ChE-403 Problem Set 1.2

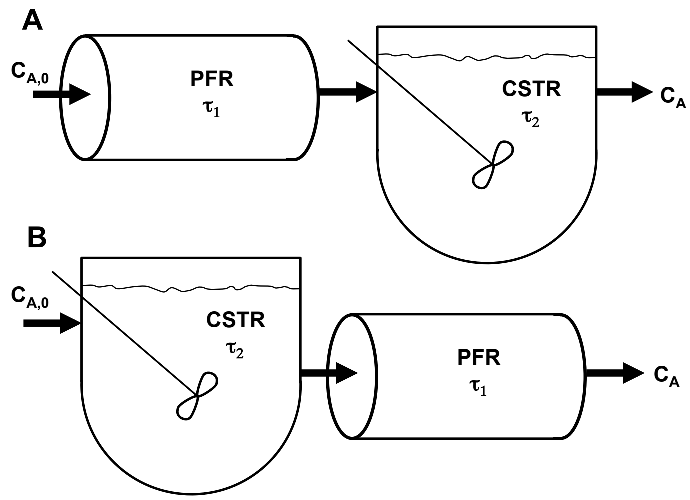
Week 2

Problem 1

Let's take a typical reaction:

$$A \rightarrow C$$

The reaction has first order kinetics. Can you calculate the concentration C_A after it has gone through these two different reactor configurations?



Solution:

<u>For A:</u>

PFR:

$$\frac{dC_A}{d\tau} = \upsilon_A r = -k\, C_A \rightarrow \frac{dC_A}{C_A} = -k\, d\tau$$

$$\ln\left(\frac{C_A}{C_{A,0}}\right) = -k\,\tau_1$$

$$C_A = C_{A,0}\exp(-k\tau_1)$$

CSTR:

$$C_A - C_{A,0}{}' = \upsilon_A r\,\tau_2 = -k\, C_A\,\tau_2$$

$$C_A = \frac{C_{A,0}{}'}{1 + k\,\tau_2}$$

$$C'_{A,0} = C_{A,0}\exp(-k\tau_1)$$

$$\rightarrow C_A = \frac{C_{A,0}\exp(-k\tau_1)}{1 + k\,\tau_2}$$

For B:

Here we don't have to redo everything, we can just take the solutions and switch $C'_{A,0}$ and $C_{A,0}$.

CSTR:

$$C_A = \frac{C_{A,0}}{1 + k\,\tau_2}$$

PFR:

$$C_A = C_{A,0}{}'\ \exp(-k\tau_1)$$

With:

$$C'_{A,0} = \frac{C_{A,0}}{1 + k\,\tau_2}$$

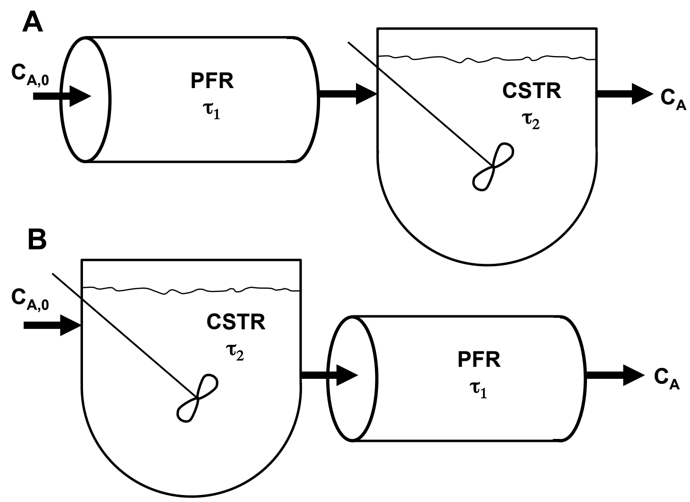
$$C_A = \frac{C_{A,0}\exp(-k\tau_1)}{1 + k\,\tau_2}$$

The same thing!

Problem 2
Let's take the same setups as for problem 1 but with the reaction:

$$2A \rightarrow C$$

i) This time the reaction has second order kinetics. Can you calculate the concentration C_A after it has gone through these two different reactor configurations?



ii) Comparing your result with that of problem 1, can you conclude something about the applicability of using RTD functions for predicting concentrations for reactions that are order 2?

Solution:
i)

<u>For A:</u>

PFR:

$$\frac{dC_A}{d\tau} = \upsilon_A r = -k\, C_A^2 \rightarrow \frac{dC_A}{C_A^2} = -k\, d\tau$$

$$-\frac{1}{C_A} + \frac{1}{C_{A,0}} = -k\tau_1$$

$$\frac{1}{C_A} = k\tau_1 + \frac{1}{C_{A,0}}$$

$$C_A = \frac{1}{\frac{1}{C_{A,0}} + k\tau_1} = \frac{C_{A,0}}{1 + C_{A,0}k\tau_1}$$

CSTR:

$$C_A - C_{A,0}{}' = \upsilon_A r\, \tau_2 = -k\, C_A^2\, \tau_2$$

$$k\, C_A^2\, \tau_2 + C_A - C'_{A,0} = 0$$

$$C_A = \frac{-1 + \sqrt{1 + 4\, k\, \tau_2\, C'_{A,0}}}{2k\, \tau_2}$$

$$C'_{A,0} = \frac{C_{A,0}}{1 + C_{A,0} k \tau_1}$$

$$\rightarrow\ C_A = \frac{-1 + \sqrt{1 + \dfrac{4\, k\, \tau_2\, C_{A,0}}{1 + C_{A,0}\, k\, \tau_1}}}{2k\, \tau_2}$$

<u>For B:</u>

Again, we don't have to redo everything, we can just take the solutions and switch $C'_{A,0}$ and $C_{A,0}$.

CSTR:

$$C_A = \frac{-1 + \sqrt{1 + 4\, k\, \tau_2\, C_{A,0}}}{2k\, \tau_2}$$

PFR:

$$C_A = \frac{C'_{A,0}}{1 + C'_{A,0} k \tau_1}$$

$$C_A = \frac{-1 + \sqrt{1 + 4\, k\, \tau_2\, C_{A,0}}}{2k\, \tau_2 + k\tau_1 \left(-1 + \sqrt{1 + 4\, k\, \tau_2\, C_{A,0}}\right)}$$

ii)

Here configurations A and B do not lead to the same concentrations. If you had run a tracer experiment for case A and B you would have gotten exactly the same profile (same E(t)) because only the CSTR influences the shape of E(t) while a PFR just delays it by τ_1 so the order of the two reactors is irrelevant. However, if an order two reaction is underway the two configurations do not lead to the same exit concentration. This demonstrates the limitations of using RTD measurements to predict kinetics for certain reactions.

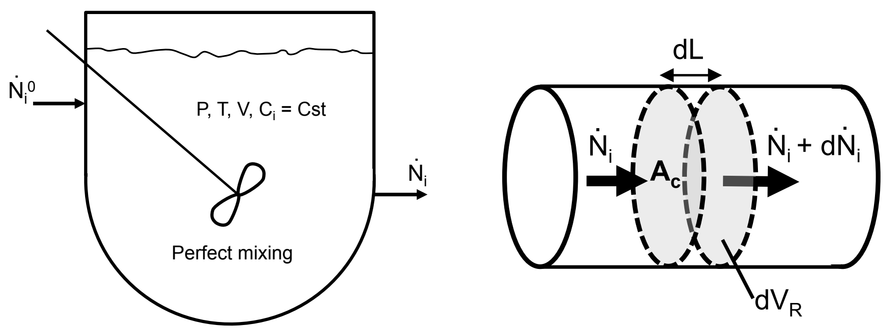
A PFR and CSTR in series are an extreme example of non-uniform mixing (no mixing followed by complete mixing or vice-versa) and therefore reinforces what we said in class (i.e. that the RTD method does not give exact results in cases of non-uniform mixing and reaction order >1). Nevertheless, if you plug numbers into the results for case A and B, you see that we get fairly similar numerical results which indicates that the RTD method is not exact but reasonably accurate even for reaction orders >1.

Problem 3
A typical autocatalytic reaction can look like:

$$\mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{B}$$

The reaction has second order kinetics.

Starting from a mass balance of the reactor, can you derive an expression for conversion of A (X_A) as a function of residence time and k in a CSTR and a PFR with $C_A^0 = C_B^0 = 1\frac{mol}{L}$?



Solution:

<u>CSTR</u>:

$$\frac{dC_A}{dt} = 0 = C_A^0(\dot{V}) - C_A(\dot{V}) + \upsilon_i r V$$

With:

$$\frac{V}{\dot{V}} = \tau$$

$$X_A = \frac{C_A^0 - C_A}{C_A^0}$$

$$X_A = -\frac{\upsilon_A r}{C_A^0}\tau = \frac{k\, C_A C_B}{C_A^0}\tau$$

$$C_A = C_A^0(1 - X_A)$$

$$C_B = C_B^0 + [C_A^0 - C_A] = C_B^0 + C_A^0 X_A$$

$$X_A = k\,(1 - X_A)(C_B^0 + C_A^0 X_A)\tau = k\,(1 - X_A)(1 + X_A)\tau = k\,(1 - X_A^2)\tau$$

$$X_A^2 + \frac{1}{k\tau}X_A - 1 = 0$$

$$X_A = \frac{-(k\tau)^{-1} + \sqrt{(k\tau)^{-2} + 4}}{2}$$

<u>PFR</u>:

$$\frac{d\dot{N}_A}{dt} = d\dot{N}_A + \upsilon_A r dV_R$$

$$\frac{d\dot{N}_A}{dV_R} = \upsilon_A r$$

With:

$$d\dot{N}_A = \dot{V} dC_A \quad and \quad \frac{dV_R}{\dot{V}} = d\tau$$

We can write:

$$\frac{dC_A}{\upsilon_A r} = d\tau$$

$$\frac{dC_A}{\upsilon_A r} = -\frac{dC_A}{k\, C_A C_B} = \frac{-(-C_A^0\, dX_A)}{k\, C_A^0\, (1 - X_A)(C_B^0 + C_A^0 X_A)} = \frac{dX_A}{k\,(1 - X_A)(1 + X_A)}$$

Rearranging we now can integrate:

$$\frac{dX_A}{(1 - X_A)(1 + X_A)} = k d\tau$$

This expression is hard to integrate as is (even if you can just pull the well-known result out of an integration table). Let's try to separate it into two expressions so that:

$$\frac{1}{(1 - X_A)(1 + X_A)} = \frac{\alpha}{(1 - X_A)} + \frac{\beta}{(1 + X_A)} = \frac{\alpha(1 + X_A) + \beta(1 - X_A)}{(1 - X_A)(1 + X_A)}$$

We can get 2 equations from this:

$\alpha + \beta = 1$ This satisfies the constants

$\alpha X_A - \beta X_A = 0$ This satisfies the variables

From this we quickly see that $\alpha = \beta = 1/2$

Our equation becomes:

$$\frac{dX_A}{(1 - X_A)} + \frac{dX_A}{(1 + X_A)} = 2k d\tau$$

$$\int_0^{X_A} \frac{dX'_A}{(1 - X'_A)} + \frac{dX'_A}{(1 + X'_A)} = 2k\tau$$

$$\ln\left(\frac{1 + X_A}{1 - X_A}\right) = 2k\tau$$

$$\frac{1+X_A}{1-X_A}=\exp(2k\tau)$$

$$X_A=-1+\exp(2k\tau)\,(1-X_A)$$

$$X_A(1+\exp(2k\tau))=\exp(2k\tau)-1$$

$$X_A=\frac{\exp(2k\tau)-1}{1+\exp(2k\tau)}=\frac{1-\exp(-2k\tau)}{1+\exp(-2k\tau)}=\tanh\,(k\tau)$$

⚠ In both solutions, we got rid of $C_A^0=C_B^0=1\,\frac{mol}{L}$ to simplify our algebra (and that's fine!). However, we have to make sure that if we plug in a value for k, we use the right units otherwise, the result is incorrect (so getting rid of these values explicitly can be dangerous).