A First Course on Kinetics and Reaction Engineering

Class 39 on Units 35 and 36

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
  - A. Alternatives to the Ideal Reactor Models
    - 33. Axial Dispersion Model
    - 34. 2-D and 3-D Tubular Reactor Models
    - 35. Zoned Reactor Models
    - 36. Segregated Flow Model
    - 37. Overview of Multi-Phase Reactors
  - B. Coupled Chemical and Physical Kinetics

Zoned Reactor Models

- Used when a reactor does not quite satisfy the assumptions of an ideal reactor model
- Treat that reactor as if it contains different zones
  - Each zone behaves like an ideal reactor
  - The zones are connected to form a network
  - Adjustable parameters associated with the network can be used to adjust the performance of the zoned model to best match the performance of the actual reactor.
    - number of zones
    - relative sizes of zones
    - fractional splits of network streams
- Useful types of zones
  - PFR zone
    - just like a PFR
  - CSTR zone
    - just like a CSTR
  - Well-mixed stagnant CSTR zone
    - like a CSTR except its inlet and outlet are connected at the same point in the zone network
    - it draws its feed and returns its product at the same point in the network

Segregated Flow Model

- Recall the age function, F, from Unit 11
  - Define F(λ) as fraction of the fluid leaving a steady state flow system that has been inside the system for a period of time (i. e. has an age) < λ
    - F is a fraction between 0 and 1 as λ varies from 0 to ∞
  - A related function, known as the residence time distribution function or the age distribution function, dF(λ), is equal to the fraction of the fluid leaving a steady state flow system that has been inside that system for a period of time between λ and dλ
    - dF(λ) = F(λ + dλ) - F(λ)
    - The integral of dF from λ = 0 to λ = ∞ should equal 1
- Segregated flow model
  - Treat each fluid element like a separate batch reactor
  - Different fluid elements have different residence times; they are distributed according to the age function
- Quantities that can be calculated from the (properly normalized) age distribution function
  - The average age of the fluid elements leaving the reactor

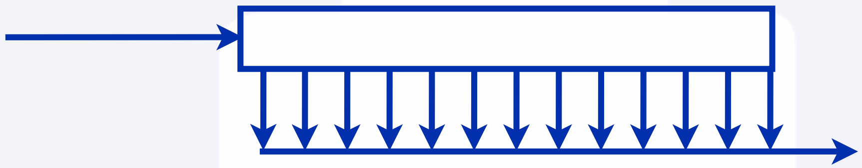
$$\overline{\lambda} = \int_{F=0}^{F=1} \lambda \, dF = \int_{\lambda=0}^{\lambda=\infty} \lambda \frac{dF}{d\lambda} d\lambda$$

  - The average value, at the reactor outlet, of any quantity, y, that depends upon the age

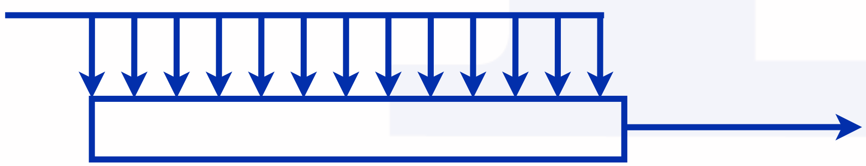
$$\overline{y} = \int_{F=0}^{F=1} y \, dF = \int_{\lambda=0}^{\lambda=\infty} y \frac{dF}{d\lambda} d\lambda$$

Variations on the Segregated Flow Model

- Segregated flow model allows for perfect micro-mixing and zero macro-mixing during processing
  - This is more easily seen in terms of a PFR analogy



  - The fraction of the inlet flow leaving at any position is equal to the value of the age function at the corresponding space time
- Macro mixing can be introduced by adding the feed so that the fraction of the total added at any point is equal to the value of the age function corresponding to the space time that element will experience
  - Upon addition, that element mixes with all the other elements already present



Questions?

Example

The age function for a laboratory reactor has been measured and found to obey the equations given below, with times in ks. Calculate the average residence time in the reactor and then use a segregated flow model to find the conversion for the first order reaction A → P if the rate constant is 0.8 ks^{-1} and the reactor is isothermal.

$0 < t < 0.4$	$F_1(t) = 0$
$t > 0.4$	$F_2(t) = 1 - \exp(-1.25(t-0.4))$

Example

The age function for a laboratory reactor has been measured and found to obey the equations given below, with times in ks. Calculate the average residence time in the reactor and then use a segregated flow model to find the conversion for the first order reaction A → P if the rate constant is 0.8 ks^{-1} and the reactor is isothermal.

$0 < t < 0.4$	$F_1(t) = 0$
$t > 0.4$	$F_2(t) = 1 - \exp(-1.25(t-0.4))$

Solution:

- First note that we will need the RTD not the age function

$$dF(\lambda) = \left(\frac{dF(\lambda)}{d\lambda}\right) d\lambda$$

Example

The age function for a laboratory reactor has been measured and found to obey the equations given below, with times in ks. Calculate the average residence time in the reactor and then use a segregated flow model to find the conversion for the first order reaction A → P if the rate constant is 0.8 ks^{-1} and the reactor is isothermal.

$0 < t < 0.4$ $\quad F_1(t) = 0$

$t > 0.4$ $\quad F_2(t) = 1 - \exp(-1.25(t-0.4))$

Solution:

- First note that we will need the RTD not the age function

$$dF(\lambda) = \left(\frac{dF(\lambda)}{d\lambda} \right) d\lambda$$

$0 < t < 0.4$ $\quad dF_1(\lambda) = 0 d\lambda$

$t > 0.4$ $\quad dF_2(\lambda) = 1.25 e^{-1.25\lambda + 0.5} d\lambda$

- The RTD should be normalized, i. e.

$$\int_{\lambda=0}^{\lambda=\infty} dF(\lambda) = 1$$

  - Check that it is

- The RTD should be normalized, i. e.

$$\int_{\lambda=0}^{\lambda=\infty} dF(\lambda) = 1$$

  - Checking here:

$$\int_{\lambda=0}^{\lambda=\infty} dF(\lambda) = \int_{\lambda=0}^{\lambda=0.4} dF_1(\lambda) + \int_{\lambda=0.4}^{\lambda=\infty} dF_2(\lambda)$$

$$= \int_{\lambda=0}^{\lambda=0.4} 0\, d\lambda + \int_{\lambda=0.4}^{\lambda=\infty} 1.25 e^{-1.25\lambda+0.5}\, d\lambda = 1$$

- The average residence time can be calculated from the RTD

$$x_{average} = \frac{\int_{x=0}^{x=\infty} x\, dN(x)}{\int_{x=0}^{x=\infty} dN(x)} \Rightarrow \overline{t} = \int_{\lambda=0}^{\lambda=\infty} \lambda\, dF(\lambda)$$

  - Calculate the average residence time

- The RTD should be normalized, i. e.

$$\int_{\lambda=0}^{\lambda=\infty} dF(\lambda) = 1$$

  - Checking here:

$$\int_{\lambda=0}^{\lambda=\infty} dF(\lambda) = \int_{\lambda=0}^{\lambda=0.4} dF_1(\lambda) + \int_{\lambda=0.4}^{\lambda=\infty} dF_2(\lambda)$$

$$= \cancel{\int_{\lambda=0}^{\lambda=0.4} 0\, d\lambda} + \int_{\lambda=0.4}^{\lambda=\infty} 1.25 e^{-1.25\lambda+0.5}\, d\lambda = 1$$

- The average residence time can be calculated from the RTD

$$x_{average} = \frac{\int_{x=0}^{x=\infty} x\, dN(x)}{\int_{x=0}^{x=\infty} dN(x)} \Rightarrow \bar{t} = \int_{\lambda=0}^{\lambda=\infty} \lambda\, dF(\lambda)$$

$$\bar{t} = \int_{\lambda=0}^{\lambda=0.4} \lambda\, dF_1(\lambda) + \int_{\lambda=0.4}^{\lambda=\infty} \lambda\, dF_2(\lambda) = \int_{\lambda=0}^{\lambda=0.4} 0\lambda\, d\lambda + \int_{\lambda=0.4}^{\lambda=\infty} 1.25\lambda e^{-1.25\lambda+0.5}\, d\lambda = 1.2$$

- In order to compute the average conversion, we need an expression for the conversion as a function of residence time for a fluid element (batch reactor)
  - Derive an expression for f_A as a function of t

$$\frac{dn_A}{dt} = -Vk\left(\frac{n_A}{V}\right)$$

$$\int_{n_A^0}^{n_A} \frac{dn_A}{n_A} = -k\int_0^{\lambda} dt$$

$$\ln\left(\frac{n_A}{n_A^0}\right) = -k(\lambda - 0)$$

$$n_A = n_A^0 \exp(-k\lambda)$$

$$f_A = \frac{n_A^0 - n_A}{n_A^0} = \frac{n_A^0 - n_A^0 \exp(-k\lambda)}{n_A^0} = 1 - \exp(-k\lambda)$$

- With this, the average conversion for the reactor can be found

$$\bar{f}_A = \int_{\lambda=0}^{\lambda=\infty} f_A \frac{dF}{d\lambda} d\lambda$$

  - Calculate the average conversion according to the segregated flow model

$$\bar{f}_A = \int_{\lambda=0}^{\lambda=0.4} f_A \frac{dF_1}{d\lambda} d\lambda + \int_{\lambda=0.4}^{\lambda=\infty} f_A \frac{dF_2}{d\lambda} d\lambda$$

$$\bar{f}_A = \int_{\lambda=0}^{\lambda=0.4} \left(1 - e^{-kt}\right) 0\, d\lambda + \int_{\lambda=0.4}^{\lambda=\infty} \left(1 - e^{-kt}\right) 1.25 e^{-1.25\lambda + 0.5}\, d\lambda = 0.643$$

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
  - A. Alternatives to the Ideal Reactor Models
    - 33. Axial Dispersion Model
    - 34. 2-D and 3-D Tubular Reactor Models
    - 35. Zoned Reactor Models
    - 36. Segregated Flow Model
    - 37. Overview of Multi-Phase Reactors
  - B. Coupled Chemical and Physical Kinetics