A First Course on Kinetics and Reaction Engineering

Class 36 on Unit 34

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
    - A. Ideal Reactors
    - B. Perfectly Mixed Batch Reactors
    - C. Continuous Flow Stirred Tank Reactors
    - D. Plug Flow Reactors
    - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors
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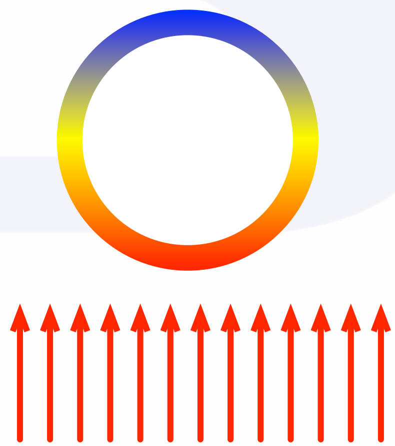
        - 37. Overview of Multi-Phase Reactors
    - B. Coupled Chemical and Physical Kinetics

2-D and 3-D Tubular Reactor Models

- The PFR model assumes
  - No mixing in the axial direction
    - Unit 33 showed how axial mixing could be added using the axial dispersion model
    - Axial mixing is usually negligible except for very short reactors
  - Perfect radial mixing
    - Now consider the possibility that mixing is *not* perfect in the radial direction
    - Often there can be temperature gradients in the radial, and sometimes azimuthal, direction
- Radial gradients
  - When heat is being added or removed through its walls, a radial temperature gradient can develop in a tubular reactor if heat transfer from the centerline to the wall is not sufficiently rapid
  - If the temperature is not uniform in the radial direction, then the rate will vary in the radial direction, leading to concentration gradients
- Azimuthal gradients
  - When heat is added or removed unevenly around the circumference of the tube, azimuthal temperature gradients can occur
    - For example, when a reactor tube passes through a furnace, the radiant heat flux is only on one half of the tube
  - Temperature gradient can cause a concentration gradient



2-D Design Equations and Boundary Conditions

- Steady state mole balance: $D_{er}\left(\frac{\partial^2 C_i}{\partial r^2}+\frac{1}{r}\frac{\partial C_i}{\partial r}\right)-\frac{\partial}{\partial z}\left(u_s C_i\right)=\sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j$
- Steady state energy balance: $\lambda_{er}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)-u_s \rho_{fluid}\tilde{C}_{p,fluid}\frac{\partial T}{\partial z}=\sum_{\substack{j=all\\reactions}} r_j \Delta H$
- Steady state momentum balance: $-\frac{dP}{dz}=f\frac{\rho_{fluid}u_s^2}{d_p}$
- Boundary conditions
  - At $z = 0$
    - $C_i(0)=C_{i,feed}$
    - $T(0)=T_{feed}$
    - $P(0)=P_{feed}$
  - At $r = 0$
    - $\left.\frac{\partial C_i}{\partial r}\right|_{r=0}=0$
    - $\left.\frac{\partial T}{\partial r}\right|_{r=0}=0$
  - At $r = R$
    - $\left.\frac{\partial C_i}{\partial r}\right|_{r=R}=0$
    - $\left.\frac{\partial T}{\partial r}\right|_{r=R}=\frac{\alpha_w}{\left(\lambda_{er}\right)_s}\left(T(R)-T_w\right)$

Questions?

Activity 34.1*

The partial oxidation of o-xylene to phthalic anhydride, reaction (1), is an exothermic reaction (ΔH = -307 kcal mol^{-1}). A heterogeneous catalyst for this reaction might consist of 3 mm particles with a bulk density of 1.3 g cm^{-3}, however this catalyst is sometimes mixed with an inert solid leading to an effective density of 0.87 g cm^{-3}. In either case, the catalyst is not perfectly selective, so that some of the o-xylene and some of the phthalic anhydride undergo total combustion to produce carbon oxides, reactions (2) and (3); the heat reaction (2) is -1090 kcal mol^{-1}. (The heat of reaction (3) equals the difference between the heats of reactions (1) and (2).) Letting A represent o-xylene, B represent phthalic anhydride and O represent oxygen, the rates for reactions (1) through (3) may be modeled using equations (4) through (6).

$$C_8H_{10} + 3\ O_2 \rightarrow C_8H_4O_3 + 3\ H_2O \qquad (1)$$

$$C_8H_{10} \xrightarrow{O_2} CO_x \qquad (2)$$

$$C_8H_4O_3 \xrightarrow{O_2} CO_x \qquad (3)$$

$$r_1 = \left(4.122\times10^{11}\ \text{mol kg}^{-1}\ \text{h}^{-1}\right)\exp\left(\frac{-27\ \text{kcal mol}^{-1}}{RT}\right)P_AP_O \qquad (4)$$

$$r_2 = \left(1.15\times10^{12}\ \text{mol kg}^{-1}\ \text{h}^{-1}\right)\exp\left(\frac{-31\ \text{kcal mol}^{-1}}{RT}\right)P_BP_O \qquad (5)$$

$$r_3 = \left(1.73\times10^{11}\ \text{mol kg}^{-1}\ \text{h}^{-1}\right)\exp\left(\frac{-28.6\ \text{kcal mol}^{-1}}{RT}\right)P_AP_O \qquad (6)$$

* This activity is based upon a case study from H. Rase, “Chemical Reactor Design for Process Plants,” Vol. II. Wiley, New York, 1977.

Consider a tubular reactor with an inside diameter of 1 inch and a length of 3 m that is cooled by perfectly mixed molten salts circulating outside the tube at a temperature equal to the feed temperature, 370 ºC. The mass velocity of the feed is 4684 kg m^{-2} h^{-1}; it consists of 0.93 mol% o-xylene in air which leads to a feed molecular weight of 29.48, a feed mole fraction of O_2 of 0.208 and a mass specific heat capacity of 0.25 kcal kg^{-1} K^{-1}, which may be assumed to be constant. Set up 2-D mole balances for o-xylene, phthalic anhydride and carbon oxides and a 2-D heat balance for this reactor assuming the superficial velocity to be constant, the wall heat transfer coefficient to equal 134 kcal m^{-2} h^{-1} K^{-1}, the effective radial conductivity to equal 0.67 kcal m^{-1} h^{-1} K^{-1} and the radial Peclet number for mass transfer (based on the superficial velocity and the catalyst particle diameter) to be constant and equal to 10. The first 75 cm of the tube is packed with the diluted catalyst, while the remainder contains the undiluted catalyst. The pressure is constant and equal to 1 atm.

Rase states that solution of the 2-D model equations reveals maximum temperatures of 400 ºC (about two-thirds of the way into the part of the bed containing the diluted catalyst) and 410 ºC (about 25 cm after entering the part of the bed containing undiluted catalyst). Model this reactor as an ideal PFR with an overall heat transfer coefficient of 82.7 kcal m^{-2} h^{-1} K^{-1} (which is equivalent to the wall heat transfer coefficient and effective radial conductivity of the 2-D model) and compare the temperature maxima predicted by the PFR model to those reported for the 2-D model.

Solution

- Read through the problem statement. Each time you encounter a quantity, write it down and equate it to the appropriate variable. When you have completed doing so, if there are any additional constant quantities that you know will be needed and that can be calculated from the values you found, write the equations needed for doing so.

Solution

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  - ΔH_1 = -307 kcal mol^{-1}, ΔH_3 = -1090 kcal mol^{-1}, d_p = 3 mm, P = 1 atm, ρ_{cat} = 1.3 g cm^{-3}, ρ_{dilcat} = 0.87 g cm^{-3}, $k_{0,1}$ = 4.122 x 10^{11} mol kg^{-1} h^{-1}, E_1 = 27 kcal mol^{-1}, $k_{0,2}$ = 1.15 x 10^{12} mol kg^{-1} h^{-1}, E_2 = 31 kcal mol^{-1}, $k_{0,3}$ = 1.73 x 10^{11} mol kg^{-1} h^{-1}, E_3 = 28.6 kcal mol^{-1}, D = 1 in, L = 3 m, T_{feed} = 370 °C, T_w = 370 °C, G = 4684 kg m^{-2} h^{-1}, $y_{A,feed}$ = 0.0093, M_{feed} = 29.48 g mol^{-1}, $y_{O,feed}$ = 0.208, α = 134 kcal m^{-2} h^{-1} K^{-1}, λ_{er} = 0.67 kcal m^{-1} h^{-1} K^{-1}, Pe_r = 10, U_{PFR} = 82.7 kcal m^{-2} h^{-1} K^{-1} and $\tilde{C}_p$ = 0.25 kcal kg^{-1}
  - $\Delta H_2 = \Delta H_3 - \Delta H_1$, $A = \pi D^2/4$, $\dot{m}_{feed} = A \cdot G$, $\dot{n}_{feed} = \dot{m}_{feed}/M_{feed}$, $\dot{V}_{feed} = \dot{n}_{feed}RT/P$, $u_s = \dot{V}_{feed} / A$, $D_{er} = u_s d_p/P_{er}$, $\rho_{fluid} = G/u_s$, $C_{A,feed} = y_{A,feed}\dot{n}_{feed}/\dot{V}_{feed}$, $C_{O,feed} = y_{O,feed}\dot{n}_{feed}/\dot{V}_{feed}$, $C_{B,feed} = 0$ and $R = D/2$
- Use the 2-D tubular reactor design equations found in Unit 34 or on the AFCoKaRE Exam Handout to generate an energy balance and mole balances on o-xylene, phthalic anhydride and carbon oxides. (Assume the stoichiometric coefficient of O_2 to equal -8.5 in reaction (2) and -5.5 in reaction (3).)

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$$\lambda_{er}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)-u_s\rho_{fluid}\tilde{C}_{p,fluid}\frac{\partial T}{\partial z}=\sum_{\substack{j=all\\reactions}} r_j\Delta H$$

$$\lambda_{er}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)-u_s\rho_{fluid}\tilde{C}_{p,fluid}\frac{\partial T}{\partial z}=r_1\Delta H_1+r_2\Delta H_2+r_3\Delta H_3$$

$$D_{er}\left(\frac{\partial^2 C_i}{\partial r^2}+\frac{1}{r}\frac{\partial C_i}{\partial r}\right)-\frac{\partial}{\partial z}\left(u_s C_i\right)=\sum_{\substack{j=all\\reactions}} \nu_{i,j}r_j$$

$$D_{er}\left(\frac{\partial^2 C_A}{\partial r^2}+\frac{1}{r}\frac{\partial C_A}{\partial r}\right)-u_s\frac{\partial C_A}{\partial z}=-r_1-r_2$$

$$D_{er}\left(\frac{\partial^2 C_B}{\partial r^2}+\frac{1}{r}\frac{\partial C_B}{\partial r}\right)-u_s\frac{\partial C_B}{\partial z}=r_1-r_3$$

$$D_{er}\left(\frac{\partial^2 C_O}{\partial r^2}+\frac{1}{r}\frac{\partial C_O}{\partial r}\right)-u_s\frac{\partial C_O}{\partial z}=-3r_1-8.5r_2-5.5r_3$$

For calculation of the rates

$$P_A=C_ART$$

$$P_B=C_BRT$$

$$P_O=C_ORT$$

- Write the boundary conditions needed to solve the 2-D tubular reactor design equations and show how to calculate any new quantities they contain.

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$$C_i\left(r,0\right)=C_{i,feed}$$

$$\left.\frac{\partial C_i}{\partial r}\right|_{r=0}=0$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=0}=0$$

$$T\left(r,0\right)=T_{feed}$$

$$\left.\frac{\partial C_i}{\partial r}\right|_{r=R}=0$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=R}=\frac{\alpha_w}{\lambda_{er}}\left(T\left(R,z\right)-T_w\right)$$

- Using the PFR design equations from Unit 17 or the AFCoKaRE Exam Handout, generate the design equations needed to model this reactor as a PFR. Identify the specific set of equations that needs to be solved and within those equations identify the independent and dependent variables, if appropriate, and the unknown quantities to be found by solving the equations.

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$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4}\left[\left(\sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j\right) - \frac{\partial}{\partial t}\left(\frac{\dot{n}_i}{\dot{V}}\right)\right]$$

$$\frac{d\dot{n}_A}{dz} = \frac{\pi D^2}{4}\left(-r_1 - r_2\right)$$

$$\frac{d\dot{n}_B}{dz} = \frac{\pi D^2}{4}\left(r_1 - r_3\right)$$

$$\frac{d\dot{n}_O}{dz} = \frac{\pi D^2}{4}\left(-3r_1 - 8.5r_2 - 5.5r_3\right)$$

$$\pi DU\left(T_e - T\right) = \frac{\partial T}{\partial z}\left(\sum_{\substack{i=\text{all}\\\text{species}}} \dot{n}_i \hat{C}_{p-i}\right) + \frac{\pi D^2}{4}\left(\sum_{\substack{j=\text{all}\\\text{reactions}}} r_j \Delta H_j\right) + \frac{\pi D^2}{4}\left[\frac{\partial T}{\partial t}\left(\sum_{\substack{i=\text{all}\\\text{species}}} \frac{\dot{n}_i \hat{C}_{p-i}}{\dot{V}}\right) - \frac{\partial P}{\partial t}\right]$$

$$\frac{dT}{dz} = \frac{\pi DU\left(T_w - T\right) - \frac{\pi D^2}{4}\left(r_1\Delta H_1 + r_2\Delta H_2 + r_3\Delta H_3\right)}{\dot{m}\tilde{C}_p}$$

Dependent vars: $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_O$ and T; independent var: z

Solve for dependent vars at $z = L$

- Assuming that the PFR design equations will be solved numerically, specify the information that must be provided and show how to calculate any unknown values.

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$$\frac{d\dot{n}_A}{dz} = \frac{\pi D^2}{4}\left(-r_1 - r_2\right) \qquad \frac{d\dot{n}_B}{dz} = \frac{\pi D^2}{4}\left(r_1 - r_3\right) \qquad \frac{d\dot{n}_O}{dz} = \frac{\pi D^2}{4}\left(-3r_1 - 8.5r_2 - 5.5r_3\right)$$

$$\frac{dT}{dz} = \frac{\pi D U\left(T_w - T\right) - \frac{\pi D^2}{4}\left(r_1\Delta H_1 + r_2\Delta H_2 + r_3\Delta H_3\right)}{\dot{m}\tilde{C}_p}$$

  - The 3 rates must be calculated using the expressions given in the problem statement; all other quantities (other than dependent and independent variables) are known constants
    - Need P_A, P_B and P_O, given values for dependent and independent variables
    - Since the fluid density is assumed constant: $P_i = \frac{\dot{n}_i R T_{feed}}{\dot{V}_{feed}}$

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  - Solving the design equations allows calculation of the dependent variables (which include T) at any value of z.
  - Do this for many values between z = 0 and z = 0.75 cm and find the maximum temperature in the zone where the catalyst is diluted
  - Then repeat for values between z = 0.75 cm and z = L and find the maximum temperature in the zone where the catalyst is not diluted
- Note, for both models, the design equations must first be solved for 0 < z < 75 cm using the density of the diluted catalyst
  - The resulting values of the dependent variables at z = 75 cm become the initial conditions (PFR) or boundary conditions (2-D tubular reactor) for the second part of the reactor (75 cm < z < L) where the equations are solved using the density of the undiluted catalyst
- Results
  - The PFR model under-predicts temperature maxima by ca. 3 and 7 K
    - This can be critical in some cases

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