

The background features a large, stylized blue and grey buffalo mascot. The buffalo is facing forward with its mouth open, showing its teeth. Below the buffalo's head, the word "BUFFALO" is written in a large, bold, white, italicized font with a grey outline. The text is centered horizontally and spans across the width of the buffalo's body.

# **A First Course on Kinetics and Reaction Engineering**

**Class 21 on Unit 20**

# 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**
    - 18. Reaction Engineering of Batch Reactors
    - 19. Analysis of Batch Reactors
    - 20. Optimization of Batch Reactor Processes
  - ▶ C. Continuous Flow Stirred Tank Reactors
  - ▶ D. Plug Flow Reactors
  - ▶ E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors



# Modeling and Optimizing Batch Reactor Operational Protocols

- Each step in the operational protocol for a batch reactor is modeled separately
  - ▶ The mole balances typically are the same for every step
  - ▶ Each step usually has slightly different energy balance design equations
    - Most commonly, the heat input terms are different in each step
- As soon as one step ends, the next step begins immediately
  - ▶ The values of the dependent variables at the end of the prior step become the initial values of the dependent variables for the current step
- The net rate of production of a product can be used as a preliminary optimization criterion for the operational protocol
  - ▶ The net rate of production accounts for both the reaction time and the turnaround time.
  - ▶ 
$$r_{i,net} = \frac{n_i^f - n_i^0}{t_{process} + t_{turnaround}}$$
- If the turnaround time is negligible, short reaction times typically correspond to high net rates, but low product purity
- If the turnaround time is comparable to the reaction time, intermediate processing times correspond to high net rates, but product purity is still greater at high processing times



Questions?



# A General Approach to Solving Quantitative Reaction Engineering Problems

- Read through the problem statement and determine (a) the type of reactor being used, (b) whether it operates transiently or at steady state, (c) whether it is heated/cooled, isothermal or adiabatic and (d - if the reactor is a PFR) whether there is a significant pressure drop
- Read through the problem statement a second time and (a) assign each quantity given in the problem statement to the appropriate variable symbol (b) choose a basis, if necessary and (c) determine what quantities the problem asks for and assign appropriate variable symbols to them
- Write a mole balance equation for each reactant and product, expanding all summations and continuous products and eliminating all zero-valued and negligible terms
- Write an energy balance design equation, expanding all summations and continuous products and eliminating all zero-valued and negligible terms
- If information about the heat transfer fluid, beyond its temperature, is provided or requested, write an energy balance on the heat transfer fluid
- 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



- 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
- 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
- Write the necessary code and solve the design equations numerically
- 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



- Recall the problem statement for Assignment 18: Reagent A undergoes an essentially irreversible isomerization reaction that obeys first-order kinetics ( $A \rightarrow B$ ). Both A and B are liquids at room temperature and both have extremely high boiling points. The rate constant at  $163\text{ }^{\circ}\text{C}$  is  $0.2\text{ h}^{-1}$  and the activation energy associated with the rate constant is  $28,960\text{ cal mol}^{-1}$ . The heat of reaction is constant and is equal to  $-20,750\text{ cal mol}^{-1}$ . The heat capacities of species A and B may be assumed to be identical and equal to  $125\text{ cal mol}^{-1}\text{ }^{\circ}\text{C}^{-1}$ . The initial charge to a perfectly mixed batch reactor contains no B, and it contains A at a concentration of  $3.6\text{ millimoles cm}^{-3}$  and at  $163\text{ }^{\circ}\text{C}$ . You need to determine how long it will take to reach 97% conversion and what the final temperature will equal if the reactor operates adiabatically.
- One might reasonably ask how the initial charge was heated to  $163\text{ }^{\circ}\text{C}$  without any reaction taking place. In a slightly more realistic scenario the initial charge ( $3.6\text{ mmol A cm}^{-3}$  and no B) to the  $100\text{ cm}^3$  reactor would be at  $300\text{ K}$ . In the first stage of processing, a heating jacket (heat transfer area of  $11.2\text{ cm}^2$ , heat transfer coefficient of  $12.1\text{ cal cm}^{-2}\text{ h}^{-1}\text{ K}^{-1}$ ) surrounding the reactor contains a well-mixed fluid at  $200\text{ }^{\circ}\text{C}$ . Once the reactor contents reaches  $160\text{ }^{\circ}\text{C}$ , the reactor is instantaneously (and magically?) switched to adiabatic operation which then continues until 97% conversion is attained. What will the total processing time be?
- Note: With the use of an “IF” statement, it is possible to solve the ODEs for both stages using a single call to the numerical ODE solver.



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





### Reactor Relationships

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

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

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

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

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

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

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

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

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



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

- ▶ During the heating stage:

$$\frac{dT}{dt} = \frac{\dot{Q} - Vr\Delta H}{n_A \hat{C}_{p,A} + n_B \hat{C}_{p,B}}$$

$$\dot{Q} = UA(T_e - T)$$

- ▶ During the adiabatic stage:

$$\frac{dT}{dt} = \frac{-Vr\Delta H}{n_A \hat{C}_{p,A} + n_B \hat{C}_{p,B}}$$



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

- ▶ During the heating stage:

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- ▶ During the adiabatic stage:

$$\frac{dT}{dt} = \frac{-Vr\Delta H}{n_A \hat{C}_{p,A} + n_B \hat{C}_{p,B}}$$

- If information about the heat transfer fluid, beyond its temperature, is provided or requested, write an energy balance on the heat transfer fluid
  - ▶ Insufficient information is given
  - ▶ Assume that the flow rate of the coolant is very large so that the temperature in the jacket remains essentially constant at 200 °C



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

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  - ▶ Insufficient information is given
  - ▶ Assume that the flow rate of the coolant is very large so that the temperature in the jacket remains essentially constant at 200 °C
- How could you solve the equations for both stages using a single call to the numerical ODE solver?



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

- ▶ During the heating stage:

$$\frac{dT}{dt} = \frac{\dot{Q} - Vr\Delta H}{n_A \hat{C}_{p,A} + n_B \hat{C}_{p,B}} \quad \dot{Q} = UA(T_e - T)$$

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  - ▶ Insufficient information is given
  - ▶ Assume that the flow rate of the coolant is very large so that the temperature in the jacket remains essentially constant at 200 °C
- How could you solve the equations for both stages using a single call to the numerical ODE solver?
  - ▶ IF  $T < 160$  °C,  $\dot{Q} = UA(T_e - T)$
  - ▶ ELSE,  $\dot{Q} = 0$



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    - 19. Analysis of Batch Reactors
    - 20. Optimization of Batch Reactor Processes
  - ▶ **C. Continuous Flow Stirred Tank Reactors**
    - 21. Reaction Engineering of CSTRs
    - 22. Analysis of Steady State CSTRs
    - 23. Analysis of Transient CSTRs
    - 24. Multiple Steady States in CSTRs
  - ▶ D. Plug Flow Reactors
  - ▶ E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors

