ABSTRACT

The water-gas shift reaction, CO + H₂O ↔ CO₂ + H₂, provides a method for extracting the energy from the toxic CO by converting it into usable H₂ along with CO₂. For such a reaction depends on activity of catalyst so study of different metal based catalyst including Cu, Fe, Ni, Pd, Rh and Ru is in centre of interest. Generally all gas phase reaction is carried out in catalytic bed and all the reaction kinetics is based on some mechanism and also depends on catalyst property. Some of mechanism and kinetics of catalytic reaction is illustrated from researcher’s literature and also from catalyst manufacturer. Mathematical model for such water gas shift reaction is beneficial for study of Concentration profile & Temperature profile. Thus we could get smooth curve for concentration profile by doing modelling and simulation of such catalytic reaction. The main aim of modeling and simulation of any reaction are to provide or compare appropriate kinetics for particular reaction and also sometimes it used to comparison among different catalysts.

Key Words: Water-gas Shift Reactor, Reversible reaction, catalysts, Thermodynamic equilibrium, Ideal plug flow reactor, fixed bed reactor.

1. INTRODUCTION

Today Hydrogen is most important energy source and also reactant for Synthesis gas phase reaction. This way we are interesting to enhance hydrogen or energy sources by different kinds of reactions. For examples we can enhance hydrogen in syntheses gas comes from reformer. Synthesis gas from reformer contain carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), nitrogen (N₂), methane (CH₄) and some inert at dry basis. So we can improve yield of hydrogen by shift conversion of CO to CO₂ by reaction with Steam. This reaction is called Water Gas Shift reaction. This type of conversion is used mostly all hydrogen/ammonia plant. The WGS reaction is reversible and exothermic (∆H° = −41.2 kJ/mol). Due to its moderate exothermic, the WGS reaction is thermodynamically unfavourable at elevated temperatures.

2. MODELING OF WGS REACTION

2.1 Thermodynamics of WGS Reaction

Water Gas Shift (WGS) is reversible reaction. So both the forward and reverse reaction is with thermodynamic equilibrium. The true dimensionless equilibrium constant can predict from Gibb’s free energy as denoted by the following reaction.

\[ R \times T \times \ln K = -\Delta G \]

Where,
- \( R \) = Ideal Gas Constant
- \( T \) = Temperature of Reaction, K
- \( K \) = Equilibrium Constant
- \( \Delta G \) = Change in Gibb’s free Energy, cal/mol

2.2 Design equation for Reactor

All fixed Bed catalytic reactor assumed to behave like ideal plug flow reactor. Equation used for the design or sizing of fixed bed reactor is

\[ F \times Ao \times \frac{dX}{dW} = -r_A \]

Where,
- \( W \) = Mass of catalyst
- \( F \times Ao \) = Molar flow rate of limiting reactant in feed
- \( X \) = Fractional conversion of limiting reactant A
- \( r_A \) = Overall rate of reaction

The differential form of the design equation must be used when analyzing reactors that have a pressure drop along the length of the reactor. Integrating with the limits \( W=0 \) at \( X=0 \) gives,

\[ W = F \times Ao \int \left( \frac{dX}{-r_A} \right) \]

This equation can be used to determine the catalyst weight \( W \) necessary to achieve a conversion \( X \) when the total pressure remains constant.

2.3 The rate law

Various manufacturers suggest rate equations for their catalysts. This rate equation is based on experiment results, mechanism and catalyst property. We will go to use Equation (1) to define rate law. [12]

\[ (-r_{CO}) = \Psi k(y_{CO} y_{H2O} - y_{CO2} y_{H2}/K)/(pb) \]
This Micro-kinetic model is given by various catalyst manufacturers and based on mole fraction of species. It consider the following factors like Specific rate constant, Activity factor, Equilibrium constant and catalyst bulk density. Here complete rate expression is based on mole fraction so unit of specific rate constant is similar to zero order reaction i.e. mole/m³ hr.

Where,
\[ k = \text{Rate Constant, lb mole/cu ft, hr} \]
\[ = \exp(15.95 - 8820/T) \text{ for iron catalyst} \]
\[ = \exp(12.88 - 3340/T) \text{ for Copper-zinc catalyst} \]

\[ K = \text{Equilibrium Constant} \]
\[ = \exp(-4.72 + 8640/T) \text{ for } 760 \leq T \leq 1060 \]
\[ = \exp(-4.33 + 8240/T) \text{ for } 1060 \leq T \leq 1360 \]

\[ P = \text{pressure} \]
\[ (-\tau_{CO}) = \text{rate of CO converted} \]
\[ T = \text{Temperature, } ^\circ R \]
\[ yi = \text{mole fraction of component indicated} \]
\[ \rho_b = \text{Catalyst Bulk density} \]
\[ \Psi = \text{activity factor} \]

For Iron catalyst
\[ \Psi = 0.816 + 0.184P \text{ for } P \leq 11.8 \]
\[ = 1.53 + 0.123P \text{ for } 11.8 < P \leq 20.0 \]
\[ = 4.0 \text{ for } P > 20.0 \]

For Copper-zinc catalyst
\[ \Psi = 0.86 + 0.14P \text{ for } P \leq 24.8 \]
\[ = 4.33 \text{ for } P > 24.8 \]

**2.4 Material Balance for WGS Reaction.**

The concentration for Species A is the number of moles of A per unit volume at given time. Concentration of species A,
\[ C_A = \frac{F_A}{v} \]

Where,
\[ C_A = \text{Concentration of species A, moles/liter} \]
\[ F_A = \text{molar flow rate of species A, moles/time} \]
\[ v = \text{volumetric flow rate, liters/time} \]

We now can write the concentrations of A, B, C, and D for the general in terms of the entering molar flow rate \((F_{Ao}, F_{Bo}, F_{Co}, F_{Do})\), the conversion \(X\), and the volumetric flow rate, \(v\).

\[ C_A = \frac{(F_A)/v}{(F_{Ao})/v}(1 - X) \]
\[ C_B = \frac{(F_B)/v}{(F_{Bo})/v} = \frac{[F_{Bo} - (b/a)F_{Ao} X]/v}{(F_{Bo})/v} \]
\[ C_C = \frac{(F_C)/v}{(F_{Co})/v} = \frac{[F_{Co} - (c/a)F_{Ao} X]/v}{(F_{Co})/v} \]
\[ C_D = \frac{(F_D)/v}{(F_{Do})/v} = \frac{[F_{Do} - (d/a)F_{Ao} X]/v}{(F_{Do})/v} \]

Where,
\[ T_o = \text{Initial Temperature of Reactant} \]
\[ T = \text{Final Temperature of Product} \]

The above equation is used for relate Concentration as function of Conversion and total mole of feed is remain constant is \(F_T\).

2.5 Combination of all three steps

We have Design equation for packed bed Reactor is
\[ \frac{dX}{dW} = \Psi k(y_{CO} y_{H2O} - y_{CO2} y_{H2})/(K F_{COo} \rho_b) \]

Now we can put mole fraction of all the compound as a function of Conversion
\[ y_{CO} = \frac{F_{COo} (1 - X)/F_T}{F_T} \]
\[ y_{H2O} = \frac{F_{COo} (\Theta_{H2O} - X)/F_T}{F_T} \]
\[ y_{CO2} = \frac{F_{COo} (\Theta_{CO2} + X)/F_T}{F_T} \]
\[ y_{H2} = \frac{F_{COo} (\Theta_{H2} + X)/F_T}{F_T} \]

\[ \frac{dX}{dW} = \Psi k y_{COo}^2 [(1 - X)(\Theta_B - X) - (\Theta_C + X)(\Theta_D + X)/K]/(F_{COo} \rho_b) \]

This is design model for Catalytic plug flow for Isothermal case. This ODE can solve from polymath, Scilab ormatleb.

Where,
\[ k = \text{Rate Constant} \]
\[ = \exp(15.95 - 8820/T) \text{ for iron catalyst} \]
\[ K = \text{Equilibrium Constant} \]
\[ = \exp\left(\frac{12.88 - 3340}{T}\right) \text{ for Copper-zinc catalyst} \]
\[ P = \text{pressure, atm} \]
\[ = \exp(-4.72+8640/T) \text{ for } 760 \leq T \leq 1060 \]
\[ = \exp(-4.33+8240/T) \text{ for } 1060 \leq T \leq 1360 \]
\[ \Psi = \text{activity factor} \]
\[ \text{For Iron catalyst} \]
\[ \Psi = 0.816 + 0.184P \text{ for } P \leq 11.8 \]
\[ = 1.53 + 0.123P \text{ for } 11.8 < P \leq 20.0 \]
\[ = 4.0 \text{ for } P > 20.0 \]
\[ \text{For Copper-zinc catalyst} \]
\[ \Psi = 0.86 + 0.14P \text{ for } P \leq 24.8 \]
\[ = 4.33 \text{ for } P > 24.8 \]

3. RESULT AND DISCUSSION

We are first take complete CO conversion based on Copper catalyst and put all the values in equation (5) and solve ODE. Only specific rate constant and catalyst bulk density is different for both catalysts.

Catalyst: Copper-Zinc catalyst
Temperature \( T = 254 \, ^\circ\text{C} = 527 \, \text{K} = 948.89 \, ^\circ\text{R} \)
Pressure \( P = 24 \, \text{atm} \)
Total Feed Rate, \( F_T = 10000 \, \text{kmol/hr} \)
\[ F_{\text{CO}} = 960 \, \text{kmol/hr} \]
\[ F_{\text{H}_2\text{O}} = 3350 \, \text{kmol/hr} \]
\[ F_{\text{CO}_2} = 550 \, \text{kmol/hr} \]
\[ F_{\text{H}_2} = 4600 \, \text{kmol/hr} \]

Now,
\[ \text{Ratio of initial moles of } \text{H}_2\text{O to CO}, \Theta_{\text{H}_2\text{O}} = 3.49 \]
\[ \text{Ratio of initial moles of } \text{CO}_2 \text{ to CO}, \Theta_{\text{CO}_2} = 0.57 \]
\[ \text{Equilibrium constant } K \text{ at } 254 \, ^\circ\text{C} = 81 \]

And value of specific reaction rate constant, \( k = 181085.61 \)
\[ \Psi = 4.33 \text{ at pressure } P=24 \text{ atm for copper catalyst} \]

Bulk density of Catalyst = 1442 kg/m³ for copper catalyst
Initial Mole fraction of CO, \( y_{\text{CO}} = 960/10000 = 0.096 \)

Substitute all the values in above equation (5) and write this equation in polymath solver as shown in table – 1.

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>X (%)</th>
<th>Weight of Catalyst, W (kg)</th>
<th>Space Velocity W/F_Ao, W/FAo, Kg Catalyst* hr/kmol CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.882646</td>
<td>600.777</td>
<td>0.625809</td>
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<td>6.510417</td>
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<td>7730.219</td>
<td>8.052311</td>
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<td>41.33834</td>
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<tr>
<td>51.67882</td>
<td>16539.62</td>
<td>17.22877</td>
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<tr>
<td>60.74803</td>
<td>21875</td>
<td>22.78646</td>
<td></td>
</tr>
</tbody>
</table>

Table – 1 Output results of Space Velocity for given case

3.2 Concentration and Temperature profile

We have two dimensional mathematical model is
\[ D_L [d^2C_A/dz^2] - [d(C_Au_z)/dz] + \rho_b r_w = 0 \]

Where,
\( C_A = \text{Concentration of species A (CO)} \)
\( z = \text{Length of reactor} \)
\( \rho_b = \text{Bulk density of Catalyst bed} \)
\( r_w = \text{Rate of reaction of CO converted} \)
\( u_z = \text{Average velocity in the bed} \)
\( l = \text{fractional length} \)
\( D_L = \text{Axial Dispersion} \)

Rate of Reaction is again we can use equation (5)
\[ (- r_{\text{CO}}) = \Psi_k y_{\text{CO}} (1 - X)(\Theta_B - X) - (\Theta_C + X)(\Theta_D + X)/K/F_{\text{CO}}(\rho_b) \]

Initial concentration of CO is found by the equation \( C = yP/RT, \) where \( R \) is universal gas constant. We can relate temperature of bed with conversion from energy balance so
\[ T = T_o + X[\Delta H_{rx}] \]

Where,
\( T = \text{Temperature of Bed, } ^\circ\text{C} \)
\( T_o = \text{Initial temperature, } ^\circ\text{C} \)
\( X = \text{Conversion} \)
\( \Delta H_{rx} = \text{Heat of reaction, KJ/mol} \)
Hydrogen Production, Vol he reactor of the WGS reaction. We can nd.

4. CONCLUSION
Water-gas shift reaction is important fuel processing reaction for enhance hydrogen in reformed gas mixture. We can find the space velocity, concentration & temperature profile though out the reactor of the WGS reaction. We can also compare the performance of Catalyst if we have activity coefficient of diff catalyst as show in figure

5. FUTURE SCOPE
We can develop generalize model for all type of operation: Isothermal as well as adiabatic.This study are developed modeling and simulation based on certain assumption by countering this assumption one’s can develop model more complex. Comparison of different catalyst is possible by using modeling and simulation and we can find out best catalyst from that study.Cost estimation of reactor is much easy by developing appropriate model for particular reaction and condition.Further work is possible on Study of mechanism of chemical reaction and development of Rate low.

6. REFERENCES


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