

## Chemical Reaction Engineering - Part 16 - more reactors

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### More reactors

So far we have learned about the three basic types of reactors: Batch, PFR, CSTR. We have also learned about the semi-batch variation of batch reactors.

There are many other types of reactors. So many types that you can make a career out of chemical reaction engineering. Some are similar to the three basic types but have variations such as incomplete mixing. Others combine reaction and separation in one process unit, such as reactive distillation columns that have solid catalyst pellets on some stages.

The good news for us at this stage includes

- we can often get a good approximation of a complex reactor by using one of the three basic reactors
- we can often model complex continuous reactors by combinations of PFRs and CSTRs, e.g., in series and parallel networks

So we can do a lot with what we have learned to at this point.

At the other extreme, complex reactors can be modeled in detail using computational fluid dynamics (CFD) simulations. This is time consuming and expensive work, so it is done when a lot of money is at stake.

Below we discuss some of the reactor types that we can model using combinations of the basic types.

### Batch to start CSTR and batch scale-up

One way to start up a CSTR could be to react initially in batch mode, then start the flow into and out of the reactor. In fermentation reactions, small batches of organisms are grown and then transferred into successively large batch reactors to minimize shock to the organisms.

### CSTRs or PFRs in series with heat exchange between for reversible reactions

Adiabatic reactors are less expensive to build than reactors with heat transfer. However, when equilibrium conversion is a limitation then your ability to achieve high conversion with an adiabatic reactor is limited.

A solution is to have a series of two or more continuous adiabatic reactors with heat exchangers between them. For endothermic reactions, such as petroleum reforming reactions, the heat exchangers would heat the reacting fluid before it enters the next reactor. For exothermic reactions, the heat exchangers cool the reacting fluid before it enters the next reactor.

You probably will not encounter this design with batch reactors. Heating or cooling batches between periods of reaction would probably be more complex than adding heat exchange to the batch reactor.

The optimal number of reactors and heat exchangers in the series is that which results in minimum cost and maximum profit. Each additional reactor and heat exchanger will reduce the total reactor volume and catalyst mass if present. That tends to reduce costs. But each additional reactor and heat exchanger will add to the cost of the system because of additional plumbing and heat exchangers. An interesting optimization problem. The optimal number of reactors and heat exchangers in the series is usually from two to five.

See the  $X_A$  vs.  $T$  plots for endothermic and exothermic reactions in CRE notes 08 thermal effects. Cooling or heating by heat exchangers for reactors in series will result in horizontal lines. CSTRs will have operating points on the plots whereas PFRs will have operating lines similar to those for batch reactors.

Another method to cool exothermic reactions between adiabatic reactors is to add additional cold feed to the reacting fluid. On an  $X_A$  vs.  $T$  plot for a reversible exothermic reaction, this will result in a line that slopes down in conversion and to lower  $T$ . This is called "cold shot cooling" or "quench cooling" and is used in some ammonia synthesis reactor designs. It has the disadvantage over cooling by heat exchange in that you lose conversion. It has the advantage that it is simple, which is of special advantage in ammonia synthesis reactors because all of the PFR catalyst beds must be enclosed in the same high-pressure reactor shell.

### CSTRs in series

Here are component balances arranged into the form we need to interpret Levenspiel inverse rate plots for reactors in series. For these equations, we use  $X_{A,i-0}$  for the inlet condition to reactor number  $i$  in series and  $X_{A,i}$  for the outlet condition to reactor number  $i$ .

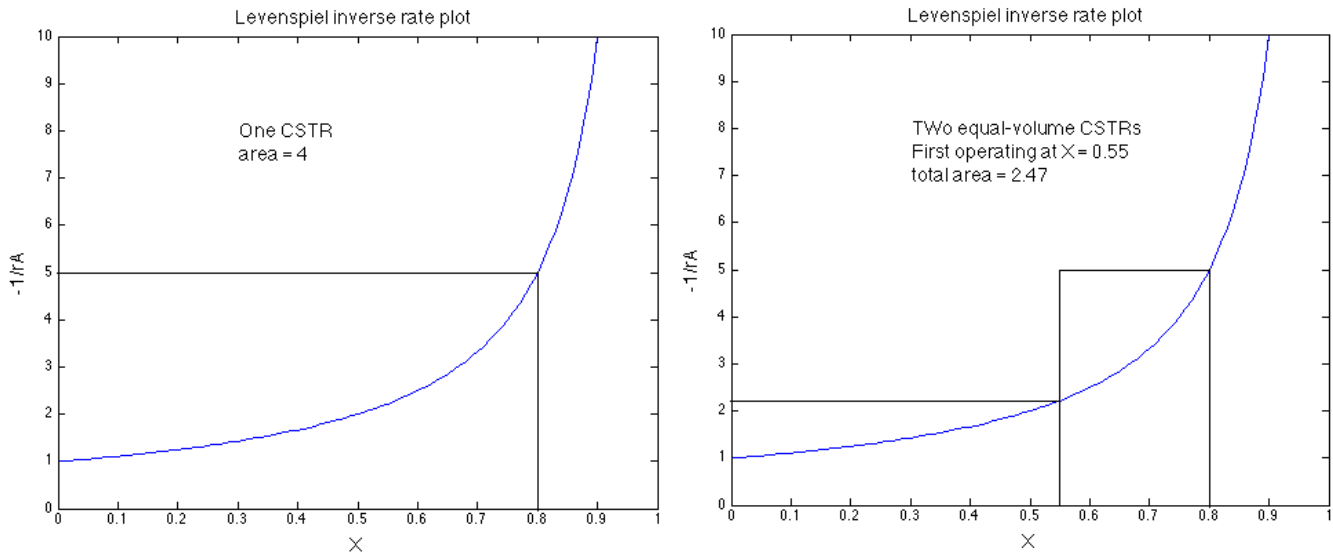
$$\int_{X_{A,i-1}}^{X_{A,i}} \left( \frac{1}{-r_A} \right) dX_A = \frac{\tau_i}{C_{A0}} \quad \text{PFR, constant } v$$

$$\left( \frac{1}{-r_A} \right)_i (X_{A,i} - X_{A,i-0}) = \frac{\tau_i}{C_{A0}} \quad \text{CSTR, constant } v$$

If we have PFRs in series with no change in conditions between reactors (e.g., no cooling), then the total PFR volume will be the same as the volume of one PFR operating at the same final conversion. You should be able to construct that case on a Levenspiel inverse rate plot. So there is no advantage in doing this except in the case that one PFR would be too large to fabricate or install.

There can be an advantage to putting CSTRs in series, even if there is no change in conditions between reactors. This can be seen clearly on a Levenspiel inverse rate plot.

The left-hand plot below shows the construction for one CSTR operating at  $X_A = 0.80$ . The area of the rectangle is  $\tau/C_{A0} = 4.0$ . The right-hand plot shows two equal-volume CSTRs in series, with the conversion in the first CSTR at  $X_A = 0.55$ . The area of each of the two rectangles is the same, and the total area is 2.47.



For equal flow rates, the total volume of the two CSTRs in series is  $2.47/4.0$  or 62% of the volume of the single CSTR. This is because the first CSTR is operating at a lower conversion and higher rate than the second CSTR in series, which is operating at the same conversion as the single CSTR.

CSTRs in series is used fairly commonly to reduce total reactor volume required while retaining advantages of using a CSTR vs. a PFR. As number in series increases, the total volume decreases. This will tend to decrease cost. However, the reactor fabrication and plumbing costs will tend to increase costs. This is another optimization problem.

The plots shown are for kinetics where the rate increases with reactant concentration (inverse rate increases with conversion). For any such kinetics, the total volume of CSTRs in series will be less than that of a single CSTR. However, for kinetics which have regions that are negative order (see LHHW discussed in CRE notes 14), and where a PFR would have a larger volume than a CSTR, then CSTRs in series can have larger total volume than a single CSTR.

You can see from the plots that, as the number of CSTRs in series becomes very large, the total volume will approach the volume of one PFR. This will be true for any rate equation - positive or negative order kinetics.

Packed bed reactors and other tubular flow reactors than do not have perfect plug flow can be modeled using CSTRs in series. Since you aren't trying to model perfect plug flow, you don't need an infinite number of CSTRs. Axial dispersion is a combination of all processes that spread molecules out along the axis of flow that would otherwise stay together in plug flow: diffusion, turbulent eddies, flow between catalyst particles, etc. The fewer CSTRs in the model, the larger the dispersion that is simulated.

### Reactors in parallel

If you have one reactor in operating and need to increase production rates, one way to do that is to add more reactors in parallel with the first. This doesn't complicate the math at all.

Some textbook authors pose problems in which a CSTR is operated in parallel with a PFR, and problems in which PFRs of different sizes are operated in parallel. These may be somewhat artificial problems as far as plant design, since I'm not aware of any situations like this in practice.

Given a reactor network, and knowing now how to model each individual reactor type, solving for the performance of the network is a relatively straight forward material balance problem.

Networks of different types of reactors in series and/or parallel may be able to predict the performance of a reactor with a complex flow pattern. Determining the reactor network that best models the complex reactor can be challenging.

### Residence Time Distribution characterization of reactors with complex flow

We need to characterize and model the flow through a reactor that has complex fluid flow patterns. The flow can be characterized by performing Residence Time Distribution (RTD) experiments.

In an RTD experiment, an inert, non-adsorbing tracer material is injected into the flow into the reactor. The amount of tracer injected is small such that it doesn't change the flow rate into the reactor significantly. The concentration of tracer is measured at the outlet of the reactor either continuously or at time intervals that are much smaller than the space time.

Different shapes of tracer input (concentration vs. time) can be chosen. The usual shapes are an impulse (injection period much smaller than space time) or a step change (step up or step down). An impulse input has the advantage that small amounts of tracer can be used relative to the amounts required for step changes. Actually, any shape of input can be used as long as it is measured and, since inert flow through a vessel is a linear process, Laplace transforms can be used to extract the residence time distribution.

The tracer input and output shapes (tracer concentration vs. time) can be analyzed in order to determine the distribution of times required for flow of tracer molecules through the reactor.

This distribution is expressed mathematically as the "**residence time distribution function**,"  $E(t)$ , also called the "**Exit age distribution function**."  $E(t)$  has dimensions of inverse time (frequency) and is defined for a system in which the flow is at steady state.

The  $E(t)$  of a flow system is also the **unit impulse response** for flow of an inert tracer through the system. In the process control field, the unit impulse response is usually denoted  $g(t)$ . The Laplace transform of  $E(t)$  is the **transfer function** for fluid flow of an inert species through the system.

For a group of tracer molecules entering a flow system at the same time,  $E(t)$  tells you the distribution of times that the molecules in this group will spend in the system before they flow out.

$$E(t) dt = \text{the fraction of tracer molecules that have a residence time between } t \text{ and } t+dt.$$

$F(t)$  is called the "**cumulative RTD function**," is dimensionless, and is the fraction of effluent which has been in the system less than time  $t$  :

$$\int_0^t E(t) dt = F(t)$$

After infinite time has elapsed, all entering molecules will have left the system.

$$\int_0^{\infty} E(t) dt = F(\infty) = 1$$

In order to measure the  $E(t)$  of a system, you can inject into the system any time-varying amount of tracer whose concentration you can measure as a function of time at both the inlet and outlet of the system. The amount of tracer injected should be small so as not to perturb the normal flow in the system.

The  $E(t)$  is a characteristic of the system, not of the type of input used in the RTD experiment. If you use a pulse input, a step input, and an arbitrary function input in separate RTD experiments, you will get different output responses but, after these are analyzed, you will get the same  $E(t)$ .

Let's say the input function of tracer is  $C_{in}^t(t)$  and the outlet function is  $C_{out}^t(t)$ . Since flow in a flow system is a linear process, the outlet function is the convolution of the RTD function,  $E(t)$ , and the inlet function:

$$C_{out}^t(t) = E(t) * C_{in}^t(t)$$

where  $E(t)$  is **convoluted** with  $C_{in}^t(t)$ , and  $*$  is the convolution operator. Taking the Laplace transform of this equation, the transform of the outlet function is equal to the product of the transform of the RTD function and the transform of the inlet function.

$$C_{out}^t(s) = E(s) C_{in}^t(s)$$

For complex input shapes, you may need to use a routine in a numerical analysis library to obtain Laplace transforms of your input and output data. The RTD function is obtained from the inverse transform:

$$E(t) = L^{-1} [E(s)] = L^{-1} \left[ \frac{C_{out}^t(s)}{C_{in}^t(s)} \right]$$

Although one can use any arbitrary tracer input that can be measured, common input functions are the approximate impulse, or pulse, and positive and negative steps. The responses to ideal impulses and steps are easy to analyze.

**Impulse Input:** You can never inject an ideal Dirac delta, or impulse, into a real flow system. However, if the duration of a real pulse of tracer is short with respect to the mean residence time of tracer in the system, then the real pulse is a good approximation of an impulse input. For such an input to a system at steady-state:

$$E(t) \approx \frac{C_{out}^t(t)}{\int_0^{\infty} C_{out}^t(t) dt}$$

Pulse inputs have the advantage that they use a relatively small amount of tracer, an advantage that is important when the tracer is expensive. If the RTD function,  $E(t)$ , is very broad, however, it may be difficult to inject an amount of tracer that is sufficiently large so as to keep the outlet concentration sufficiently high to be measured accurately. In such a case, another type of input, such as a step, would be better to use.

**Positive Step or Step Up:** You can never inject an ideal step function, but if the time over which the rise in tracer concentration occurs is short with respect to the mean residence time of tracer in the system, then the real step is a good approximation of an ideal step.

$$F(t) \approx \frac{C_{out}^t(t)}{C_{in}^t}$$

$$E(t) = \frac{dF(t)}{dt} \approx \frac{d}{dt} \left[ \frac{C_{out}^t(t)}{C_{in}^t} \right]$$

**Negative Step or Step Down:**

$$F(t) \approx 1 - \left[ \frac{C_{out}^t(t)}{C_{in}^t} \right]$$

$$E(t) = \frac{dF(t)}{dt} \approx - \frac{d}{dt} \left[ \frac{C_{out}^t(t)}{C_{in}^t} \right]$$

Make sure you are familiar with the shapes of the impulse and positive- and negative-step responses of flow in PFRs, CSTRs, and laminar flow in tubes.

### Modeling reactors with complex flow

For zero-order reactions, knowledge of the mean residence time is sufficient information to determine reactant conversion. For flow reactors with constant volumetric flow rate, the mean residence time is equal to the space time.

For first-order reactions, knowledge of the residence time distribution function,  $E(t)$ , is sufficient information to determine reactant conversion, at least for isothermal systems.

For first-order reactions, once we know  $X_A(\tau)$  we can use the "**segregated flow model**" to compute the conversion.

$$\bar{X}_A = \int_0^{\infty} X_A(t)E(t)dt$$

For other reactions, we need to have information in addition to  $E(t)$  about the flow patterns in the reactor to determine reactant conversion. That is, we need information about the patterns of fluid flow through the reactor.

For example, a PFR-CSTR-in-series combination has the same  $E(t)$  as a CSTR-PFR-in-series combination. Conversions for zero- and first-order reactions are the same for both combinations. But reactions with more complex kinetics will show different conversions in the two different reactor combinations.

One situation that may be encountered is a CSTR that is not well mixed. Such a reactor might be modeled with one CSTR connected to the main inlet and outlet streams and a second CSTR that exchanges material only with the first CSTR.

### Modeling axial dispersion in reactors

The process of "**axial dispersion**" can be present in packed bed catalytic reactors and other tubular flow reactors than do not have perfect plug flow. Axial dispersion is a combination of all processes that spread molecules out along the axis of flow that would otherwise stay together in plug flow: diffusion, turbulent eddies, flow between catalyst particles, etc.

There are two approaches to modeling reactors with significant axial dispersion: (a) a CSTR-in-series model, and (b) solving the second-order ODE component balance.

For the CSTR-in-series model the fewer CSTRs in the model, the larger the dispersion that is simulated. The number of CSTRs is adjusted so that the  $E(t)$  of the model matches that measured for the real reactor.

For the component balance, the second-order ODE is

$$\begin{aligned} \text{accum} &= \text{in-out by flow} + \text{in-out by dispersion} + \text{gen by rxn} \\ A_x \Delta z \frac{d\bar{C}_A}{dt} &= A_x \bar{u} (\bar{C}_A|_z - \bar{C}_A|_{z+\Delta z}) + A_x (-D_a) \left( \frac{d\bar{C}_A}{dz} \Big|_z - \frac{d\bar{C}_A}{dz} \Big|_{z+\Delta z} \right) + r_A A_x \Delta z \end{aligned}$$

where  $\bar{u}$  is average fluid velocity ( $\text{m s}^{-1}$ ) and  $D_a$  is the axial dispersion coefficient. Specifying steady-state, dividing by  $\Delta z$  and taking the limits as  $\Delta z$  approaches zero produces the second-order ODE to be integrated:

$$\bar{u} \frac{d\bar{C}_A}{dz} - D_a \frac{d^2 \bar{C}_A}{dz^2} - r_A = 0$$

Two boundary conditions (BC) are required. There are two different sets of BC. (1) "Closed system" or Danckwerts BC: at  $z = 0$ ,  $C_{in} = C(z=0^-) = -(D/u) dC/dz$  (at  $z=0$ ) +  $C(z=0^+)$ ; at  $z = L$ ,  $dC/dz = 0$ . (2) Open system BC:  $C(0) = C_{in}$ ,  $C(L) = C_{out}$ . This second-order ODE can be separated into two, coupled first-order ODEs and integrated using Euler's method or other algorithm.

Adjust  $D_a$  until computed  $E(t)$  for inert flow fits experimental  $E(t)$ , or estimate  $D_a$  from a correlation. The value of  $D_a$  is significantly higher than the molecular diffusion coefficient of the reactant in the fluid.

### Laminar flow reactor

A type of flow pattern that immediately comes to mind is laminar flow in a cylindrical reactor or tube. How do we calculate reactant conversions for this type of reactor? This seems like a simple case. It's not so simple.

How we treat laminar flow in a tube depends on the relative importance of convective flow and molecular diffusion, as given by the product of the Reynolds number (Re) and the Schmidt number (Sc), which are dimensionless:

$$Re = \frac{d_t u \rho}{\mu} = \frac{d_t \bar{u}}{\nu} = \frac{\text{convective mass transport}}{\text{diffusive momentum transport}} < 2000 \text{ for laminar flow in tube}$$

$$Sc = \frac{\mu}{\rho D_{AB}} = \frac{\nu}{D_{AB}} = \frac{\text{diffusive momentum transport}}{\text{diffusive mass transport}}$$

$$Re Sc = \frac{d_t u}{D_{AB}} = \frac{\text{convective mass transport rate}}{\text{diffusive mass transport rate}} = \frac{(\bar{u} / d_t)(s^{-1})}{(D_{AB} / d_t^2)(s^{-1})}$$

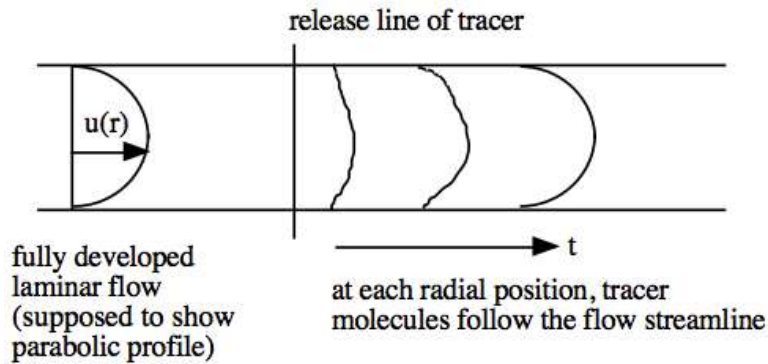
$$Re Sc = \frac{(d_t^2 / D_{AB})(s)}{(d_t / \bar{u})(s)} = \frac{\text{characteristic time for diffusion across tube diameter}}{\text{mean residence time for flow down tube}}$$

For diffusion of O<sub>2</sub> in **air** at 300 K, Sc = approx. 1.

For diffusion of small molecules in **liquid water** at 300 K, Sc = approx. 2000.

**Large ReSc.** For ReSc > approx. 50, convection dominates and a **segregated flow model** can be used to model reaction in laminar flow reactors. This will often be the situation for **laminar flow with liquids**, e.g., liquid water at 300 K with  $0.02 < Re < 2000$ .





Since reactant molecules at each radial position will travel down the reactor independently of molecules at other radial positions, we can consider the flow of reactant molecules as "segregated". Reactant molecules flowing down the center of the reactor will spend less time in the reactor than molecules traveling near the wall. The average conversion will be equal to the conversion  $X_A(t)$  averaged over radial position, i.e., the integral of  $X_A(t)$  weighted by  $E(t)$  :

$$\bar{X}_A = \int_0^{\infty} X_A(t) E(t) dt$$

We can get  $X_A$  as a function of position down the reactor and, therefore, residence time, from our species balance. The  $E(t)$  for a laminar-flow tubular reactor can be determined from the parabolic velocity profile:

$$E(t) = 0 \quad t < \frac{\tau}{2}$$

$$= \frac{\tau^2}{2t^3} \quad t \geq \frac{\tau}{2}$$

In terms of the dimensionless residence time distribution function  $E'(\Theta)$ ,

$$E'(\Theta) = \tau E(t) = \frac{1}{2\Theta^3} \quad \Theta \geq 0.5 \quad \text{where } \Theta \equiv \frac{t}{\tau}$$

For the case of an essentially irreversible, isothermal, first-order reaction:

$$X_A(t) = 1 - e^{-kt}$$

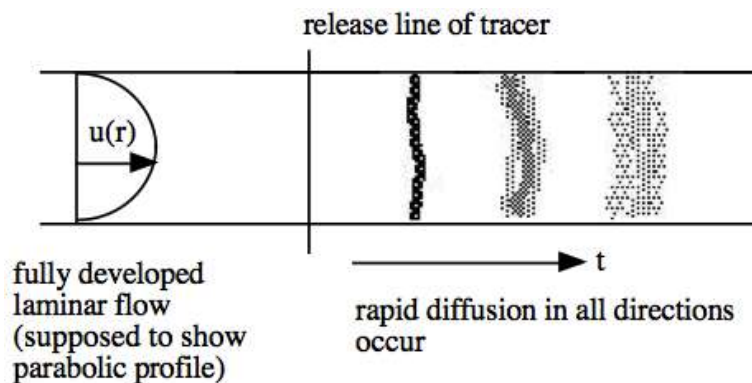
$$\bar{X}_A = \int_{\tau/2}^{\infty} (1 - e^{-kt}) \left( \frac{\tau^2}{2t^3} \right) dt$$

This integral can be approximated numerically. In Matlab:

```
k = 1;
tau = 1;
dt = 0.01;
t = [tau/2:dt:100];
E = tau^2./(2*t.^3);
X = 1 - exp(-k*t/tau);
Xave = sum(X.*E)*dt
```

For  $k = 1$  and  $\tau = 1$ , the conversion for the laminar flow reactor at large  $Re_{Sc}$  estimated numerically is 0.56. This compares to 0.63 for this reaction in a PFR with the same  $\tau$ , or an 11% lower conversion for this case with the laminar flow reactor.

**Small  $Re_{Sc}$ .** For  $Re_{Sc} < \text{approx. } 5$ , radial diffusion is fast with respect to axial convection. This will often be the situation for **laminar flow with gases**, e.g., air at 300 K with  $Re < 5$ .



The fluid flow profile is still parabolic. Reactant molecules released near the center diffuse toward slower traveling fluid near the outer wall. Molecules released near the wall diffuse toward faster traveling fluid near the center. We can choose between two models: the dispersion model or the CSTRs in series (tanks in series) model.

The dispersion model requires us to integrate a second-order ordinary differential equation to compute conversion:

$$-\bar{u} \frac{d\bar{C}_A}{dz} - D_{AB} \frac{d^2\bar{C}_A}{dz^2} - r_A = 0$$

In the case of laminar flow at small  $Re_{Sc}$  that we are considering, the axial dispersion coefficient  $D_a$  approximately equals the molecular diffusivity  $D_{AB}$ .

For short reactors with laminar flow of gases (small  $L/d_i$ ), there will be a large deviation from conversions determined for a PFR with the same mean residence time. For long reactors with laminar

flow of gases (small  $L/d_t$ ), there will be a small deviation from conversions determined for a PFR with the same mean residence time.

To use the CSTRs in series model, we need to determine the number of CSTRs to use. The number of tanks will depend on the length to diameter ratio of the tube ( $L/d_t$ ):

$$n_{CSTR} = 0.5 \left( \left( \frac{L}{d_t} \right) \text{ReSc} + 1 \right) \text{ rounded to nearest integer, for ReSc} < \text{approx. } 3$$

To compute conversion with this model, we just compute the conversion for the  $i$ -th reactor in series inside of a repeat structure, with the outlet flow of the  $i-1$  reactor becoming the inlet flow to the  $i$ -th reactor. For the case of  $\text{ReSc} = 1$ ,  $(L/d_t) = 100$ ,  $n_{CSTR} = 50$ .

For short reactors with laminar flow of gases (small  $L/d_t$ ),  $n_{CSTR}$  will be a small number and there will be a large deviation from conversions determined for a PFR with the same mean residence time. For long reactors with laminar flow of gases (small  $L/d_t$ ),  $n_{CSTR}$  will be a large number and there will be a small deviation from conversions determined for a PFR with the same mean residence time.

**Intermediate ReSc.** At intermediate ReSc between the two cases discussed above, a dispersion model with a dispersion coefficient less than  $D_{AB}$  can be used. This might be obtained with reaction in high-pressure, low-temperature gases, and with liquids in creeping flow (very small Re).

#### PFR with recycle

This is a system with reaction occurring in a PFR, but with the outlet stream physically split (no chemical separation) and part of it recycled and mixed with the inlet stream at a point just before the inlet to the PFR section. Reaction occurs only in the PFR section and not, for example, in the recycle stream.

Recycle reactors are most commonly used with solid catalysts, where the PFR section is a packed bed of catalyst pellets or a catalytic monolith. As we shall see below, recycle reactors approach the behavior of CSTRs at high recycle ratio.

With no flow in or out, a recycle reactor can closely approach the behavior of a batch reactor.

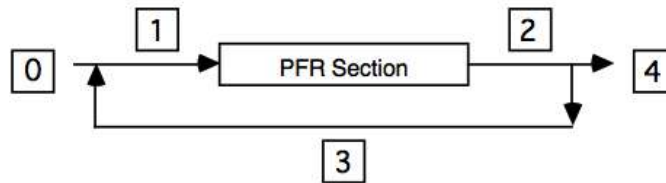
CSTRs are excellent for laboratory kinetic studies, since the entire contents of the reactor are at the same conditions (neglecting gradients inside catalyst pellets) and at steady-state. Recycle reactors can also operate as batch reactors. Therefore, recycle reactors are good choices to use to get kinetic information over solid catalysts. There are two types of laboratory recycle reactors: internal recycle ("Berty reactor") and external recycle reactors.

At intermediate recycle ratios, the behavior of a recycle reactor is intermediate between that of a PFR and a CSTR. Thus, they can be useful for complex kinetics where the smallest reactor can be obtained with a reactor with this intermediate behavior. Remember that PFRs give the smallest reactor for a specified conversion with positive-order reactions, whereas CSTRs give the smallest reactor with negative-order reactions. Intermediate reactor behavior is desirable, for example, when the kinetics are

positive order at low reactant concentrations and negative order at high reactant concentrations.

Here is a procedure for deriving the design equations for a recycle reactor for a system described by a single independent stoichiometric equation. First sketch the system and label the streams:

Recycle Reactor Stream Labels:



Define "recycle ratio," R:

$$R = \frac{F_{\text{total}3}}{F_{\text{total}4}} = \frac{\left(\frac{F_{A3}}{y_{A3}}\right)}{\left(\frac{F_{A4}}{y_{A4}}\right)} = \frac{F_{A3}}{F_{A4}}$$

Also,  $R = (v_3/v_4)$ , when  $v_3$  and  $v_4$  are evaluated at the same temperature and pressure.

Identify the uniform volume element in the PFR section: a differential volume element. Now do a mole balance for the PFR section. Convert all species variables to ones in terms of a single dependent variable. Below we work with the fractional conversion,  $X_A$ , of the key, limiting species A:

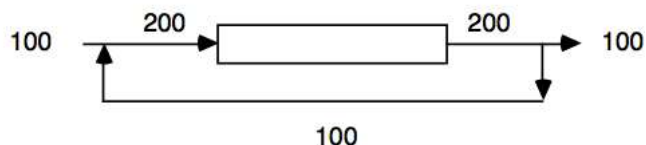
$$X_A = \left(\frac{F_A^{\text{off}} - F_A}{F_A^{\text{off}}}\right)$$

where  $F_A^{\text{off}}$  is the molar flow rate of A that you would have at the point of evaluation of  $X_A$  if everything were kept the same except that the reaction were turned "off." To work with a specific example, here is a case with  $R = 1$  and 50% conversion across the entire recycle reactor. The numbers are the molar flow rate of the limiting reactant:

"Reaction ON"



"Reaction OFF"



At the PFR inlet,  $X_{A1} = (1 - 150/200) = 0.25$ . At the outlet of the PFR,  $X_{A4} = X_{A3} = X_{A2} = (1 - 100/200) = 0.50$ .

Doing the mole balance for the PFR section will result in an equation containing variables at the intermediate points 1 and 2 in the system. For example:

$$\frac{dF_A}{dz} = A_x r_A, \text{ integrated from } F_{A1} \text{ at } z = 0 \text{ to } F_{A2} \text{ at } z = L$$

where  $r_A$  is a function of feed composition,  $F_A$ , and temperature and pressure, and where  $V_{\text{recycle-pfr}} = A_x L$ . In terms of fractional conversion,

$$\frac{dX_A}{dz} = \left( \frac{A_x}{f_{A1}^{\text{off}}} \right) (-r_A), \text{ integrated from } X_{A1} \text{ at } z = 0 \text{ to } X_{A2} \text{ at } z = L$$

where  $r_A$  is a function of feed composition,  $X_A$ , and temperature and pressure, and  $A_x$  is the cross sectional area of the constant cross-section PFR. When temperature or the pressure of gases vary with position  $z$  down the PFR section, the mole balance equation needs to be solved along with equations for  $dT/dz$  and  $dP/dz$ .

In simple cases – constant  $T$  and  $P$ , or where  $T$  and  $P$  can be expressed as functions of  $X_A$  (adiabatic; pressure drop in gas with constant viscosity and negligible  $\Delta F_{\text{total}}$ ) – the mole balance is separable and can be expressed, for example, as:

$$V_{\text{recycle-pfr}} = F_{A1}^{\text{off}} \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{(-r_A)}$$

Now, we want to get expressions for  $F_{A1}^{\text{off}}$  and  $X_{A1}$  in terms of  $R$  and inlet and outlet variables at points 0 and 4, since  $R$  and the inlet and outlet variables will be specified or are unknowns to be determined. Note that  $X_{A2} = X_{A4}$ .

First, get  $F_{A1}^{\text{off}}$  in terms of  $R$  and inlet and/or outlet variables. Since we want an expression for a variable when the "reaction is turned off," mentally keep the flows going but turn the reaction off. Since we are concerned with stream 1, do a mole balance around the mixing point at the inlet of the reactor: streams 0 and 3 combine to make stream 1:

$$\begin{aligned} F_{A1}^{\text{off}} &= F_{A0}^{\text{off}} + F_{A3}^{\text{off}} \\ &= F_{A0}^{\text{off}} + R F_{A4}^{\text{off}} \\ &= F_{A0}^{\text{off}} + R F_{A0}^{\text{off}} \\ &= F_{A0} (R + 1) \end{aligned}$$

Now we want to get an expression for  $X_{A1}$ . Since this is a "conversion" and conversion involves "reaction," we want to do a mole balance around the inlet mixing point with the "reaction turned on":

$$F_{A1} = F_{A0} + F_{A3}$$

$$F_{A1}^{\text{off}} (1 - X_{A1}) = F_{A0}^{\text{off}} (1 - X_{A0}) + F_{A3}^{\text{off}} (1 - X_{A3})$$

we have just determined  $F_{A1}^{\text{off}}$ , and since  $F_{A0}^{\text{off}} = F_{A0}$ ;  $X_{A0} = 0$ ;  $F_{A3}^{\text{off}} = R F_{A4}^{\text{off}} = R F_{A0}$ ; and  $X_{A3} = X_{A4}$ ; we have

$$F_{A0} (R + 1) (1 - X_{A1}) = F_{A0} + R F_{A0} (1 - X_{A4})$$

solving for  $X_{A1}$ :

$$X_{A1} = X_{A4} \left( \frac{R}{R + 1} \right)$$

Now the PFR-section mole balance can be integrated from this value of conversion at its entrance to  $X_{A2} = X_{A4}$  at its outlet:

$$V_{\text{recycle-pfr}} = F_{A0} (R + 1) \int_{X_{A4} \left( \frac{R}{R + 1} \right)}^{X_{A4}} \frac{d X_A}{(-r_A)}$$

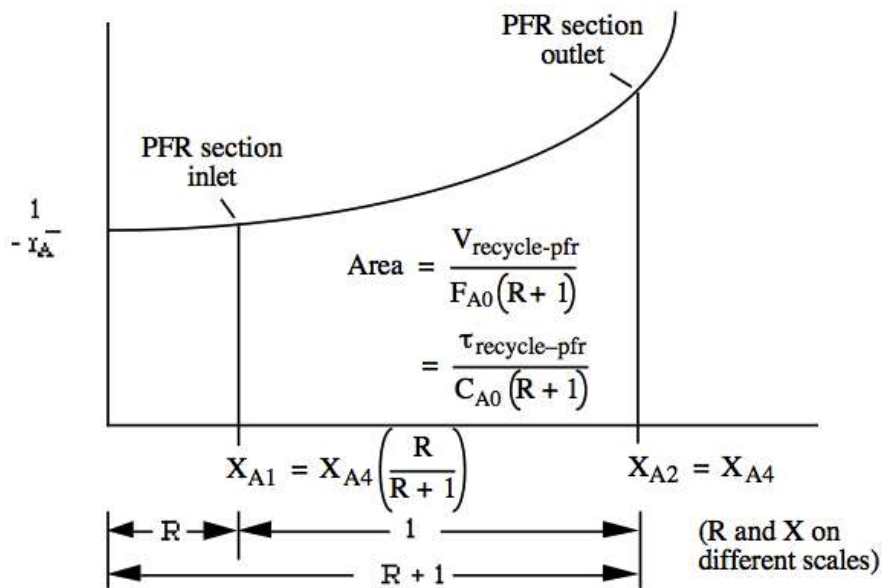
The next step is to evaluate the concentration terms in  $r_A$  using the mole table and the following:

$$C_j = \frac{F_j}{v} \quad C_A = \frac{F_A}{v} \quad F_A = F_{A1}^{\text{off}} (1 - X_A) = F_{A0} (R + 1) (1 - X_A)$$

For ideal gases in flow reactors,  $Pv = F_{\text{total}} R_g T$ :

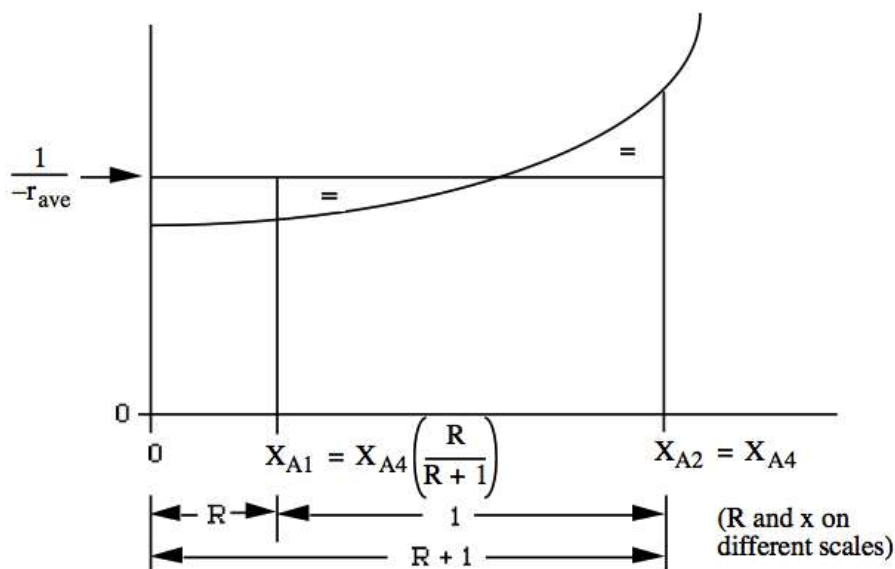
$$v = F_{\text{total}} \left( \frac{R_g T}{P} \right) \quad \text{and} \quad F_{\text{total}} = \text{function} \left( F_{j1}^{\text{off}}, X_A \right)$$

The "inverse rate vs. conversion" plot for a recycle reactor looks like this for a positive-order reaction:



The volume of the PFR section of the recycle reactor,  $V_{\text{recycle-pfr}}$ , is equal to  $F_{A0}(R+1)$  times the area under the curve between  $X_{A1}$  and  $X_{A2} = X_{A4}$ . For  $R \ll 1$ , a recycle reactor is similar to a PFR: they are identical at  $R = 0$ . For  $R \gg 1$ , a recycle reactor is very similar to a CSTR. Note that when  $R \gg 1$ ,  $V_{\text{recycle-pfr}}$  is large, even though the area under the curve between the inlet and outlet  $X_A$ 's is small, because the factor  $(R+1)$  becomes large. Note, in the figure below, that the area of the large rectangle between the origin  $[0, 0]$  and  $[(1/-r_{A,\text{ave}}), X_{A2}]$ , is proportional to the PFR-section volume:

$$\text{Area of rectangle between } [0,0] \text{ and } \left[ \frac{1}{-r_{A,\text{ave}}}, X_{A2} \right] = \left( \frac{R+1}{1} \right) \left( \frac{V_{\text{recycle-pfr}}}{F_{A0}(R+1)} \right) = \frac{V_{\text{recycle-pfr}}}{F_{A0}}$$



Using this plot, show that the behavior of a recycle reactor approaches that of a CSTR at  $R \gg 1$  for any type of kinetics. For example, note that  $X_{A1}$  approaches  $X_{A2}$ , so the conditions within the PFR section are approximately constant.

Verify that a recycle reactor will require a larger reactor volume (e.g., volume or weight of catalyst) for a given conversion with a positive-order reaction than required with a straight PFR.

Sketch the inverse rate plot for a negative-order reaction and compare the behavior of a recycle reactor to a CSTR.

Sketch the inverse rate plot for a reaction that is positive order at low reactant concentration (high conversion) and negative order at high reactant concentration (low conversion). Can you show conditions under which a recycle reactor will let you use a smaller reactor or catalyst volume than either a PFR or CSTR?

### Membrane reactor

This type of reactor has been studied in the laboratory for hydrocarbon dehydrogenation reactions. By selectively removing the hydrogen product through a permeable reactor wall, conversion can exceed equilibrium conversion with no separation. The permeable wall might be a porous ceramic tube coated on one side with a thin palladium coating. The annulus between this tube and an outer tube would contain the flow of hydrogen product.

A membrane reactor can be modeled in a way similar to that for a semi-batch reactor with selective product removal. See CRE notes 10.

This is a type of hybrid, reactor-separator process unit.

### Reactive distillation

Another type of hybrid, reactor-separator process unit is a distillation column in which reactions occur in addition to separation of components. An example is "catalytic distillation" in which porous solid catalyst pellets are placed on some of the stages. By separating products as they are formed, conversion can exceed equilibrium conversion with no separation.

Methanol dehydration to dimethyl ether (DME) and water is an example reaction. DME is potentially useful as a sootless diesel fuel.

### Packed bed reactors

The reactors are usually packed with catalyst pellets. If you are given a rate equation, then you can model the reactor in one of the several ways you know: PFR, CSTRs in series, dispersion model.

The catalyst pellets are porous in order to obtain high active area per unit reactor volume. This means that reactants must diffuse and be carried from the bulk fluid flow to the pellet and then diffuse into the pellets. Products must diffuse out.



The rate equation you are given may not apply if you want to change the size of the catalyst pellets or the concentration of active material in the pellets. That is because the ratio of mass transport to reactivity may change and affect the rate of reaction.

This process of coupled mass transfer (and heat transfer) and reaction complicates the situation such that it becomes of great interest to chemical engineers! Diffusion and reaction in porous catalysts is the subject of a second course in reaction engineering.

### Multi-phase reactors

Reactions in which there is only one phase present are called "homogeneous reactions."

We have learned about reactions of components carried in a fluid-phase that are catalyzed by solids.

When two phases are present that participate in the reaction, we use the term "heterogeneous reaction." Solid catalysts of reactants in the fluid phase are called "heterogeneous catalysts." The reaction happens when components from the fluid phase adsorb over the surface of the catalyst and react on the surface. There are also cases in which both homogeneous and heterogeneous reactions can occur in the same reactor.

We have modeled heterogeneous reactions catalyzed by solids in the same way as homogeneous reactions. We simply replaced the fluid volume by the weight or volume of the catalyst. This can be done when we have a reaction rate equation that is a function of fluid-phase composition and the properties of the catalyst (size, porosity, active material concentration, etc.) and transport properties (external mass transfer coefficient, heat transfer coefficients) are constant. This type of model of a heterogeneous reaction is called a "pseudo-homogeneous" model, since the math equations have the same form as for homogeneous reactions.

When we need to model the effects of changes in the catalyst or changes in mass transport properties, then we need more equations in addition to the basic balance equations for homogeneous and pseudo-homogeneous models.

In addition to solid-catalyzed reactions, there are other types of heterogeneous reaction systems, including gas-liquid, and gas-liquid-solid reactions. Hydrotreating of heavy petroleum fractions can be carried out by liquid trickling down over solid catalyst particles with a flow of  $H_2$  between the particles. In ReactorLab, the glucose oxidation reactor involves reactants in the liquid,  $O_2$  supplied by air bubbles, and solid catalyst particles. See Division 2 Catalytic Reactors, Lab 5 Glucose Oxidation 3 phase.

### Fluidized bed reactors

Consider a bed of solid particles, either inert or catalytically active, with gas flow upward through the bed. As the gas flow rate is increased, the pressure drop across the bed will increase. At a critical gas velocity, the fluid drag on the solid particles will be sufficient to separate the particles somewhat such that they can move relative to each other. The gas-particle mixture at this point can flow like a fluid. As the gas velocity is increased further, regions of low particle density, gas bubbles, form. Bubbles drag solid particles upward and help to mix the solids in the bed. At even higher gas velocities, solid

particles will be carried upward and can flow to another part of the reactor system.

Fluidized bed reactors have an important use in "cracking" high molecular weight hydrocarbons into smaller molecules. In petroleum refineries, "catalytic crackers" or "cat crackers" convert low-value gas oils into molecules that are useful in high-value gasoline.

### Electrochemical reactors

Batteries and fuel cells and metal plating systems are electrochemical reactors. These are usually the subject of a separate graduate course.

### Fermentation reactors

These are reactors in which living organisms grow and convert reactants into useful products. Food, beverages and pharmaceuticals are typical products. In addition to modeling the conversion of reactants you also need to model the growth of the living organisms.

### So many reactors, so little time...

There are many types of interesting reactors. There are so many that you can make a career out of chemical reaction engineering.

### Simulations in ReactorLab

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

#### Division 4 Flow Patterns

Lab 1 PFR CSTR Comparison

Lab 2 Packed Bed RTD

#### Division 6 Electrochemical Reactors

Lab 1 Fuel Cell