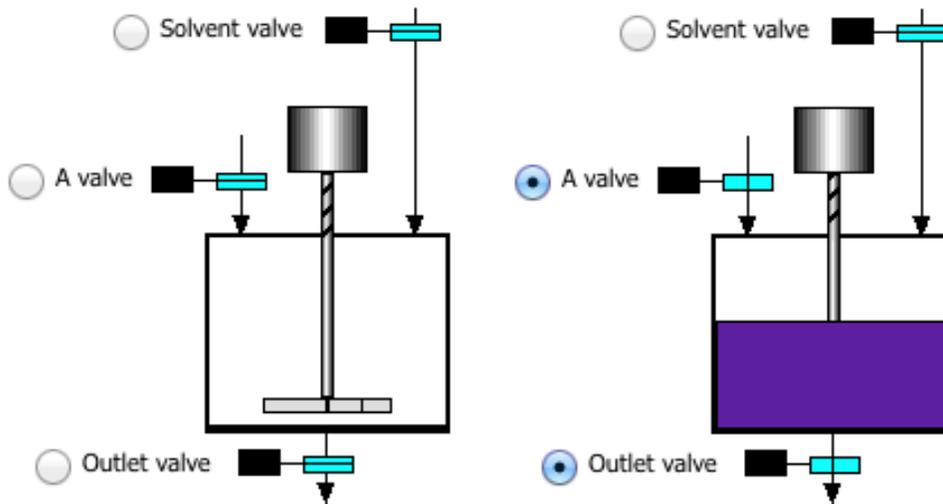


Chemical Reaction Engineering - Part 14 - intro to CSTRs

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Continuous Stirred Tank Reactors - CSTRs

Here are a couple screenshots from the ReactorLab, Division 1 Lab 7. On the left is an empty reactor showing the mixer blades. On the right there is a continuous flow of reactant into the reactor through the "A valve" and an equal flow rate of products out of the reactor through the "Outlet valve."



The reactor on the right is operating as a CSTR. This CSTR looks like a batch reactor but has continuous flow of fluid through it.

A CSTR has some of the same characteristics as a batch reactor: its contents can be well mixed and uniform in temperature and composition. And a CSTR has some of the same characteristics as a PFR: it can produce product continuously.

Component balance

Consider the reaction of A to products in an isothermal CSTR.

$$\begin{aligned} \text{accum} &= \text{in} - \text{out} + \text{rxn} \\ \frac{dN_A}{dt} &= F_{A0} - F_A + r_A V \end{aligned}$$

Use these equations for molar flow rates and concentrations in a CSTR - the same equations used with PFRs and other flow reactors.

$$C_i = \frac{F_i}{v} \quad ; \quad F_i = v C_i$$

$$\frac{d(C_A V)}{dt} = v_0 C_{A0} - v C_A + r_A V$$

The component balance for an unsteady-state (dynamic) CSTR is an ODE.

For constant volume and flow rate

$$V \frac{dC_A}{dt} = v_0 C_{A0} - v C_A + r_A V$$

$$\frac{dC_A}{dt} = \left(\frac{v_0}{V} \right) (C_{A0} - C_A) + r_A$$

$$\frac{dC_A}{dt} = \left(\frac{1}{\tau} \right) (C_{A0} - C_A) + r_A \quad \text{for constant } V \text{ and } v$$

Under steady-state conditions we get an algebraic equation

$$\frac{dC_A}{dt} = 0 = \left(\frac{1}{\tau} \right) (C_{A0} - C_A) + r_A$$

$$C_A = C_{A0} + r_A \tau$$

For an essentially irreversible 1st-order reaction

$$C_A = C_{A0} - k C_A \tau$$

$$C_A = \frac{C_{A0}}{1 + k \tau}$$

$$C_{A0} (1 - X_A) = \frac{C_{A0}}{1 + k \tau}$$

$$X_A = \frac{k \tau}{1 + k \tau} \quad \text{1st-order, essentially irreversible reaction in steady-state CSTR}$$

It is good practice to check solutions such as this to see if it is reasonable. One way is to check to make sure the solution approaches the correct limits. As the space time approaches zero, the conversion approaches zero. As the space time approaches infinity, the conversion approaches one. Solution checks out at the limits at least.

For a steady-state CSTR we get an algebraic equation. There is no variation in space (well mixed) nor time (steady state).

This is a qualitative difference from a batch reactor (varies with time, dynamic) and from a steady-state PFR (variation with position). Both of those reactors give us ODEs for component balances.

We can use the same solutions for a constant volume batch reactor as for a steady-state PFR with constant volumetric flow rate. For a CSTR, we are going to have to get new solutions for the same reaction systems.

Solutions for dynamic CSTRs will require integration of ODEs. These differential equations will differ from those for a batch reactor by the addition of the flow in and out terms.

Solutions for steady-state CSTRs will require solution of algebraic equations. An alternative is integration of the dynamic reactor equations to steady state.

Reversible 1st-order reaction

Consider the reaction $A \rightleftharpoons B$ with no B in the feed to the CSTR, and constant V and v

$$C_A = C_{A0} + r_A \tau$$

$$C_A = C_{A0} + (-k_f C_A + k_b C_B) \tau$$

$$C_{A0}(1 - X_A) = C_{A0} - k_f \tau C_{A0}(1 - X_A) + k_b \tau C_{A0} X_A$$

$$(1 - X_A) = 1 - k_f \tau (1 - X_A) + k_b \tau X_A$$

$$X_A = \frac{k_f \tau}{1 + (k_f + k_b) \tau}$$

At large space time

$$X_A \rightarrow X_{A,eq} = \frac{k_f}{k_f + k_b}$$

Second-order reaction

Consider a 2nd-order reaction of A to products in a reaction that is essentially irreversible with constant V and v

$$C_A = C_{A0} + r_A \tau$$

$$C_A = C_{A0} - k C_A^2 \tau$$

$$(k \tau) C_A^2 + C_A - C_{A0} = 0$$

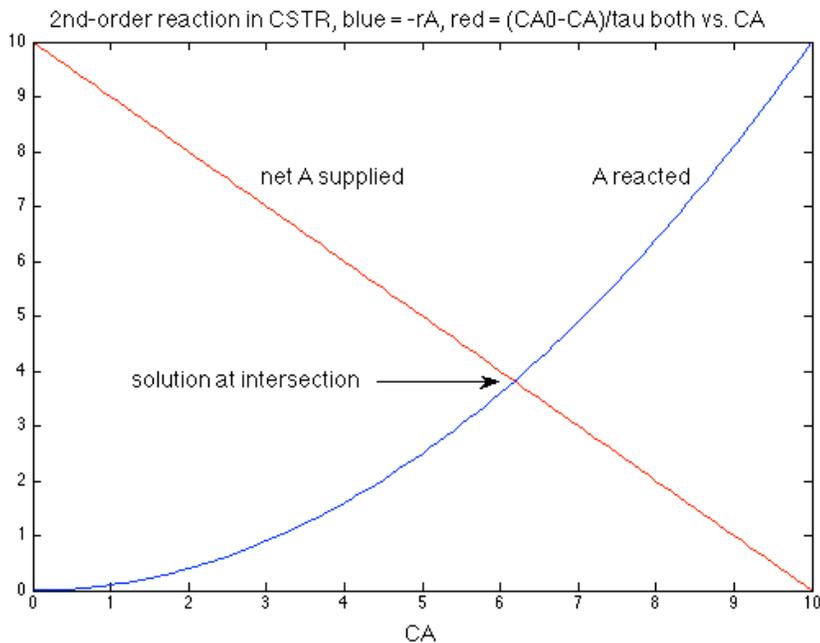
In terms of conversion

$$X_A^2 - \left(2 + \frac{1}{k\tau C_{A0}}\right) X_A + 1 = 0$$

These are quadratic equations (2nd-order polynomials) with solutions you know (the $-b \pm \text{square root of } b^2 \dots$ solution).

There are two solutions to each 2nd-order polynomial but only one will be a "physical solution." That is, only one solution will be positive and less than C_{A0} for the concentration equation, or positive and less than one for the conversion equation.

The fact that there will be only one physical solution can be seen by the graphical solution to the equation.



```
% second order reaction in cstr
% constant V and v, essentially irreversible
k = 0.1; % m3/mol/s, rate coefficient
tau = 1; % s, space time = V/v0
cao = 10; % mol/m3, inlet concentration of reactant
c = 0:0.1:cao; % mol/m3, reactant conc in reactor
y1 = k*c.^2; % mol/m3/s, -rA
y2 = (cao - c)/tau; % mol/m3/s, net supply of reactant by flow
% at steady state, supply by flow = consumption by reaction
% (cao - c)/tau = k*c^2
plot(c,y1,'b',c,y2,'r')
title('2nd-order reaction in CSTR, blue = -rA, red = (CA0-CA)/tau both vs. CA',...
'FontSize',14), xlabel('CA', 'FontSize',14);
% find solution
cc = 0.1; % convergence criterion, adjust depending on c array increment
[rows cols vals] = find(abs(y1-y2)<cc);
Css = c(cols)
```

Reaction with inhibition kinetics

Consider the essentially irreversible reaction of A to products in a CSTR with constant V and v and the following rate equation

$$-r_A = \frac{k C_A}{(1 + K C_A)^2}$$

This type of rate equation can be seen with some reactions catalyzed by solid catalysts or enzymes. See Langmuir Hinshelwood-Hougen Watson (LHHW) kinetics in CRE notes 02. At low C_A the rate is first-order. At high C_A the rate is negative order.

$$C_A = C_{A0} + r_A \tau$$

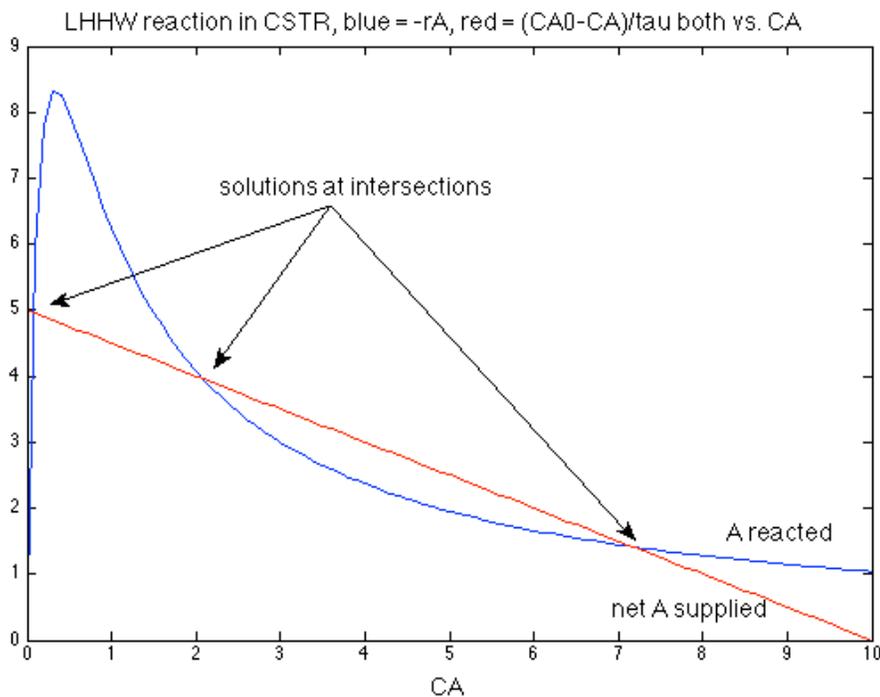
$$C_A = C_{A0} - \frac{k C_A}{(1 + K C_A)^2} \tau$$

$$\frac{k C_A}{(1 + K C_A)^2} = \frac{C_{A0} - C_A}{\tau}$$

$$K^2 C_A^3 + (2K - C_{A0} K^2) C_A^2 + (k \tau + 1 - 2K C_{A0}) C_A - C_{A0} = 0$$

This is a cubic polynomial (3rd-order polynomial) which will have three solutions for C_A . How many of the three will be physical solutions?

We can use a graphical solution for this problem.



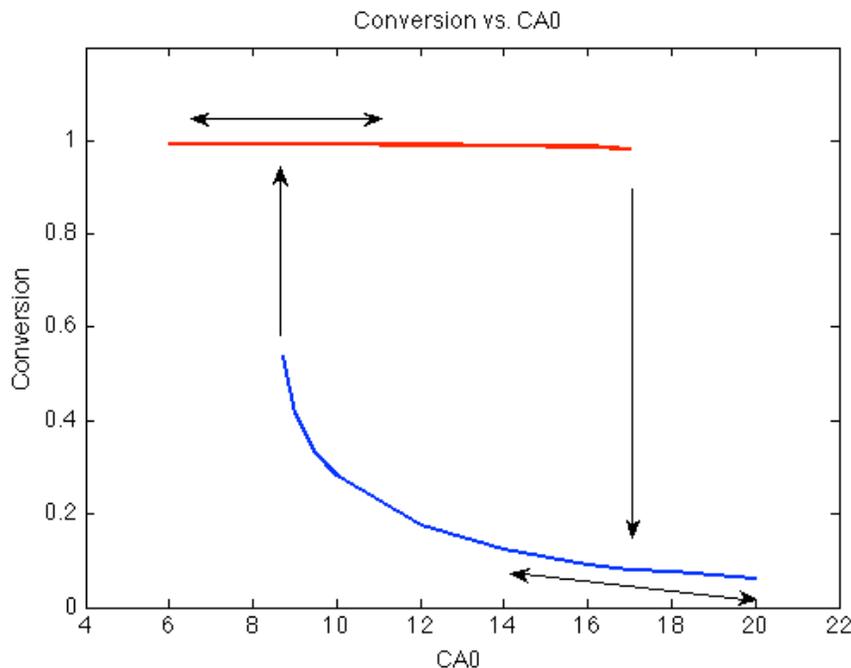
There can be three physical solutions for this rate equation under some conditions. For other values of C_{A0} and τ , there may be one or two physical solutions. For example, reducing C_{A0} from 10 to 8.7 or less will result in only one intersection, and that will be at low C_A and high reaction rate in the reactor. Alternatively, reducing τ from 2.0 to 1.15 s or less, such that the slope of the "net A supplied" line becomes steep, will result in only one intersection, and that will be at high C_A near C_{A0} and low reaction rate. ($k = 100 \text{ s}^{-1}$, $K = 3 \text{ m}^3/\text{mol}$, $C_{A0} = 10 \text{ mol/m}^3$, $\tau = 2 \text{ s}$ for this plot)

This is a case of multiple steady states. This is an interesting field. We will see that multiple steady states can also be obtained with exothermic reactions in CSTRs a little later in these notes.

For the case shown in the plot, the middle solution is an "unstable steady-state" solution. That is, for small perturbations, the system will leave this solution and go to one of the outer "stable steady-state" solutions. This can be seen by integrating the unsteady-state component balance. This can also be seen by doing a "thought experiment." Say that the system is at the middle steady state and an additional small amount of reactant is thrown into the reactor. C_A on the plot will jump a small amount above that at the steady state value. This will cause the system location on both the "A reacted" (rate line) and "net A supplied" (supply line) lines to move to the right a small distance. But the location on the supply line is now higher than the location on the rate line so the system is getting more A than is being reacted. So the system will move to the high C_A steady state on the right as a result of this perturbation.

To which multiple state will your system go? That depends on where your system is coming from. It depends on the history of your system. If you start flow to the CSTR with a very low inlet C_{A0} , you will stay in the high-conversion steady state (low C_A), until the intersection of the supply line with the peak of the rate line is lost. Alternatively, if you start in a low-conversion state (high C_A), and then decrease C_{A0} , you will stay in the low-conversion state steady state until the intersection of the supply line with the "dip" in the middle of the rate line is lost.

If you plot the steady-state X_A as C_{A0} or τ is varied, you will see abrupt jumps in state and a hysteresis loop in the plot of X_A vs. the varied parameter. Below is a plot of X_A vs. C_{A0} showing the hysteresis loop.



CSTRs compared with batch reactors and PFRs

The choice of which type of reactor to use is affected by several factors, including cost, controllability and safety.

In the absence of cost and other data, we can compare the sizes of the different types of reactors required for a given reaction. A larger reactor or larger catalyst requirement will tend to increase costs.

Levenspiel plots (inverse rate plots) are a good way to compare reactor sizes.

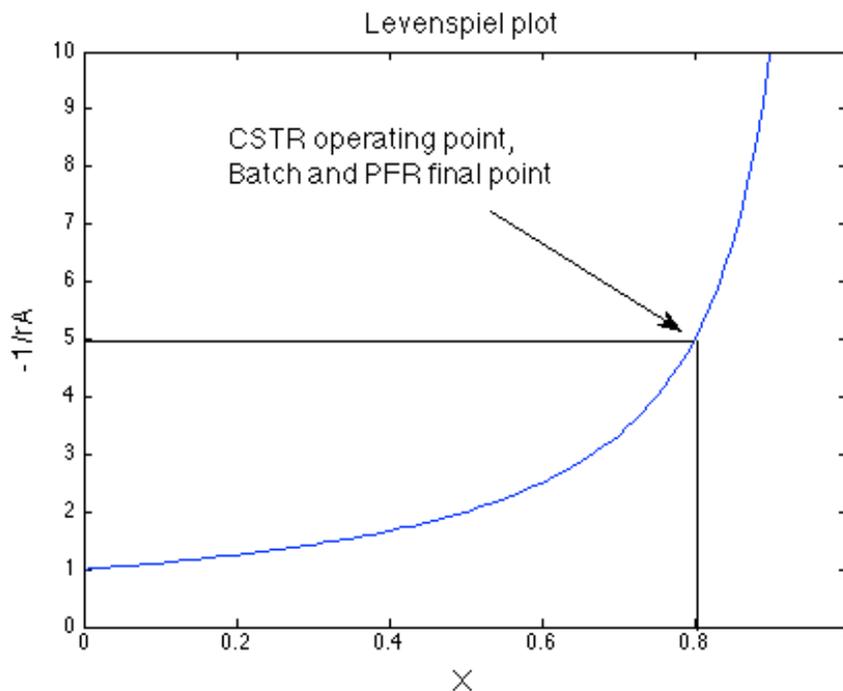
Here are component balances for the three reactors arranged into the form we need to interpret the plots.

$$\int_0^{X_{A,final}} \left(\frac{1}{-r_A} \right) dX_A = \frac{t_{rxn}}{C_{A0}} \quad \text{Batch reactor, constant } V$$

$$\int_0^{X_{A,final}} \left(\frac{1}{-r_A} \right) dX_A = \frac{\tau}{C_{A0}} \quad \text{PFR, constant } v$$

$$\left(\frac{1}{-r_A} \right)_{final} X_{A,final} = \frac{\tau}{C_{A0}} \quad \text{CSTR, constant } v$$

Here is the plot for an essentially irreversible, first-order reaction. The initial or inlet reactant conversion is zero. The final conversion in the batch reactor is 0.80, the outlet conversion in the PFR is 0.80, and the conversion across the steady-state CSTR is 0.80.



From the equations, we can see that the space time for the CSTR is proportional to the area of the rectangle, whose upper-right corner is at the CSTR operating point.

The batch reaction time, and the PFR space time are proportional to the area under the curve from $X_A = 0$ to $X_A = 0.80$.

So the space time or residence time required in the CSTR for this reaction is larger than required by the batch reactor and PFR.

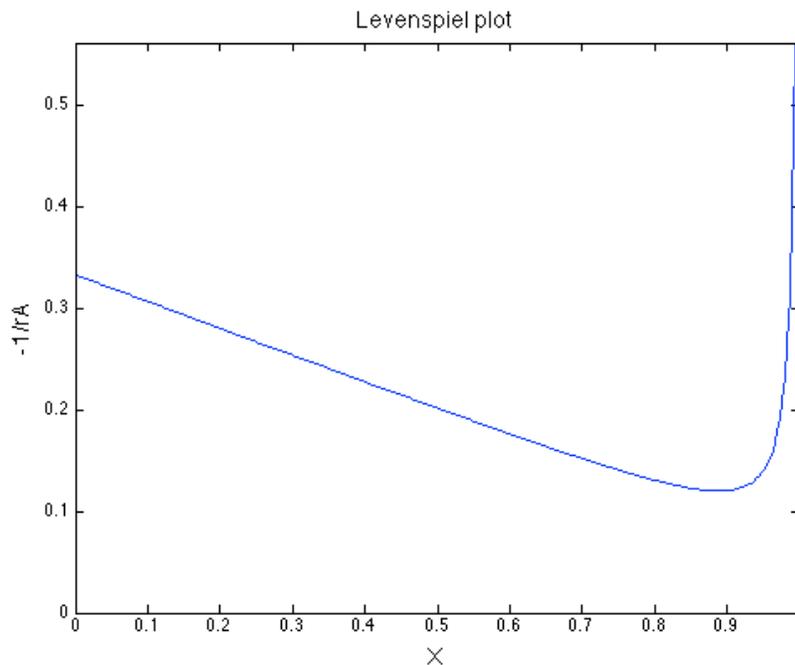
Larger residence time means a larger reactor is required. Note that the areas approach infinity as the conversion approaches infinity. That means the reactor sizes required approach infinity. For these kinetics we can never get exactly to 100% conversion.

Why does the CSTR need more residence time? Why does the CSTR need to be larger? The reason is that the high concentration of reactant in the feed is instantly diluted and reduced to the final reactant concentration as soon as the feed enters the CSTR. Low reactant concentration means low reaction rate and large residence time.

In contrast, the reactant concentration is high, and the rate is high for these kinetics, early during the batch reaction and near the inlet of the PFR.

Remember that the size required for a batch reactor also depends on the batch changeover time.

The result that a larger CSTR is required is the case for any kinetics in which the rate increases with increasing reactant concentration. What about the LHHW kinetics we looked at above? ($k = 100 \text{ s}^{-1}$, $K = 3 \text{ m}^3/\text{mol}$, $C_{A0} = 3 \text{ mol}/\text{m}^3$, $\tau = 2 \text{ s}$ for this plot)



How would the required size for a CSTR compare to that of a PFR for an outlet conversion of 0.5? Of 0.9? Of the maximum conversion of 98% shown.

When a reaction has a region in which the rate is negative order in reactant, then a smaller CSTR can perform the same as a larger PFR. Why would this be true? Think in terms of what happens when the feed to a CSTR is mixed into the reactor contents.

Gases in CSTRs

In a PFR, for gases with a change in total moles, temperature or pressure, the volumetric flow rate of gas changes with position down the reactor.

In contrast, conditions within a CSTR are uniform. However, we need to consider the change in volumetric flow rate out of the CSTR for gases.

Consider the reaction of gases $A \rightarrow 2B$ under isothermal conditions in a steady-state CSTR. The reaction is essentially irreversible and first-order in A.

$$\begin{aligned} F_A &= F_{A0} - F_{A0} X_A \\ F_B &= \quad + 2 F_{A0} X_A \\ \hline F_{tot} &= F_{A0} + F_{A0} X_A \end{aligned}$$

Assume the ideal gas law applies

$$v = v_0 (1 + X_A) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$$

For cases where the steady-state T and P can change with conditions, you will need to write the energy balance and a pressure equation, where the pressure in the reactor may change with a change in flow rate of gas through an outlet valve. Here, specify $T = T_0$ and $P = P_0$

$$v = v_0 (1 + X_A)$$

The component balance is

$$\text{accum} = \text{in} - \text{out} + \text{rxn}$$

$$0 = F_{A0} - F_A + r_A V$$

$$0 = F_{A0} - F_A - k C_A V$$

$$0 = F_{A0} - F_{A0} (1 - X_A) - k \left(\frac{F_A}{v} \right) V$$

$$0 = F_{A0} - F_{A0}(1 - X_A) - k \left(\frac{F_{A0}(1 - X_A)}{v_0(1 + X_A)} \right) V$$

We can see that the change in volumetric flow rate with conversion affects concentrations and, thus, the rate of reaction.

$$0 = F_{A0} X_A - k \tau \left(\frac{F_{A0}(1 - X_A)}{(1 + X_A)} \right)$$

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

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

A graphical solution will show that there will be only one physical solution for this case ($0 < X_A < 1$).

Follow the same procedure for other stoichiometry and kinetics.

Warning: In some problem statements you may be given inlet conditions at standard T and P , e.g., 1 atm, 25 °C. Be sure to correct all values to the T and P inside the reactor before solving, including the inlet conditions.

Kinetic studies with CSTRs

Laboratory CSTRs have an advantage over the other reactor types when it comes to kinetic studies: at steady state, the rate is constant throughout the reactor and can be determined from the inlet and outlet conditions. In contrast, in a batch reactor, the rate is changing with time and, in a steady-state PFR, the rate is changing with position inside the reactor.

So, with a steady-state CSTR, you get a head start on the differential method of analysis: you get the rate at known conditions without having to differentiate. Otherwise, the methods we learned for batch reactors in CRE notes 07 data analysis still apply.

Simulations in ReactorLab - CSTRs

Get ReactorLab at <http://www.ReactorLab.net>

Division 1 Isothermal Reactors

Lab 1 Nth Order Reactions - CSTR

Lab 5 Reversible Reactions - CSTR

Lab 7 Dynamic Mixed Tank - can be run in batch or CSTR mode

Division 2 Catalytic Reactors

Lab 2 First Order Reactions (gas) - CSTR

Lab 3 First Order Reactions (liquid) - CSTR (liquid so constant v)

Division 4 Flow Patterns

Lab 1 PFR CSTR Comparison

Division 5 Multiple Reactions

Lab 3 Parallel Reactions

Lab 4 Series Reactions

(each can be run in batch or CSTR mode)

Division 7 Biological Reactions

Lab 1 Enzyme Reactions - CSTR

Lab 2 Immobilized Enzymes - CSTR