A First Course on Kinetics and Reaction Engineering

Class 27 on Unit 26

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
    - 25. Reaction Engineering of PFRs
    - 26. Analysis of Steady State PFRs
    - 27. Analysis of Transient PFRs
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors

The Steady State PFR Design Equations

- Mole balance on i

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$$

- Energy balance

$$\pi D U \left(T_e - T\right) = \left(\sum_{\substack{i=all \\ species}} \dot{n}_i \hat{C}_{pi} \right) \frac{dT}{dz} + \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} \left(r_j \Delta H_j \right)$$

- Momentum balance (unpacked tube)

$$\frac{dP}{dz} = -\frac{G}{g_c} \left(\frac{4}{\pi D^2} \right) \frac{d\dot{V}}{dz} - \frac{2 f G^2}{\rho D}$$

- Momentum balance (packed bed)

$$\frac{dP}{dz} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[\frac{150\left(1-\varepsilon\right)\mu}{\Phi_s D_p G} + 1.75 \right]$$

Identifying and Solving Quantitative Reaction Engineering Problems

- Identifying quantitative reaction engineering problems
  - In a quantitative reaction engineering problem one is typically given
    - the reactions that are taking place
    - their rate expressions (with values for all of the kinetic parameters appearing in them)
    - the thermal properties of the fluids involved
    - selected specifications for the reactor
    - specifications on how the reactor operates
  - One is then typically asked
    - either to determine additional reactor specifications or operating procedures needed to meet specified reactor performance criteria
    - or to calculate selected reactor performance metrics
- General approach to solving quantitative reaction engineering problems
  - Read through the problem statement and determine
    - the type of reactor being used
    - whether it operates transiently or at steady state
    - whether it is heated/cooled, isothermal or adiabatic
    - (if the reactor is a PFR) whether there is a significant pressure drop
  - Read through the problem statement a second time
    - assign each quantity given in the problem statement to the appropriate variable symbol
    - if all of the given quantities are intensive, select a value for one extensive variable as the basis for your calculations
    - determine what quantities the problem asks for and assign appropriate variable symbols to them

- Write a mole balance equation for each reactant and product; expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- Write an energy balance design equation (unless the reactor is isothermal and the problem does not ask any questions related to heat transfer); expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- If the reactor is a PFR and there is a significant pressure drop, write a momentum balance; expand all summations and continuous products, and eliminate all zero-valued and negligible terms
- Identify the type of the design equations (in the case of steady state PFRs, they will be initial value differential equations)
  - identify the independent and dependent variables
    - if the number of dependent variables is greater than the number of equations, choose one dependent variable and express it and its derivatives in terms of the remaining dependent variables
- Determine what you will need to provide in order to solve the design equations numerically and show how to do so (again, in the case of steady state PFRs, they will be initial value differential equations)
  - Assuming they are written in the form $\frac{d\underline{y}}{dx} = \underline{f}\left(\underline{y},x\right)$, you must provide initial values of x and $\underline{y}$, a final value for either x or one element of $\underline{y}$, and code that evaluates $\underline{f}$ given x and $\underline{y}$
- After the design equations have been solved numerically, yielding values for the independent and dependent variables, use the results to calculate any other quantities or plots that the problem asked for

Questions?

Oxidative Dehydrogenation of Ethane to Ethylene

The irreversible oxidative dehydrogenation of ethane to ethylene, reaction (1), has a heat of reaction of -25 kcal mol^{-1}. It is first order in ethane; the pre-exponential factor for the rate coefficient is equal to 1.4 x 10^8 min^{-1} and the activation energy is 30 kcal mol^{-1}. The feed consists of 5% ethane in air at 350 °C and 2 atm; the heat capacity of the gas can be approximated to equal 3.5R and the pressure drop is negligible. The reactor has a diameter of 25 mm and is 2 m long Calculate the conversion and outlet temperature for an adiabatic PFR operating at space times of 1, 10 and 50 min (a) assuming constant density and (b) accounting for the change in density.

$$C_2H_6 + \frac{1}{2}\,O_2 \rightarrow C_2H_4 + H_2O \qquad (1)$$

$$A + \frac{1}{2}\,B \rightarrow Y + Z \qquad (2)$$

Read through the problem statement and determine the type of reactor being used, whether it operates transiently or at steady state, whether it is heated/cooled, isothermal or adiabatic and (if the reactor is a PFR) whether there is a significant pressure drop

Read through the problem statement a second time and assign each quantity given in the problem statement to the appropriate variable symbol, if all of the given quantities are intensive, select a value for one extensive variable as the basis for your calculations and determine what quantities the problem asks for and assign appropriate variable symbols to them

Schematic

$$\mathrm{A} + \frac{1}{2}\,\mathrm{B} \rightarrow \mathrm{Y} + \mathrm{Z}$$

$$r = \left(1.4\times10^{8}\ \mathrm{min}^{-1}\right)\exp\left(\frac{-30\ \mathrm{kcal\ mol}^{-1}}{RT}\right)C_A$$

$$\Delta H = -25\ \mathrm{kcal\ mol}^{-1}$$

$$\dot{n}_A^0 = 0.05\dot{n}_{total}^0$$

$$\dot{n}_B^0 = (0.21)0.95\dot{n}_{total}^0$$

$$\dot{n}_I^0 = (0.79)0.95\dot{n}_{total}^0$$

$$\dot{n}_Y^0 = \dot{n}_Z^0 = 0$$

$$T^0 = (350 + 273.15)\ \mathrm{K}$$

$$\dot{n}_A =$$

$$\dot{n}_B =$$

$$\dot{n}_I = \dot{n}_I^0$$

$$\dot{n}_Y =$$

$$\dot{n}_Z =$$

$$T =$$

$$D = 25\ \mathrm{mm}$$

$$L = 2\ \mathrm{m}$$

$$\dot{Q} = 0$$

$$P = 2\ \mathrm{atm}$$

$$\tau = (1\ ,10\ \mathrm{or}\ 50)\ \mathrm{min}$$

Solution

- Write a mole balance equation for each reactant and product, expanding all summations and continuous products and eliminating all zero-valued and negligible terms

Reactor Relationships

$$\tau = \frac{V}{\dot{V}^0}\ ;\ SV = \frac{1}{\tau};\ \frac{dn_i}{dt} = V\left(\sum_{\substack{j=\text{all}\\\text{reactions}}} \nu_{i,j} r_j\right);\ \dot{Q} - \dot{W} = \left(\sum_{\substack{i=\text{all}\\\text{species}}} n_i \hat{C}_{p,i}\right)\frac{dT}{dt} + V\left(\sum_{\substack{j=\text{all}\\\text{reactions}}} r_j \Delta H_j\right) - V\frac{dP}{dt} - P\frac{dV}{dt};$$

$$\dot{n}_i^0 + V \sum_{\substack{j=\text{all}\\\text{reactions}}} \nu_{i,j} r_j = \dot{n}_i + \frac{d}{dt}\left(\frac{\dot{n}_i V}{\dot{V}}\right);$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=\text{all}\\\text{species}}} \left(\dot{n}_i^0 \int_{T^0}^{T} \hat{C}_{p-i}\, dT\right) + V \sum_{\substack{j=\text{all}\\\text{reactions}}} \left(r_j \Delta H_j(T)\right) + V\left(\sum_{\substack{i=\text{all}\\\text{species}}} \frac{\dot{n}_i \hat{C}_{p-i}}{\dot{V}}\right)\frac{dT}{dt} - P\frac{dV}{dt} - V\frac{dP}{dt};$$

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

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3}\frac{G^2}{\rho \Phi_s D_p g_c}\left[\frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75\right];$$

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

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all}\\\text{reactions}}} \nu_{i,j} r_j\ ;\ \dot{Q} - \dot{W} = \sum_{\substack{i=\text{all}\\\text{species}}} \dot{n}_i\left(\hat{h}_i - \hat{h}_{i,stream}\right) + \frac{dT}{dt}\sum_{\substack{i=\text{all}\\\text{species}}} \left(n_i \hat{C}_{pi}\right) + V \sum_{\substack{j=\text{all}\\\text{reactions}}} \left(r_j \Delta H_j\right) - \frac{dP}{dt}V - P\frac{dV}{dt};$$

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

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

Design Equations

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j$$

- Mole balances for A, B, Y and Z

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4} r$$

$$\frac{d\dot{n}_B}{dz} = \left(-\frac{1}{2}\right)\frac{\pi D^2}{4} r$$

$$\frac{d\dot{n}_Y}{dz} = \frac{\pi D^2}{4} r$$

$$\frac{d\dot{n}_Z}{dz} = \frac{\pi D^2}{4} r$$

- Write an energy balance design equation, expanding all summations and continuous products and eliminating all zero-valued and negligible terms

Reactor Relationships

$$\tau = \frac{V}{\dot{V}^0}\ ;\ SV = \frac{1}{\tau};\ \frac{dn_i}{dt} = V\left(\sum_{\substack{j=\text{all}\\ \text{reactions}}} \nu_{i,j} r_j\right);\ \dot{Q} - \dot{W} = \left(\sum_{\substack{i=\text{all}\\ \text{species}}} n_i \hat{C}_{p,i}\right)\frac{dT}{dt} + V\left(\sum_{\substack{j=\text{all}\\ \text{reactions}}} r_j \Delta H_j\right) - V\frac{dP}{dt} - P\frac{dV}{dt};$$

$$\dot{n}_i^0 + V\sum_{\substack{j=\text{all}\\ \text{reactions}}} \nu_{i,j} r_j = \dot{n}_i + \frac{d}{dt}\left(\frac{\dot{n}_i V}{\dot{V}}\right);$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=\text{all}\\ \text{species}}}\left(\dot{n}_i^0 \int_{T^0}^{T} \hat{C}_{p-i}\, dT\right) + V\sum_{\substack{j=\text{all}\\ \text{reactions}}}\left(r_j \Delta H_j(T)\right) + V\left(\sum_{\substack{i=\text{all}\\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p-i}}{\dot{V}}\right)\frac{dT}{dt} - P\frac{dV}{dt} - V\frac{dP}{dt};$$

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

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3}\frac{G^2}{\rho \Phi_s D_p g_c}\left[\frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75\right];$$

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$$\frac{dn_i}{dt} = \dot{n}_i + V\sum_{\substack{j=all\\ reactions}} \nu_{i,j} r_j\ ;\ \dot{Q} - \dot{W} = \sum_{\substack{i=all\\ species}} \dot{n}_i\left(\hat{h}_i - \hat{h}_{i,stream}\right) + \frac{dT}{dt}\sum_{\substack{i=all\\ species}}\left(n_i \hat{C}_{pi}\right) + V\sum_{\substack{j=all\\ reactions}}\left(r_j \Delta H_j\right) - \frac{dP}{dt}V - P\frac{dV}{dt};$$

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

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

Design Equations

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$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j$$

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4} r$$

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- Energy balance

$$\pi D U\left(T_e - T\right) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right)\frac{dT}{dz} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \Delta H_j\right)$$

$$\frac{dT}{dz} = \frac{-\frac{\pi D^2}{4} r \Delta H}{\left(\dot{n}_A + \dot{n}_B + \dot{n}_I + \dot{n}_Y + \dot{n}_Z\right)\hat{C}_p}$$

- If information about the heat transfer fluid, beyond its temperature, is provided or requested, write an energy balance on the heat transfer fluid

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    - The reactor is adiabatic, so a heat transfer fluid energy balance is not needed
- If the reactor is a PFR and there is a significant pressure drop, write a momentum balance, expanding all summations and continuous products and eliminating all zero-valued and negligible terms

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- If the reactor is a PFR and there is a significant pressure drop, write a momentum balance, expanding all summations and continuous products and eliminating all zero-valued and negligible terms
    - The problem statement specifies that the pressure drop is negligible, so a momentum balance is not needed
- Identify the type of the design equations as algebraic, ordinary differential or partial differential equations
    - if they are algebraic, identify a set of unknowns, equal in number to the number of equations
    - if they are differential, identify the independent and dependent variables, and if the number of dependent variables is greater than the number of equations, choose one dependent variable and express it and its derivatives in terms of the remaining dependent variables

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- If the reactor is a PFR and there is a significant pressure drop, write a momentum balance, expanding all summations and continuous products and eliminating all zero-valued and negligible terms
  - The problem statement specifies that the pressure drop is negligible, so a momentum balance is not needed
- Identify the type of the design equations as algebraic, ordinary differential or partial differential equations
  - The design equations are initial value ODEs
  - The independent variable is z
  - The dependent variables are $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, $\dot{n}_Z$ and T
- Determine what you will need to provide in order to solve the design equations numerically and formulate the equations you need in order to do so

- Determine what you will need to provide in order to solve the design equations numerically and formulate the equations you need in order to do so

If the solution to a problem involves solving a set of initial value ordinary differential equations, you must state that it is necessary to solve a set of initial value ODEs numerically and you must (a) explicitly identify the equations to be solved, the independent variable and the dependent variables by writing the equations in the form, (derivative i) = f_i(independent variable, dependent variable list) = expression. Then you must list values or show how to calculate (b) initial values of the independent and dependent variables, (c) the final value of either the independent variable or one of the dependent variables and (d) every quantity that appears in those functions, assuming you are given values for the independent and dependent variables. Once you have provided (a), (b) and (c), you may assume that the final values of the remaining independent and dependent variables have been found numerically, and you may use those values as needed to complete the problem.

Numerical Solution

$$\frac{d\dot{n}_A}{dz} = -\frac{\pi D^2}{4} r \qquad \frac{d\dot{n}_B}{dz} = \left(-\frac{1}{2}\right)\frac{\pi D^2}{4} r \qquad \frac{d\dot{n}_Y}{dz} = \frac{\pi D^2}{4} r \qquad \frac{d\dot{n}_Z}{dz} = \frac{\pi D^2}{4} r$$

$$\frac{dT}{dz} = \frac{\pi D U\left(T_e - T\right) - \frac{\pi D^2}{4} r \Delta H}{\left(\dot{n}_A + \dot{n}_B + \dot{n}_I + \dot{n}_Y + \dot{n}_Z\right)\hat{C}_p}$$

- Initial conditions (at z = 0)

$$\dot{n}_A(0) = \dot{n}_A^0 = 0.05\dot{n}_{total}^0,\ \dot{n}_B(0) = \dot{n}_B^0 = (0.21)0.95\dot{n}_{total}^0,$$

$$\dot{n}_Y(0) = \dot{n}_Z(0) = 0,\ T(0) = T^0 = (350 + 273.15)\ \text{K}$$

$$\dot{n}_{total}^0 = \frac{P\dot{V}^0}{RT^0}; \qquad \dot{V}^0 = \frac{V}{\tau} = \frac{1}{\tau}\left(\frac{\pi D^2}{4}\right)L$$

- Final condition: z = L
- Code to evaluate the right hand sides of the equations above, given z, molar flow rates of A, B, Y and Z and T

$$r = k_0 \exp\left\{\frac{-E}{RT}\right\} C_A; \quad C_A = \frac{\dot{n}_A}{\dot{V}} = \frac{\dot{n}_A P}{\left(\dot{n}_A + \dot{n}_B + \dot{n}_X + \dot{n}_Y + \dot{n}_I\right)RT} \ \text{or}\ C_A = \frac{\dot{n}_A}{\dot{V}^0}$$

$$\dot{n}_I = (0.79)0.95\dot{n}_{total}^0$$

- After the design equations have been solved numerically, use the results to calculate any other quantities or make any plots that the problem asked for

- After the design equations have been solved numerically, use the results to calculate any other quantities or make any plots that the problem asked for
  - Solving the design equations will yield the values of $\dot{n}_A$, $\dot{n}_B$, $\dot{n}_Y$, $\dot{n}_Z$ and T at z = L
  - The problem asked for the outlet temperature, which is obtained by solving the design equations and the conversion which is calculated as follows:

$$f_A = \frac{\dot{n}_A^0 - \dot{n}_A}{\dot{n}_A^0}$$

Result

Space Time, τ (min)	***T and f_A Ignoring Density Change***	***T and f_A Including Density Change***
1	624 K, 0.0043	624 K, 0.0043
10	632 K, 0.0483	632 K, 0.0479
50	797 K, 0.978	772 K, 0.838

Where We're Going

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- Part III - Chemical Reaction Engineering
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