \) where the \( \text{Nu} \) is the Nessult number, the \( K \) is the Thermal conductivity of gases (W/m.K). The \( D_s \) is the equivalent pellet diameter (m). This is defined as the diameter of a sphere with the same external surface area per unit volume of the catalyst pellet

\[
D_s = \frac{0.5 \times (R_i - N \times R_o)^2 H_p}{(R_i - N \times R_o)^2 + R_o \times H_p}
\]

where the \( R_i \) is the radius of the hole in the catalyst pellet of cylindrical shape (m), the \( R_o \) is the External radius of catalyst pellet of cylindrical shape (m), the \( H_p \) is the height of pellet (m), the \( N \) is the number of holes in the pellet of catalyst.

2.2.2 Model B

The mass balance of i-component along the reactor length can be calculated by the following equations:

\[
\frac{\partial F_{(i)} / \partial \ell}{\partial t} = -\rho_c (1 - \varepsilon_b) A (\eta_1, R_1)
\]

(24)
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\[
\frac{\partial F_{(H_2O)}}{\partial \ell} = -\rho_C(1-\epsilon_B)A(\eta_1R_1 + \eta_2R_2) \tag{25}
\]

\[
\frac{\partial F_{(H_2)}}{\partial \ell} = \rho_C(1-\epsilon_B)A(3\eta_1R_1 + \eta_2R_2) \tag{26}
\]

\[
\frac{\partial F_{(CO)}}{\partial \ell} = \rho_C(1-\epsilon_B)A(\eta_1R_1 - \eta_2R_2) \tag{27}
\]

\[
\frac{\partial F_{(CO_2)}}{\partial \ell} = \rho_C(1-\epsilon_B)A(\eta_2R_2) \tag{28}
\]

The temperature of gases has been given

\[
\frac{\partial T_g}{\partial \ell} = \frac{\rho_C(1-\epsilon_B)A(\eta_1R_1(-\Delta H^0_{r,1}) + \eta_2R_2(-\Delta H^0_{r,2}))}{F_{CH4}.C_{P.CH4} + F_{H2O}.C_{P.H2O} + F_{H2}.C_{P.H2} + F_{CO}.C_{P.CO} + F_{CO2}.C_{P.CO2} + F_{N2}.C_{P.N2} + F_{Ar}.C_{P.Ar}} \tag{29}
\]

The value of temperature on the catalyst surface has been evaluated relative to the gases temperature by many authors

\[
T_S = T_g + \left[ \frac{\rho_C(1-\epsilon_B)(\eta_1R_1(-\Delta H^0_{r,1}) + \eta_2R_2(-\Delta H^0_{r,2}))}{6(1-\epsilon_B)h D_s} \right] \tag{30}
\]

In order to validate the model, the simulation results from both (A) and (B) modeling compared against the available data of Basra Fertilizer Plant.

3. Results and discussion

The theoretical results predicated from both mathematical models (A&B) have been drawn and compared as shown in figures 2 to 6. Figure 2 depicts the profile of methane molar flowrate as a function of catalyst bed length for both models A and B. Anyway, for model A when the length of catalyst zone varies between (0-2.80) m methane molar flowrate has decreased from (183.690 to 19.001) Kmol/hr, while it decreases to (39.165) Kmol/hr for Model (B) for the same axial coordinate of the catalyst zone. The profile of hydrogen flow rate as a function of catalyst zone length is presented in figure 3. Also, the profile of the total molar flow rate of outlet gases from secondary reformer is presented in figure 4.
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Figure 2: The calculation of values of methane molar flow rate as a function of axial coordinate of catalyst bed relative to inlet operation conditions (T=1369.644K & P=32bar)

Figure 3: The calculation of values of hydrogen molar flow rate as a function of axial coordinate of catalyst bed relative to inlet operation conditions (T=1369.644K & P=32bar)

Figure 4: The calculation of values of Total molar flow rate of outlet gases from secondary reformer as a function of axial coordinate of catalyst bed relative to inlet operation conditions (T=1369.644K & P=32bar)
Also, figure 5 depicts the temperature profile of gases as a function of catalyst zone length for both Models (A & B). Anyway, for Model (A) when the length of the catalyst zone varies between (0-2.80) m the temperature of gases has decreased from (1369.644 to 1282.630) K, while it decreased to (1288.970) K for the Model (B) with the same axial coordinate of the catalyst zone.

**Figure 5:** the calculation of values of Temperature of gases as a function of axial coordinate of catalyst bed relative to inlet operation conditions (T=1369.644K & P=32bar)

Figure 6, depicts that temperature of catalyst surface for Model A has decreased from (1362.1 to 1282.01) K for a distance of (2.80) m from the catalyst zone, while it decreased to (1287.85) K for the Model B with the same axial distance of catalyst zone.

**Figure (6)** the calculation of values Temperature of catalyst surface as a function of axial coordinate of catalyst bed relative to inlet operation conditions (T=1369.644K & P=32bar)

The values of deviation of Models (A&B) relative to plant data have been calculated and tabulated in Table (2). However, this table show the Model (A) is better than Model (B) through a different point of view because the Carbon Dioxide Reforming reaction is described. It takes more variables of some parameters such as the methane consumption reaction for Model (A) is larger than that from Model (B). Besides, the Hydrogen production from Model (A) is larger than that from Model (B). The total conversions of methane in the secondary reformer relative to Models (A&B) were **95.5 %** and **90.8%**
respectively, while the actual conversion of industrial plant data was 95.6%. Consequently, the deviations of the total conversions of methane relative to Models (A) and (B) relative to the actual plant were 0.1% and 5% respectively then, Model (A) appear good agreement with the industrial plant data as shown in table 2.

Table 2: Shows comparison between results of models (A&B) at outlet of secondary reformer reactor relative to Basra Fertilizer Plant

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Plant Data</th>
<th>Simulation Data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Model A</td>
<td>Model B</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>969</td>
<td>1009.630</td>
<td>1015.970</td>
</tr>
<tr>
<td>Pressure (Bar)</td>
<td>31.570</td>
<td>31.918</td>
<td>31.918</td>
</tr>
<tr>
<td>Components</td>
<td>Mole flow rates (Kmol/hr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>18.640</td>
<td>19.001</td>
<td>39.165</td>
</tr>
<tr>
<td>H₂O</td>
<td>3992.350</td>
<td>3985.640</td>
<td>4048.480</td>
</tr>
<tr>
<td>H₂</td>
<td>3449.710</td>
<td>3455.730</td>
<td>3352.550</td>
</tr>
<tr>
<td>CO</td>
<td>785.200</td>
<td>777.861</td>
<td>800.384</td>
</tr>
<tr>
<td>CO₂</td>
<td>563.600</td>
<td>570.589</td>
<td>527.902</td>
</tr>
<tr>
<td>Total molar flowrate(Kmol/hr)</td>
<td>10205.504</td>
<td>10204.400</td>
<td>10164</td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>2.511</td>
<td>2.516</td>
<td>2.441</td>
</tr>
<tr>
<td>(CO+H₂)/N₂</td>
<td>3.083</td>
<td>3.082</td>
<td>3.024</td>
</tr>
</tbody>
</table>

4. Conclusions

The effect of chemical reactions number in a catalyst zone of industrial secondary reformer reactor in the State Company of Fertilizers South Region in the Basra/Iraq has been investigated and two models (A) and (B) have been studied. The first model (A) has assumed three reactions while the second model (B) assumed two reactions, all these reactions of model (A&B) took place in a catalyst zone. The effecting of Carbon Dioxide Reforming reaction equation has been studies on the design and the performance of industrial secondary reformer reactor. The theoretical results of Model (A) are closer to the plant data than Model (B), the deviations of the total conversions of methane in the secondary reformer relative to Models (A) and (B) relative to the actual plant were 0.1% and 5% respectively. However, Carbon Dioxide Reforming reaction equation has effected on the catalyst bed models of the secondary reformer design and performance.

Acknowledgments

The authors wish to thank the State Company Fertilizers Plant South Region in Basra/Iraq for its introduce industrial data and support.

6. References

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