

Notes for CHE5314 course @ UCV

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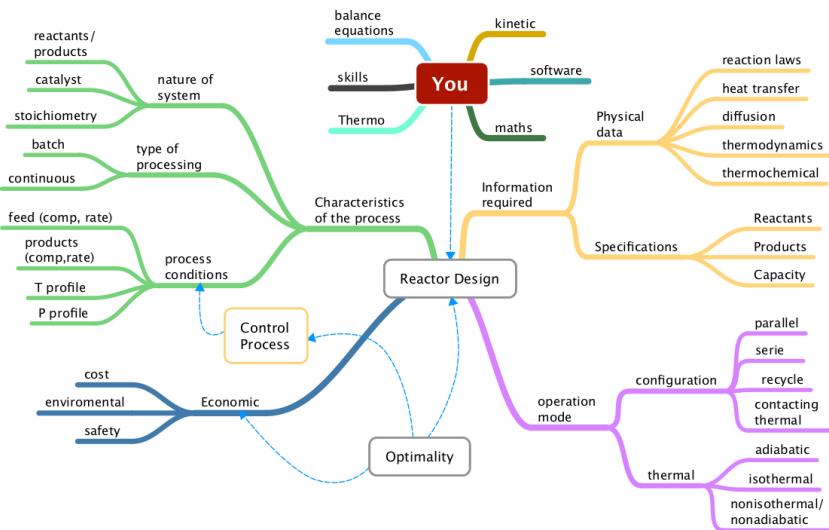
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Introduction

```
img <- readPNG("figures/Reactor_Design_map.png")
grid.raster(img)
```



This is an *online* book written in **Markdown** and **LaTeX** where I published the personal notes that I used to use while I was lecturing Chemical Reactor Design at the Central University of Venezuela, Caracas, Venezuela.

Because it is an informal recompilation of my notes, this material is not a comprehensive book where you will find details in concepts of the area. However, it is a relatively straightforward guide for an intermediate undergraduate student of Chemical Engineering who has taken an introductory course on Chemical reaction kinetics.

Besides concepts and mathematical deductions, I added typical problems solved in Python. Most of the illustrations given are modifications of examples taken from classic textbooks like Fogler or

Roberts.

Chapter 1

Key concepts related to Chemical Reactors Design

In a homogeneous system, the rate of a chemical reaction can be easily estimated because it depends on the temperature system and the concentrations of both reactants and products. However, the prediction on heterogeneous systems is more complicated because of the effect of mass and heat transfer rate over the reaction rate.

1.1 Fundamental of Kinetics and Reaction Equilibrium

It is essential to review some definitions related to design a chemical reactor before starting with our main subject. The first one is **reaction rate**. For a homogeneous reaction, the reaction rate is defined either as the amount of product formed or the amount of reactant consumed per unit volume of the liquid or gas phase per unit time.

$$r \equiv \frac{\text{moles consumed or produced}}{\text{reactor volume} \times \text{time}}$$

The reaction rate is based on moles of reactant consumed or produced per unit mass of catalyst per unit time for solid-catalyzed reactions.

$$r \equiv \frac{\text{moles consumed or produced}}{\text{mass of catalyst} \times \text{time}}$$

The second important is **conversion**, X , which is defined as the fraction of the more critical or limiting reactant consumed.

$$X_A \equiv \frac{\text{moles A reacted}}{\text{moles of A fed}}$$

The **yield** is the quantity created by the desired product compared to the quantity that would have been generated if there were no by-products and the primary reaction was completed.

$$Y \equiv \frac{\text{moles of product formed}}{\text{maximum moles of product, } X = 1.0}$$

For $nA \rightarrow B$

$$Y \equiv \frac{F_B}{F_A/n}$$

Finally, the **selectivity** is the amount of desired product divided by the amount of reactant consumed. This ratio often changes as the reaction progresses, and the selectivity based on the final mixture composition should be called an *average selectivity*.

For $nA \rightarrow B$

$$\bar{S} = \frac{\text{B formed}}{\text{A used}} = \frac{F_B}{F_A X_A/n} = \frac{Y}{X_A}$$

1.1.1 Power-Law Kinetics

1.1.1.1 Irreversible Reaction

For an irreversible reaction where two reactants forming a product



- The overall reaction rate r can be expressed as the moles of components A being consumed per unit time per unit volume.
- Additionally, the overall reaction rate has a temperature dependence governed by the specific reaction rate $k(T)$ and a concentration dependence.

In terms of molar concentrations for components A and B , the overall rate reaction could be expressed as:

$$r = k(T) C_A^\alpha C_B^\beta$$

where α and β are the order of reaction for each reactants.

The actual reaction mechanism determines the form of the kinetic expression.

- More than one mechanism may provide the same expression of the rate.
- Only in elementary reaction steps the reaction order equal to the stoichiometry.

The temperature-dependent specific reaction $k(T)$ is represented by Arrhenius equation

$$k(T) = k_0(T) \exp [(-E/R/T)]$$

where $k_0(T)$ is the pre-exponential factor, usually a big positive number that has units with respect to each component based on the concentration units and the order of the reaction, E is the activation energy, R is the universal gas-constant, and T is the absolute temperature.

If $n = \alpha + \beta$ then

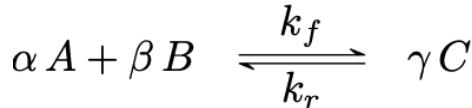
$$k(T) = \frac{[\text{Concentration}^{(1-n)}]}{\text{time}}$$

It is essential to know that:

1. If temperature increase the $k_0(T)$ will be increased.
2. $k_0(T)$ will be more sensitive to temperature changes at higher activation energy.

1.1.1.2 Reversible Reaction

Consider next reversible reaction



The forward rate reaction in terms of molar concentrations of reactants A and B will be:

$$r_f = k_f(T) C_A^\alpha C_B^\beta$$

$$k_f(T) = k_{0_f}(T) \exp(-E_f/R/T)$$

The reverse rate reaction will be:

$$r_r = k_r(T) C_C^\gamma$$

$$k_r(T) = k_{0_r}(T) \exp(-E_r/R/T)$$

The net overall rate reaction will be:

$$r = r_F - r_R = k_F(T) C_A^\alpha C_B^\beta - k_R(T) C_C^\gamma$$

Under chemical equilibrium conditions, the net overall rate reaction is equal to zero, which leads to:

$$K_{\text{eq}} = \frac{k_f(T)}{k_r(T)} = \frac{C_A^\alpha C_B^\beta}{C_C^\gamma}$$

$$K_{\text{eq}} = \frac{k_{0_f}(T) \exp(-E_r/R/T)}{k_{0_r}(T) \exp(-E_r/R/T)} = \frac{k_{0_f}}{k_{0_r}} \exp\left(\frac{E_r - E_f}{RT}\right)$$

It is important to know that:

- If $E_R = E_F$, then K_{eq} is independent of temperature
- If $E_R > E_F$, then the process is exothermic, so if temperature increases, then the exponential factor decreases and K_{eq} decreases.
- If $E_R < E_F$, then the process is endothermic (energy is required in order to transform reactants into products), so if temperature increases, then the exponential factor increases, and K_{eq} increases.

The van't Hoff equation of thermodynamics gives the temperature dependence of the chemical equilibrium constant.

$$\frac{d \ln K_{\text{eq}}}{dT} = \frac{\Delta H_R^\circ(T)}{RT^2}$$

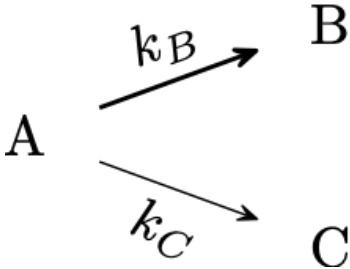
$$\Delta H_R^\circ(T) = E_f - E_r$$

1.1.2 Multiple Reactions

In a reacting system might occur more than one chemical reaction. We are frequently interested in just one called the principal, while others are side-reactions. The latter produce undesired components that diminish the yield of the desired product.

1.1.2.1 Parallel Reactions

In this case, the reactants form other undesired products in parallel with the primary reaction. For example:



If we assume first-order kinetics, the reactions occur in a simple batch isothermal reactor at volume constant. The concentrations of each component could be express as:

$$\frac{dC_A}{dt} = -(k_B + k_C) C_A$$

$$\frac{dC_B}{dt} = k_B C_A$$

$$\frac{dC_C}{dt} = k_C C_A$$

If at $t = 0$, $C_A = C_{A0}$, $C_B = 0$ and $C_C = 0$ then

$$\frac{C_A}{C_{A0}} = e^{-(k_B+k_C)t}$$

$$\frac{C_B}{C_{A0}} = \frac{k_B}{k_B + k_C} (1 - e^{-(k_B+k_C)t})$$

$$\frac{C_C}{C_{A0}} = \frac{k_C}{k_B + k_C} (1 - e^{-(k_B+k_C)t})$$

From `scipy.integrate`, we can use the function `solve_ivp` to solve ODEs using several Runge-Kutta's methods.

```
solution = solve_ivp(fun, (0, tfin), c0,
                      t_eval=np.linspace(0, tfin, 100))
```

The graphical solution for this sample is available (file).

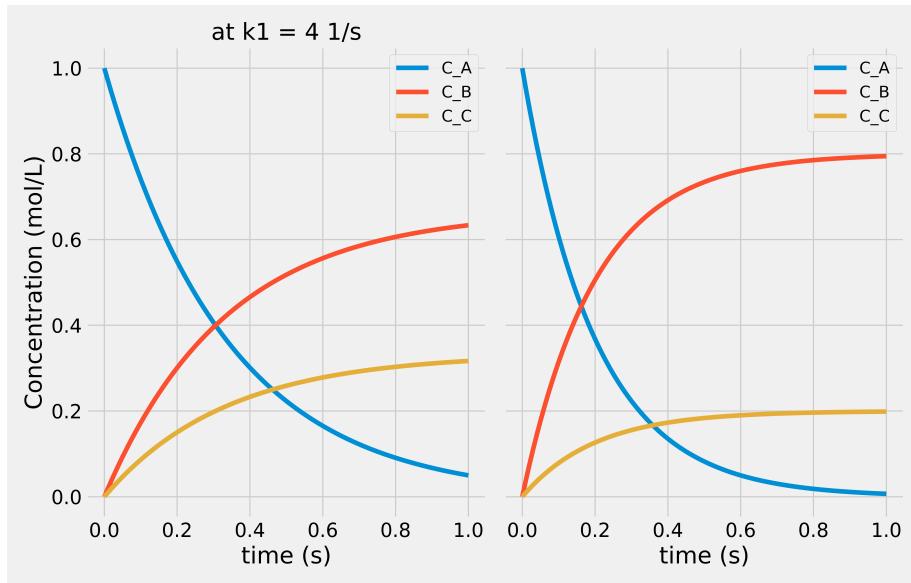


Figure 1.1: Concentrations vs time for parallel reactions.

In figure 1.1, we could see that more product B is generated at higher k_B values concerning k_C . This behavior is represented in terms of the **Selectivity (S)** to the desired product:

$$S = \frac{C_B}{C_C}$$

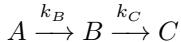
Our job as engineers is to optimize the reactor's operation, so in this case, we must find the best operating temperature to maximize selectivity. In the case the reactor has more than one reactant, the selectivity is affected by their concentrations.

1.1.2.2 Series Reactions

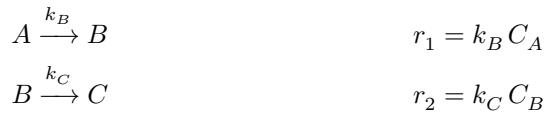
For series reactions, an intermediate is formed that can then further react. For a reaction system:

The reactions in standard form are:

For a batch reactor, the mass balances on A, B, and C are:



The reactions in standard form are:



For a batch reactor, the mass balances on A, B, and C are:

$$\begin{aligned} \frac{dC_A}{dt} &= -k_B C_A \\ \frac{dC_B}{dt} &= k_B C_A - k_C C_C \\ \frac{dC_C}{dt} &= k_C C_B \end{aligned}$$

If at $t = 0$, $C_A = C_{A0}$, $C_B = 0$ and $C_C = 0$ then

$$\begin{aligned} \frac{C_A}{C_{A0}} &= e^{-k_B t} \\ \frac{C_B}{C_{A0}} &= \frac{k_B}{k_C - k_B} (e^{-k_B t} - e^{-k_C t}) \\ \frac{C_C}{C_{A0}} &= 1 - \frac{C_A(t)}{C_{A0}} - \frac{C_B(t)}{C_{A0}} \end{aligned}$$

The graphical solution for this sample is available (file).

The figure 1.2 shows typical composition profiles. And on the C_B profile, we notice that there is a peak at some point in time. Therefore, the batch should be stopped at that time to maximize selectivity.

1.2 Temperature effects over chemical kinetics

Temperature changes affect the reaction rate, and hence the mode of reactor operation in two ways: temperature dependence of (1) the rate parameters and (2) the equilibrium constant. Several kinds of behavior occur, some of which are represented in fig. @ref(fig:temperature_effect).

The temperature dependence of reactions rate constants will meet the Arrhenius law where A is the pre-exponential factor and E is the activation energy.

Whereas the exponential dependence of rate constants on temperature means that the reaction rate changes rapidly as temperature changes. Moreover, the larger the value of activation energy, the more significant the reaction rate difference for a given temperature change.

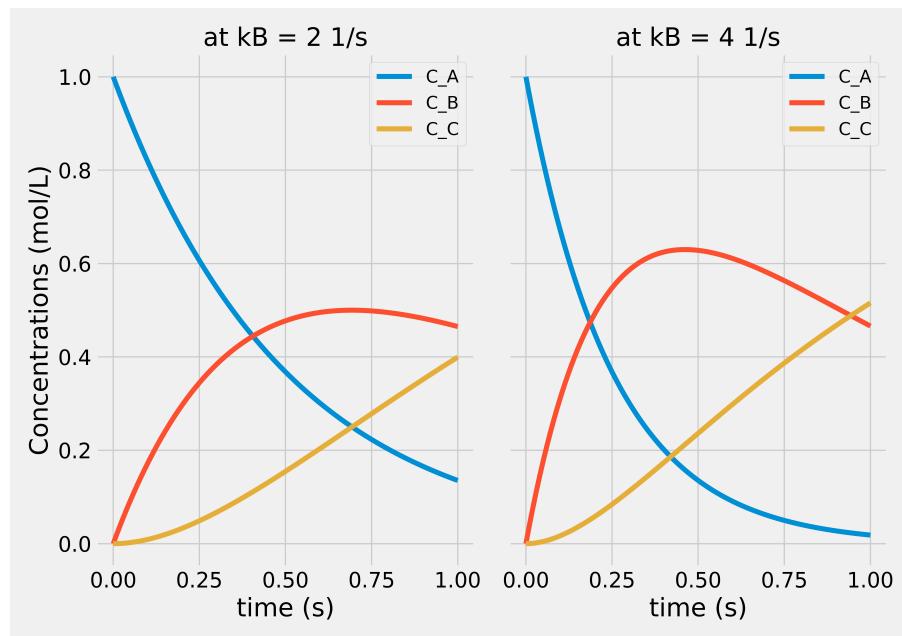


Figure 1.2: Concentrations vs time for series reactions.

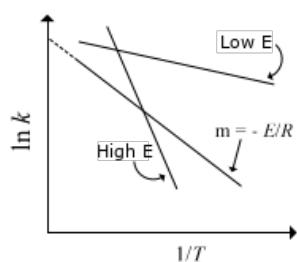


Figure 1.3: Typical Arrehnius plot

The temperature dependence of the chemical equilibrium constant (K) is given by the van't Hoff equation.

$$\frac{d \ln K}{dT} = \frac{\Delta H_R}{RT^2}$$

Thus for an exothermic reaction, an increase in temperature decreases the equilibrium yield and vice-versa.

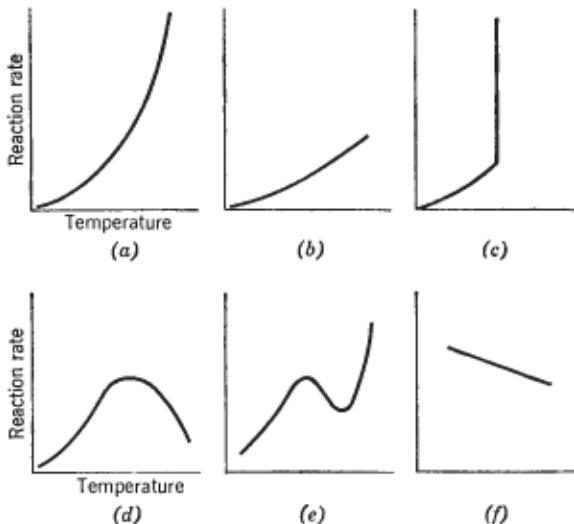


Figure 1.4: Effect of temperature on reaction rate [@walas1989]

In Figure 1.4, (a) Normal behavior, kinetic rate increases rapidly with rising temperature. (b) The behavior of particular heterogeneous reactions dominated by resistance to diffusion between phases. (c) Typical explosions, where the rapid rise takes place at the ignition temperature. (d) Catalytic reactions are controlled by the rate of adsorption (in which the amount of adsorption decreases at elevated temperatures) and enzyme reactions (where high temperatures destroy the enzyme). (e) Some reactions, such as oxidation of carbon, are complicated by side reaction, which becomes significant as the temperature rises. (f) Diminishing rate with increasing temperature, for example, the reaction between oxygen and nitric oxide where the equilibrium conversion is favored by lower temperatures. The rates appear to depend on the displacement from equilibrium.

The values of the heat of reaction $\Delta H_{R,j}(T)$ must be known, which must be calculated from

$$\Delta H_R(T^\circ) = \sum_i \nu_i \Delta H_{fi}^\circ$$

where the superscript “ \circ ” denotes the standard conditions.

Except in unusual cases, e.g., reactions at supercritical conditions, a temperature correction is the

only thing that is necessary to calculate the value of $\Delta H_R(T)$ from $\Delta H_R(T^\circ)$ using,

$$\Delta H_R(T) = \Delta H_R(T^\circ) + \int_{T^\circ}^T \nu_i C_{P_i} dT$$

Which equation is valid on the assumption that no phase change takes place between T° and T

1.3 Equation rate when density of fluid is variable

Changes in the volume yield a difference in concentrations. For example, let us consider the following reaction is taking place in a gas-phase.



At any time, and at any point inside the reactor, it is known that:

$$PV = Z R n T \quad (1.2)$$

Therefore, it is possible to correlate the volume V at $t = 0$ with any $t = t$ by

$$V = V_0 \left(\frac{P}{P_0} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{n_T}{n_{T_0}} \quad (1.3)$$

The stoichiometric coefficients in reaction represent the increase in the total number of moles per mole of A reacted by symbol δ

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (1.4)$$

Therefore, using this parameter δ is possible to calculate the total of moles (n) at any time t by

$$n = n_0 + \delta n_{A0} X_A \quad (1.5)$$

where n_0 represents the total moles at $t = 0$, N_{A0} initial moles of A and X is the fractional conversion of A .

Combining this relationship with the previous volume equation

$$V = V_0 \left(\frac{P}{P_0} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) (1 + \varepsilon_A X_A) \quad (1.6)$$

where $\varepsilon_A = \delta y_{A0}$ and it represents the change in the total number of moles for complete conversion to the total number of moles fed to the reactor.

The concentrations to be substituted into the rate equation can be expressed as

$$C_A = \frac{N_A}{V} = \frac{N_{A0}}{V_0} \frac{(1 - X_A)}{(1 + \varepsilon_A X_A)} \left(\frac{P}{P_0} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \quad (1.7)$$

and in terms of the partial pressures,

$$\begin{aligned} P_A &= P \frac{N_A}{N} = P \frac{N_{A0}}{N_0} \frac{(1 - X_A)}{(1 + \varepsilon_A X)} \\ &= P_{A0} \frac{(1 - X_A)}{(1 + \varepsilon_A X)} \left(\frac{P}{P_0} \right) \end{aligned} \quad (1.8)$$

When a reactor operates under isothermal conditions, and the pressure drop is neglected, thus

$$V = V_0 (1 + \varepsilon_A X_A) \quad (1.9)$$

1.4 Ideal Reactors

Industrial chemical reactors can be large and complex pieces of equipment. However, many of these reactors can be modeled with reasonable accuracy using an ideal reactor model. There are two types of ideal reactors, stirred tanks for liquids' reactions and tubular for gas or liquid reactions.

Stirred-tank reactors include batch reactor, semi-batch reactor, and continuous stirred-tank reactors (CSTRs). The criterion for ideality in-tank reactors is that the liquid is perfectly mixed, which means no gradients in the vessel's temperature or concentration.

Tubular reactors are considered ideal if there is a plug flow of fluid. There are no radial gradients of concentration or velocity, nor is there no axial diffusion or conduction.

Although these ideal conditions are impossible to reach into real industrial reactors, the classical idealizations can be used for studying both steady-state design and the dynamic control of chemical reactors. In this class, we discuss the classical types of reactors qualitatively: batch reactor (BR), continuous stirred-tank reactor (CSRT), plug flow reactor (PFR).

Chapter 2

Ideal Chemical Reactor Design

Process design has to do with specific matters relating to the process itself, in our cases, such as operation conditions, size, configuration, and operation mode of the reactor.

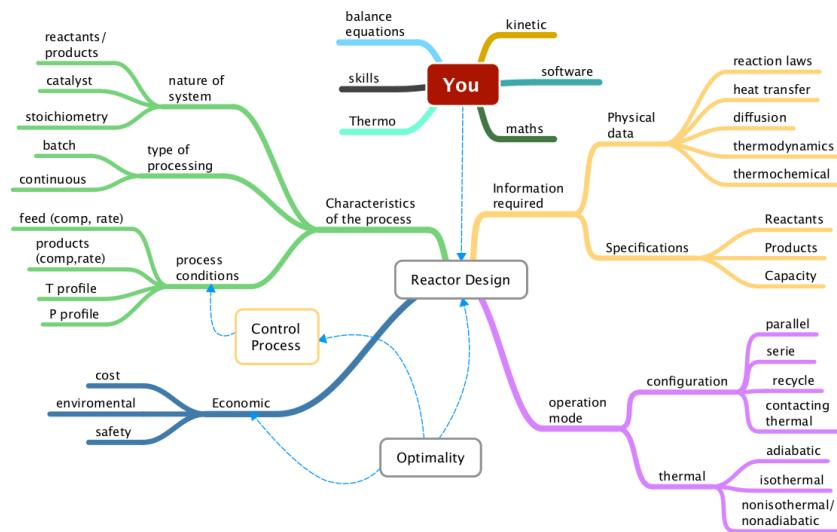


Figure 2.1: Conceptual Map of Chemical Reactor Design

In this course, we will focus on the phenomena taking place in basic reactor types.

The phenomena occurring in a reactor may be broken down into reaction, mass, heat, and momentum transfer. Therefore, reactors' modeling and design are based on the reaction rate equation, the continuity, energy, and momentum equations. The modeling and design of reactors are based on

the equations describing these phenomena: the reaction rate equation and the continuity, energy, and momentum equations (Froment, Bischoff, and De Wilde 2011).

Additionally, we will study two situations (1) the design of a new chemical reactor for a new process, (2) the analysis of the performance of an existing reactor for a current process. In many cases, as chemical engineers, we must consider several items shown in figure 2.1 when starts the design or analysis of a reactor.

2.1 Fundamental Balances

2.1.1 Material Balance

As a chemical engineer, our main modeling tools are the material balance and energy balance. We should remember two aspects: the material balance of a reactor must consider the rate at which species are converted from one chemical form to another and the rate at which energy is transformed by the process.

We will perform a mole balance on species j in a system volume, where j represents the particular chemical species of interest.



Figure 2.2: System volume scheme

Based on figure 2.2, the mole balance expressed in mole/time would be

$$F_{j0} + G_j - F_j = \frac{dN_j}{dt} \quad (2.1)$$

where F_{j0} is rate flow in j , G_j is the generation rate of j by chemical reaction, F_j is rate flow out j , and dN_j/dt means accumulation rate of j .

In equation (2.1), the generation/consumption of j (G_j) will be expressed as the product of the reaction volume, V , and the rate of reaction, r .

The symbol r is expressed in molar units per unit time and volume, and it is always **positive** when the reaction proceeds in the direction of the arrow. Thus, the integral form of the general mole balance for any chemical specie j yields.

$$F_{j0} - F_j + \int_0^V r_j dV = \frac{dN_j}{dt} \quad (2.2)$$

In mathematical terms, the equation (2.2) is called the continuity equation for j . If j reacts in more than one phase, such an equation is needed for each phase. This equation will develop the design equations for different ideal reactors: batch, semi-batch, and continuous-flow.

The mechanisms by which j can enter or leave the volume element are flow and molecular diffusion, and they are irrelevant. However, it is essential to realize that a fluid's motion is not really ordered and challenging to describe.

For this reason, as a first approach, it is therefore natural to consider two extreme conceptual cases: first, where there is no mixing of the streamlines, and second, where the mixing is complete. These two extremes may be formulated with sufficient approximation by the tubular plug flow reactor, and the continuous flow stirred tank with complete mixing.

In a plug flow reactor, all fluids elements move with equal velocity along parallel streamlines. The plug flow is the only mechanism for mass transport, and there is no mixing between fluid elements. The reaction leads to a concentration gradient in the axial flow direction.

Reactors with complete mixing may be subdivided into batch and continuous types. In batch-reactor types with complete mixing, the composition is uniform throughout the reactor. Consequently, the continuity equations may be written for the entire contents, not over a volume element. As the bulk composition varies with time, a first-order ordinary differential equation is obtained, with time as a variable. The form of this equation is analogous to that for the plug flow case.

In the continuous flow type, an element of the entering fluid is instantaneously mixed with the reactor's contents so that it loses its identity. This type also operates at a constant concentration level. In the steady-state, the continuity equations are algebraic.

Both types of continuous reactors considered are idealized conceptual cases. They are important cases because they are easy to calculate and give the extreme values of the conversions between those realized in a real reactor. With its intermediate level of mixing, the design of a real reactor requires information about this mixing.(Froment, Bischoff, and De Wilde 2011)

2.1.2 Energy Balance

The real chemical reactors are almost operated under nonisothermal conditions because reactions generate or absorb large amounts of heat. Detailed reactor sizing and analysis require the energy balance to be solved in conjunction with one or more material balances.

For a generic open system, the energy balance is:

$$Q - W_s + \dot{H}_{\text{in}} - \dot{H}_{\text{out}} = \frac{dE}{dt}$$

The terms in energy balances have the following meanings:

- Q is the rate of heat transfer **into** the reactor.
- W_s means the rate at which shaft work is done by the system on the surrounding. If shaft work is done on the contents of the reactor, e.g., by an agitator, the value of W_s is negative.
- \dot{H}_{in} is the rate at which enthalpy is transported into the reactor.
- \dot{H}_{out} is the rate at which enthalpy is transported out of the reactor.
- dE/dt is the rate at which the system's total energy, E , changes with time.

In chemical reactors, it is typically assumed the internal energy is the dominant contribution over the kinetic and potential energies. Thus, the general energy balance will be

$$\frac{dU}{dt} = Q - W_s + \dot{H}_{\text{in}} - \dot{H}_{\text{out}} \quad (2.3)$$

For single reactors, the inlet and outlet molar flow are related through the extents of reaction (ξ). If “ R ” independent reactions occur, and if the extents of reaction are zero in the stream that enters the reactor.(Roberts 2009)

$$F_i - F_{i0} = \sum_{j=1}^R \nu_{j,i} \xi_j$$

where $\nu_{j,i}$ refers to stoichiometric coefficient of the component i in the reaction j .

Therefore,

$$\dot{H}_{\text{in}} - \dot{H}_{\text{out}} = \sum_{i=1}^C F_{i0} \bar{H}_{i0} - \sum_{i=1}^C \left(F_{i0} + \sum_{j=1}^R \nu_{j,i} \xi_j \right) \bar{H}_i$$

where \bar{H}_i refers to the partial molar enthalpy of the component i .

Assuming that feed and product streams are ideal solutions, the partial molar enthalpies \bar{H}_i can be replaced by pure component enthalpies, H_i , Thus,

$$\dot{H}_{\text{in}} - \dot{H}_{\text{out}} = \sum_{i=1}^C F_{i0} (H_{i0} - H_i) - \sum_{j=1}^R \xi_j \left(\sum_{i=1}^C \nu_{i,j} H_i(T) \right)$$

The term $\sum \nu_{i,j} H_i^\circ$ is just the enthalpy of reaction for reaction j , evaluated at exit conditions. Since the temperature of the effluent stream is T ,

$$\sum_{i=1}^C \nu_{i,j} H_i = \Delta H_{R,j}(T)$$

where $\Delta H_{R,j}(T)$ is the heat of reaction j , evaluated at the temperature T .

If the pressure difference between the feed and the product streams is not substancial, and if there are no phase changes

$$H_{i0} - H_i = \int_T^{T_0} C_{P_i} dT \approx \bar{C}_{P_i} (T_0 - T)$$

where, T_0 is the temperature of the inlet stream, C_{P_i} is the constant-pressure molar heat capacity of specie i , and \bar{C}_{P_i} is the average constant-pressure molar heat capacity over the temperature range T_0 to T

So, eq. (2.3) becomes to

$$\frac{dU}{dt} = Q - W_s - \sum_{i=1}^C \left(F_{i0} \int_{T_0}^T C_{P_i} dT \right) - \sum_{j=1}^R \xi_j \Delta H_{R,j}(T) \quad (2.4)$$

Equation (2.4) is the energy balance for a whole reactor in which multiple reactions are taken place. In this equation, the term $(\sum F_{i0} \int C_{P_i} dT)$ represents the rate of sensible heat, and it is usually written on a **molar** basis. The term $\sum \xi_j \Delta H_{R,j}(T)$, means the heat rate (generated or consumed) related to the reaction.(Roberts 2009)

If only one reaction is taking place, eq. (2.4) can be written in terms of the fractional conversion. For a single reaction, where A is a reactant,

$$\xi = -\frac{F_{A0} - F_A}{\nu_A} = -\frac{F_{A0} X_A}{\nu_A}$$

Substituting this relationship into eq. (2.4) and assuming steady-state condition gives (Roberts 2009)

$$Q - W_s - \sum_{i=1}^c \left(F_{i0} \int_{T_0}^T C_{P_i} dT \right) + F_{A0} X_A \frac{\Delta H_R(T)}{\nu_A} = 0 \quad (2.5)$$

or

$$Q - W_s - \sum_{i=1}^c \left(F_{i0} \int_{T_0}^T C_{P_i} dT \right) - \frac{\Delta H_R(T)}{\nu_A} r_A V = 0$$



When $\nu_A = -1$ is chosen, the basis for ΔH_R has been fixed to 1 mole of A, i.e., the units of ΔH_R must be energy/mole of A

The form of the energy balance results from considerations closely related to those for different continuity equations. When the mixing is so intense that the concentration is uniform over the reactor, it may be accepted that the temperature is also uniform.

When plug flow is postulated, it is natural to accept that the concentration in a section perpendicular to flow is considered to be uniform. It is natural to also consider the temperature to be uniform in this section. It follows that when the heat is exchanged with the surroundings, the temperature gradient has to be situated entirely in a thin “film” along the wall. This also implies that the resistance to heat transfer in the central core is zero in a direction perpendicular to the flow, which is not right for certain catalytic reactors.

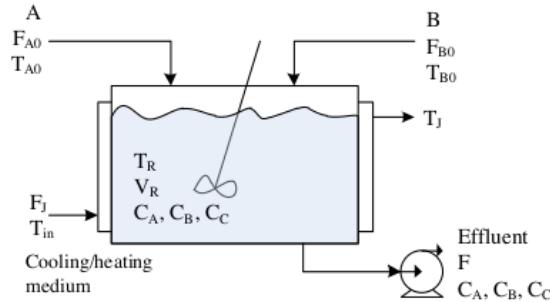
2.1.3 Momentum Balance

The momentum balance can be obtained by the application of Newton's second law on a moving fluid.

In a chemical reactor, only pressure drop and friction forces have to be considered in most cases. Several specific pressure drop equations will be discussed later on PFR and on a fixed catalytic reactor.

2.2 The Continuous-Stirred-Tank Reactor (CSTR)

When the demand for a single chemical product reaches a high level, there will be an economic incentive to continuously manufacture it, using a reactor dedicated to that product. One of those is The *Continuous-Stirred-Tank Reactor or CSTR*.



The CSTR is a well-mixed vessel consisting of a baffled tank with mixing induced by an impeller and operates at a steady-state. The mass flow rate into the tank is equal to the mass flow rate out of it at steady-state, and the feed and product properties are not functions of time. Furthermore, the reactor volume is constant.

A well-mixed vessel means a working fluid with neither radial, axial, nor angular gradients in properties. In other words, both the composition and temperature of the fluid are uniform over the entire volume. That is, they do not vary with position. Those assumptions are

The central assumption is that the incoming fluid concentration will become instantaneously equal to outgoing upon entering the vessel. As a consequence of well-mixing behavior, the effluent stream must have precisely the same composition and temperature as the contents of the reactor. The feed must be immediately mixed with the reactor's contents in a time interval that is very small compared to the mean residence time of the fluid flowing through the vessel to meet this ideal mixing pattern. (Froment, Bischoff, and De Wilde 2011)

The CSTR is frequently chosen when temperature control is a critical aspect when the conversion must occur at constant composition, when a reaction between two phases has to be carried out, or when a catalyst must be kept in suspension. (Froment, Bischoff, and De Wilde 2011)



In practice, it is possible to reach a perfect mixing condition if the mixing time is much less than the residence time inside the reactor, usually when the fluid is low viscosity.

2.2.1 The design equation for a CSTR

An ideal CSTR is quite similar to a perfectly mixed batch reactor. The most significant difference is that mass flows into and out of a CSTR. Thus, the mass flow in and out of the reactor in eq. (2.1) will not cancel.

Writing the material balance for this system:

$$\frac{dN_j}{dt} = F_{\text{in},j} - F_j + r_j V \quad (2.6)$$

where $F_{\text{in},j}$ is the molar flow in of j , F_j is the molar flow out of j , V is the reactor volume, r_j is the production rate of specie j , and N_j means the number of moles of specie j

At steady-state, the left-hand side of eq. (2.6) is zero, thus

$$\begin{aligned} F_{\text{in},j} - F_j + r_j V &= 0 \\ V &= \frac{F_{\text{in},j} - F_j}{-r_j} \end{aligned} \quad (2.7)$$

Equation (2.7) is **the design equation** for an ideal CSTR. For a single reaction, it is useful to write it down in terms of the conversion of reactant A.

$$\begin{aligned} F_{A,\text{in}} &= F_{A0}(1 - X_{A,\text{in}}) \\ F_A &= F_{A0}(1 - X_A) \end{aligned}$$

leading to

$$\frac{V}{F_{A0}} = \frac{X_A - X_{A,\text{in}}}{-r_A}, \quad r_A = -r \quad (2.8)$$

where ν_A represents moles of A , and r the global rate equation.



The material balance equation is usually solved for V in steady-state operation or determines the changes of outlet properties concerning time in the unsteady-state process for a particular V .

These characteristics of a CSTR generates an inherent weakness in its operation related to the fractional conversion:

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

If a high conversion is desired, the reactant concentration must be small. But the reaction rate depends directly on the reactant concentration, so to compensate for this restriction, we must design larger reactors.

Constant-Density System

If the reactor volume is constant and the volumetric flow rate of the inflow and outflow streams are the same, the eq. (2.6) in terms of volumetric flow rates, is

$$\begin{aligned} F_j &= v C_j \\ \frac{dC_j}{dt} &= \frac{1}{t} (C_{j,0} - C_j) + r_j \end{aligned} \quad (2.9)$$

where $C_{0,j}$ is the concentration of specie j at initial conditions, C_j is the concentration into the reactor, and \bar{t} is used to refer to the **mean residence time**, which is given by

$$\bar{t} = \frac{V}{v} \quad (2.10)$$

where v is the volumetric flow rate evaluated at exit conditions.

For $X_{A,\text{in}} = 0$, the effluent volumetric flow rate can be related to inlet flow rate by

$$v = v_0 (1 + \nu X_A) \quad (2.11)$$

where v_0 is the volumetric flow rate evaluated at entrance conditions, and $\nu = \sum_j \nu_j$

Since the volumetric flow rate is a function of X , T , and P , the mean residence time, \bar{t} , depends on those variables. Instead of using the reactor residence time to describe performance, an equal quantity called **space-time** define as:

$$\tau = \frac{V}{v_0} \quad (2.12)$$

This definition of space-time applies to any continuous reactor.

For a homogeneous reaction, space-time has the dimension of time. It is related to the average time a volume element of fluid spends in the reactor.

Although space-time is not necessarily equal to the mean residence time, they behave similarly, and it is possible to relate eq. (2.10) and eq. (2.12)

$$\bar{t} = \frac{\tau}{1 + \varepsilon_A X_A} \quad (2.13)$$

If the volume change in the reactor is negligible, then $\varepsilon_A = 0$. Finally, if the working fluid has constant density

$$V = \frac{(C_{A0} - C_A) v}{r_A} \quad \bar{t} = \tau \quad (2.14)$$

Space-time influences reaction behavior in a continuous reactor in the same way that real-time does on a batch reactor's behavior. In both cases, the fractional conversion will increase if reactants spend more time or space-time increases.

Therefore, if the fluid density is constant, eq. (2.8) becomes

$$\tau = \frac{C_{A0} - C_A}{-r_A}, \quad r_A = -r \quad (2.15)$$

The equation (2.8) may be interpreted graphically from a plot of reciprocal rate $1/(-r_A)$ as function of X_A , as shown by curve EB in fig. 2.3. Point B is the *operating point* of the reactor, which represents the steady-state condition in the reactor. Area ABCD represents the ratio V/F_{A0} for the CSTR.

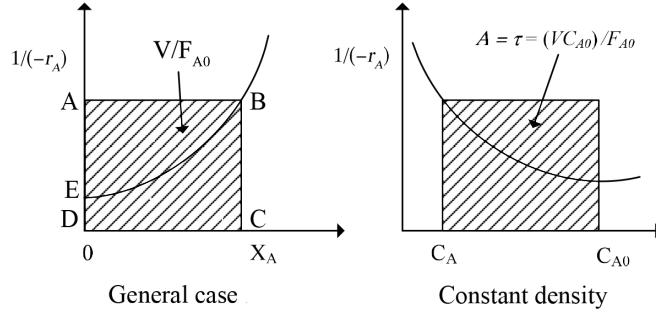


Figure 2.3: Graphical representation of the performance equations for CSTR

Another parameter commonly used for CSTR design is the inverse of τ , called **space velocity**, which can be regarded as the number of reactor volumes of feed processed per unit time at the feed conditions.

$$SV = \frac{v_0}{V} = \frac{1}{\tau} \quad (2.16)$$

Space velocity is more useful in the field of heterogeneous catalysis. Its definition is not unique. For example, it can also be defined as GHSV, which means gas-hourly space velocity. It may be defined as the volumetric flow rate of gas entering the catalyst divided by the catalyst's weight.

Variable-Density System

For variable-density cases, the design equation for a CSTR is:

$$\begin{aligned} \frac{V}{v} &= \tau = \frac{V}{v_0 (1 + \varepsilon_A X_A)} = \frac{C_{A0} - C_A}{r_A(C_A)} \\ \tau &= (1 + \varepsilon_A X_A) \frac{C_{A0} - C_A}{r_A(C_A)} \end{aligned} \quad (2.17)$$

2.2.2 CSTR in series

CSTRs of equal sizes in series

Consider a system of N CSTRs connected in series, as shown in the figure 2.4. Though the concentration is uniform in each reactor, there is a change in concentration as fluid moves from one reactor to another.

The feed molar flow rate of reactant A is F_{A0} , the effluent conversion of A from the first reactor is X_{A1} , while the output conversion of A from the second reactor is X_{A2} so on.

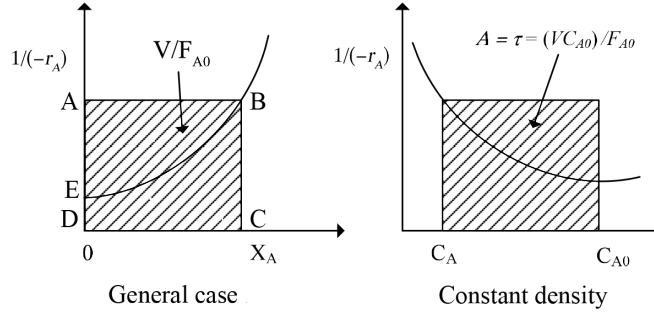


Figure 2.4: Sketch of ideal CSTRs in series

(R) It is crucial to be consistent in defining the fractional conversion for a series of reactors.

For a series of three CSRTs in serie

$$\begin{aligned} X_{A,1} &= (F_{A0} - F_{A,1}) / (F_{A0}) \\ X_{A,2} &= (F_{A0} - F_{A,2}) / (F_{A0}) \\ X_{A,3} &= (F_{A0} - F_{A,3}) / (F_{A0}) \end{aligned}$$

The conversion X_{A1} is the fractional conversion of A in the stream leaving the first reactor. In contrast, X_{A2} is the overall conversion of A in the second reactor's effluent, which means the conversion for the first and second reactors combined. Thus, the overall conversion for the series of three CSTRs is equal to X_{A3} . (Roberts 2009)

The mole balance for reactant A can be written for any reactor j in the series will be

$$-r_{A,j} = \frac{F_{A,j-1} - F_{A,j}}{V_j} \quad (2.18)$$

The molar flow rates from a reactor j and $j - 1$ expressed in terms of conversion are:

$$\begin{aligned} F_{A,j-1} &= F_{A0}(1 - X_{A,j-1}) \\ F_{A,j} &= F_{A0}(1 - X_{A,j}) \end{aligned}$$

The change in the molar flow rate of A in any reactor is defined as

$$F_{A,j-1} - F_{A,j} = F_{A0} (X_{A,j} - X_{A,j-1})$$

Therefore, the design equation for a reactor j is written in terms of conversion as:

$$\frac{V_j}{F_{A0}} = \frac{(X_{A,j} - X_{A,j-1})}{-r_A(X_{A,j})} \quad (2.19)$$

This equation can be rearranged in terms of the conversion from reactor j

$$X_{A,j} = X_{A,j-1} - \frac{r_{A,j} V_j}{F_{A0}} \quad (2.20)$$

Equation (2.20) can be solved for each reactor sequentially to calculate the incremental conversion from each reactor. Equation (2.21) can be generalized to apply to the Nth reactor in a series of CSTRs

$$\frac{V_N}{F_{A0}} = \frac{(X_{A,N} - X_{A,N-1})}{-r_A(X_{A,N})} \quad (2.21)$$

A typical case is to evaluate the behavior of a series of N equal-size CSTRs that operate isothermally, with a first-order kinetic and no volume change ($v = v_0$).

In this case, it is convenient to write mass balances on specie A in terms of concentrations and τ instead of fractional conversion.

$$\begin{aligned} C_{A0} - C_{A1} &= \tau_1 r(C_{A1}) \\ C_{A1} - C_{A2} &= \tau_2 r(C_{A2}) \\ C_{A2} - C_{A3} &= \tau_3 r(C_{A3}) \\ &\vdots \\ C_{A,n-1} - C_{An} &= \tau_n r(C_{An}) \end{aligned}$$

Usually the initial concentration of A is known. Therefore, the system of equations can be rewritten as:

$$\begin{aligned} C_{A1} &= \frac{C_{A0}}{(1 + \tau_1 k)} \\ C_{A2} &= \frac{C_{A0}}{(1 + \tau_1 k)(1 + \tau_2 k)} \\ &\vdots \\ C_{Ai} &= \frac{C_{A(i-1)}}{(1 + \tau_i k)} = \frac{C_{A0}}{\prod_k (1 + \tau_k k)} \end{aligned}$$

In general,

$$\frac{C_{A,i-1}}{C_{A,i}} = 1 + k \tau_i \quad \text{or} \quad \tau_i = \frac{C_{A,i-1} - C_{A,i}}{k C_{A,i}} \quad (2.22)$$

Assuming all reactors have the same volume (V_i), which means they have the same τ , then the total residence time in the series of N equal-residence-time CSTR is equal $\sum_k \tau_k = N \tau$ and $C_{A,N}$, the concentration from the N -th reactor is given in terms of C_{A0} by:

$$\frac{C_{A,N}}{C_{A0}} = \frac{C_{A,1}}{C_{A0}} \frac{C_{A,2}}{C_{A,1}} \dots \frac{C_{A,N-1}}{C_{A,N}} = \frac{1}{(1 + \tau_N k)^N} \quad (2.23)$$

Substituting for $C_{A,N}$ in terms of conversion

$$C_{A0} (1 - X_{A,N}) = \frac{C_{A0}}{(1 + \tau_N k)^N} \Rightarrow X_{A,N} = 1 - \frac{1}{(1 + \tau_N k)^N} \quad (2.24)$$

Figure 2.5 shows the variation of conversion vs. the number of reactors in series for a first-order reaction. It also indicates that the Damkholer number is a crucial parameter to decide the optimal number of CSTRs required to reach an overall conversion.

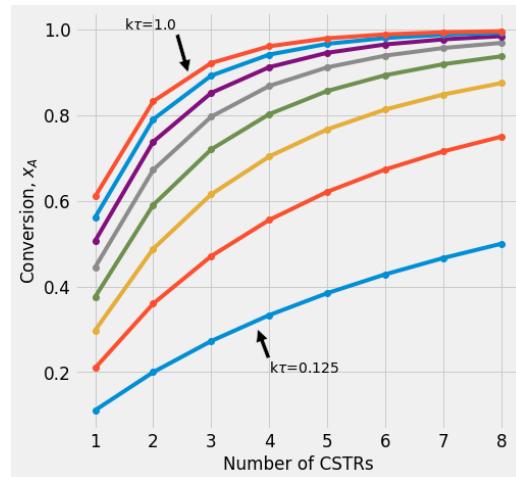


Figure 2.5: Plot of conversion as function of number of CSTRs in serie

In general, while the Damkholer number increases, the system will require fewer CSTRs to get the desired level of conversion. (Numerical solution)

The total capital cost is an important parameter rather than the total reactor volume in a practical situation. Increasing the number of CSTRs in series will reduce the total cost by reducing the required volume. However, it will also increase the price since more agitators, valves, piping, etc., will be required. The economic optimum usually occurs at a value of N as low as 2 or 3. (Roberts 2009)

The optimal operation of a multistage CSTR can be considered from the point of view of minimizing the total volume V for a given throughput (F_{A0}) and fractional conversion (X_A). So it will be necessary an objective function for V from the material balance together with a rate law and energy balance as required

CSTRs of different sizes in series

For reactions with slight density change is possible to find the outlet composition from a series of CSTRs by a graphical procedure due to the design equation of each CSTRs could be written as:

$$-\frac{1}{\tau_N} = \frac{(-r_A)_N}{C_{A,N} - C_{A,N-1}} \quad (2.25)$$

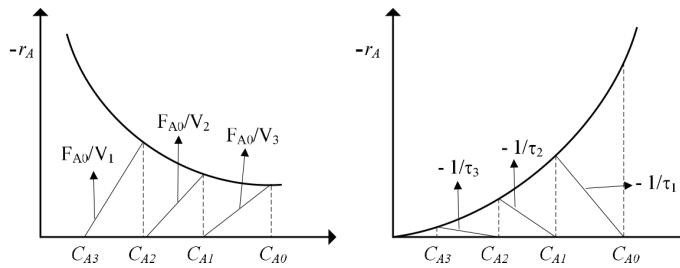


Figure 2.6: Graphical solution for multistage CSTRs - first-order reaction

Figure 2.6 shows a way to represent the material balances for each stage from a plot $1/(-r_A)$ as a function of C_A .

Another interesting situation is finding the best setup to achieve a given conversion. Let us illustrate the use of this method considering two CSTRs in series under isothermal conditions, as shown in the Figure 2.7

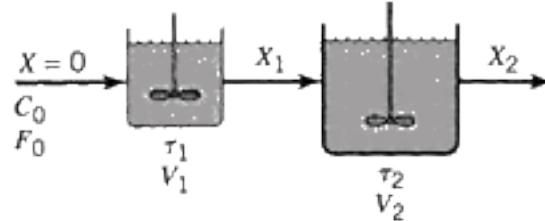


Figure 2.7: Graphical representation of two CSTRs in series

For the first CSTR, the design equation becomes

$$\frac{V_1}{F_{A0}} = \frac{X_{A1}}{-r_A(X_{A1})} \quad (2.26)$$

while for the second one is:

$$\frac{V_2}{F_{A0}} = \frac{X_{A2} - X_{A1}}{-r_A(X_{A2})} \quad (2.27)$$

These relations are graphically represented in the Figure 2.8. The cascade of CSTRs operates between known initial and final conversion levels, and the total reaction volume is represented by the sum of the shaded areas.

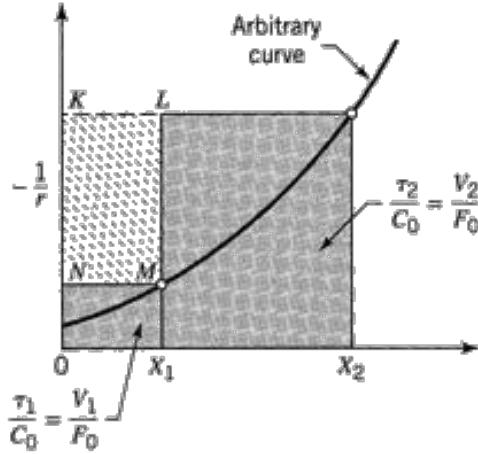


Figure 2.8: Graphical representation of two CSTRs in series

When the rectangle $KLMN$ is made as large as possible, the overall volume is minimized. Therefore, point X_{A1} is the critical parameter to get the reactors' optimal size.

For reaction rate expressions of the n -th-order form, it can be shown that there is always one and only one point that minimizes the total volume when $n > 0$. (C. G. J. Hill and Root 2014)

The total reaction volume is:

$$V_1 + V_2 = F_{A0} \frac{X_{A1}}{(-r_A)_1} + F_{A0} \frac{X_{A2} - X_{A1}}{(-r_A)_2} \quad (2.28)$$

The derivative of eq. #ref(eq:totalVolume) respects to X_{A1} is:

$$\frac{d(V_1 + V_2)}{dX_{A1}} = \frac{F_{A0}}{(-r_A)_1} + F_{A0} X_{A1} \left(\frac{d(1/(-r_A)_1)}{dX_{A1}} \right) - \frac{F_{A0}}{(-r_A)_2} = 0 \quad (2.29)$$

simplifying leads to

$$\frac{d(1/(-r_A)_1)}{dX_{A1}} = \frac{1/(-r_A)_2 - 1/(-r_A)_1}{dX_{A1}} \quad (2.30)$$

Therefore, the minimum reaction volume will be found when the intermediate fractional conversion X_{A1} is selected. The slope of the reaction rate curve at this conversion level is equal to the slope of the rectangle's diagonal $KLMN$, as is shown in figure 2.9.

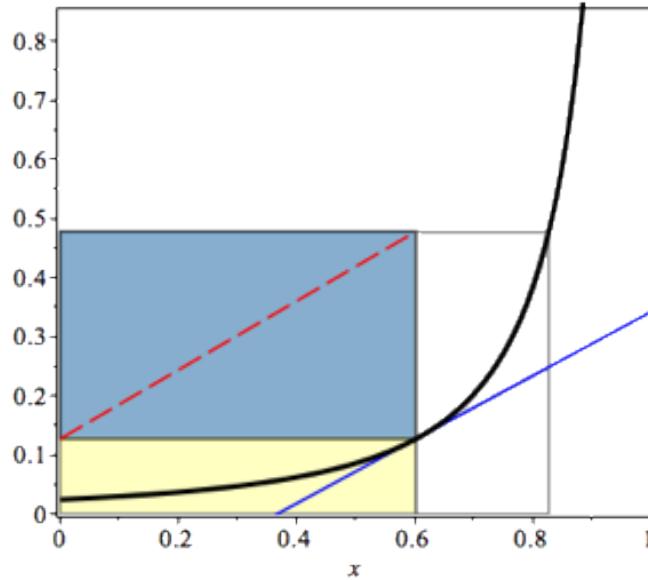


Figure 2.9: Graphical representation of the minimum total reaction volume for two CSTRs in series

Generally, the optimum size ratio is dependent on the form of the reaction rate expression and on the conversion task specified. Table 2.1 summarizes the optimal configuration for CSTRs in series from a kinetic-order point of view.

Table 2.1: Thumb-rules for optimal configuration for CSTRs in series

| kinetic-order n | Optimal configuration |
|-------------------|----------------------------|
| $n = 1$ | same size |
| $n > 1$ | first tank with $<$ volume |
| $n < 1$ | first tank with $>$ volume |

In engineering practice, the designer tends to select CSTRs with the same volume to minimize installation and operational costs.

2.2.3 Energy Balance

Now let us find out how to apply the general energy balance (eq.(2.3)) to a CSTR. Usually, for an ideal CSTR operating at a steady-state ($dU/dt = 0$), it is considered the work done by the stirrer neglected, so the energy balance yields to:

$$Q - \sum_{i=1}^c F_{i0} \left(\int_{T_0}^T C_{P_i} dT \right) - \sum_{j=1}^r \xi_j \Delta H_{R_j}(T) = 0 \quad (2.31)$$

From thermodynamics, we know that for a reaction j

$$\xi_j = \frac{F_i - F_{i0}}{\nu_i} = -\frac{F_{i,0} X_i}{\nu_i} \quad (2.32)$$

Thus

$$Q - \sum_{i=1}^c F_{i0} \left(\int_{T_0}^T C_{P_i} dT \right) + \sum_{j=1}^R \left(\frac{F_{i,0} X_i}{\nu_i} \right)_j \Delta H_{R_j}(T) = 0 \quad (2.33)$$

This equation written for a reactant A ($\nu_A = -1$), considering only one chemical reaction is taken place, becomes to

$$Q - \sum_{i=1}^c F_{i0} \left(\int_{T_0}^T C_{P_i} dT \right) - F_{A,0} X_A \Delta H_R(T) = 0 \quad (2.34)$$

or

$$Q - \sum_{i=1}^c F_{i0} \left(\int_{T_0}^T C_{P_i} dT \right) + \Delta H_R(T) r_A V = 0 \quad (2.35)$$

while for a product P

$$Q - \sum_{i=1}^c F_{i0} \left(\int_{T_0}^T C_{P_i} dT \right) + \frac{\nu_P}{\nu_A} F_{A,0} X_A \Delta H_R(T) = 0 \quad (2.36)$$

Equation (2.34) (or (2.36)), if the system's heat transfer characteristic is known, requires a reaction rate expression and the design equation to determine the fluid's temperature and composition leaving the reactor.

Using the energy balance to analyze the performance or sizing an ideal CSTR is not as complicated mathematically, so let us consider some typical heat transfer modes.

Jacket-Cooled

Consider the ideal CSTR shown in Figure 2.10. Heat is added to or removed from the reactor by a heat-transfer fluid that flows through the jacket. Depending on the reactor temperature and whether the reactor is being heated or cooled, the heat-transfer fluid may be cooling water, chilled brine, chilled glycol solution, hot oil, or some other fluid. The fluid is a source of (or a sink for) the heat transferred through the reactor wall.

The transit energy rate is \dot{W} . The temperature of the fluid at a point in the jacket is T_c . The fluid enters the jacket at $T_{c,i}$ and leaves at $T_{c,o}$. The feed enters the reactor at temperature T_0 . The molar flow rates of each component of the feed are designated $F_{i,0}$, and its corresponding concentrations are designated $C_{i,0}$. The reactor operates at a temperature, T , which is the effluent temperature too.

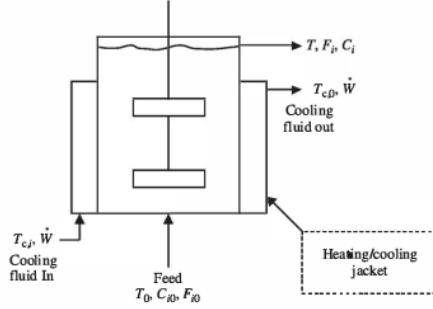


Figure 2.10: Schematic diagram of an ideal CSTR with heat transfer through a heating/cooling jacket

The molar flow rates in the output stream are designated F_i , and the corresponding concentrations are C_i .

If a single reaction occurs in a CSTR and one mole of reactant A is consumed in an elemental first-order reaction, the eq. (2.37) yields to:

$$Q - \left(\sum_{i=1}^c F_{i0} \bar{C}_{p,i} \right) (T - T_0) - F_{A0} X_A \Delta H_R(T) = 0 \quad (2.37)$$

The Q term in eq. (2.37) depends on the removal scheme used. In general, the rate for heat transfer is:

$$q = U (T_c - T)$$

where: q is the heat flux into the reactor ($\text{J}/\text{m}^2 \cdot \text{h}$), and U means the overall heat-transfer coefficient ($\text{J}/\text{m}^2 \cdot \text{h} \cdot \text{K}$).

If $T < T_c$, heat is transferred into the reactor and $q > 0$. The total heat transfer rate, Q , is obtained by integrating the flux, q , over the whole area of the exchanger. For example, if the temperature of the fluid is the same at every point in the exchanger.

$$Q = U A_J (\bar{T}_c - T)$$

where \bar{T}_c is the constant temperature of the heat-transfer fluid, and it is equal to the outlet temperature, $T_{c,o}$. A_J is the total area of the heat exchanger.

Substituting in (2.37),

$$-F_{A0} X_A \Delta H_R(T) = U A_J (T - T_c) + \left(\sum_{i=1}^c F_{i0} \bar{C}_{p,i} \right) (T - T_0) \quad (2.38)$$

To understand the physical meaning of the terms in eq. (2.38), consider an exothermic reaction. The term $[-F_{A0} X_A \Delta H_R(T)]$ represents the enthalpy change related to change in composition because of the chemical reaction. While $U A_J (T - T_c)$ is the rate at which heat is transferred out

of the CSTR. Finally, $\left(\sum_{i=1}^c F_{i0} \bar{C}_{p,i} \right) (T - T_0)$ represents the increase in sensible heat of the feed as it goes from T_0 to T .

Now, we define two functions corresponding to the left-hand side and right-hand of eq. (2.38), respectively.

The first function is:

$$HPR(T) = -F_{A0} X_A \Delta H_R(T) \quad (2.39)$$

The function $HPR(T)$ represents the **heat generation* rate in the reactor, proportional to the reaction heat (ΔH_R) and conversion degree (X_A). For an exothermic reaction, this term will be > 0 and a strong temperature function.

The second function, $HWR(T)$, is defined from two right-hands terms of the eq. (2.40).

$$HWR(T) = UA_J (T - T_c) + \left(\sum_{i=1}^c F_{i0} \bar{C}_{p,i} \right) (T - T_0) \quad (2.40)$$

Eq (2.40) is called the **removal** term because it represents the total heat transfer rate per unit volume of the reaction mixture. In summary, it represents the sensible heat from T_0 to T and the heat transferred to the heat-transfer fluid.

Both $HPR(T)$ and $HWR(T)$ allow identifying when the CSRT operates under steady-state conditions and which of them is stable. If $HPR(T) \neq HWR(T)$, the CSTR is **not** at steady-state.

Figure 2.11 shows a typical $HPR(T)$ and $HWR(T)$ vs T plot for an ideal CSTR, assuming an irreversible, exothermic and first-order reaction is taking place.

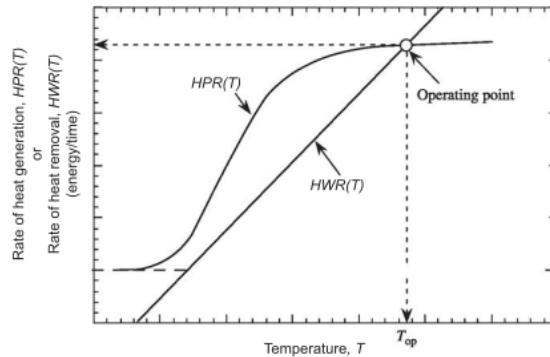


Figure 2.11: Typical $HPR(T)$ and $HWR(T)$ curves versus temperature, T , for an irreversible, exothermic reaction in an ideal CSTR

The intersection of the $HPR(T)$ curve with the $HWR(T)$ line is the reactor's operating point. Therefore it is a **graphical** solution to the design equation and the energy balance for the CSTR.

The $HWR(T)$ is linear when C_P is assumed constant, while the $HPR(T)$ curve is generated following pseudo-algorithm:

INPUT: Assumed reaction temperature, T;
OUTPUT: HPR-HWR curve;

WHILE output is **not** generated

```

select T from input;
calculate kinetic constants with input;
solve design equation for  $X_A$ ;
calculate  $HPR(T)$ 
plot  $HPR(T)$  vs.  $T$ 
IF output_is_True:
    end;
```

For reasons of convenience, several different expressions for heat production and heat removal are used. For the heat production with constant density reactions, we have:

1. the heat production per unit time: $(-\Delta H_r) v C_{A0} X_A$
2. the heat production per unit of volume of reaction mixture: $(-\Delta H_r) C_{A0} X_A$
3. the heat production per unit of volume of reaction mixture divided by ρC_P , the sensible heat per unit of volume of the reaction: $(-\Delta H_r) C_{A0} X_A / \rho C_P$. This represents the fraction of the maximum possible temperature increase, which is reached in the reactor.

For heat removal, similar expressions can be defined. As long as the HPR and HWR are unit-consistent, all will lead to the same conclusions concerning the reactor design and operation. (Westertep, Van Swaaij, and Beenackers 1984)

Multiple steady-states analysis

Another essential aspect of CSRT design is to determine if multiple steady-states are raised. This situation is possible because a non-linear equation can have more than one solution. Nevertheless, how is it possible to determine this particular situation?

Let us consider some changes to the situation shown in Figure 2.11. Suppose that the temperature of the feed, T_0 , or the cooling fluid temperature, T_c , is reduced. The result of this modification will be to increase the intercept of the HWR(T) line on the y-axis without changing the slope of the line. It means that HWR(T) line shifts to the left, parallel to the original curve, so that it could be more than one operating point. This situation is known as **multiple steady-states**.

In order to determine if there are multiple steady-states for a CSTR. We are going to follow the next steps:

1. Let us fixed inlet conditions.
2. Let us establish a range for T we are interested in.
3. For each T in the temperature range, let calculate k and X_A (or C_A).
4. Again, for each T , the cooling fluid temperature T_c is calculated.
5. Finally, the set of values for T , X_A , and T_c is substituted into the reactor energy balance. When the left-hand side of equation (2.37) is equal to 0, a steady-state will have been reached.

The heat-transfer fluid consumption is calculated from an energy balance around the perfectly mixed jacket at temperature T_J . Constant physical properties of the cooling medium are assumed.

$$F_c \rho_c C_{P_c} T_{c,\text{in}} = F_c \rho_c C_{P_c} T_J - Q \quad (2.41)$$

where F_c is flow rate of coolant (m^3/s), ρ_c means density of coolant (kg/m^3), C_{P_c} is heat capacity of coolant ($\text{J kg}^{-1} \text{K}^{-1}$), $T_{c,\text{in}}$ represents the supply temperature of cooling medium (K), and T_J is the output temperature of cooling medium (K).

The typical reactor design situation is given the feed conditions, the kinetic information, and the desired conversion. The problem is to determine the temperature and the size of the reactor. The next illustrations show how the principles described above are applied in the design of a CSTR. See Exercise 2.1

Exercise 2.1 (Operation of a cooled exothermic CSTR). An irreversible exothermic reaction is carried out in a CSTR.



The reaction is first-order in reactant A and has a heat reaction given by ΔH_R which is based on reactant A . Negligible heat losses and constant densities can be assumed. A well-mixed cooling jacket surrounds the reactor to remove the heat of reaction. Cooling water is added to the jacket at a rate of F_J and at an inlet temperature of T_{J0} .

The volume V of the contents of the reactor and the volume V_J of water in the jacket are both constant. The reaction rate constant changes as function of the temperature according to the equation.

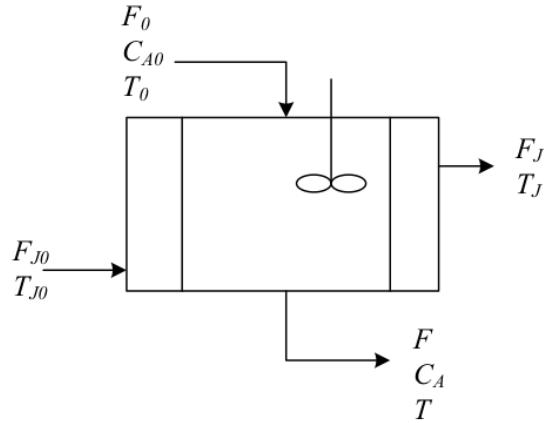
$$k = k_0 \exp(-E/RT)$$

The feed flow rate F_0 and the cooling water flow rate F_J are constant. The jacket water is assumed to be completely mixed. Heat transfer from the reactor to the jacket can be calculated from:

$$Q = U A_J (T_J - T)$$

where Q is the heat transfer rate, U is the overall heat transfer coefficient, and A_J is the heat transfer area.

1. Formulate the material and energy balances that apply to the CSTR and the cooling jacket.
2. Calculate the steady-state value of C_A , T_J , and T for the operating conditions.
3. Identify all possible steady-state operating conditions, as this system may exhibit multiples steady states.
4. Solve the unsteady-state material and energy balances to identify if any of the possible multiple steady states are unstable.



Solution

- (a) There are three balance equations that can be written for the reactor (respect to reactant A) and the cooling jacket.2.1

$$\begin{aligned} F_0 C_{A0} - F C_A - k C_A V &= 0 \\ \rho C_P (F_0 T_0 - FT) - \Delta H_R(T) V k C_A + U A_J (T_J - T) &= 0 \\ \rho_J C_{P_J} F_J (T_{J0} - T_J) - U A_J (T_J - T) &= 0 \end{aligned}$$

- (b) The operation conditions for the reactor are:

| Sym | Value | Sym | Value |
|----------|----------------------------|--------------|------------------------------|
| F_0 | 40 ft ³ /h | U | 150 btu/h-ft ² -R |
| F | 40 ft ³ /h | A_J | 250 ft ² |
| C_{A0} | 0.55 lbmol/ft ³ | T_{J0} | 530 R |
| V | 48 ft ³ | T_0 | 530 R |
| F_J | 49.9 ft ³ /h | ΔH_R | -30 000 btu/lbmol |
| C_P | 0.75 btu/lb-R | C_{P_J} | 1 btu/lb-R |
| k_0 | 7.08E10 h ⁻¹ | E | 30 000 btu/lbmol |
| ρ | 50 lb/ft ³ | ρ_J | 62.3 lb/ft ³ |
| R | 1.9872 btu/lbmol-R | | |

All these values were implemented into modeling equations into a Python script link. The solution obtained was:

| Variable | Value |
|--------------------------------|--------|
| C_A (lbmol/ft ³) | 0.521 |
| T (R) | 537.25 |
| T_J (R) | 537.25 |

When we are dealing with exothermic reactions, several steady states may be possible in a CSTR, which can easily calculate them if we rewrite the equations like so:

$$C_A = \frac{F_0 C_{A0}}{F + V k}$$

$$T_J = \frac{\rho_J C_{P_J} F_J T_{J_0} + U A_J T}{\rho_J C_{P_J} F_J + U A_J}$$

Now, these equations are solved for a range $500 \leq T \leq 700$, next their results are evaluated into energy balance function (eq. @ref{eq:ec003020b}) on the reactor.

$$f(T) = \rho C_P (F_0 T_0 - FT) - \Delta H_R(T) V k C_A + U A_J (T_J - T) \quad (2.42)$$

These equations are solved for a range from 500 to 700. Next, their results are evaluated into energy balance function on the reactor. The results obtained are plotted vs T_R in figure 2.12.

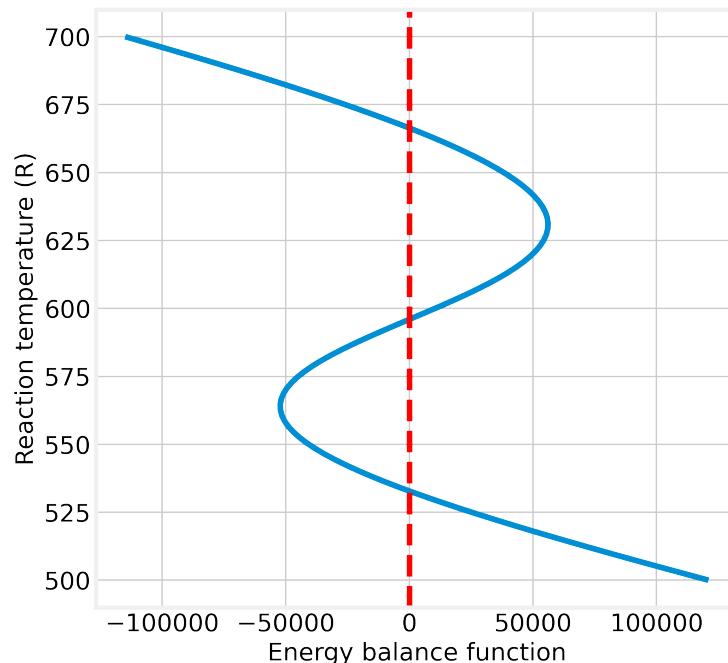


Figure 2.12: Graphical indication of multiple steady-states solutions

Figure 2.12 shows the system has three operating-points. Now, how a CSTR can operate at multiple steady-states is necessary to know which is (or which of them) stable for the operating condition. Thus, the next step in designing a non-isothermal CSTR must be to carry out a steady-state analysis.

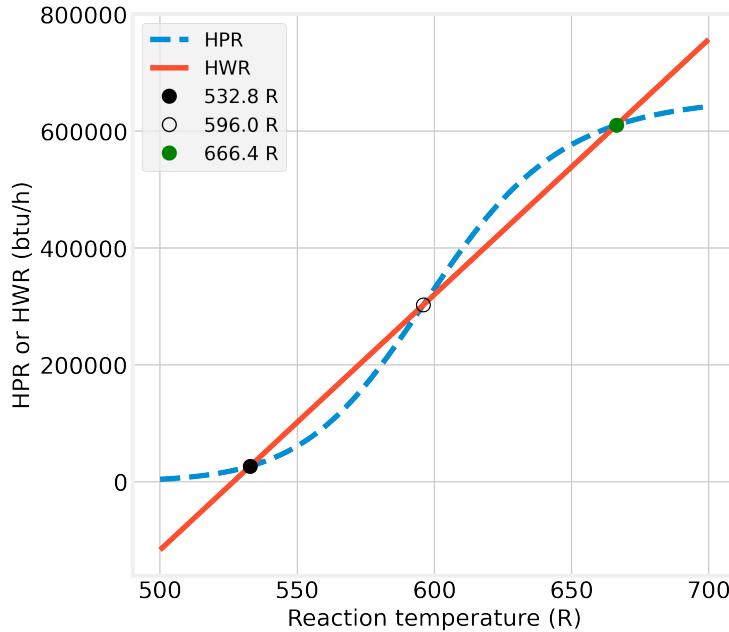


Figure 2.13: Graphical solutions of the heat balance for a CSTR

Usually, the stability analysis can be done from the plot $HPR(T)$ - $HWR(T)$ vs. reaction temperature.

Figure 2.13 shows HPR is a sigmoidal curve because of the rate constant's exponential temperature dependence. The shape of the curve depends in large part on the value of the activation energy.

All possible reactor operating temperatures must satisfy both functions, HPR and HWR , such that the two functions have equal values. These operating points are represented in Fig. 2.13 by circles.

Additionally, Figure 2.13 shows that the HWR line intercepts the HPR curve in three points at the same temperatures shown in Figure 2.12. Gray dots represent stable conditions, and especially the latter point is of practical interest since it represents a high degree of conversion.

The stable conditions are related to the fact that the heat removal line's slope should be greater than that of the heat production line. Under that condition, more heat is removed on a positive deviation from the operating point than produced heat so that the reaction temperature will return to the steady-state value.

Figure 2.13's black circle is an unstable operating condition because the situation is reversed than for gray dots. Since the heat production curve slope is here more significant than that of the heat removal line, any positive temperature deviation will be amplified until the reactor works in the upper stable operating point and vice versa.

In summary, the lower stable steady-state operating point in Figure 2.12 corresponds to low rates of heat generation and removal. This combination may result from one or more of the following factors:

1. Small values of ΔH_R ;
2. Low value of the reaction rate constant;
3. Short average residence time;
4. Small value of the feed rate, and
5. Fast removal of heat from the reactor, which does not cause the temperature to rise to higher values.

On the other hand, the higher stable steady-state operating point in Figure 2.12 corresponds to the reactant's nearly complete consumption. This outcome is favored by:

- a. An enormous value of ΔH_R ;
- b. A more considerable value of the reaction rate constant;
- c. Longer average residence time;
- d. Larger reactant throughput, and
- e. A slower heat removal regime by a heat exchanger.

Whether the reactor operates at a lower or higher stable point depends on how it is started up. The **unsteady energy** and material balances must be solved simultaneously to determine the effect of startup conditions.

The type of stability analysis carried out above is not mathematically rigorous. However, it is a handy way to understand the concept of stable and unstable operating points. In mathematical terms, the above analysis has shown that a steady-state operating will be unstable if

$$\left[\frac{\partial HPR(T)}{\partial T} \right]_{\text{operating point}} > \left[\frac{\partial HWR(T)}{\partial T} \right]_{\text{operating point}}$$

and will be stable if

$$\left[\frac{\partial HPR(T)}{\partial T} \right]_{\text{operating point}} < \left[\frac{\partial HWR(T)}{\partial T} \right]_{\text{operating point}}$$

The first inequality is a sufficient criterion for instability so that the operating point will be intrinsically unstable in this situation. The second inequality is a sufficient criterion for stability, provided that the CSTR is adiabatic. If the reactor is not adiabatic, the second condition is necessary but not sufficient.

It is important to remark that the curve HPR/HRW vs. T performed in Fig. 2.12 corresponds to a simple reaction rate expression $r_A = -kC_A$. As the reaction change's characteristics, the shape of that curve will change, and the resulting analysis will need to be accordingly modified.

Figure 2.14 presents qualitative forms of the HPW/HWR curve for (a) a reversible reaction, (b) a pair of consecutive exothermic reactions, and (c) for two consecutive reactions, where the first is exothermic and the second is endothermic.

Internal Coil

If an internal coil is used, the cooling medium flows in plug flow through the coil. The temperature differential driving force for heat transfer is a log mean average of the differential temperatures at the coil's two ends.

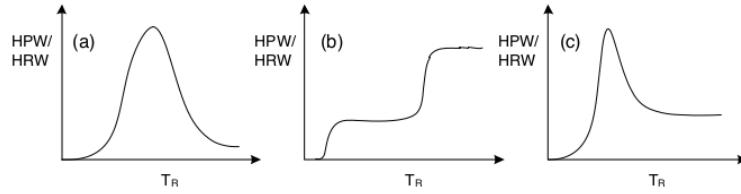


Figure 2.14: Qualitative shape of HPR/HPWR curve for several kind of reactions

$$\begin{aligned}\Delta T_{\text{in}} &= T_R - T_{C,\text{in}} \\ \Delta T_{\text{out}} &= T_R - T_{C,\text{out}} \\ (\Delta T)_{LM} &= \frac{\Delta T_{\text{in}} - \Delta T_{\text{out}}}{\ln \left(\frac{\Delta T_{\text{in}}}{\Delta T_{\text{out}}} \right)}\end{aligned}\quad (2.43)$$

where: $T_{C,\text{in}}$ is the supply temperature of cooling medium (K) and $T_{C,\text{out}}$ is the temperature of cooling medium leaving the coil (K).

The energy balance on the coil is again given by the eq. (2.41). While the heat transfer rate is given by

$$Q_{\text{coil}} = U A_{\text{coil}} \Delta T_{LM} \quad (2.44)$$

There are several issues to be resolved in the design of a cooling coil but these will not be considered for this course.

Exercise 2.2 (Non-rigorous coil design for a CSTR). As illustration, let us design (non-rigorous) a coil heat exchanger for a CSTR presented in part 1 of the illustration 2.1. The following coil specification are used in this illustration:

1. the pipe diameter is 5/8 in.
2. the loop diameter constitutes 80% of the diameter of the vessel.
3. The spacing between the loop flights is the diameter of the pipe.
4. Only one coil is used.
5. The reactor vessel has an aspect ratio (L/D) of 2.

Solution. In order to solve this problem, it is required two iterative calculations. One to determine the size of the reactor, including the coil heat exchanger, and the second one to determine the coolant flow rate required

In the first iterative calculation, it must include following equations:

| | | |
|-----------------------|--|--|
| Length of the reactor | | $L_R = 2 D_R$ |
| Number of coils | | $N = \frac{L_R}{2D_{coil}}$ |
| Length of coil | | $L_{coil} = 0.8 D_R \pi N$ |
| Volume of coil | | $V_{coil} = \frac{\pi D_{coil}^2}{4} L_{coil}$ |

This problem was implemented in Python and the results obtained were:

Reactor size parameters including coil heat exchanger:

Reactor diameter: 1.55 m

Reactor volume: 6.0 m

Coil heat exchanger parameters:

Transfer area: 19.09 m²

Number of loops: 98

Coil volume: 0.08 m³

Coil length: 382.87 m

Cooling fluid parameters:

Exit temperature: 436.15 K

Log-mean temperature difference: 7.10 K

Coolant flowrate: 34.88 cm³/s

The main advantage of a coil over a jacket is more transfer area.

Reactors in series

In the general energy balance (eq. (2.4)), the extent of reaction, ξ_j , in the inlet stream was taken to be zero. When dealing with CSTRs in series, this balance must include the change in extension of reaction or fractional conversion per each CSRT referred to in the first reactor. (Roberts 2009)

Then, if only one reaction is taking place, the Eq. (2.4) becomes

$$Q - \left(\sum_{i=1}^c F_{i0} \bar{C}_{p,i} \right) (T_{\text{out}} - T_{\text{in}}) - F_{A0} (X_{A,out} - X_{A,in}) \Delta H_R(T) = 0 \quad (2.45)$$

If more than one reaction occurs, and if the extents of reaction in the feed to a reactor or segment are denoted ξ_k^0 , then eq. (2.4) becomes

$$\frac{dU}{dt} = Q - \left(\sum_{i=1}^c F_{i0} \bar{C}_{p,i} \right) (T_{\text{out}} - T_{\text{in}}) - \sum_{j=1}^R (\xi_j - \xi_j^0) \Delta H_{R,j}(T) \quad (2.46)$$

It is essential to point out that in Eqs. (2.45) and (2.46), Q is the rate at which heat is transferred into the reactor section under consideration, i.e., for which the inlet temperature is T_{in} , and the outlet temperature is T_{out} .

Finally, it is necessary, the temperature correction for the heat of reactions is based on:

$$\Delta H_{R,j}(T) = \Delta H_R^\circ(T^\circ) + \int_{T^\circ}^T \sum \nu_i C_{p,i} dT$$

where $\Delta H_R^\circ(T^\circ)$ is usually calculated from enthalpies of the formation of components involved in the chemical reaction.

Exercise 2.3 (Heat transfer requirement for multiple CSTRs). Reactant A undergoes an essentially irreversible isomerization reaction that obeys first-order kinetics. An irreversible exothermic reaction



Both A and B are liquids at room temperature ad both have too high boiling points. Consider the possibility of using one or more CSTRs operating in series. If each CSTR operates at 163C and if the feed stream consists of pure A entering at 20C.

Determine the reactor volumes and heat transfer requirements to produce 2 million pounds in 7000 h for

1. A single CSTR.
2. Three identical CSTRs in series.

Data and assumptions

1. Reaction rate expression: $r = k C_A$.
2. Rate constant at 163C = 0.8 h-1.
3. Heat of reaction = -83 cal/g.
4. Molecular weight = 250.

The heat capacities of species A and B may be assumed to be identical and equal to 0.5 cal/g-C. Their densities may be assumed to be equal to 0.9 g/cm3. The conversion final is 97%

Solution

1. For a CSTR. From the CSTR's design equation

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

Additionally,

$$X_A = 1 - \frac{C_A}{C_{A0}}$$

So, combining two last equations with k and X_A values

$$0.97 = -\frac{1}{1 + 0.8\tau} + 1 \Rightarrow \tau = 40.42 \text{ h}$$

From problem data given:

$$F_{A0} = 1.297 \cdot 10^5 \frac{\text{g}}{\text{h}}$$

$$v = 144.13 \frac{\text{L}}{\text{h}}$$

$$\mathbf{V_R = 5825.13 L}$$

The Q is calculated from Eq. (2.36)

$$\mathbf{Q = -1.1687 \cdot 10^6 \frac{cal}{h} = -4634.85 \frac{btu}{h}}$$

2. For a three-CSTR series For the last reactor,

$$C_{A3} = \frac{C_{A0}}{(1 + k\tau)^3}$$

This equation could be rewritten in

$$X_{A3} = -(1 + k\tau)^{-3} + 1$$

Thus, $\tau = 2.77$ h, therefore $\mathbf{V_R = 399.645 L}$

The heat requirement for each reactor is calculated from τ and the fractional conversion reached in each of them. Thus,

$$\begin{aligned} C_{A1} &= \frac{C_{A0}}{1 + k\tau} \Rightarrow & \mathbf{X_{A1} = 0.689} \\ C_{A2} &= \frac{C_{A0}}{(1 + k\tau)^2} \Rightarrow & \mathbf{X_{A2} = 0.9034} \end{aligned}$$

Finally,

$$\mathbf{Q_1 = \left(F_{A0} \int_{20}^{163} C_P dT + F_{A0} X_{A1} \Delta H_R \right) \frac{1}{252.16} = 7350.97 \frac{btu}{h}}$$

$$\mathbf{Q_2 = (F_{A0} [X_{A2} - X_{A1}] \Delta H_R) \frac{1}{252.16} = -9144.44 \frac{btu}{h}}$$

$$\mathbf{Q_3 = (F_{A0} [X_{A3} - X_{A2}] \Delta H_R) \frac{1}{252.16} = -2841.39 \frac{btu}{h}}$$

2.3 Plug-flow reactor (PFR)

Plug flow is a simplified and idealized picture of a fluid's motion, whereby all the fluid elements move with a uniform velocity along parallel streamlines. This perfectly ordered flow is the only transport mechanism accounted for in the plug flow reactor model.

In summary, the essential features of a PFR are:

1. The volumetric flow may vary continuously in the direction of the flow because of a change in density,
2. Each element of fluid is a closed system; that is, there is no axial mixing (it seems a CSTR),
3. fluid properties may change continuously in the axial direction but are constant radially at a given axial position,
4. Each element of fluid has the same residence time, t , as any other.

This kind of reactor is usually used:

1. When a high flow rate of the reacting system is needed (fast reactions).
2. Large scale.
3. High temperature.
4. Homogeneous or heterogeneous reactions.
5. Continuous operations.

In a PFR, the composition of the fluid varies from point to point along a flow path. Thus the material balance for a reaction component must be made for a differential element dV , as shown in Figure 2.15.

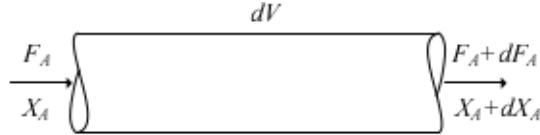


Figure 2.15: Plug-flow reactor volume element

Under steady-state operation, the material balance is expressed in terms of the molar flow.

$$dV = \frac{dF_A}{r_A} \quad (2.47)$$

Equation (2.47) is the ***design equation*** for an ideal PFR.

For a single reaction, it may be convenient to write Eq. (2.47) in terms of fractional conversion of a key reactant

$$F_A = F_{A0} (1 - X_A) \quad (2.48)$$

$$dF_A = - F_{A0} dX_A \quad (2.49)$$

$$\frac{dV}{F_{A0}} = - \frac{dX_A}{r_A} \quad (2.50)$$

The equation (2.50) could be rewritten as a differential equation representing the gradient of X_A for a position (z) in a PFR. Assuming that the reactor is a cylinder of radius R. The volume of the reactor from the inlet to position is $V(z) = \pi R^2 z$, so:

$$\frac{dX_A}{dz} = - \frac{\pi R^2 r_A}{F_{A0}} \quad (2.51)$$

Under the traditional approach for sizing reactors, the equation (2.50) is rewritten depending on the reacting fluid density. As far as I understand, it is unnecessary because of software like Python or Matlab, making more straightforward numerical calculations. Despite that, let us study how the equation design changes on a constant- and variable- density fluid.

2.3.1 Design equation

Constant-Density System

If the reacting fluid keeps its density constant during the chemical reaction, then Equation (2.50) can be written in terms of the initial concentration of limiting reactant (C_{A0}) and the spacial time (τ)

$$d\tau = -C_{A0} \frac{dX_A}{r_A} \equiv \frac{dC_A}{r_A} \quad (2.52)$$

A graphical interpretation of equations (2.50) and (2.52) is illustrated in Figure 2.16

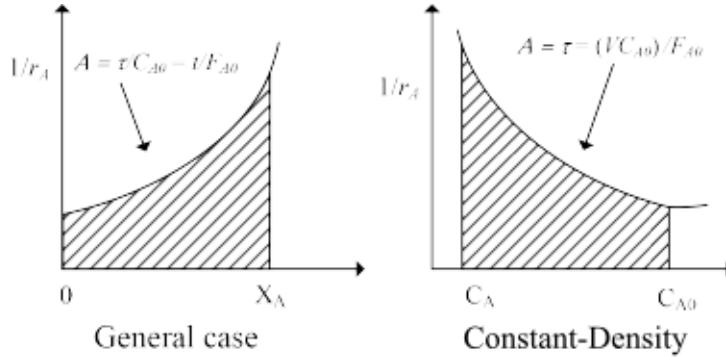


Figure 2.16: Graphical interpretation of design equation for a PFR

The shape of figure 2.16 is based on the assumption that $-r_A$ decreases as X_A increases. Thus equation (2.50) states that (V/F_{A0}) for an ideal PFR is the area under the curve of $(1/-r_A)$ vs. X_A , between the inlet and outlet fractional conversion.

Variable-Density System

When the reacting system's density is not constant throughout a PFR, the size of a PFR must be calculated using the general design equation (Eq. (2.50)).

For example for an irreversible first-order reaction, which $r_A = -k C_A$. The kinetic equation will be written as

$$r_A = -k C_A = -k \frac{F_A}{v} = -k F_{A0} \frac{(1-X_A)}{v}$$

Thus, the equation design is

$$\tau = -C_{A0} \int_0^{X_A} \frac{dX_A}{r_A} = C_{A0} \int_0^{X_A} \frac{v dX_A}{k F_{A0} (1-X_A)} = \frac{1}{k v_0} \int_0^{X_A} \frac{v dX_A}{1-X_A} \quad (2.53)$$

Taking into account that, in this case, $v = v_0 (1 + \varepsilon_A X_A)$ then (2.53) becomes

$$\tau = \frac{1}{k} \int_0^{X_A} \frac{(1 + \varepsilon_A X_A)}{1 - X_A} dX_A \quad (2.54)$$

As it was mentioned before, for ideal PFR, all fluid elements take the same length of time in the reactor. This time is called **mean residence time** (\bar{t}) and, in general, it could be calculated by:

$$\bar{t} = \int_0^V \frac{dV}{v} \quad (2.55)$$

where v is the volumetric flow rate.

The space-time and the mean residence time are identical when there is no density change in the reactor. For analyzing kinetic data obtained from tubular reactors, the τ is a more useful variable than t because the former is an independent variable. In contrast, the latter only can be obtained if the progressive changes occurring within the reactor are known beforehand.



information For systems of constant density, the performance equations are identical for a BR and PFR, which means τ for PFR is equivalent to t for the BR

To demonstrate how to use the expressions for PFR, let us solve the next problem.

Exercise 2.4 (Effect of the rate laws over PFR performance). Consider the effect of reaction on conversion in a PFR whose volume is 1.5 dm^3 . The irreversible liquid phase reaction $A \rightarrow B$ is taking place in which the feed concentration is $C_{A0} = 1.0 \text{ mol/dm}^3$ and the volumetric flow rate is $v_0 = 0.9 \text{ dm}^3/\text{min}$. The reaction rate constant for various reaction orders is fixed at 1.1 for this comparison with units consistent with the concentration mentioned above and flow rate.

1. Plot the conversion in a PFR as a function of reactor volume for zero-, first-, second-, and third-order reaction to a reactor volume of 1.5 dm^3 .
2. Repeat for feed concentrations of C_{A0} at 0.5 and 2.0 mol/dm^3 .

Solution. For the PFR, a differential mole balance gives the following differential equation for converting A

$$\frac{dX}{dV} = -\frac{r_A}{F_{A0}} \quad (2.56)$$

where the rate law is

$$r_A = -k C_A^n$$

and $n = 0, 1, 2$, or 3 according to the reaction's order. As an initial condition for eq. (2.56) is that there is no conversion at the reactor inlet. Additionally, if constant temperature and pressure are considered, then the concentration of reactant A could be expressed using conversion as:

$$C_A = C_{A0} (1 - X_A)$$

Part 1 of this problem was solved in Python, and the graphical results are given

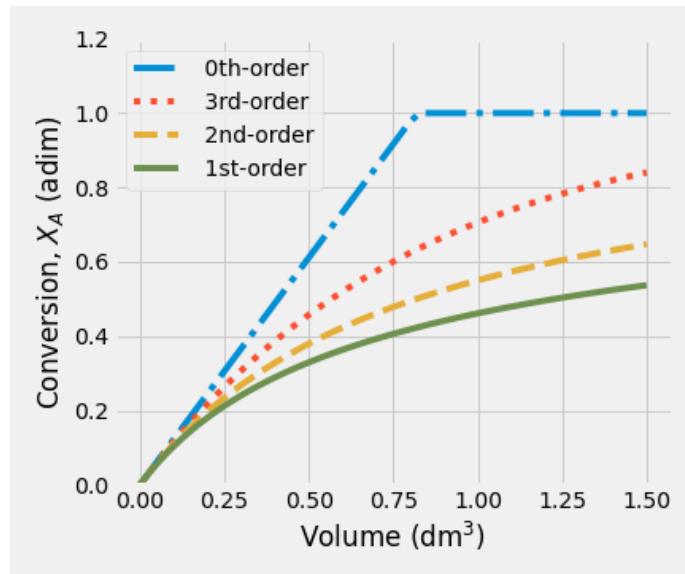


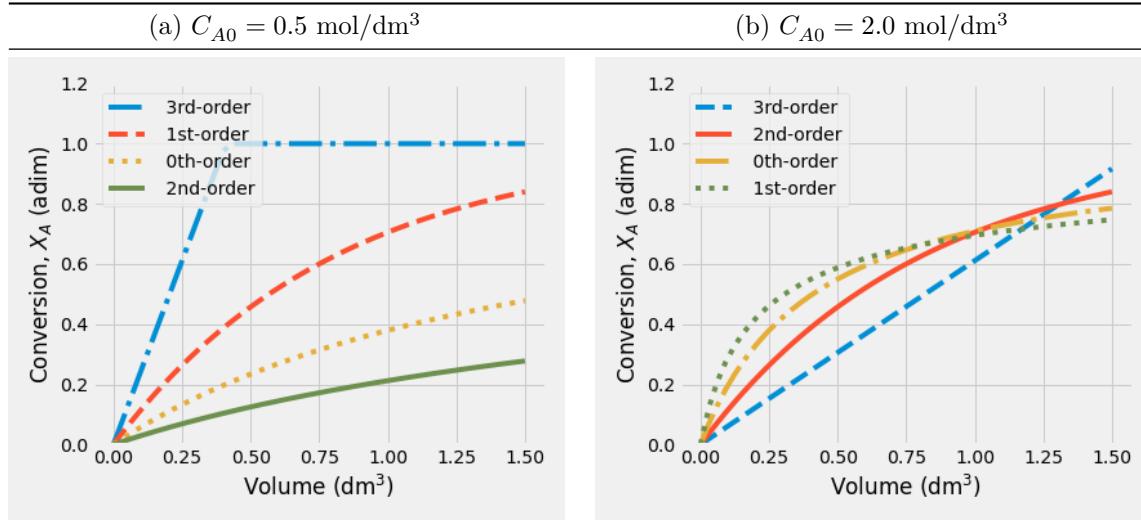
Figure 2.17: Fractional conversion vs volume for various reaction orders

Figure 2.17 shows clearly the effect of reaction on conversion in a PFR, for zero-order kinetic will obtain higher conversion than other cases. As we expect, for a zero-order kinetic, fractional conversion shows an independent behavior of concentration A . That is why a linear function is observed when the fractional conversion is less than one.

In those cases, when order-kinetic is more significant than zero, fractional conversion shows an exponential behavior, and the final conversion value decreases inversely to order-kinetic.

The results for item 2 were plotted. When the initial concentration of A decreases to $0.5 \text{ mol}/\text{dm}^3$, fractional conversion changes in the same way. The main difference with item 1 is that final conversion values, for order-kinetic greater than zero, are less.

The results obtained when the initial concentration of A was increased to $2.0 \text{ mol}/\text{dm}^3$ are shown.



2.3.2 Energy balance

This section will derive an energy balance for a PFR, considering the volume element in Figure 2.18. Additionally, it will be assumed temperature and composition of the reaction mixture are uniform over the cross-section of the PFR and depend only on the distance L from the feed point.

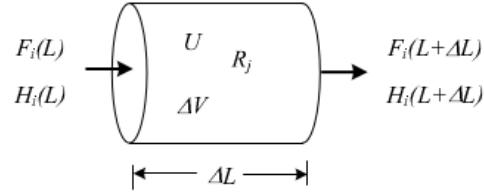


Figure 2.18: PFR reactor volume element

According to Fig. 2.18, the steady-state energy balance over a differential volume of the reactor becomes, if any work done by the reaction mixture is neglected:

$$\frac{dQ}{dV} - \frac{d}{dV} \left(\sum_{i=1}^c F_i H_i \right) = 0 \quad (2.57)$$

The enthalpy term can be broken apart into two terms:

$$\frac{dQ}{dV} - \sum_{i=1}^c \left(\frac{dF_i}{dV} H_i \right) - \sum_{i=1}^c \left(F_i \frac{dH_i}{dV} \right) = 0 \quad (2.58)$$

The differential of enthalpy is

$$\frac{dH_i}{dV} = C_{Pi} \frac{dT}{dV} + \left[V_i - T \left(\frac{\partial V_i}{\partial T} \right)_P \right] \frac{dP}{dV} \quad (2.59)$$

If the pressure changes over enthalpy are neglected

$$\frac{dH_i}{dV} = C_{Pi} \frac{dT}{dV} \quad (2.60)$$

The second term in Fig. (2.57) is related to a molar balance over specie i . If we consider that only one reaction is taking place in the PFR:

$$\frac{dF_i}{dV} = \nu_i r \quad (2.61)$$

Substituting (2.61), (2.60) into (2.58) to give

$$\frac{dQ}{dV} - \sum_{i=1}^c (H_i \nu_i) r - \sum_{i=1}^c (F_i C_{Pi}) \frac{dT}{dV} = 0 \quad (2.62)$$

This equation is equivalent to:

$$\frac{dQ}{dV} = \Delta H_R r + \sum_{i=1}^c (F_i C_{Pi}) \frac{dT}{dV} \quad (2.63)$$

Equation (2.63) provided the concentration and temperature profiles in the PFR as a function of V , solving it simultaneously with Eq. (2.61), when the rate of heat transfer to the reactor is known.

In most cases, the equation (2.63) is written in terms of 1 mole of the key reactant A.

$$\frac{dQ}{dV} = \sum_{i=1}^c (F_i C_{Pi}) \frac{dT}{dV} - \Delta H_{R,A} r_A, \quad r_A = -r \quad (2.64)$$

Therefore,

$$\frac{dT}{dV} = \frac{\frac{dQ}{dV} + \Delta H_{R,A} r_A}{\sum_{i=1}^c (F_i C_{Pi})}, \quad r_A = -r \quad (2.65)$$

Temperature and concentration profiles as function of PFR length

In case that the tube diameter is constant, it could be useful to express Eq. (2.63) considering the differential element of length ($dL()$) rather than the differential element of volume, dV .

The volume of the reactor is related to the axial length, L , and the vessel diameter, D . Thus, over a differential element of volume:

$$dV = \frac{\pi D^2}{4} dL = A_t dL \quad (2.66)$$

where A_t is the cross-sectional tube area.

Substituting this relationship into Eq. (2.61), the molar-balance equation then becomes for A

$$\frac{dF_A}{dL} = \frac{\pi D^2}{4} r_A \quad (2.67)$$

or, for constant-density, considering that $F_i = A_t u C_i$

$$u \frac{dC_i}{dL} = \nu_i r \quad (2.68)$$

where u is the linear velocity with which the fluid flows through the tube, and C_i is the concentration of the specie i .

Incorporating Eq. (2.66) into the energy balance, (2.63), gives

$$\frac{dQ}{dL} = \sum_{i=1}^c (F_i C_{Pi}) \frac{dT}{dL} - \frac{\pi D^2}{4} \Delta H_{R,A} r_A \quad (2.69)$$

Now, the simultaneous solution of Eq. (2.67) and Eq. (2.69) gives the temperature and concentration profiles along the reactor's axial length, provided that the rate of external heat transfer is known.

External Heat Transfer to PFR

In such cases, when a PFR operates with heat transfer to the surroundings to control the temperature within a specified range, it is possible to impose a constant heat flux at the reactor's wall, which could be implemented example, electrical heating.

The rate of heat transfer depends on the local temperature difference between the fluid in the reactor and the heat transfer fluid, as follow:

$$\frac{dQ}{dV} = U (T_\infty - T) \frac{dA}{dV} \quad (2.70)$$

where: U is overall heat transfer coefficient, T_∞ is the temperature of the surrounding heat transfer fluid, T is the temperature inside of the reactor, A is the heat transfer area of the reactor upon which U is based.

A represents the heat transfer area of the external wall of the tube, thus.

$$dA = p_w dL \quad (2.71)$$

p_w is the perimeter length of the tube wall. Suppose the tube is cylindrical, then $A = \pi D$. Thus, for a typical PFR illustrated in Figure 2.18, with a length equals to dL

$$\frac{dQ}{dV} = U (T_\infty - T) \frac{\pi D dL}{(\pi D^2 / 4) dL} = U (T_\infty - T) \frac{4}{D} \quad (2.72)$$

Substituting Eq. (2.72) into Eq. (2.62)

$$U(T_{\infty} - T) \frac{4}{D} = \sum_{i=1}^c (F_i C p_i) \frac{dT}{dV} - \Delta H_{R,A} r_A \quad (2.73)$$

This equation is one form of the energy balance for a PFR with external heat exchange. It is widespread to rewrite the energy balance as

$$\frac{dT}{dV} = \frac{1}{\sum_{i=1}^c F_i C_{P_i}} \left(\frac{4U(T_{\infty} - T)}{D} + \Delta H_{R,A} r_A \right) \quad (2.74)$$

Writing Eq. (2.74) in terms of the length by substituting Eq. (2.64)

$$\frac{dT}{dL} = \frac{1}{\sum_{i=1}^c F_i C_{P_i}} \left(\pi U D (T_{\infty} - T) + \frac{\pi D^2}{4} \Delta H_{R,A} r_A \right) \quad (2.75)$$

Any form of energy balance equation must be combined with the molar balance over PFR to obtain the temperature and concentration profiles along the reactor. In cases in which pressure could not be neglected, the momentum balance must be added.

One standard method of reactor operation is having a phase change taking place in the heat transfer fluid, that is, a boiling or condensing fluid use. In this operating mode, T_{∞} is constant, and the energy balance equation is solving based on that supposition.

Another useful assumption is considering an average heat capacity value (composition independent) which gives the following equation.

$$\frac{dT}{dL} = \frac{\pi U D}{\dot{m} \bar{C}_P} (T_{\infty} - T) + \frac{\pi D^2}{4\dot{m} \bar{C}_P} \Delta H_{R,A} r_A$$

From temperature analysis, there are four essential differences between PFRs and CSTRs.

1. The variation properties with axial position down the length of the reactor. In CSTR, the maximum reaction temperature is reached at the exit of the reactor under steady-state conditions. However, in a PFR, the peak temperature usually occurs at an intermediate axial position in the reactor. (assuming irreversible and exothermic reaction).
2. In a CSTR, a change over an input variable has an immediate effect on variables inside the reactor. In contrast, a PFR takes time for the disturbance to work its way through the reactor to exit. Thus there are significant dynamic lags and dead time between changes made at the inlet of the reactor and temperatures and compositions further down the reactor's length.
3. It is mechanically impossible to control the reaction temperature at each axial position down the PFR. Only a single temperature can be controlled, which can be the peak temperature or exit temperature.
4. In CSTR, the inlet temperature is not the most critical process variable but, in the case of a PFR, it is a design and control variable.

The primary assumption about flow pattern in a PFR is relatively reasonable for an adiabatic reactor. However, for non-adiabatic reactors, radial temperature gradients are inherent features. However, if tube diameters are kept small, the plug flow assumption is more suitable.

Exercise 2.5 (Heat transfer requirement for a PFR). Consider a reaction



Feed contains 80% A and 20% inert by weight. The molecular weight of A is 160 and that of inert is 80. The feed comes at a mass flow rate of 1 kg/s. The reaction is second order in A .

Reaction data:

- The rate constant is $k = 10^4 \exp(9000/T_R) \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
 - The specific heat capacity of A and B are 100 J/mol/K and 200 J/mol/K, respectively.
 - The heat of reaction is 20 000 J/mol A reacted.
 - The feed temperature is 400 K and the volumetric flow rate at the inlet is 1 L/s.
1. If it is adiabatically in a PFR of 1 m³, what is conversion?
 2. If heating coil are employed, and we are given that $U = 3 \times 10^2 \text{ W m}^{-2}$, $A = 2\text{-m}^2$ per m³ of PFR and $T_J = 500 \text{ K}$, what is the conversion?

Solution. The solution of this problem is available in this link

Since it is a liquid-phase reaction, no significant change in density is assumed.

1. Under adiabatic conditions, we have to solve two equations:

$$\frac{dX_A}{dV} = -\frac{r_A}{F_{A0}}$$

$$\frac{dT}{dV} = \frac{\Delta H_R r_A}{F_A C_{P_A} + F_I C_{P_I} + F_B C_{P_B}}$$

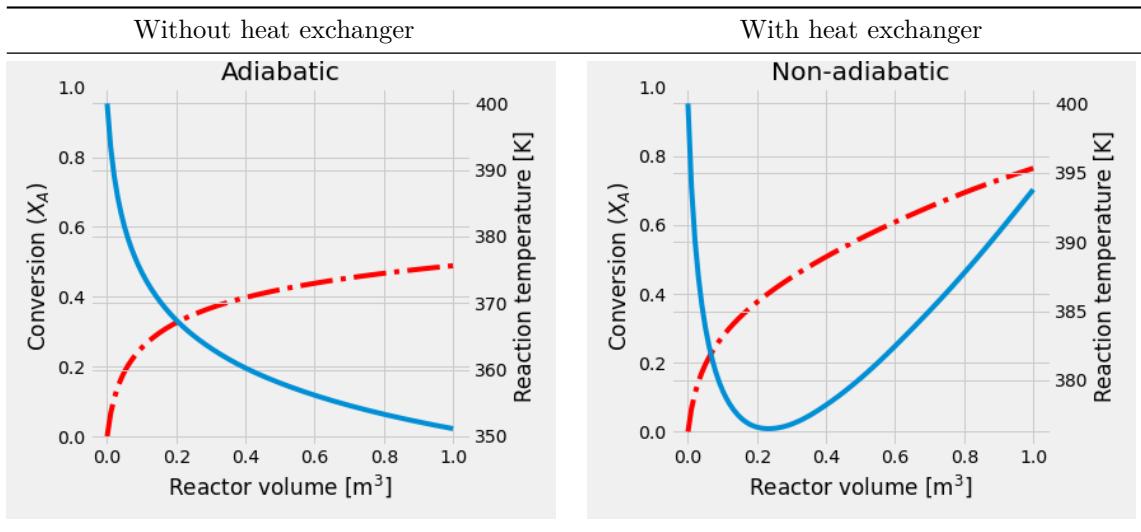
This system of equations was solved, and the reaction temperature was 351 K, while the conversion of A equals 48.89%.

In the next figure is shown the temperature and conversion profile obtained. In the beginning, the temperature is high, as well as the concentration of A. Later both temperature and conversion drop drastically, so the reaction rate is slowing down a lot.

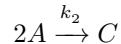
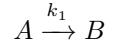
2. When the heating coil is used, the heat balance must change to include the quantity of heat-related to the heat exchanger.

$$\frac{dT}{dV} = \frac{U \left(\frac{A}{V_{\max}} \right) (T_J - T) + \Delta H_R r_A}{F_A C_{P_A} + F_I C_{P_I} + F_B C_{P_B}}$$

In this case, the output is at 394 K, and the conversion is 76.53%. Temperature and conversion profiles are shown in figure Y



Exercise 2.6 (Parallel Reactions in a PFR with Heat Effects). Consider next set of reactions which occurs in gas-phase



with $r_1 = k_1 C_A$ and $r_2 = k_2 C_A^2$. Pure A is fed at a rate of 100 mol/s, a temperature of 150 °C and a concentration of 0.1 mol/dm³. Determine the temperature and flow rate profiles down the reactor.

Solution. This problem was solved from following set of equations:

Kinetics equations:

$$r_1 = k_1 C_A$$

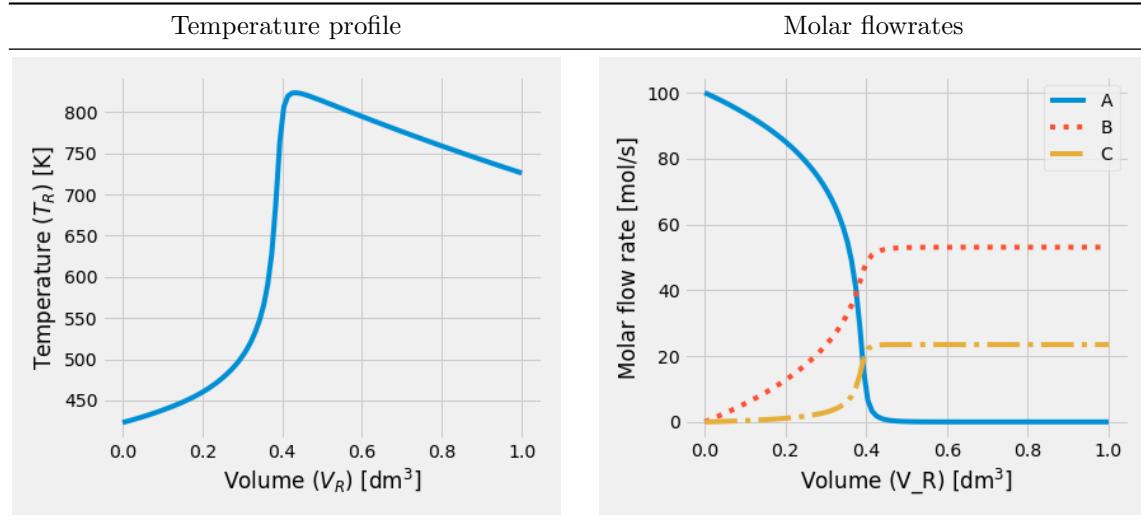
$$r_2 = k_2 C_A^2$$

Mole balances:

$$\begin{aligned}\frac{dF_A}{dV} &= r_A = -r_1 - 2r_2 \\ \frac{dF_B}{dV} &= r_B = r_1 \\ \frac{dF_C}{dV} &= r_C = r_2\end{aligned}$$

Energy balance:

$$\frac{dT}{dV} = \frac{Ua(T_J - T) + r_{A1} \Delta H_{R1} + r_{A2} \Delta H_{R2}}{F_A C_{P_A} + F_B C_{P_B} + F_C C_{P_C}}$$



2.3.3 Recycle PFR

A recycling reactor is an ideal tubular reactor that part of the effluent stream back to the reactor inlet. As shown in Figure 2.19. Recycle can control the temperature in the reactor and adjust the product distribution if more than one reaction is taking place.

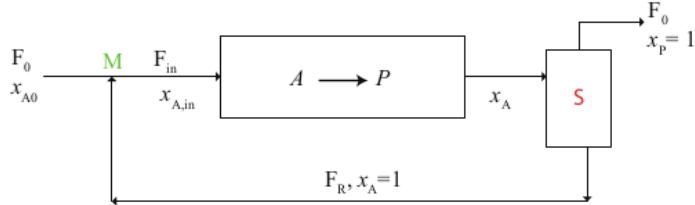


Figure 2.19: Recycle PFR

Based on the flowsheet in Fig. 2.19, the feed to the process is denoted by the subscript “o” with is mixed at the point M with the recycle stream, denoted by a subscript “R”. The mixed stream, which is denoted by a subscript “in”, is then fed to the reactor.

At point S, the outlet stream from the reactor, which is denoted by a subscript “out”, is split into recycle stream and the final stream leaving the process (denoted by a subscript “f”). The recycle ratio, R , as defined as

$$R = \frac{v_R}{v_f} = \frac{F_{\text{tot},R}}{F_{\text{tot},f}} = \frac{F_{A,R}}{F_{A,f}}$$

where v and F are the volumetric and molar flow, respectively.

If the fresh feed F_o contains a molar fraction $x_{A,o}$, and the reactor product a molar fraction x_A of the specie A, then the molar balance for A at point M is

$$F_{A,in} = F_{A,0} + F_{A,R} = F_{A,0} + R F_{A,f}$$

On the other hand, the A balance at point S is

$$F_{A,out} = F_{A,f} + F_{A,R} = F_{A,f} + R F_{A,f} = (1 + R) F_{A,f} \Rightarrow F_{A,f} = \frac{F_{A,out}}{1 + R}$$

Combining those last two equations, the desired expression for the initial value of the molar flow rate of A will be:

$$F_{A,in} = F_{A,0} + R \frac{F_{A,out}}{1 + R}$$

The material balance may obtain the volume of the recycled PFR for the reactant A into the reactor, which is

$$\frac{V}{F_{in}} = - \int_{X_{A,in}}^{X_A} \frac{dX_A}{r_A} \quad (2.76)$$

However, there are at least two ways to define the conversion of a system like this. One is the per-pass conversion given in eq. (2.78) and the other is the overall conversion given in equation (2.78).

$$X_{A,pass} = \frac{F_{A,in} - F_{A,out}}{F_{A,in}} \quad (2.77)$$

$$X_{A,overall} = \frac{F_{A,0} - F_{A,f}}{F_{A,0}} \quad (2.78)$$

It is essential to consider that the reactor's volumetric flow rate is greater than the volumetric flow rate entering the process when the rate expression contains concentrations.

The definition of concentration (eq. (2.79)) is used as usual. For a gas-phase system, the volumetric flow rate, in the denominator, is written using an appropriate equation of state.

$$C_i = \frac{F_i}{v} \quad (2.79)$$

On the other hand, if the fluid is a liquid of constant density, the reactor's volumetric flow rate must be used according to Eq. (2.80)

$$C_i = \frac{F_i}{v_{in}} = \frac{F_i}{v_0(1 + R)} \quad (2.80)$$

When the recycled PFR operates at non-isothermal temperature, the initial condition for the temperature is found at point M while noting that $T_{out} = T_R = T_f$. Assuming that no phase change occurs in any of the streams, the heat balance would be:

$$\sum_i \left(F_{i,0} \int_{T_0}^{T_{in}} C_{P,i} dT \right) + \sum_i \left(F_{i,R} \int_{T_R}^{T_{in}} C_{P,i} dT \right) = 0 \quad (2.81)$$

Therefore, the temperature of the stream “in”

$$T_{in} = T_0 \frac{\sum_i (F_{i,0} C_{P,i}) + T_R \sum_i (F_{i,R} C_{P,i})}{\sum_i (F_{i,in} C_{P,i})} (\#eq : ectemp_i n) \quad (2.82)$$

In summary, the performance of a non-isothermal recycle PFR must be calculate

$$\frac{dF_i}{dz} = \frac{\pi D^2}{4} \sum \nu_{i,j} r_j \quad (2.83)$$

$$\pi D U (T_e - T) = \left(\sum F_i C_{P,i} \right) \frac{dT}{dz} + \frac{\pi D^2}{4} \sum r_j \Delta H_j \quad (2.84)$$

$$F_i (z = 0) = F_{i,in} = F_{i,0} + \frac{R}{1+R} F_{i,out} \quad (2.85)$$

$$T (z = 0) = T_{in} \quad (2.86)$$

This EDO system must be solved using successive substitution because the flow rate and temperature of stream “in” usually are not provided. To calculate the initial values of these variables is necessary to know the molar flow rate and temperature of the stream “out”. However, $F_{i,in}$ and T_{in} are needed to integrate the design equation and calculate $F_{i,out}$ and T_{out} .

The problem could be solved by calculating an initial guess for the conditions of stream “in”, assuming that there is no recycle stream. The previous calculation provides an educated-guess for the composition and temperature of the recycle stream ‘‘R’’. The rest of the calculations are performed using these values as initial conditions.

Under isothermal operation and assuming that $F_0 = F_f$, and noting that $x_{A,R} = x_{A,out} = x_{A,f}$, the problem is much easier to solve. A balance for A at point M.

$$F_0 x_{A,0} + F_R x_{A,R} = F_{in} x_{A,in}$$

Now, a balance on the reactor

$$F_{in} = F_{out} = F_f (1 + R) \equiv F_0 (1 + R)$$

Therefore

$$\begin{aligned} x_{A,in} &= \frac{F_0 x_{A,0} + F_R x_{A,f}}{F_{in}} \\ &= \frac{F_0 x_{A,0} + F_0 R x_{A,f}}{F_{out}} = \frac{F_0 (x_{A,0} + R x_{A,f})}{F_0 (1 + R)} \end{aligned}$$

where $x_{A,k}$ referred to molar fraction of A in the stream k

Then, the total reactor feed contains a molar fraction $x_{A,in}$, given by

$$x_{A,in} = \frac{x_{A,o} + R x_A}{1 + R} \quad (2.87)$$

The fractional conversion in the stream entering the reactor $X_{A,\text{in}}$ is not zero since this stream is a combination of fresh feed and the recycle stream. Thus the fractional conversion at the reactor inlet is:

$$\begin{aligned} X_{A,\text{in}} &= \frac{x_{Ao} - x_{A,\text{in}}}{x_{Ao}} \\ &= \frac{1}{x_{Ao}} \left(x_{Ao} - \frac{x_{Ao} + R x_A}{1 + R} \right) \\ X_{A,\text{in}} &= \frac{R}{1 + R} X_A \end{aligned} \quad (2.88)$$

Substituting (2.88) in (2.76)

$$V = -F_0 (1 + R) \int_{\frac{R}{1+R} X_A}^{X_A} \frac{dX_A}{r_A} \quad (2.89)$$

In this case, X_A represents the overall conversion which means

$$X_A = \frac{\text{moles of A reacted overall}}{\text{mole of fresh feed}}$$

For the particular case where density changes are negligible, we may write (2.89) in terms of concentrations,

$$\tau = (1 + R) \int_{\frac{C_{A0} + R C_{Af}}{1+R}}^{C_{Af}} \frac{dC_A}{r_A} \quad (2.90)$$

Equation (2.89) is the mole balance for a recycled reactor, which has two characteristic limiting cases:

| Limiting case | Reactor volume |
|------------------------|--|
| $R \rightarrow 0$ | $\frac{V}{F_o} = - \int_0^{X_A} \frac{dX}{r_A(X)}$ |
| $R \rightarrow \infty$ | $\frac{V}{F_o} = - \frac{X_A}{r_A(X_A)}$ |

 information When $R \rightarrow 0$, V corresponds to an ideal PFR without recycling, while $R \rightarrow \infty$, V will be an ideal CSTR's volume.

It could be interesting to know the **per pass conversion of A**, which is the fraction of the total feed of reactant A converted in a single pass through the reactor.

$$X_A = \frac{\text{moles of A reacted in a single pass}}{\text{mole of A feed to the reactor}}$$

In this case, the total molar flow rate of A into the reactor is $F_o + R F_{out}$, and to set the fractional inlet conversion of A, equal to zero for the combined stream that enters the reactor. (Roberts 2009)

On this basis, the design equation becomes

$$\frac{V}{F_o + R F_{out}} = - \int_0^{X_A} \frac{dX}{r_A}$$

where

$$X_A = \frac{(F_o + R F_{out}) - (R + 1) F_{out}}{F_o + R F_{out}} = \frac{F_o - F_{out}}{F_o + R F_{out}}$$

$$X_A = \frac{F_o - F_o (1 - X_A)}{F_o + R F_o (1 - X_A)} = \frac{X_A}{1 + R (1 - X_A)}$$

This equation is difficult to solve because X_A appears on both sides of it. Therefore, the previous method is much simpler. The following example may serve to illustrate this reactor type.

Exercise 2.7 (Autocatalytic reaction). Determine the required reactor volume to treat $0.1 \text{ m}^3/\text{min}$ of a fluid having a $C_{A0} = 10 \text{ mmol/m}^3$ to 90% conversion. Additionally, it is known next experimental data:

| | | | | | | | | |
|--------------------------------|-----|---|----|---|----|----|----|----|
| C_{A0} , mmol/m ³ | 2 | 5 | 6 | 6 | 11 | 14 | 16 | 24 |
| C_A , mmol/m ³ | 0.5 | 3 | 1 | 2 | 6 | 10 | 8 | 4 |
| τ , min | 30 | 1 | 50 | 8 | 4 | 20 | 20 | 4 |

Suppose that the reactor is:

1. a CSTR.
2. a PFR.
3. a recycle reactor with $R = 30$.
4. the recycle reactor with minimum volume.

Solution. In this reaction system, the fluid density is constant, so it is possible to rewrite (2.89) in terms of concentration (which is an advantage for us because the fitting of experimental data was already done).

$$C_{A,in} = \frac{C_{A0} + R C_A}{1 + R}$$

$$\tau = -(1 + R) \int_{C_{A,in}}^{C_A} \frac{dC_A}{r_A}$$

It is necessary add a negative sign because A is the reactant in the reaction. Those equations were implemented in a Python script to solve the problem both graphically and analytically. Figure 2.20 shows the comparison between continuous-flow reactors for an autocatalytic reaction.

Fig. 2.20, for each case, shaded area represents the value of the integral $\int dC_A/r_A$. In summary, the volume for:

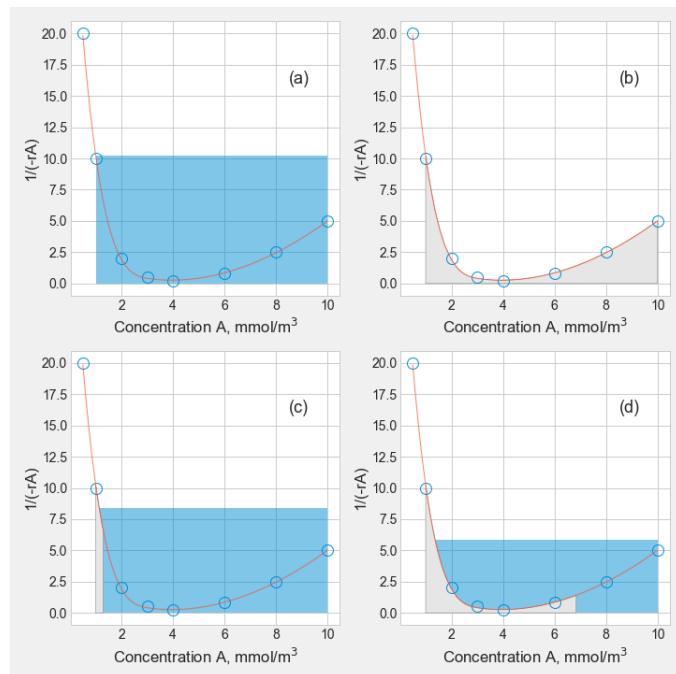


Figure 2.20: Comparison continuous-flow reactors with autocatalytic kinetics: (a) CSTR, (b) PFR, (c) PFR with $R = 1$, (d) PFR at optimal recycle

1. a CSTR is 9.24 m^3 .
2. a PFR is 1.769 m^3 .
3. a PFR with $R = 30$ is 7.49 m^3 .
4. Finally, the optimal R for a PFR is 0.5455. Therefore, its volume is 1.23 m^3 .

In general, PFRs require less volume than CSTRs of equal fractional conversion, but this generalization is not valid in the case of autocatalytic reactions. In the example solved before, although the volume required for a PFR (case (b)) is smaller than a CSTR (case (a)), it is not minimum.

For autocatalytic reactions, back-mixing of reacted material with fresh feed is often beneficial in optimizing the overall reactor design, as it was proved in both cases (c) and (d).

2.4 Analysis of Equilibrium-Limited Adiabatic Reactors

Suppose we are asked to analyze the behavior of a single reaction taking place in an adiabatic reactor. One of the questions we might want to answer is: "What is the maximum conversion that can be achieved?"

Of course, the maximum conversion is obtained when the reaction reaches chemical equilibrium. This situation will be reached for an infinite reactor volume or an infinite weight of the catalyst. Nevertheless, the composition and temperature of the effluent from any reactor will be determined by the reaction's kinetics.

In any case, a reactor's performance is susceptible to the temperature of the inlet stream, which is especially true for PFRs, and for reactors that operate adiabatically. Thus, it is vital to consider the type of reaction we are dealing with: exothermic, endothermic, irreversible, or reversible.

Temperature, composition, and reaction rate are uniquely related to any single homogeneous reaction, and this way is represented graphically in one of three ways, as shown in Figure 2.21.

2.4.1 Adiabatic reactors

The simplest and cheapest mode of reactor design and operation is the adiabatic model. If heat is added to or withdrawn from the reactor as the reaction proceeds, the heat-exchange surface must be designed into the reactor, increasing the capital cost substantially. However, an adiabatic reaction is practicable when the resulting temperatures stay in a workable range. That is, when they did not drop so that the rate becomes too small or rise until the rate becomes uncontrollable. The following conditions are favorable to adiabatic operation:

1. When the heat of reaction is small.
2. When it is possible to adjust the initial temperature to not take the system out of the workable range.
3. When the heat capacity of the equipment or the solvent or any inert materials that may be present is sufficient to moderate the temperature effect.
4. When an inert material is present or introduced without harm, it can moderate temperature changes by vaporization or condensation.

The construction of an adiabatic reactor is relatively simple, and the capital cost is relatively low, so its design should always be considered. A more complex design should be used only when there

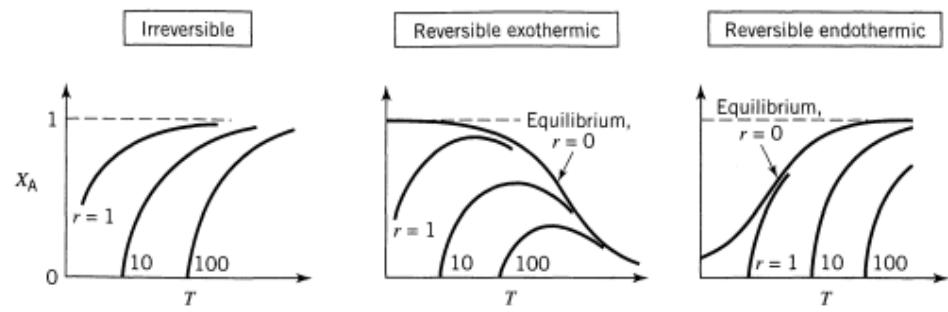


Figure 2.21: General shape of the temperature-conversion plot for different reaction types [@levenspiel2004]

are compelling reasons.

For the design of nonisothermal operation, these necessary data are needed: (Walas 1989)

1. The specific reaction rate as a function of temperature.
2. The system's thermal data, such as the heat capacities and sensible and latent enthalpies of all participants and inert materials present, as functions of temperature.
3. The heat of reaction at some base or reference temperature.
4. Heat fluxes or heat-transfer coefficients.

For an adiabatic flow reactor operating at a steady-state with no shaft work, when only one reaction takes place, eq. (2.5) simplifies to

$$\left(\sum_{i=1}^c F_{i0} \bar{C}_{P_i} \right) (T_0 - T) - F_{A0} X_A \Delta H_{R,A}(T) = 0 \quad (2.91)$$

Rearranging,

$$T = T_0 - \left(\frac{F_{A0} \Delta H_{R,A}(T)}{\sum_{i=1}^c F_{i0} \bar{C}_{P_i}} \right) X_A \quad (2.92)$$

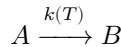
Equation (2.92) shows that the temperature, T , is proportional to the fractional conversion, X_A , for an adiabatic flow reactor at a steady state. If the fractional conversion is known, the corresponding temperature can be calculated.

Let T_{ad} be the temperature that corresponds to complete conversion (i.e., $X_A = 1$)

$$\Delta T_{ad} = \left(\frac{F_{A0} (-\Delta H_R(T_{ad}))}{\sum_{i=1}^c F_{i0} \bar{C}_{p,i} (T_0 \rightarrow T_{ad})} \right) \quad (2.93)$$

where ΔT_{ad} is called ***adiabatic temperature change***.

Exercise 2.8 (Comparing PFRs performance). Plot a C_A and T profiles vs τ for the reaction



with $r = k(T) C_A$

The reaction is taken place in an adiabatic PFR for $E = 30$ kcal/mol, $k_0 = 2.6 \times 10^{20}$ min $^{-1}$, $\Delta H_r = -20$ kcal/mol, $\rho C_P = 1000$ cal/L-K, $T_0 = 300$ K y $C_{A0} = 2$ mol/L.

Solution. For any continuous flow reactor working under adiabatic mode, the energy balance is

calculated by

$$T = T_0 + \left(\frac{F_{A0} (-\Delta H_R(T))}{\sum_{i=1}^c F_{i0} \bar{C}_{p,i}} \right) X_A$$

This equation could rewrite it, taking advantage of the reacting fluid is constant-density,

$$F_i = \rho v_i$$

where v represents the volumetric flow.

Substituting this expression into the energy balance, and rearranging it

$$\begin{aligned} T &= T_0 + \left(\frac{F_{A0} (-\Delta H_R(T))}{v \rho C_P} \right) X_A \\ &= T_0 + \left(\frac{-\Delta H_R(T)}{\rho C_P} \right) C_{A0} X_A \\ T &= T_0 + \left(\frac{-\Delta H_R(T)}{\rho C_P} \right) (C_{A0} - C_A) \end{aligned}$$

The design equation for a PFR,

$$d\tau = \frac{dC_A}{r_A} = -\frac{dC_A}{k(T)C_A} \quad (2.94)$$

Summarizing, the set of equations to be solved is:

$$\begin{aligned} d\tau &= -\frac{dC_A}{k(T)C_A} \\ T &= T_0 + \left(\frac{-\Delta H_R(T)}{\rho C_P} \right) (C_{A0} - C_A) \\ k(T) &= k_0 \exp(-E/R/T) \end{aligned}$$

This system of equations was implemented and solved with Python, and the graphical solution for the concentration and temperature profiles are shown in Fig. 2.22.

It is interesting to compare the concentration profile for the adiabatic PFR with the solution for the reactor maintained isothermally at 300 K. These solutions are plotted in Figure 2.23.

From Figure 2.23, it is worthy to point out when the PFR operates in adiabatic mode, a shorter τ to attain complete conversion is required than under isothermal operation. Otherwise, the isothermal reactor curve exhibiting a standard exponential decay, but the adiabatic reactor shows an acceleration in rate as the reaction proceeds because the temperature increases.

The same problem was solved for an adiabatic CSTR, and both profiles obtained were compared with PFR profiles in Figure 2.24.

Figure 2.24 shows that the temperature profile and concentration profile have a similar shape. The difference is that temperature increases while concentration decreases for this exothermic reaction.

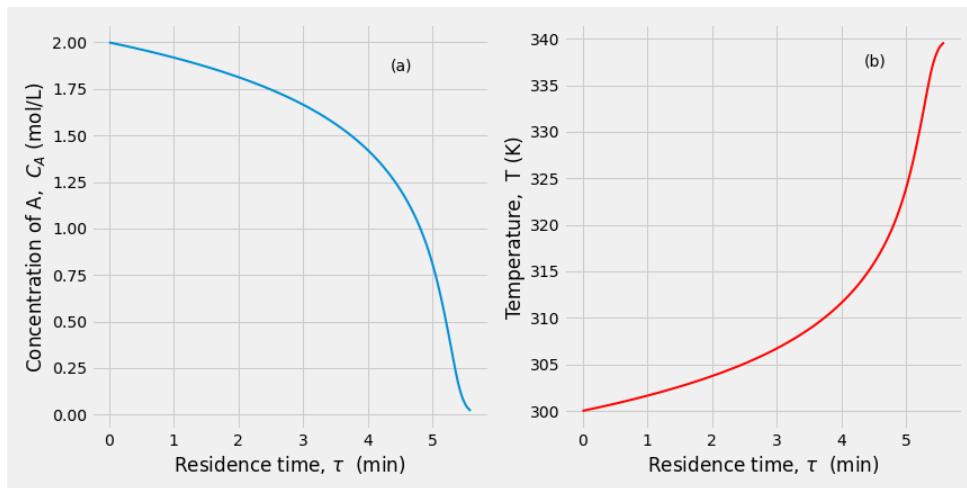


Figure 2.22: Profiles for an adiabatic PFR: (a) Concentration, (b) Temperature

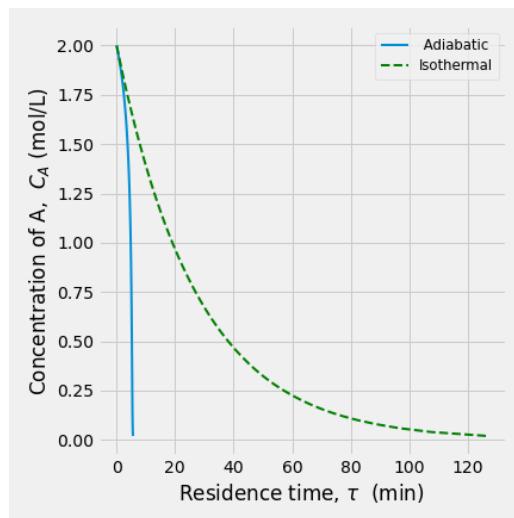


Figure 2.23: Comparison of concentration profile for a PFR

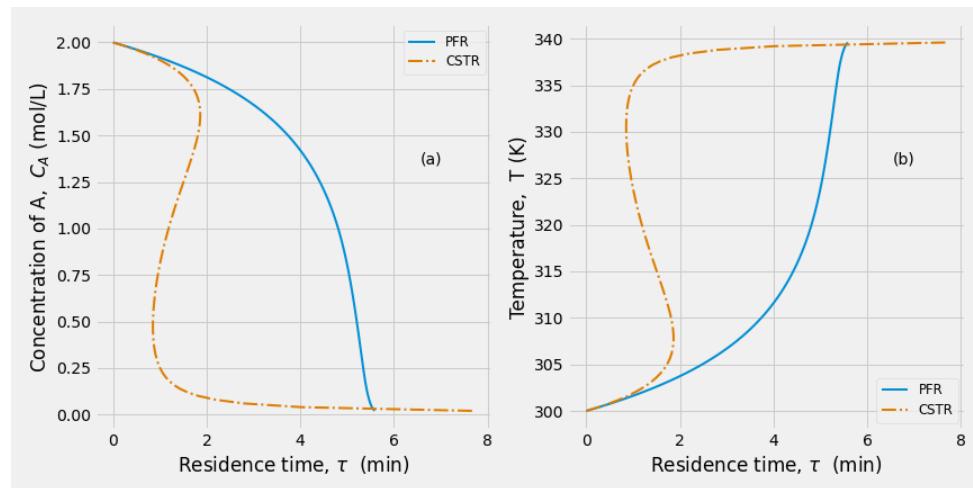


Figure 2.24: Comparison of concentration and temperature profile for an adiabatic CSTR and adiabatic PFR: (a) Concentration profile, (b) Temperature profile

Otherwise, from the comparison between PFR and CSTR, it is possible to note that, in this example, the CSTR requires a shorter residence time for a given conversion than a PFR. Finally, CSTR profiles' shapes suggest multiple steady states approximately at $\tau = 1.5$ min.

To identify those operating points, we will rewrite the material and energy balance for our adiabatic CSTR.

The material balance is

$$\begin{aligned} v C_{A0} - v C_A + r_A V &= 0 \\ C_{A0} - C_A &= -r_A \tau \\ C_{A0} - C_A &= k(T) C_A \tau \\ C_A &= C_{A0} \frac{k(T)}{1 + \tau k(T)} \end{aligned} \quad (2.95)$$

The energy balance is

$$\begin{aligned} v \rho C_P (T_o - T) - k(T) C_A \Delta H_r V &= 0 \\ \frac{\rho C_P}{\tau} (T_o - T) - k(T) C_A \Delta H_r &= 0 \end{aligned} \quad (2.96)$$

The first term of Eq. (2.95) represents the removal of heat, and the second one is associated with generating heat. When both terms have the same value, then the CSTR will be operating at steady-state conditions.

Now, to identify possible steady-state operating points. First, we set a residence time, in our case 1.5 min. Second, we set the evaluating temperature range, which is 300 - 340 K. Finally, Eq. (2.95) is substituted into Eq. (2.96) and the resulting equation is evaluated for each temperature from the temperature range.

Figure 2.25 shows the energy balance for our CSTR at $\tau = 1.5$ min, following the procedure described before, and it is possible to identify three operating points. These points are approximately 302.5 K, 317.5 K, and 337.5 K, respectively.

2.4.2 Selecting the best reactor for adiabatic operation

In any case, it is important to know the optimum temperature progression because it will assure the minimum V/F_{A0} for a given conversion of reactant. This optimum may be isothermal, or it may be a changing temperature: in time for a batch reactor, along the length of the PFR, or from stage to stage for a series of mixed flow reactors.

In order to select the best adiabatic continuous-flow reactor for carrying out a reaction, it is suitable to analyze the $1/r$ plot because either for isothermal or nonisothermal reactors, τ is still the area under curves of plots $1/r$ versus $C_{A0} - C_A$.

In general, the size of reactor required for a given duty and a given temperature progression is found as follows:

1. Draw the reaction path on the X_A vs. T plot, which is the operating line for the operation.

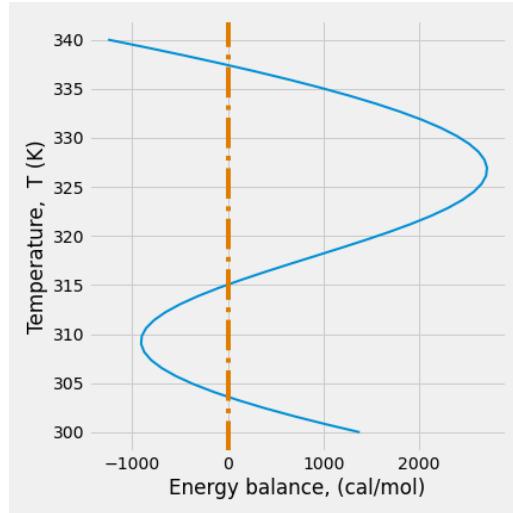


Figure 2.25: Locations of steady-state operating points for an adiabatic CSTR at $\tau = 1.5$ min

2. Find the rates at various X_A along this path.
3. Plot the $1/r_A$ vs. X_A curve for this path.
4. Find the area under this curve, which gives V/F_{A0}

This procedure is general, applicable for any kinetics, temperature progression, reactor type, or reactor series. Thus, once the operating line is known, the reactor size can be found. For exothermic reactions, this procedure is illustrated in Figure 2.26 for three paths.

The optimum temperature progression in any reactor is as follows: At any composition, it will always be at the temperature where the rate is a maximum. The locus of the maximum rates is found by examining the $r(T, C)$ curves of Figure W.

To illustrate this procedure, let us work with the previous example. In figure 2.27 values of $1/r_A$ are plotted versus $C_{A0} - C_A$

Figure 2.27 shows that r_A increases then decreases so that $1/r_A$ has a global minimum.

2.4.3 Optimization of endothermic equilibrium reactions

The temperature dependence of the chemical equilibrium constant is given by the van't Hoff equation:

$$\left(\frac{\partial (\ln K)}{\partial T} \right)_P = \frac{\Delta H_R}{R T^2} \quad (2.97)$$

For endothermic reaction, the value of $\Delta H_R > 0$, therefore increasing the temperature, leads to an increase in the K value.

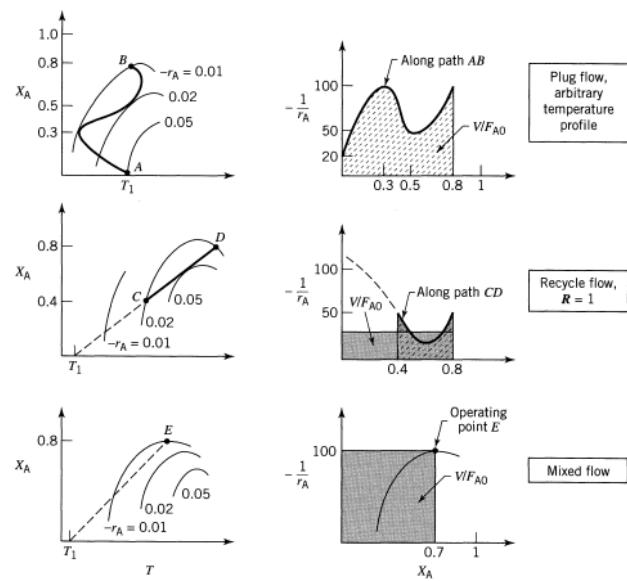


Figure 2.26: Finding the reactor size for different types of flow [@levenspiel2004]

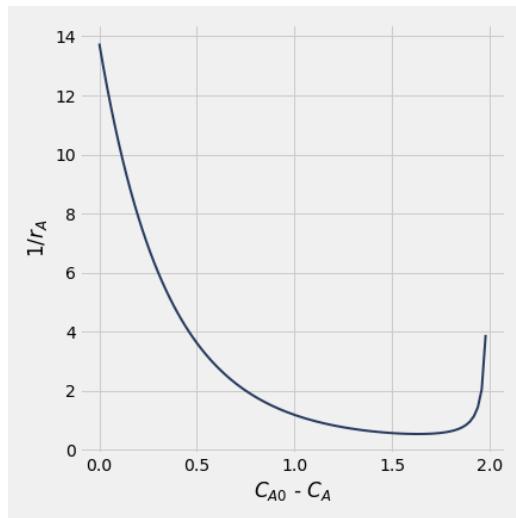


Figure 2.27: Plot of $1/r_A$ vs $C_{A0} - C_A$

As a high temperature also increases the reaction rate, high temperatures are desirable to maximize rate and conversion in endothermic reactions, and higher temperatures will lead to smaller reactors. (Figure 2.28)

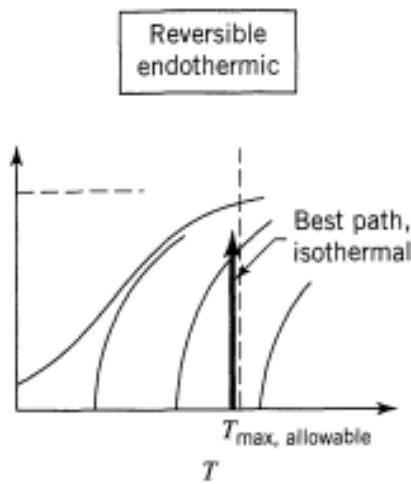


Figure 2.28: Operating line for minimum reactor size for an endothermic reversible reaction

2.4.4 Optimization of exothermic equilibrium reactions

When an exothermic reaction occurs in an adiabatic reactor, the effect of temperature on its performance is crucial.

In an exothermic reaction, the $\Delta H_R < 0$; therefore, increasing the reaction temperature decreases the equilibrium chemical constant (K) value, with a concomitant decrease in the equilibrium yield. This situation is disadvantageous on the kinetic side because a high reaction rate occurs at high temperatures.

Figure 2.29 shows a typical equilibrium composition line for an exothermic reaction. When the reaction temperature is low, the fractional conversion is close to unity, but while temperature increases, the conversion decreases.

Fig. 2.29 also shows two lines that represent operation modes for the reactor: adiabatic and isothermal modes. For adiabatic mode, the line governs the relationship between the temperature and the fractional conversion, assuming ΔH_R and C_P are constant, as presented in equations Eq. (2.92) and Eq. (2.130).

In this operation mode, the temperature and the fractional conversion will increase along this line until the equilibrium curve is encountered at T_e and X_e . At this point, the rate is zero, so any additional change, neither composition nor temperature, will not occur.

If the same reactor operates isothermally, the change of composition will follow the vertical line, and the final fractional conversion will be determined, again, for the chemical equilibrium curve.

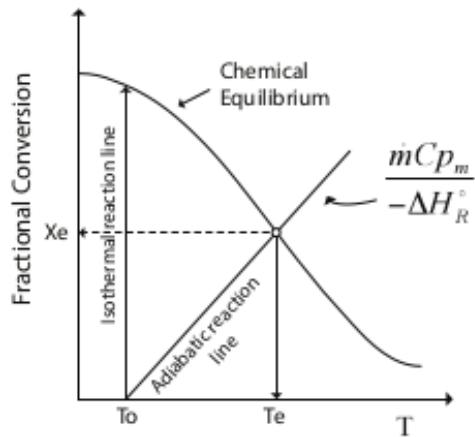


Figure 2.29: Typical graphic for an equilibrium composition vs. reaction temperature for an exothermic reaction

Although the final conversion (X) will be higher for an isothermal mode than for an adiabatic mode at the same initial temperature (T_0), the isothermal operation may not be practical because of the required reactor volume.

For this reason, it is necessary to determine the optimal temperature progression along the reactor to maximize the conversion for the minimum possible reactor volume, which is shown as a dashed line in figure 2.30.

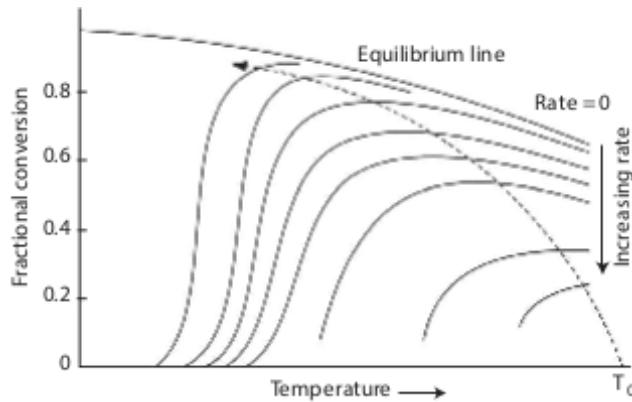


Figure 2.30: Typical lines of constant reaction rate corresponding to set of values of temperature and conversion for an exothermic reaction

In figure 2.30, each solid line represents a locus of the set of temperature and conversion that gives a specified value of rate. At a constant reaction rate, the conversion initially rises rapidly with increasing temperature and then begins to fall due to a faster reverse reaction's rising rate. The

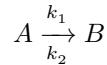
top line (equilibrium line) corresponds to a reaction rate of zero.

The dashed line gives a trajectory of maximum reaction rates as a function of the conversion called ‘‘the locus of maximum reaction rates’’. This locus is independent of the type of reactor used, and for a given conversion, the reactor volume is minimum if the temperature of operation is selected to correspond to the maximum reaction rate.

The temperature at which the conversion rate is a maximum will be somewhat lower than T_e and is determined by the condition.

$$\frac{\partial r_j}{\partial T} = 0 \quad (2.98)$$

Exercise 2.9 (The locus of maximum reaction rates). Derive an equation for the locus of maximum reaction rates for a simple reversible-exothermic reaction



Assuming $C_{B0} = 0$, $r_1 = k_1 C_A$, $r_2 = k_2 C_B$, and

$$\begin{aligned} k_1 &= k_{10} \exp(-Ea_1/RT) \\ k_2 &= k_{20} \exp(-Ea_2/RT) \end{aligned}$$

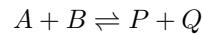
with $Ea_2 > Ea_1$

Solution. The corresponding maximum reaction rate can be derived as a function of temperature, which is:

$$r_{\text{opt}}(T) = \frac{C_{A0} k_{10} k_{20} (-Ea_1 + Ea_2)}{\frac{Ea_2}{Ea_1 k_{10} e^{RT}} + \frac{Ea_1}{Ea_2 k_{20} e^{RT}}}$$

More details about the solution of this problem is available on this link [Python](#)

Exercise 2.10 (Calculation of the optimal temperature). Derive an equation for the optimal temperature for a simple reversible-exothermic reaction



$$\begin{aligned} r_1 &= k_1 C_A C_B, & k_1 &= k_{10} \exp(-E_1/RT) && \text{forward reaction} \\ r_2 &= k_2 C_P C_Q, & k_2 &= k_{20} \exp(-E_2/RT) && \text{reverse reaction} \end{aligned}$$

with $E_2 > E_1$

Solution. Following the same procedure shown in the last illustration, the optimal temperature is

$$T_{\text{opt}} = \frac{E_1 - E_2}{\ln \left(\frac{k_{10} E_1 C_A C_B}{k_{20} E_2 C_P C_Q} \right) R} \quad (2.99)$$

The system will reach the chemical equilibrium at $r = 0$ and

$$K = \frac{C_P C_Q}{C_A C_B} = \frac{k_{10} \exp(-E_1/RT)}{k_{20} \exp(-E_2/RT)} \quad (2.100)$$

Substituting Eq. (2.100) into (2.99)

$$\frac{T_{\text{opt}}}{T_e} = \frac{E_1 - E_2}{-E_2 + E_1 - \ln \left(\frac{E_2}{E_1} \right) R T_e} \quad (2.101)$$

When the difference between the absolute temperature T_e and T_{opt} is relatively small, (2.101) may be approximated by

$$\frac{T_e - T_{\text{opt}}}{T_e} \approx \frac{R T_e}{-\Delta H_R} \ln \left(\frac{E_2}{E_1} \right) \quad (2.102)$$

More details about the solution of this problem is available on this link [Python](#)

In practice, it may be challenging to achieve an optimal temperature profile within a reactor. Therefore other designs are often used.

1. For relatively fast reactions that are equilibrium limited, the adiabatic reactor is commonly used in the industry.
2. Where very high conversions are desired, it is common to use multiple reactors in series, with cooling between each reactor.

Figure 2.31 shows a typical conversion path for multiple adiabatic reactors in series. Each diagonal line represents one reactor, which operates adiabatically until the fixed conversion is reached. For example, X_1 then the process stream is cooled by passing it through a heat exchanger until a predetermined temperature (in this stage, there is no conversion). Afterward, the process stream enters the next reactor (Bed 2) and so on.

In designing reactor systems with interstage cooling, one crucial question that must be addressed is how the reactor stages should be sized. Should all the temperature differences between inlet and outlet be equal? Or is there some optimum distribution of ΔT 's? The latter would imply an optimum in the number of reactor stages and (in the case of catalytic reactions) an optimum distribution of mass of catalyst between the reactor stages.

In the end, the exact number of the reactor and the degree of cooling between them depends on the reaction involved and operating and capital costs. However, it is clear that the system is very complex, and the optimum to be arrived at would depend on the type of objective function(s) that are adopted.

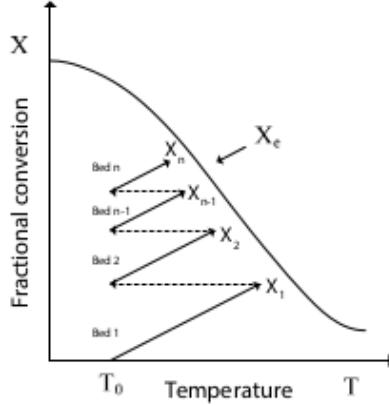


Figure 2.31: Typical conversion path for multiple adiabatic reactors in series for exothermic reactions

When dealing with a series of PFR, the application of Eq. (2.101) is quite tricky. However, the optimum temperature profile can be found based on the assumption that the criterion Eq. (2.98) and hence also equation Eq. (2.101) must be valid for any cross-section of the reactor.

The volume of a PFR is proportional to the integral

$$\int_0^{X_{A,L}} \frac{dX_A}{r_A} \quad (2.103)$$

From the optimum temperature policy, this integral should be a minimum which leads to the condition

$$\int_0^{X_{A,L}} \frac{\partial r_A}{\partial T} \frac{dX_A}{r_A^2} = 0 \quad (2.104)$$

In order to the highest possible final conversion for a given number of sections based on a given entrance temperature of the first section, the conditions must be met: For each section, N equation X becomes to

$$\int_{X_{A,0}}^{X_{A,L}} \frac{\partial r_A}{\partial T} \frac{dX_{A,N}}{r_A^2} = 0 \quad (2.105)$$

where $X_{A,N}$ and T are related by

$$T_N = T_{N,0} = \Delta T_{\text{ad}} (X_{A,N} - X_{A,0}), \quad \Delta T_{\text{ad}} = \frac{-\Delta H_R C_{A0}}{\rho C_P} \quad (2.106)$$

Between two sections ($N - 1$) and N

$$R_{A(N-1),L} = R_{AN,0} \quad (2.107)$$

$$X_{A(N-1),L} = X_{AN,0} \quad (2.108)$$

The procedure will be illustrated using a temperature conversion diagram of a given exothermic equilibrium reaction with a given feed composition.

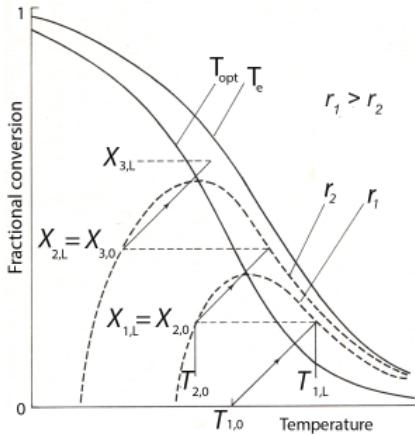


Figure 2.32: Sketch of optimal temperature progression

Figure 2.32 contains a curve for T_e (chemical equilibrium) and T_{opt} (optimum temperature profile) at which the conversion rate is at a maximum, both for the corresponding fractional conversion. Two lines of constant conversion rate have also been drawn.

The feed enters the first stage at temperature $T_{1,0}$ ($X_{1,0} = 0$) and the reaction is heated up proportionally to X following equation (2.106). When the $T_1 - X_1$ line intersects with the curve for T_{opt} , the sign of $\partial R/\partial T$ changes from positive to negative, which occurs at $T_{1,L}, X_{1,L}$ located on curve $R = R_1$ so reaction mixture must be cooled at temperature $T_{2,0}$ and then the mixture entering the second stage has the same conversion rate R_1 , and so on until the desired number of stages has been passed.

In the case that the process has a maximum of permissible temperature T^* so that only a corresponding degree of conversion $X^* < X_{A1,L}$ can be reached in stage number 1. This section then no longer has the minimum volume since Eq. (2.105) is no longer applicable.

Therefore, Eq. (2.105) must be replaced by

$$\Delta T_{\text{ad}} \int_0^{X_{A1,L}^*} \frac{\partial r_A}{\partial T} \frac{dX_{A1}}{r_A^2} + \frac{1}{r_A(X^*)} = \frac{1}{r_{A2,0}} \quad (2.109)$$

to find the proper entrance temperature to the second section.

Exercise 2.11 (Reversible exothermic reaction). Consider next chemical reaction is taking place in a CSTR that has two feed streams, F_{A0} and F_{B0} (m^3/s) with concentrations C_{A0} and C_{B0} (kmol/m^3).



Assuming a first-order kinetic, determine the operating temperature that maximize the fractional conversion of A in a CSTR with volume equals to (a) 50 m^3 , (b) 100 m^3 and (c) 200 m^3 .

| Variable | Description |
|---------------------------------|--|
| $F_{A0} = 4.377 \times 10^{-3}$ | Feed flowrate of A, m^3/s |
| $C_{A0} = 8.01$ | Feed concentration of A, kmol/m^3 |
| $F_{B0} = 4.377 \times 10^{-3}$ | Feed flowrate of B, m^3/s |
| $C_{B0} = 8.01$ | Feed concentration of B, kmol/m^3 |
| $k_f = 4.239 \times 10^6$ | Forward preexponential factor, $\text{m}^3/\text{s}/\text{kmol}$ |
| $k_r = 3.631 \times 10^{16}$ | Reverse preexponential factor, $\text{m}^3/\text{s}/\text{kmol}$ |
| $E_f = 69.71 \times 10^6$ | Forward activation energy, J/kmol |
| $E_r = 139.4 \times 10^6$ | Reverse activation energy, J/kmol |

Solution. The net reaction rate is the difference between the forward and reverse reactions.

$$r = k_f C_A C_B - k_r C_C C_D$$

The component balances can be written

$$\begin{aligned} F_{A0} C_{A0} &= F C_A + V_R r \\ F_{B0} C_{B0} &= F C_B + V_R r \\ 0 &= F C_C - V_R r \\ 0 &= F C_D - V_R r \end{aligned}$$

And assuming constant density, the volumetric flow rate of the effluent will be equal to the volumetric of the two feeds

$$F = F_{A0} + F_{B0}$$

This problem was solved in Python, and the results are presented in Figure 2.33.

The reaction's activation energy is greater than the activation energy of the forward reaction from the data given. For this reason, figure 2.33 shows that at low temperatures, the conversion is scanty because of detained specific reaction rates. At high temperatures, the conversion is also low, this time because of a low equilibrium constant.

For each volume reactor studied, at the beginning of the curve, the fractional conversion of A is reaction-rate limited and equilibrium limited at high temperature.

In the following table, the maximum conversion of A and its correspondence reaction temperature for each volume reactor is presented.

| Reactor volume (m^3) | Conversion X_A | Temperature (K) |
|---------------------------------|------------------|-----------------|
| 50 | 0.5242 | 352.52 |
| 100 | 0.5725 | 347.47 |
| 200 | 0.6789 | 341.41 |

Now, let us add the same size CSTR to the previous problem and determine the optimum operating temperature and final fractional conversion.

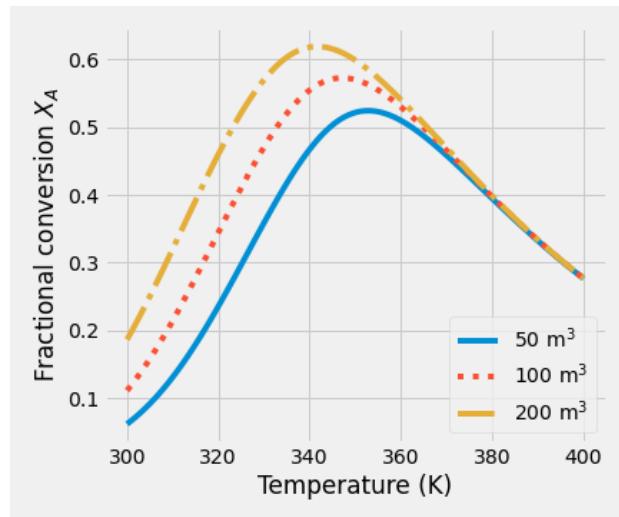


Figure 2.33: Conversion vs reaction temperature for a reversible reaction in a CSTR

Exercise 2.12 (Reversible exothermic reaction). For the elementary solid-catalyzed liquid-phase reaction



1. Make a plot of equilibrium conversion as a function of temperature.
2. Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K.
3. What conversion could be achieved if two interstage coolers is available that had the capacity to cool the exit stream to 350 K?. Assume in each reactor, 95% of equilibrium conversion is achieved.
4. Plot the optimal operating temperature profile.
5. Determine the heat duty of each exchanger for a molar feed rate of A of 40 mol/s.
6. Calculate the volume of each reactor to get those conversion.
7. For a 1 m³ RFP, determine the inlet temperature which maximize the fractional conversion achieved.

Solution. This problem was solved in Python

First, the equilibrium conversion temperature and the adiabatic heat balance line are plotted in Figure 2.34.

The figure 2.34 was produced by solving the next system of equations:

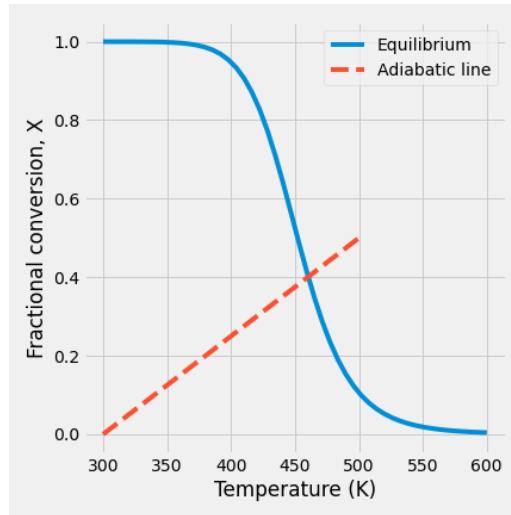


Figure 2.34: Equilibrium conversion vs. reaction temperature for a reversible reaction

$$K = \frac{k_{10}}{k_{20}} \exp \frac{(E_2 - E_1)}{RT}$$

$$X_e = \frac{K}{1 + K}$$

If the reactor is operated adiabatically, with $T_{in} = 300$ K, the adiabatic line (dashed green line on Fig. 2.34) is obtained from:

$$T = T_{in} + (X_A - X_{A,in}) \frac{(-\Delta H_R^\circ)}{C_{P_A}}$$

Then, assuming 95% of equilibrium conversion at each stage, three reactors with interstage cooling are modeled, and the results are presented in Figure 2.35.

In Figure 2.35, the actual path is represented by a dashed line while the locus of the optimal temperature is the red line. The latter was calculated from Eq. (2.101).

In the following table, the summary of results is presented.

| Reactor | Final conversion X_A | Final Temperature (K) | Cooling load (kW) | Volume Reactor (L) |
|---------|---------------------------|--------------------------|----------------------|-----------------------|
| First | 0.3809 | 452.38 | 189 | 1215.38 |
| Second | 0.5826 | 430.66 | 161 | 624.87 |
| Third | 0.7388 | 412.47 | 125 | 804.70 |

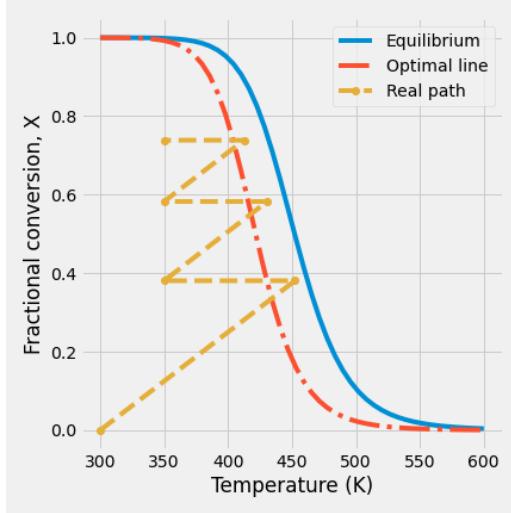


Figure 2.35: Equilibrium conversion vs. reaction temperature for a reversible reaction

The cooling load represents the heat that a heat exchanger must be retired to cool the outlet stream of the reactor (bed) to 350 K, as required by the problem. The heat requirement by each cooling interstage was calculated from:

$$Q = \sum_{i=1}^2 F_{i,\text{in}} C_{P_i} (T - 350)$$

The volume reactor is the volume required by each PFR (bed) to achieve the 95% of the equilibrium conversion set by the problem. And it was calculated from the mass balance in each reactor by:

$$\begin{aligned} r_A &= k_f C_{A0} (1 - X_A) - k_r C_{A0} X_A \\ \frac{dV}{dX} &= \frac{F_{A0}}{r_A} \end{aligned}$$

In Figure 2.36, the fractional conversion profile as a function of volume reactor for each bed is presented.

2.5 The Batch Reactor (BR)

A batch reactor (BR) is a spatially uniform closed system whose concentration parameters are established at time zero. To ensure that the reactor content is well mixed, they are mechanically agitated, and in most cases, it is necessary to implement a heat-transfer system to ensure an isothermal operation mode. Therefore, it is assumed that in an ideal batch reactor.

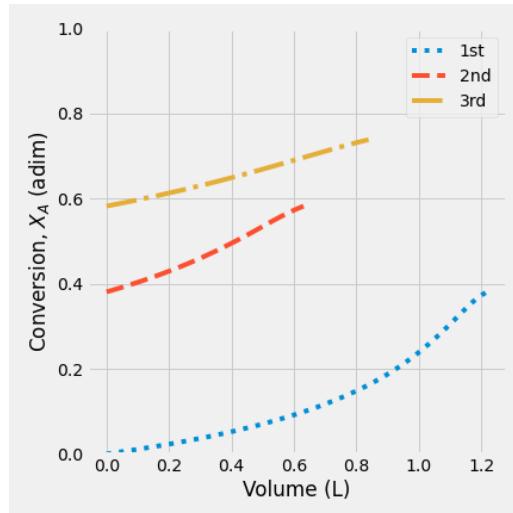


Figure 2.36: Conversion profile as function of volume reactor

 information At any time, the batch is uniform in composition and temperature at every point in the reactor.

Batch reactors are generally used for liquid-phase reactions. When a solid catalyst has to be kept in suspension or two liquid phases, an agitator is required. Since the batch reactor (BR) has no flow streams, and as a consequence that the reaction mixture is homogeneous, that is, all contents are in a single phase. Perfect mixing is also assumed, which means that there are no spatial variations in temperature and composition. The composition changes with time, however. Temperature sequencing may be favorable for the selectivity of achieving complete conversion in a safe way. (Froment, Bischoff, and De Wilde 2011)

If all reactants are charged to the reactor, its concentration initially is large, which means that the reaction rate and the heat transfer load are high at the beginning of the batch cycle unless the temperature keeps low for external heat-transfer equipment.

For better control of temperature, this type of operation may not be advisable, and the reactant(s) may have to be added progressively to the vessel's contents. The reactor is then said to operate in semi-batch mode. (Froment, Bischoff, and De Wilde 2011)

Characteristics:

- These reactors usually have a cylindrical-tank shape.
- Reactor is charged from the top.
- Nothing else is put or taken out until the reaction is done.
- Tank is efficiently heated or cooled by a heat-exchanger jacket.
- Each batch is a closed system.
- The total mass of each batch is fixed.
- The volume or density of each batch may vary (as the reaction proceeds).

- The energy of each batch may vary (as the reaction proceeds).
- The reaction time t for all elements of fluid is the same.
- The operation of the reactor is inherently unsteady-state.
- These reactors are very flexible. Thus, a single reactor may be used to produce many different products.

Uses:

- Small scale production.
- Intermediate or one-shot production.
- Testing new processes that have not been fully developed.
- Manufacture of expensive products.

2.5.1 The isothermal batch reactor

In spite of the perfect mixing assumption, for a single reaction the mole balance (Eq. (2.1)) for the key component j for the entire reactor volume reduces to:

$$\frac{dN_j}{dt} = V r_j (C_j) \quad (2.110)$$

Where t is the residence time in the reactor, which is the same as "clock" time, N_j describes the moles of the component j , V is the portion of the overall reactor volume in which the reaction takes place.

Equation (2.110) is referred to as the **design equation** for an ideal batch reactor, and it is valid no matter how many homogeneous reactions are taking place. Moreover, in despite of any operation mode, it allows us to answer two questions related to the design of a BR:

1. What is the reaction time necessary to achieve a conversion X for a reactant?

$$t = \int_0^t dt = \int_{N_{jO}}^{N_j} \frac{1}{V} \frac{dN_j}{r_j}$$

2. What is the reaction volume (size of reactor) required for a specific production flow rate?

Constant-Volume Batch Reactor

If the reactor volume is constant, then the mass density of the system, ρ (mass/volume), must also be constant since the mass of material in a batch reactor does not change with time. In this case, it is possible to rewrite the molar balance (Eq. (2.110)) directly in terms of concentrations.

$$r_j (C_j) = \frac{1}{V} \frac{dN_j}{dt} = \frac{d}{dt} \left(\frac{N_j}{V} \right) = \frac{dC_j}{dt} \quad (2.111)$$

 information **Remember:** In Eq. (2.111), the reaction rate must be expressed in terms of concentration of specie j .

For batch reactors, it is important to know how much time is required for reactants to achieve a certain conversion X . For this reason, the molar balance is in terms of conversion. Let us assume we are dealing with a reactant specie, A .

$$N_A = N_{A0} (1 - X_A) \quad (2.112)$$

differentiating (2.112) with respect to time

$$r_A (X_A) = -\frac{N_{A0}}{V} \frac{dX_A}{dt} = -C_{A0} \frac{dX_A}{dt} \quad (2.113)$$

Equation (2.113) is the basic mole balance for the constant-volume batch reactor. And this solution is:

$$t = C_{A0} \int_0^{X_A} \frac{dX_A}{r_A} = - \int_{C_{A0}}^{C_A} \frac{dC_A}{r_A} \quad (2.114)$$

 information The assumption of constant volume is valid for the most industrial batch reactor. The mass density is approximately constant for a large majority of liquids, even if the temperature changes moderately as the reaction proceeds. Moreover, if a vessel is filled with gas, the gas volume will be constant because the vessel's dimensions are fixed and do not vary with time. (Roberts 2009)

Variable-Volume Batch Reactor

In a variable-volume batch reactor, the volume of the reacting mixture changes over time for two reasons:

1. external means (e.g., filling a reaction vessel or adding a second reactant), which is often termed "semi-batch" operation, and
2. changes in densities of reactants or products (e.g., molar expansion of gases), which is not commonly used in industry because of the small mass capacity. However, at the laboratory level, gas-phase reactors have been utilized.

If V change over time, Eq. (2.110) in terms of concentrations would be:

$$r_j = \frac{1}{V} \frac{dN_j}{dt} = \frac{1}{V} \frac{dC_j V}{dt} = \frac{dC_j}{dt} + \frac{C_j}{V} \frac{dV}{dt}$$

which is more complex than Eq. (2.111).

However, for a critical reactant, an alternating way is to rewrite Eq. (2.113) in terms of fractional conversion because a change in the volume yields a change in concentrations.

Usually, a batch reactor operates isothermally, and the pressure drop is neglected thus

$$V = V_0 (1 + \varepsilon_A X) \quad (2.115)$$

From this relationship, the design equation for a batch reactor (Eq. (2.110)) is written as

$$r_A(X_A) = -\frac{1}{V_0(1 + \varepsilon_A X_A)} \frac{dN_A}{dt} \quad (2.116)$$

and their solutions are:

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A) V_0 (1 + \varepsilon_A X_A)} = C_{j0} \int_0^{X_A} \frac{dX_A}{(-r_A) (1 + \varepsilon_A X_A)} \quad (2.117)$$

All these equations apply to both isothermal and nonisothermal operations, and they can be represented graphically, as shown schematically in Figure 2.37, to know the reaction time.

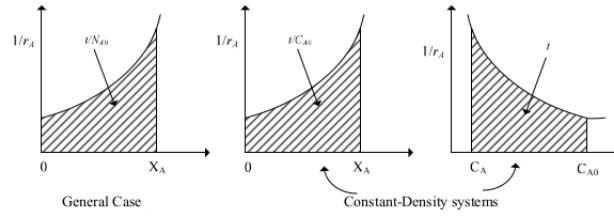


Figure 2.37: Graphical representation of the performance equations for batch reactors, isothermal or nonisothermal.

2.5.2 The nonisothermal batch reactor

It is not always possible, or even desirable, to carry out a reaction under isothermal conditions in practice. In this situation, both the energy and mass balances must be solved simultaneously.

It is known that a batch reactor is a closed system. Otherwise, in most cases, the work done by the stirrer is neglected unless the mixture is highly viscous and the stirring operation draws significant power. Under this scenario, Eq. (2.3) becomes

$$\frac{dU}{dt} = Q - W_s \quad (2.118)$$

By convenience, let us rewrite Eq. (2.118) in terms of enthalpy,

$$\frac{dH}{dt} - P \frac{dv}{dt} - v \frac{dP}{dt} = Q - P \frac{dv}{dt}$$

Thus

$$\frac{dH}{dt} - v \frac{dP}{dt} = Q \quad (2.119)$$

Doing some math, over a multicomponent system of \mathcal{C} components, Eq. (2.119) becomes to

$$\sum_{i=1}^{\mathcal{C}} n_i \frac{dH_i}{dt} + \sum_{i=1}^{\mathcal{C}} H_i \frac{dn_i}{dt} - v \frac{dP}{dt} = Q$$

Now, including some thermodynamic relationships over a chemically-reactive system

$$\sum_{i=1}^{\mathcal{C}} n_i C_{P_i} \frac{dT}{dt} + \sum_{i=1}^{\mathcal{C}} n_i \left(v_i - T \left(\frac{\partial v_i}{\partial T} \right)_P \right) \frac{dP}{dt} + \sum_{i=1}^{\mathcal{C}} H_i \frac{dn_i}{dt} - v \frac{dP}{dt} = Q$$

Thus,

$$\sum_{i=1}^{\mathcal{C}} n_i C_{P_i} \frac{dT}{dt} - T \sum_{i=1}^{\mathcal{C}} n_i \beta_i v_i \frac{dP}{dt} + \sum_{i=1}^{\mathcal{C}} H_i \frac{dn_i}{dt} = Q \quad (2.120)$$

where β_i is volume expansivity of specie i

If "R" reactions are taking place into a batch reactor,

$$\frac{dn_i}{dt} = V \sum_{j=1}^R \nu_{j,i} r_j$$

so that

$$\sum_{i=1}^{\mathcal{C}} H_i \frac{dn_i}{dt} = \sum_{i=1}^{\mathcal{C}} H_i \left(V \sum_{j=1}^R \nu_{j,i} r_j \right) = V \sum_{j=1}^R \Delta H_{R_j}(T) r_j$$

Combining this relationship with Eq. (2.120),

$$Q = \sum_{i=1}^{\mathcal{C}} n_i C_{P_i} \frac{dT}{dt} - T v \beta \frac{dP}{dt} + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \quad (2.121)$$

where $\beta = \sum_{i=1}^{\mathcal{C}} n_i \beta_i$

The batch reactor can be operated in either constant-(e.g., in an autoclave) or variable-(e.g., in an open vessel) volume mode. The form of the energy balance equation (Eq. (2.120)) depends on which of these two modes is used.

Batch Reactor at constant-pressure

A batch reactor operating at **constant pressure** or the fluid is incompressible, then Eq. (2.121) reduces to

$$Q = \sum_{i=1}^{\mathcal{C}} n_i C_{P_i} \frac{dT}{dt} + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \quad (2.122)$$

In general, when dealing with a batch reactor, it will be required to calculate the reaction temperature and fractional conversion as a function of time under given conditions of heat supply or removal, or to calculate the heating or cooling requirements for obtaining a desired temperature and reactor capacity.

For a single reaction,

$$Q = \sum_{i=1}^c n_i C_{P_i} \frac{dT}{dt} + V \Delta H_R(T) r \quad (2.123)$$

If A is the key reactant, and setting $\nu_A = -1$

$$Q = \sum_{i=1}^c N_i C_{P_i} \frac{dT}{dt} - \Delta H_{R,A}(T) r_A V, \quad r_A = -r \quad (2.124)$$

where r is the global reaction rate.

Thus, the temperature profile is just calculated from this relationship.

$$\frac{dT}{dt} = \frac{q A_k + \Delta H_R(T) r_A V}{\sum_{i=1}^c N_i C_{P_i}}, \quad r_A = -r \quad (2.125)$$

Where Eq. (2.125) is the appropriate simplified heat balance and A_k is the heat exchanger surface. The term $q A_k$ represents any addition or removal of heat from the reactor. For a heat exchange coil, q would have the form:

$$q = U (T_r - T) \quad (2.126)$$

where T_r is the temperature of the heating or cooling medium.

For adiabatic operation, $q = 0$, and it is very important to dig a little bit under this type of operation. Under this operation mode, Eq. (2.125) becomes to:

$$\frac{dT}{dt} = \frac{\Delta H_R(T) r_A V}{\sum_{i=1}^c N_i C_{P_i}}, \quad r_A = -r \quad (2.127)$$

which is equivalent to

$$\frac{dT}{dt} = \frac{\Delta H_R(T) \left(\frac{dN_A}{dt} \right)}{\sum_{i=1}^c N_i C_{P_i}}$$

Eliminating the time derivative term

$$\left(\sum_{i=1}^c N_i C_{P_i} \right) dT = \Delta H_R(T) dN_A \quad (2.128)$$

When only one reaction is taking place $N_i = N_{i,0} + \nu_i N_{A,0} X_A$, so

$$\left(\sum_{i=1}^c N_{i,0} C_{P_i} + N_{A,0} X_A \sum_{i=1}^c \nu_i C_{P_i} \right) dT + \Delta H_R(T) N_{A,0} dX_A$$

At constant pressure,

$$\sum_{i=1}^c \nu_i C_{P_i} \approx \frac{d \Delta H_R(T)}{dT}$$

Combining both equations

$$\left(\sum_{i=1}^c N_{i,0} C_{P_i} + N_{A,0} X_A \frac{d \Delta H_R(T)}{dT} \right) dT + \Delta H_R(T) N_{A,0} dX_A = 0$$

so

$$\sum_{i=1}^c N_{i,0} C_{P_i} dT + N_{A,0} d[\Delta H_R(T) X_A] = 0 \quad (2.129)$$

Assuming that C_{P_i} and ΔH_R are known and constant for the reaction temperature range, the integration of Eq. @ref(eq:ec003_039) is straightforward:

$$\left(\sum_{i=1}^c N_{i,0} C_{P_i} \right) (T - T_0) + N_{A,0} \Delta H_R(T) X_A = 0$$

Rearranging,

$$T = T_0 + \left(\frac{N_{A,0} (-\Delta H_R(T))}{\sum_{i=1}^c N_{i,0} \bar{C}_{P_i}} \right) X_A \quad (2.130)$$

The equation (2.130) can be used to check the maximum reactor temperature change that can be attained with adiabatic operation by setting the fractional conversion of A equal to one. This temperature change is called **adiabatic temperature change**



Physically, it is the amount that the temperature will increase or decrease as the reaction goes to completion under adiabatic conditions.

Finally, if $(N_{A,0}(-\Delta H_R(T)) / \sum_{i=1}^c N_{i,0} \bar{C}_{P_i})$ is constant, independent of temperature, the Eq. (2.130) can be written as

$$T = T_0 + \Delta T_{ad} X_A \quad (2.131)$$

This equation represents a simplified version of the energy balance for an adiabatic reactor, valid when ΔT_{ad} is constant.

(R)

information The operating point of an adiabatic CSTR at steady-state must lie somewhere on the line that represents the adiabatic energy balance. For an adiabatic PFR at a steady-state or for an adiabatic batch reactor, the energy balance describes the reaction's path, including the exit condition for a PFR and the final condition for a batch reactor. For an adiabatic reactor, if point (X, T) does not lie on the line, the energy balance is not satisfied.

Exercise 2.13 (Heat requirement for a BR). In a batch reactor, having a volume $V_R = 5 \text{ m}^3$, a constant-density exothermic reaction $A \rightarrow P$ is carried out in the liquid phase. For the conversion rate we have

$$\begin{aligned} r_A &= -k C_A \quad [\text{kmol/m}^3 \text{s}] \\ C_P &= 4.2 \cdot 10^6 \text{ J/m}^3 \text{ }^\circ\text{C} \\ k &= 4 \cdot 10^6 \exp(-7900/T) \quad [\text{s}^{-1}] \\ \text{MW}_A &= 100 \text{ kg/kmol} \\ \Delta H_R &= -1.67 \cdot 10^6 \text{ J/kg} \\ C_{A0} &= 1 \text{ kmol/m}^3 \end{aligned}$$

The initial temperature T_0 of the reaction is $20 \text{ }^\circ\text{C}$ and the maximum allowable reaction temperature is $95 \text{ }^\circ\text{C}$. The reactor contains a spiral for heat exchange purpose; its surface area A is 3.3 m^2 and it can be operated with steam ($T_s = 120 \text{ }^\circ\text{C}$, $U_s = 1360 \text{ W/m}^2 \text{ }^\circ\text{C}$) and cooling water ($T_c = 15 \text{ }^\circ\text{C}$, $U_c = 1180 \text{ W/m}^2 \text{ }^\circ\text{C}$). The time required for filling and emptying the reactor are 600 and 900 s, respectively.

The problem to be solved is calculated the duration of one reaction cycle and the steam consumption for a relative conversion $X_A \geq 0.9$ and for the following policies of operation:

1. Preheat to $55 \text{ }^\circ\text{C}$, let the reaction proceed adiabatically, start cooling when $95 \text{ }^\circ\text{C}$ or $X_A = 0.9$ is reached, cool down to $45 \text{ }^\circ\text{C}$.
2. Heat up to $95 \text{ }^\circ\text{C}$, let the reaction proceed isothermally until $X_A = 0.9$, cool down to $45 \text{ }^\circ\text{C}$.

Solution. To solve the problem, we are going to apply the energy balance for a batch reactor that operates at constant-pressure (eq. (2.125)). This equation will combine with the mass balance equation and the kinetic rate law of the reaction, following the operation policies described before.

Case I. First policy of operation (see Figure 2.38)

Step 1. Heating up. During this step, the chemical reaction is not taking place. It is just a preheat of the reaction mixture. The energy balance for an incompressible fluid without external heat exchange and chemical conversion becomes to

$$\frac{dT(t)}{dt} = \frac{U_s A (T_s - T(t))}{C_P V_R}$$

Where T_s and U_s is the operating temperature and the global heat transfer coefficient for steam, respectively.

This ODE was integrated from $T = 20^\circ\text{C}$ and $T = 55^\circ\text{C}$ (ec. (2.132)) and it is found that the latter temperature is reached after 2015.69 seconds.

$$T(t) = T_s + \exp\left(-\frac{U A t}{C_P V_R}\right) (20 - T_s) \quad (2.132)$$

Step 2. Reaction under adiabatic operation. Now, it is necessary to combine mass balance, kinetic rate with energy balance. Thus, the ODEs system to be solved is

$$\begin{aligned} \frac{dX_A}{dt} &= k(1 - X_A) \\ \frac{dT}{dt} &= -\frac{\Delta H_{R_A}^{\circ} C_{A0}}{C_P} \frac{dX_A}{dt} \end{aligned}$$

This system required 4063.6 seconds for reached 90% of conversion. The final temperature was 90.79°C .

Step 3. Cooling down. This stage will be solved under same assumptions set out in first stage but using water as refrigerant fluid.

$$\frac{dT(t)}{dt} = \frac{U_c A (T_c - T(t))}{C_P V_R}$$

In this stage, the system was cooled to 45°C in 4997.43 seconds.

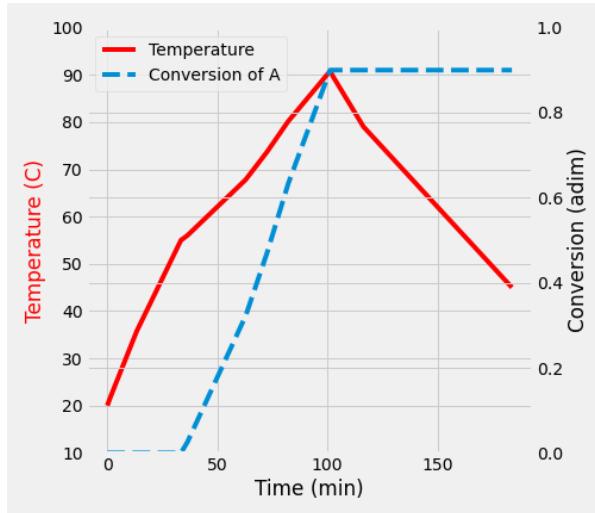


Figure 2.38: Conversion and temperature in a batch reactor (Case I)

Case II. Second policy of operation. (see Figure 2.39).

Step 1. In first step, the heating up and reaction will be simultaneous. Therefore, the equations to

be solved are:

$$\frac{dX_A}{dt} = k(1 - X_A)$$

$$\frac{dT}{dt} = \frac{U_s A (T_s - T(t))}{C_P V_r} - \frac{\Delta H_{R_A}^{\circ} C_{A0}}{C_P} \frac{dX_A}{dt}$$

The reaction was stopped when the reaction temperature was 95 °C. This temperature was reached in 3442.17 seconds, and the conversion of A was 67.8%

Step 2. In the second step, the reaction proceeded at a constant temperature. The equation required to solve this step is just the mass balance of A with k evaluated at 95 °C. Under this circumstance, the conversion of 90% was reached in 609.38 seconds.

$$\frac{dX_A}{dt} = k(T)(1 - X_A)$$

Step 3. The final step was cooling down the reaction mixture until 45 °C. This temperature was reached in 5290.39 seconds.

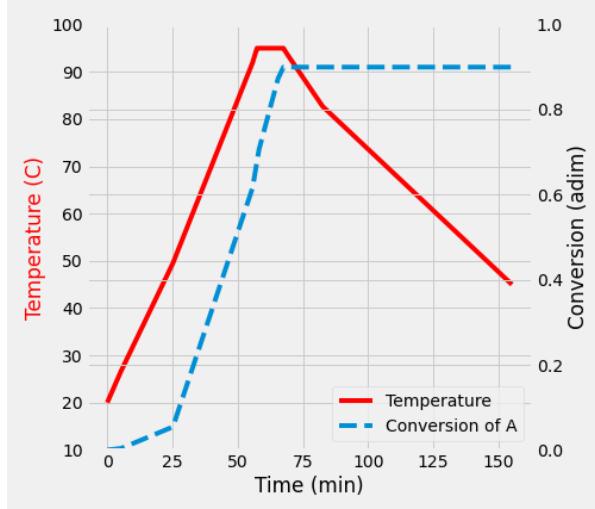


Figure 2.39: Conversion and temperature in a batch reactor (Case II)

The total time operation in case I (including filling and emptying times) was 11676.5 seconds or 3.24 hours. For case II, the total time required was 9341.94 or 2.59 hours, which implies a decrease of 20%.

However, it is essential to include an economic function to optimize the operation scheme because steam and cooling water requirements are different in both cases.

The solution for this problem is available in Python

Exercise 2.14 (Dynamic simulation of a non-isothermal batch reactor). The chemical reaction is a liquid-phase, irreversible, exothermic, and first-order, which is taking place into a BR.

Let us assume that A is fed to the reactor at 294 K, the diameter of the reactor is 2 m, and it is equipped with a jacket heat transfer and an additional external heat exchanger, which heat transfer area is four times the jacket area. The operating temperature is 340 K, and initially, the reactor is heated with a hot fluid until the reaction begins to generate heat, and then it is cooled by a cold fluid.

A split-range-heating/cooling system is used to heat or cool the reactor as it is required. A reactor temperature controller's setpoint is ramped up from 300 K to 340 K in 45 min. The hot-stream temperature is 373 K while the cold-stream one is 294 K. The maximum flow rate of each stream is one kg/s.

The process has two operating restrictions:

1. It is required the maximum conversion of A is equal to 99.99% and,
2. the reaction stops if the batch temperature is equal or greater than 400 K.

Solution. This problem is described by following ODEs

$$\begin{aligned}\frac{dC_A}{dt} &= -k C_A \\ \frac{dT}{dt} &= \frac{1}{\rho C_P V_R} (Q - \Delta H_R(T) k C_A V_R) \\ \frac{dT_J}{dt} &= \frac{F_{\text{cold}} T_{\text{cold}} + F_{\text{hot}} T_{\text{hot}}}{V_J} - \frac{(F_{\text{hot}} + F_{\text{cold}}) T_J}{V_J} - \frac{Q}{V_J \rho_J C_{P_J}}\end{aligned}$$

where J refers to jacket heat exchanger

with:

$$Q = U A (T_J - T) \quad k = k_0 \exp\left(\frac{-E}{R T}\right)$$

This problem was solved in Python, and its results are shown in Figure 2.40.

Figure 2.40 (a) shows the reactor temperature profile compared to setpoint temperature (340 K). This figure is consistent with the regular mode operation of a BR depicted for high exothermic reactions.

In (b), the behavior of the hot fluid and cold fluid rate is observed. The maximum flow rate of the cold stream occurs at the end of the ramp when the temperature ($T_{R,\max}$) exceeded 340 K (approx. 350K). Now, the reaction slows down, and when T starts to drop, the cooling flow rate is gradually reduced to maintain T at the desired level.

In general, at $T_{R,\max}$ for the reaction

$$U A (T_{R,\max} - T_{\text{cold}}) = \Delta H_R(T) V_R r_A(T_{R,\max})$$

For a batch reactor is crucial that the cooling system could maintain $T_{R,\max}$ and that the sensibility of $T_{R,\max}$ towards the cooling medium inlet temperatura T_{cold} , $dT_{R,\max}/dT_{\text{cold}}$ should be lower than 1 in order to have a dampening effect.

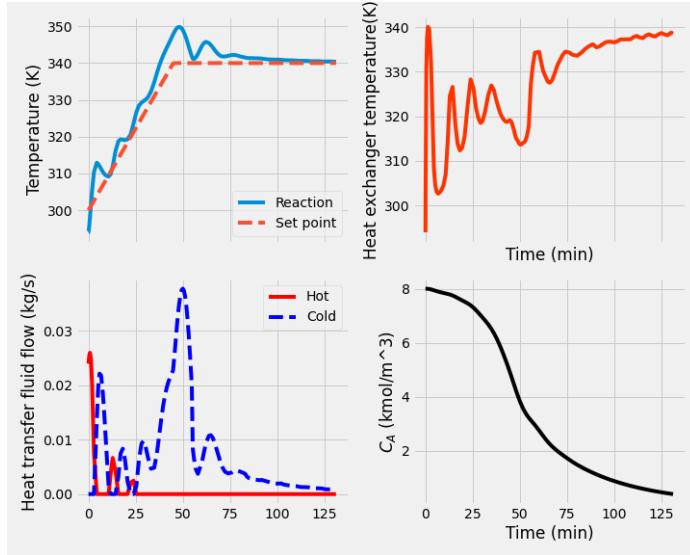


Figure 2.40: Dynamic simulation of a batch reactor

In (c) is shown that at $T_{R,\max}$ the concentration of A dropped to about half its initial value. The final conversion of A was reached in **291.29 min**

The same problem was solved for two different diameters for the reactor to analyze the effect over reactor performance and stability of the reaction. The results obtained are shown in figure 2.41.

Figure 2.41 shows when the reactor size is decreased, its response is unstable, with a 10K overshoot of the desired temperature, whereas when the diameter is increased to 3 m, the reactor runs away

Batch Reactor at constant-volume

Nevertheless, when the reactor operates at constant volume, the boundary work is zero so let us rewrite the energy balance for a batch reactor (from Eq. (2.121)) in reasonable terms. The variation of the pressure can be derived from the total differential of volume.

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P,n} dT + \left(\frac{\partial V}{\partial P} \right)_{T,n} dP + \sum_{i=1}^c \bar{V}_i dn_i \quad (2.133)$$

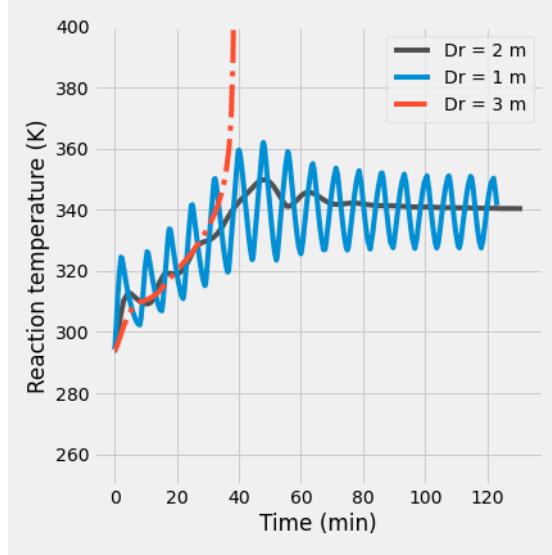


Figure 2.41: Effect of size reactor over dynamic behavior of a BR

Other useful relationships are:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_{P,n_k} \quad (2.134)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial v}{\partial P} \right)_T \quad (2.135)$$

$$C_P = C_V + T v \frac{\beta^2}{\kappa_T} \quad (2.136)$$

Now, forming time derivatives for Eq. (2.133),

$$\frac{dP}{dt} = -\frac{\left(\frac{\partial V}{\partial T} \right)_{P,n} \frac{dT}{dt} + \sum_{i=1}^c \bar{V}_i \frac{dn_i}{dt}}{\left(\frac{\partial V}{\partial P} \right)_{T,n}} = \frac{\beta}{\kappa_T} \frac{dT}{dt} + \frac{1}{V \kappa_T} \sum_{i=1}^c \bar{V}_i \frac{dn_i}{dt} \quad (2.137)$$

Substituting Eq. (2.137) into Eq. (2.121)

$$\begin{aligned} Q &= \sum_{i=1}^c n_i C_{P_i} \frac{dT}{dt} - T V \beta \frac{dP}{dt} + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \\ &= \sum_{i=1}^c n_i C_{P_i} \frac{dT}{dt} - T V \beta \left(\frac{\beta}{\kappa_T} \frac{dT}{dt} + \frac{1}{V \kappa_T} \sum_{i=1}^c \bar{V}_i \frac{dn_i}{dt} \right) + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \end{aligned}$$

This equation could rewrite it,

$$\begin{aligned}
 Q &= \left(C_P - TV \frac{\beta^2}{\kappa_T} \right) \frac{dT}{dt} - \frac{T\beta}{\kappa_T} \sum_{i=1}^C V_i \frac{dn_i}{dt} + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \\
 &= C_V \frac{dT}{dt} - \frac{T\beta}{\kappa_T} \sum_{i=1}^C V_i \left(V \sum_{j=1}^R \nu_{i,j} r_j \right) + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \\
 &= C_V \frac{dT}{dt} - \left(\sum_{j=1}^R \left(\frac{T\beta}{\kappa_T} \sum_{i=1}^C \nu_{i,j} V_i \right) r_j \right) V + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j \\
 &= C_V \frac{dT}{dt} - V \sum_{j=1}^R \frac{T\beta}{\kappa_T} \Delta V_j + V \sum_{j=1}^R \Delta H_{R_j}(T) r_j
 \end{aligned}$$

Therefore, the energy balance for a batch reactor that operates at **constant volume** is

$$Q = C_V \frac{dT}{dt} - V \sum_{j=1}^R \left(T \frac{\beta}{\kappa_T} \Delta V_j - \Delta H_{R_j}(T) r_j \right)$$

For most liquid reactions, $\Delta V_j \approx 0$ is usually a good approximation. With this approximation $\Delta H_R \approx \Delta U_R$ and $C_P \approx C_V$.

In a gas-phase reacting system, there are two cases: there is no change in moles on reaction, and it follows that

$$\sum_{j=1}^R \nu_j = 0 \text{ and } \sum_{j=1}^R \Delta V_j = 0$$

In the second case, there is a change in moles on reaction. Thus $\sum \nu_j = \Delta N$ and $\sum \Delta V_j \neq 0$.

The use of a jacket surrounding the reactor is probably the most common method providing heat transfer because it is relatively inexpensive in terms of equipment cost. However, the most effective heat exchange equipment configuration will be determined by the amount of heat that must be added or removed from the reactor to keep optimum conversion of the key reactant into the desired product.

2.5.3 The Semi-Batch Reactor

When addition of reactants, together with removal of liquid and vapor, is also considered, the equations becomes for example (Froment, Bischoff, and De Wilde 2011):

Continuity equations for specie j :

$$\frac{C_j V}{dt} = F_1 C_{j,0} - F_2 C_j - F_{3,v} C_{j,v} - V \sum_{i=1}^R \nu_{ij} r_i$$

F_1 is the liquid feed rate, and F_2 is the liquid withdrawal rate, and F_3 is the vapor withdrawal rate.

Energy equation:

$$\rho c_P V \frac{dT}{dt} = F_1 c_P \rho T_1 - F_2 c_P \rho T - F_{3,v} \sum C_{j,c} \Delta H_v + Q + V \sum_{i=1}^R r_i (-\Delta H_i)$$

Accounting for the change in volume:

$$\frac{dV}{dt} = F_1 - F_2 - F_{3,l}$$

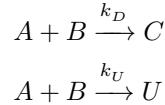
with

$$F_{3,l} = F_{3,v} \frac{273}{273+T} P \frac{1}{22.4} \frac{1}{C_{t,l}}$$

where T is in degrees Celsius and $C_{t,l}$ is the total liquid concentration.

One may choose to operate a semi-batch reactor to control the reaction or heat release during the reaction by slowly adding one reactant in the feed stream or maximizing the selectivity to a specific product.

In order to illustrate the last option, let us consider two elementary liquid-phase reactions simultaneously. One of them produces an undesired product U .



whose rate equations are:

$$\begin{aligned} r_D &= k_D C_A^2 C_B \\ r_U &= k_U C_A C_B^2 \end{aligned}$$

The instantaneous selectivity, $S_{D/U}$, is

$$S_{D/U} = \frac{k_D}{k_U} \frac{C_A}{C_B}$$

From this expression, to increase the production of D , we need to keep the concentration of A high as possible or B low as feasible.

As shown in figure, let us consider that the specie A is placed in the reactor initially and B is added continuously while reaction is taking place. The molar balance for A

$$r_A V = \frac{d N_A}{dt} = \frac{d (C_A V)}{dt} = V \frac{d C_A}{dt} + C_A \frac{d V}{dt}$$

The molar balance over B is

$$F_{B0} + r_B V = \frac{d N_B}{dt} \equiv v_0 C_{B0} + r_B V = V \frac{d C_B}{dt} + C_B \frac{d V}{dt}$$

The reaction volume varies with time as follow,

$$v_0 \rho_0 = \frac{d(\rho V)}{dt}$$

For a constant-density system, $\rho_0 = \rho$, and

$$v_0 = \frac{dV}{dt}$$

with the initial condition $V = V_0$ at $t = 0$, integrating for the case of constant V_0 yields

$$V = V_0 + v_0 t$$

Substituting into molar balance of A and B

$$\begin{aligned} \frac{dC_A}{dt} &= r_A - \frac{v_0}{V} C_A \\ \frac{dC_B}{dt} &= r_B - \frac{v_0 (C_{B0} - C_B)}{V} \end{aligned}$$

We need to solve this EDOs system in order to measure the performance of the reactor.

2.5.4 Optimal Operation Policies

Two main types of situations are considered (Froment, Bischoff, and De Wilde 2011)

1. Optimal batch operation time for the sequence of operations in a given reactor.
2. Optimal temperature (or other variables) variations during the reaction, aiming to minimize the reactor size.

The volume reactor is considered constant in order to simplify the mathematical model.

Optimal Batch Operation Time

Suppose the reaction (Eq. (2.138)) is taking place in a batch reactor of volumen V on a continual basis.



The production rate is calculated based on reaction time, t , and the turnaround time, t_t , between batches. This turnaround time might involve: charge the reactor with reactants, heat the contents to a specified temperature, the reaction time, cool the reactor contents down to ambient temperature, drain the contents of the reactor, cleaning and prepare the reactor for the next batch.

Thus, the total time per batch or cycle time is:

$$t_c = t + t_t$$

The rate of production of C on a continual basis is then

$$\begin{aligned}\text{Prod}(C) &= \frac{\text{moles of C formed}}{\text{batch}} \times \frac{\text{batch}}{\text{time}} \\ &= \frac{n_C - n_{C0}}{t_c}\end{aligned}$$

This equation is, in terms of fractional conversion of A

$$\text{Prod}(C) = \frac{C_{A0} (X_A - X_{A0}) V}{t + t_t} \quad (2.139)$$

Where V is the volume of reactor, t is obtained from (2.110), and the other quantities C_{A0} , X_A , and t_t must be specified.

Usually, it is necessary to answer at least one of the following questions:

1. How long should t be? or
2. How high should X_A be?

In any case, an optimization problem should be solved to answer them. This optimization problem could have two points of view:

1. Economic: Compare the economics of further conversion to a different use of equipment.
2. Chemical: How about the quality of the product?

From chemical point of view, if product stability is assumed. The productivity Pr will be maximized when $dPr/dt = 0$, so let us set t_t is constant:

$$\frac{dPr}{dt} = C_{A0} V \left[\frac{\frac{dX_A}{dt}(t + t_t) - X_A}{(t + t_t)^2} \right] = 0 \quad (2.140)$$

As consequence of Eq. (2.140), it is possible to calculate the optimum time from:

$$\frac{dX_A}{dt}(t_{\text{optimum}} + t_t) - X_A = 0 \quad (2.141)$$

Specify kinetics is required to solve Eq. (2.141).

Otherwise, if it is possible to get data of operation costs like:\ C_1 : the cost per unit time during production.\ C_2 : the cost per unit time when the reactor does not produce, and\ C_3 : the additional expenses per period

And, the average total costs per unit molar (or mass) of product (\bar{P}_r) equal

$$\bar{P}_r = \frac{C_1 t + C_2 t_t + C_3}{C_{A0} X_A}$$

Solving these equations is possible to calculate the optimum load of the installation.

Optimal Temperature Policies

When you want to answer questions like:

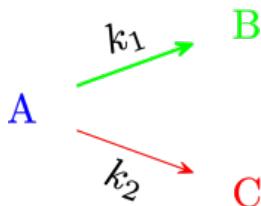
1. What is the best single temperature of operation?
2. What is the best temperature progression during the reaction time or, in other words, the best trajectory?

For single reactions, the results are relatively straightforward. If the reaction is *irreversible*, and if the rate increases with temperature, the optimal temperature for either maximum conversion from a given reactor operation, or minimum time for the desired conversion, is the highest temperature possible. This highest temperature, T_{\max} , is imposed by other considerations such as reactor materials and catalyst physical properties. Similarly, for reversible *endothermic* reactions where the equilibrium conversion increases with temperature ($E_{\text{for.}} > E_{\text{rev.}}$), the highest allowable temperature is the best policy.

The case of reversible exothermic reactions is complicated because even though the rate may increase with temperature, once the equilibrium conversion is reached, higher temperatures hurt the equilibrium conversion. Thus, there is an optimum intermediate temperature where reasonably rapid rates are obtained with a sufficiently high equilibrium conversion. I will dig into that subject later.

2.6 Dealing with complex reactions

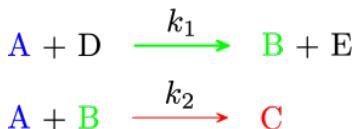
In principle, complex reactions are defined by parallel, consecutive reactions or any combinations of them. In parallel reactions, the key reactant is consumed by two different reaction pathways to form different products.



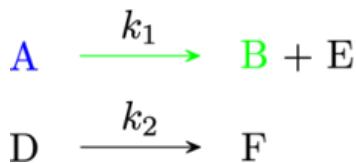
In series reactions, the reactants form an intermediate product, which reacts further to form another product.



While, multiple reactions involve a combination of both series and parallel reaction, such as:



Finally, independent reactions occur when there are many reactants in feedstocks which react in different reaction pathway to different products.



On any chemical scheme shown before, we must design or analyze a reactor system in which multiple reactions occur. In general, our work would have two simultaneous objectives:

1. To produce the **desired** product at the specified production rate using the most miniature reactor. (maximize the reaction rate)
2. To minimize the formation of **low-value by-products**. (maximize the reaction yield)

Nevertheless, there are no general rules for achieving both objectives because they are usually incompatible. Although in most cases, product distribution controls.

Frequently, there is a trade-off between reaction rate and yield. Ultimately, this trade-off requires economic analysis. Typically, the final analysis often favors selectivity over rate because there is a significant and *continuing* cost penalty associated with converting a valuable raw material into low-value by-products.

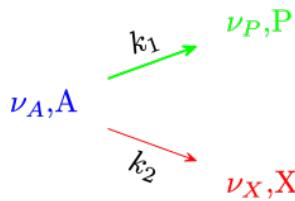
There are two types of problems that arise in multiple-reaction systems:

1. The first is analogous to the kind of problem associated with single reactions. In this category are questions such as: Given a system of reactions with known kinetics, what reaction time (or space-time) will be required to obtain a specified concentration of reactant or product, and what concentrations of the other species will exist at this time?
2. The second type of problem does not involve reaction time or space-time. The question here is given a system of reactions with known kinetics, and given the concentration of one component at some (unspecified) time (or space-time), what are the concentrations of the other species at that time (or space-time)? This type of problem is referred to as a "*time-independent*" problem. Time-independent problems can be solved by forming the ratio of various reaction rates to eliminate time (or space-time) as an explicit variable. However, the solution to such problems provides no information about the time or reactor volume required to obtain a given composition.

Although fractional conversion still is a valid concept, even when more than one reaction takes place. However, the conversion of a single reactant is not sufficient to describe the progress of more than one reaction or to define the complete composition of a system in which more than one reaction occurs. Thus, it is more convenient to deal with concentrations rather than fractional conversions and examine product distribution. (Roberts 2009)

In industrial practice, high conversion rates are essential, but the yield of desired products plays a tremendous role in chemical reactor design. Thus, attempts are often made at the expense of reactor capacity to increase the production of desired products and suppress the formation of undesired ones.

For a reaction system like this one



The ability to convert a reactant into the desired product, **P**, minimizing the formation of undesired product, **X**, is measured by **Yield**. The **overall yield** to desired product *P* with respect to reactant *A* is defined as

$$\tilde{Y}_P = \frac{\text{All moles of } P \text{ formed}}{\text{All moles of } A \text{ reacted}} = \frac{\nu_A}{\nu_P} \frac{N_P - N_{P0}}{N_A - N_{A0}} \quad (2.142)$$

The overall yield refers to the performance of the entire reactor as a whole. Either it operates continuously or in batch mode. Therefore, \tilde{Y}_P is dependent on the reaction conditions and the reactor type.

However, it is often convenient to use a second type of yield called **instantaneous yield**, Y_P , which determines to what extent reactant *A* is being converted into *P* at some place or at some moment in the reactor. It is defined as the ratio of reaction rate of a given product to the reaction rate of the key reactant *A*.

$$Y_P = -\frac{r_P}{r_A} \quad (2.143)$$

Here, Y_P will be 1 when all of the *A* that reacts is converted into the desired product, *P*.

The overall yield is the average of the instantaneous yield integrates over the reactor. The overall yield concerns us because it represents the product distribution at the reactor outlet. Both types of yields are related to each other, and they are always positive.

The rates of the reactions that take place will vary with time in a batch reactor because the composition, and perhaps the temperature, will vary with time. Therefore, the instantaneous yield for a batch reactor will not necessarily be the same as the overall yield. Similarly, for a PFR, the composition and temperature will vary from point to point, so the overall yield will, if necessary, be the same as the instantaneous yield.

In contrast, for a CSTR, the overall and instantaneous yields are equal. As a consequence, the fluid composition and temperature do not vary inside the reactor.

There is a third parameter called **global yield**, η_P , that frequently is used to describe the behavior of system in which more than one reaction takes place. The **global yield** is defined as

$$\eta_P = \frac{\text{All moles of } P \text{ formed}}{\text{All moles of } A \text{ fed}} = \frac{N_P - N_{P0}}{N_{A0}} \quad (2.144)$$

The definitions of overall and global yield are similar. However, the last one is based on the amount of reactant that is *fed*.

The sum of all global yield of all products will not equal to unity as long as some *A* remains unconverted. The global and overall yield is related through the fractional conversion.

$$\frac{\text{moles of } P \text{ formed}}{\text{moles of } A \text{ fed}} = \frac{\text{moles of } A \text{ reacted}}{\text{moles of } A \text{ fed}} \times \frac{\text{moles of } P \text{ formed}}{\text{moles of } A \text{ reacted}}$$

$$\eta_P = X_A \tilde{Y}_P \quad (2.145)$$

where X_A is the fractional conversion of reactant A . Or in differential mode

$$d\eta_P = d(X_A \tilde{Y}_P) = Y_P dX_A \quad (2.146)$$

In case there is no product P present in the reactor feed, the ρ of the reaction mixture is constant over the entire reactor, the stoichiometric coefficients of A and P in the reaction equation are equal, the defining equations above simplify to

$$\begin{aligned}\tilde{Y}_P &= \frac{C_P}{C_{A0} - C_A} \\ \eta_P &= \frac{C_P}{C_{A0}}\end{aligned}$$

For convenient reasons, it could be rather to use a selectivity ratio instead of yield. Thus, the parameter **instantaneous selectivity** is defined as the ratio of reaction rate of the desired product P to the reaction rate of the undesired product X .

$$S_{PX} = \frac{r_P}{r_X} = \frac{k_p C_A^m}{k_x C_A^n} \quad (2.147)$$

There are other definitions of selectivity, for example, the formation of the desired product divided by the formation of all products, all based on moles.

$$S_P = \frac{\text{All moles of P formed}}{\text{All moles of all products formed}}$$

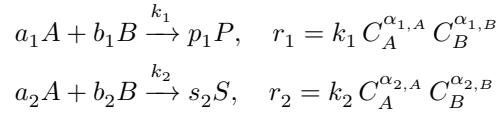
Another useful quantity is the **Rate of Production** of a given product P . We mean the amount of desired product produced by the reactor per unit time F_P , usually in moles/time. If specie A is the reactant and specie P is the desired product, then

$$F_P = \tilde{Y}_P F_{A0} = S_P x X_A F_{A0} \quad (2.148)$$

It is difficult to develop general guidelines regarding selecting and designing a reactor for a consecutive parallel reaction network than for a parallel-reaction or consecutive-reaction network separately. It is necessary to analyze various factors related to the particular situation considered. A list of steps is as follows:

1. A kinetics analysis.
2. A stoichiometric analysis to determine the maximum number of independent material balance equations and kinetics rate laws required.
3. A material balance analysis.
4. Selection of an appropriate numerical scheme to be used to solve the problem.
5. Calculation of selectivity, yield, or production rate concerning the reactor's size and type/configuration.

Qualitatively, let us analyze the following competitive reactions:



The instantaneous yield of P is:

$$\begin{aligned} Y_P &= \frac{r_P}{-r_A} = \frac{p_1 r_1}{a_1 r_1 + a_2 r_2} = \frac{\frac{p_1}{a_1}}{1 + \frac{a_2 r_2}{a_1 r_1}} \\ &= \frac{\frac{p_1}{a_1}}{1 + \frac{a_2 k_2}{a_1 k_1} C_A^{(\alpha_{2,A} - \alpha_{1,A})} C_B^{(\alpha_{2,B} - \alpha_{1,B})}} \end{aligned}$$

The maximum value of instantaneous yield will be

$$Y_{P,\max} = \frac{p_1}{a_1}$$

Therefore, a normalized yield would be

$$\frac{Y_P}{Y_{P,\max}} = \frac{1}{1 + \frac{a_2 k_2}{a_1 k_1} C_A^{(\alpha_{2,A} - \alpha_{1,A})} C_B^{(\alpha_{2,B} - \alpha_{1,B})}}$$

Based on the previous equation, maximizing the value of yield implies:

1. if $\alpha_{2,A} < \alpha_{1,A}$, $\alpha_{2,B} < \alpha_{1,B}$, keep C_A and C_B as high as possible, so PFR is better than CSTR.
2. if $\alpha_{2,A} = \alpha_{1,A}$, $\alpha_{2,B} < \alpha_{1,B}$, keep C_B as high as possible, so PFR is better than CSTR.
3. if $\alpha_{2,A} = \alpha_{1,A}$, $\alpha_{2,B} > \alpha_{1,B}$, keep C_B as low as possible, so CSTR is better than PFR.

Chapter 3

Distribution of Residence times

Reactors treated in this course have been modeled under specific flow considerations that lead to simplicity in the mole and energy balances and are valid in many industrial reactors.

Unfortunately, as it is shown in Figure 3.1, there are other cases where the deviation of those industrial reactors from ideal behavior may be sufficiently large that the use of an ideal reactor model will give an unacceptably significant error because of the careless treatment that these models do to the fluid flow pattern within the reactors.

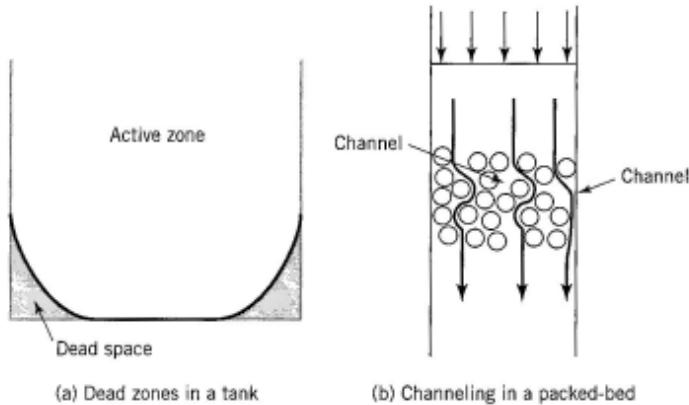


Figure 3.1: Examples of nonideal flow in a CSTR and packed-bed vessel. [@missen1999]

If the flow pattern does not follow the ideal models, it must be necessary to apply a more complex methodology for the reactor performance analysis. Nevertheless, before going deeper into these methodologies, it is essential to emphasize that the factors that govern the performance of a chemical

reactor can be grouped into two broad classifications:

1. The **amount of time** that a reactant molecule spends in the reactor. The longer that reactant can spend in the reactor, the more chance they can react. The time that molecules spend in the reactor is called **the residence time**, which is a crucial parameter in the flow reactor performance, and the **distribution of residence time** is a key factor in determining the extent of reaction.
2. The **extent of mixing** within the reactor. When dealing with two or more different molecules that must react, molecular collision must occur as a first step. Therefore, the concentration at the molecular level is essential.

The degree of mixing depends not only on the reactor configuration and operating conditions but also on the fluid and reactants' properties.

Mixing is a complex phenomenon that can be analyzed on both a macroscopic and microscopic scale. The RTD functions provide a measure only of macroscopic mixing. (Missen, Mims, and Bradley 1999)

However, non-ideal flow results in irregularities relating to the micromixing of fluid elements of differing ages at the microscopic level, too. Therefore, in this section of the course, we will see how the classical approach of Residence Time Distribution (RTD) provides a method for evaluating the effect of flow patterns within the reactor on chemical conversion levels.

3.1 RTD functions

First of all, the study of non-ideal flow behavior is based on the RTD of non-reacting species in an arbitrary flow system with constant density fluid. From this point, it will be explained its relationship to a chemically reacting species present in the reactor.

Residence time theory deals with the age of particles within a flow system. The particles may be atoms, molecules, or fluid elements conserved as they flow through the system.



information The residence time, or age, of a particle in the system is the elapsed time between the time at which the particle enters the system and the time it leaves.

This approach assumes specific essential considerations:

1. If a particle reenters the system after it leaves, the aging of that particle resumes from the value it had as its previous exit.
2. A particle is not allowed to remain in the system forever.
3. All particles must have an original entrance and a final departure.
4. The age of the particle when it finally leaves the system will be its residence time.

Regardless the state of mixing or type of flow, we use the classical definition of mean residence time \bar{t} of an element of fluid volume within a fully contained, continuous flow reactor with a total fixed volume of V operated at steady state which is:

$$\bar{t} = \frac{V}{v} \quad (3.1)$$

where v is the steady volumetric flow rate.

It is vital to point out that a fully contained vessel has no diffusion or dispersion at the vessel's entrance or exit so that a fluid element once inside the reactor cannot escape back into the input stream or once removed from cannot return to the vessel.

This assumption is more precisely related to the boundaries of the reactor. It is assumed a plug flow in both the inlet tube and the outlet tube. Such boundary conditions are called "closed-closed." Figure 3.2 gives others boundary conditions than closed-closed that they are essential for specific experimental techniques to assess the mixing parameters inside the reactor, but they will not consider in this course.

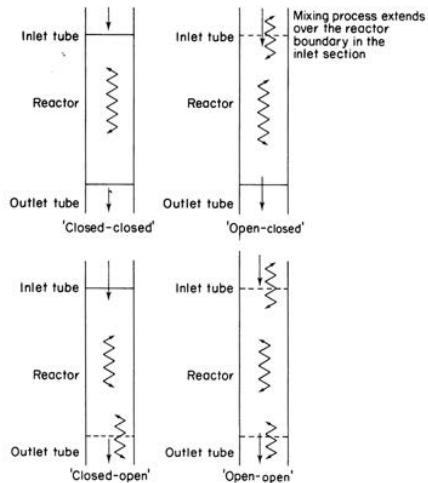


Figure 3.2: Boundary conditions of reactors in relation to the residence time distribution. [©west-terp1984]

Now, let us introduce some mathematical concepts. Let $dV = v dt$ represent a fluid element which entered the system t time ago. Also, let $\mathbf{P}(t)$ represent the probability that the element remains in the reactor during the period t . The total volume of the fluid in the reactor must be

$$V = v \int_0^\infty \mathbf{P}(t) dt \quad (3.2)$$

Now, let us introduce some mathematical concepts. Let $dV = v dt$ represent a fluid element which entered the system t time ago. Also, let $\mathbf{P}(t)$ represent the probability that the element remains in the reactor during the period t . The total volume of the fluid in the reactor must be

Now, let $\mathbf{F}(t)$ represent the probability of a fluid element leaving the system during the period t so $\mathbf{P}(t) + \mathbf{F}(t) = 1$. The foregoing equation then becomes

$$\frac{V}{v} = \int_0^{\infty} (1 - F(t)) dt \quad (3.3)$$

which upon integration by parts gives

$$\frac{V}{v} = [1 - F(t)] \cdot \infty - [1 - F(t)] \cdot 0 + \int_{F(0)}^{F(\infty)} t dF(t) \quad (3.4)$$

with boundary conditions of $F(t) = 0$ at $t = 0$, and 1 at $t = \infty$ (chance of 100% removal in an infinitive time) so that

$$\frac{V}{v} = \int_0^1 t dF(t) = \bar{t} \quad (3.5)$$

$$F(t) \rightarrow 1 \text{ when } t \rightarrow \infty$$

$F(t)$ is called “*Cumulative Distribution Function*”. This function is dimensionless, and **represents the fraction of effluent that has been in the reactor for less time than t , and leaves the reactor with age less than t .**

The typical shape of $F(t)$ function is shown on Figure 3.3. From this figure, it is possible to note that 80% of the molecules spend 40 min or less in the reactor, and 20% of the molecules spend longer than 40 min in the reactor.

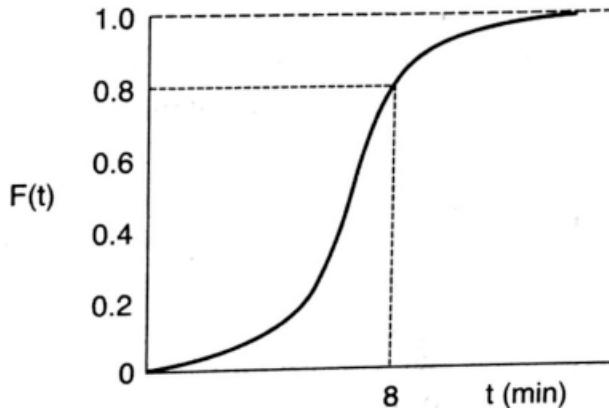


Figure 3.3: Typical cumulative distribution curve **F**. [@fogler2008]

The distribution of residence times is represented by an external residence time distribution or an exit age distribution, $E(t)$. This function is called **Residence Time Distribution Function** or (RTD-function) which **defines a fraction of exiting fluid elements with residence times lies between time t and $t + dt$.**

Since $\mathbf{E}(t)$ is a fraction, $\mathbf{E}(t)$ has units of time⁻¹. In addition, the fraction of fluid that leaves the reactor over all time, this means between $t = 0$ and $t = \infty$ must be 1. Therefore

$$\int_0^{\infty} \mathbf{E}(t) dt = 1 \quad (3.6)$$

The fraction of fluid *in the effluent stream* that was *in the reactor* for a time between $t = 0$ and $t = t$ is given by

$$\int_0^t \mathbf{E}(t) dt$$

Another way of saying the same thing is that $\int_0^t \mathbf{E}(t) dt$ is the fraction of fluid in the exit stream with an *exit age* less than t . This fraction can be represented graphically as shown in Figure 3.4.

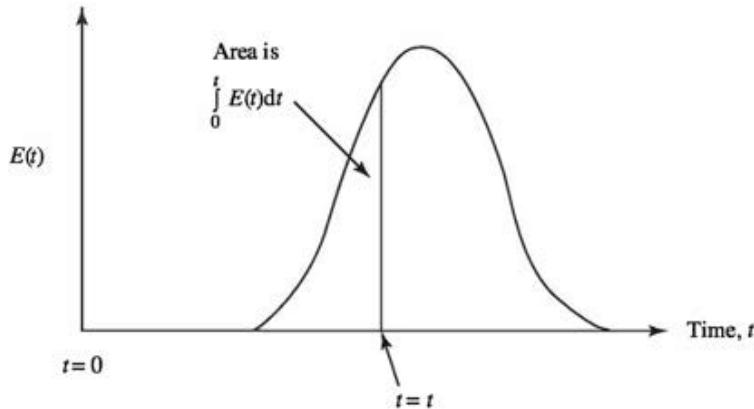


Figure 3.4: Typical RTD curve **E**. [@roberts2009]

The fraction of the fluid that spends a given duration, t inside the reactor, is given by the value of $\mathbf{E}(t) dt$. Therefore, $\mathbf{E}(t)$ curve is related to $\mathbf{F}(t)$ because the fraction of the fluid that leaves the reactor with age less than t is equal to the sum over all times less than t of $\mathbf{E}(t)\Delta t$, or expressed continuously. (Roberts 2009)

$$\mathbf{F}(t) = \int_0^t \mathbf{E}(t) dt \quad (3.7)$$

Equation (3.7) could be rewritten as

$$\frac{d\mathbf{F}(t)}{dt} = \mathbf{E}(t) \quad (3.8)$$

Therefore from Eq. (3.5)

$$\bar{t} = \int_0^\infty t \mathbf{E}(t) dt \quad (3.9)$$

This procedure is called normalizing the distribution, and Figure 3.5 shows that.

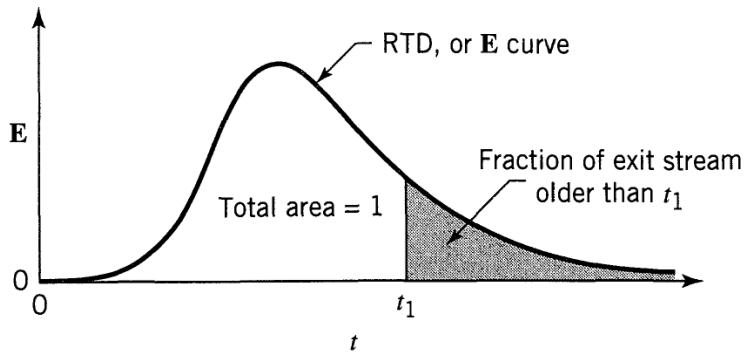


Figure 3.5: The typical exit age distribution curve **E** (RTD) [@levenspiel2004]

The RTD function may be used directly to analyze reactors, or related functions may be used depending on the application.

Another useful distribution curve is the Washout function, \mathbf{W} , which sometimes is called “Complement function”. This function gives **the fraction of effluent that has been in reactor (with the residence times) for longer than time t** . It could be calculated from

$$\mathbf{W}(t) = \int_t^\infty \mathbf{E}(t) dt \equiv 1 - \mathbf{F}(t) = 1 - \int_0^t \mathbf{E}(t) dt \quad (3.10)$$

So,

$$\mathbf{F}(t) + \mathbf{W}(t) = 1 \quad (3.11)$$

Furthermore, the relationship between the functions in derivative form is

$$\frac{d\mathbf{F}(t)}{dt} = -\frac{d\mathbf{W}(t)}{dt} = \mathbf{E}(t) \quad (3.12)$$

A typical $\mathbf{F}(t)$ and the corresponding $\mathbf{W}(t)$ function curve are illustrated in Figure 3.6

Another distribution function of interest in some application is the “Internal Age Distribution”, \mathbf{I} , which is **the fraction of fluid inside the vessel with age between t and $t + dt$** . It has

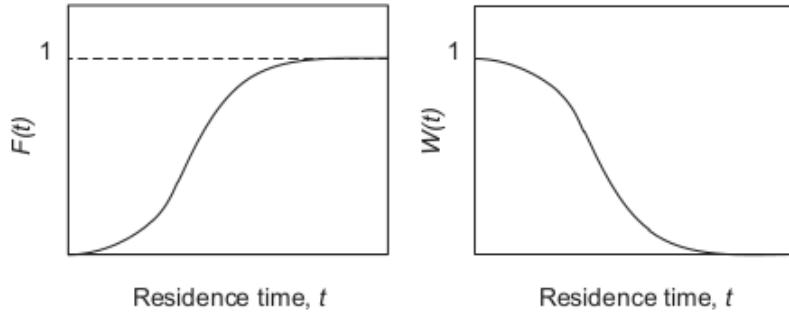


Figure 3.6: The typical $F(t)$ and $W(t)$ curves. [@hayes2013]

properties similar to $\mathbf{E}(t)$, so

$$\int_0^\infty \mathbf{I}(t) dt = 1$$

The time $t = 0$ refers to an arbitrary initial time and not the start of the flow of fluid into the vessel. In physical terms, this equation states that all fluid has an age between 0 and ∞ .

As a consequence, the fraction of vessel contents younger than a specified age t is,

$$\int_0^t \mathbf{I}(t') dt' = 1$$

While the fraction older than t is

$$\int_t^\infty \mathbf{I}(t') dt' = 1 - \int_0^t \mathbf{I}(t') dt'$$

Similar to $\mathbf{E}(t)$, the mean age fluid elements inside the vessel is,

$$\bar{t}_1 = \int_0^\infty t \mathbf{I}(t) dt = \text{mean internal age}$$

As might be expected, there is an interrelationship between \mathbf{I} and \mathbf{E} since the fluid entering a vessel at a given time obviously either leaves it or stays inside. Therefore:

$$\bar{t} \mathbf{I}(t) = 1 - \int_0^t \mathbf{E}(t) dt = \mathbf{W}(t) \quad (3.13)$$

or

$$\mathbf{I}(t) = \frac{\mathbf{E}(t)}{1 - \mathbf{F}(t)} \Rightarrow \mathbf{E}(t) = -\bar{t} \frac{d\mathbf{I}(t)}{dt} \quad (3.14)$$

Finally, the **Intensity function**, $\Lambda(t)$ is defined as **fraction of fluid in the vessel of age t will leave at time between t and $t + dt$** . The intensity is useful in detecting the existence of dead space and bypassing.

The intensity function can be related to \mathbf{E} and \mathbf{I} functions from

$$\begin{bmatrix} \text{Amount of fluid} \\ \text{leaving between} \\ t \text{ and } t + dt \end{bmatrix} = \begin{bmatrix} \text{Amount not leaving} \\ \text{before time } t \end{bmatrix} \cdot \begin{bmatrix} \text{Fraction of age } t \\ \text{that will leave} \\ \text{between times } t, t + dt \end{bmatrix}$$

$$v \mathbf{E}(t) dt = V \mathbf{I}(t) \cdot \Lambda(t) dt$$

Therefore

$$\Lambda(t) = \frac{1}{\bar{t}} \frac{\mathbf{E}(t)}{\mathbf{I}(t)} \quad (3.15)$$

Combining the last two equations

$$\Lambda(t) = \frac{-\bar{t} \frac{d\mathbf{I}(t)}{dt}}{\bar{t} \mathbf{I}(t)} = -\frac{d[\ln(\bar{t}\mathbf{I}(t))]}{dt} \quad (3.16)$$

3.2 Means and moments

In addition to characterizing the RTD using the three functions $\mathbf{E}(t)$, $\mathbf{F}(t)$ and $\mathbf{W}(t)$, the residence time can also be characterized using the moments of the RTD functions. There are several types of moments. (Hayes and Mmbaga 2013)

The first type is the moment around the origin, which is defined in terms of density function as

$$\mu_n = \int_0^\infty t^n \mathbf{E}(t) dt \quad (3.17)$$

The value of n determines which moment is calculated. For example, the first moment about the origin is the **mean residence time**, \bar{t}

$$\mu_1 = \bar{t} = \int_0^\infty t \mathbf{E}(t) dt \quad (3.18)$$

As we already know, the mean residence time is the average time that molecules spend in the system. In a constant-density system $\bar{t} = V/v = \tau$

 information Equation (3.17) can provide a helpful check on operating data because the volumetric flow rate is relatively easy to set and measure. However, the volume of the reactor filled by a fluid is not always so easy to determine.

Rather than compute the moments about the origin, it is common for the moments of the RTD function to be calculated about the mean residence time. These moments are called central moments, and are defined as

$$\mu'_n = \int_0^\infty (t - \bar{t})^n \mathbf{E}(t) dt \quad (3.19)$$

The variance, σ_t^2 , of the RTD is the second central moment:

$$\sigma^2 = \mu'_2 = \int_0^\infty (t - \bar{t})^2 \mathbf{E}(t) dt \quad (3.20)$$

An alternative form may be more convenient to use is obtained by expanding the square in Eq. (3.20)

$$\sigma_t^2 = \left(\int_0^\infty t^2 \mathbf{E}(t) dt \right) - \bar{t}^2 \quad (3.21)$$

The variance measures the spread of the distribution about the mean characterized by the standard deviation, σ_t . The third central moment, the skewness, measures the symmetry of the distribution about the mean:

$$\sigma^3 = \mu'_3 = \int_0^\infty (t - \bar{t})^3 \mathbf{E}(t) dt \quad (3.22)$$

All moments must be calculated meticulously for a complete summary of a distribution. In practice, these three parameters are typically appropriate for a good RTD characterization.

3.3 Normalized RTD functions

It is common when using residence time theory to work with normalized RTD, defined as the residence time divided by the mean residence time. This dimensionless time is given by (Hayes and Mmbaga 2013)

$$\theta = \frac{t}{\bar{t}}$$

The density functions for the two cases are related by

$$\mathbf{E}(\theta) d\theta = \mathbf{E}(t) dt$$

Because $\bar{t} d\theta = dt$, it follows that

$$\mathbf{E}(\theta) = \bar{t} \mathbf{E}(t) = \frac{\bar{t} C(t)}{\int_0^\infty C(t) dt}$$

The other relationships do not change. The normalized cumulative distribution function is

$$\mathbf{F}(t) = \int_0^t \mathbf{E}(t) dt = \int_0^{\theta} \mathbf{E}(\theta) d\theta = \mathbf{F}(\theta)$$

The normalized washout function is

$$\mathbf{W}(\theta) = \int_{\theta}^{\infty} \mathbf{E}(\theta) d\theta$$

Finally, the moments about the origin and the central moments for the normalized RTD functions are

$$\begin{aligned}\nu_{(1,\theta)} &= \int_{\theta}^{\infty} \theta \mathbf{E}(\theta) d\theta = \bar{\theta} = 1 \\ \nu_{\theta}^2 &= \int_{\theta}^{\infty} (\theta - \bar{\theta})^2 \mathbf{E}(\theta) d\theta = \int_{\theta}^{\infty} \theta^2 \mathbf{E}(\theta) d\theta - 1 = \frac{\theta^2}{t^2}\end{aligned}$$

For numerical work with tracer data directly, it is common to use the dimensional $\mathbf{E}(t)$, \bar{t} , and σ_t^2 . The dimensionless quantities are used with the performance models. Figure 3.7 shows a summary of RTD functions expressed by dimensionless time.

$$\begin{aligned}\theta &= \frac{t}{V/v}; \quad \theta = \frac{t}{\bar{t}} \\ \mathbf{E}(t) dt &= \mathbf{E}(\theta) d\theta; \quad \Lambda(t) dt = \Lambda(\theta) d\theta \\ \mathbf{F}(t) &= \mathbf{F}(\theta); \quad \mathbf{W}(t) = \mathbf{W}(\theta); \quad \mathbf{C}(t) = \mathbf{C}(\theta) = \frac{c(t)}{c(0)} \\ \mathbf{E}(t) &= \frac{d\mathbf{F}(t)}{dt} = -\frac{d\mathbf{W}(t)}{dt} = \frac{\mathbf{C}(t)}{\bar{t}} = \frac{\mathbf{E}(\theta)}{\bar{t}} \\ \mathbf{F}(t) &= \int_0^t \mathbf{E}(t) dt = 1 - \mathbf{W}(t) = \mathbf{F}(\theta) \\ \Lambda(t) &= \frac{\mathbf{E}(t)}{\mathbf{W}(t)} = \frac{\mathbf{E}(t)}{1 - \mathbf{F}(t)} = \frac{\mathbf{E}(t)}{\bar{t} \mathbf{I}(t)} = \frac{1}{\bar{t}} \Lambda(\theta) \\ \mathbf{C}(t) &= \bar{t} \mathbf{E}(t) = \bar{t} \frac{d\mathbf{F}(t)}{dt} = \mathbf{C}(\theta) \\ \int_0^{\infty} \mathbf{E}(t) dt &= \int_0^{\infty} \mathbf{E}(\theta) d\theta = 1 \\ \int_0^{\infty} \mathbf{I}(t) dt &= 1 = \frac{1}{\bar{t}} \int_0^{\infty} \mathbf{W}(t) dt = \int_0^{\infty} \mathbf{W}(\theta) d\theta \\ \int_0^{\infty} \mathbf{C}(t) dt &= \int_0^{\infty} t \mathbf{E}(t) dt = \bar{t} = \bar{t} \int_0^{\infty} \mathbf{C}(\theta) d\theta\end{aligned}$$

Figure 3.7: Relationships between Residence Time Functions

3.4 Experimental determination of RTD

The RTD is measured experimentally by injecting a tracer, which is an inert chemical compound into the reactor at some time $t = 0$ and then measuring its concentration, C , in the effluent stream as a function of time. The tracer must meet the following requirements:

1. it must be a nonreactive species that is easily detectable at low concentrations, e.g., by electrical conductivity, light absorption, or nuclear radiation.
2. it should have physical properties similar to those of the reacting mixture, such as density, and be completely soluble in the mixture to avoid flow changes due to viscosity and molecular diffusion of the tracer in the solution.

3. it should not adsorb on the walls or other surfaces in the reactor.
4. The tracer should be inexpensive and easy to handle.
5. The tracer should be stable and conserved so that it can be accounted for by a material balance relating the response to the input; if tracer decays, its half-life should be such that $t_{1/2}(\text{tracer}) > 25\bar{t}(\text{fluid})$.

The two most used methods of injection are *pulse input* and *step input*.

3.5 Determination of $E(t)$ from Pulse input

The direct experimental determination of $E(t)$ requires a sharp pulse of tracer to be injected into the system. Essentially, an amount of tracer N_0 is required to be injected into the vessel's inlet at a single instant of time at $t = 0$. Figure 3.8 shows typical concentration-time curves at the inlets and outlet of an arbitrary reactor. (Hayes and Mmbaga 2013)

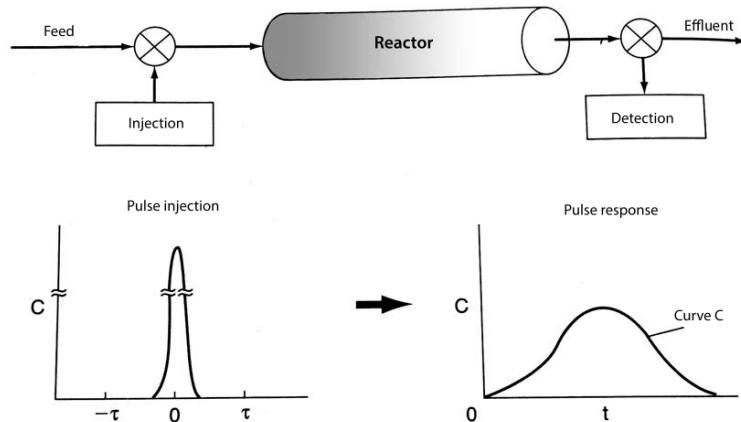


Figure 3.8: Typical pulse impulse curves for RTD measurement

Mathematically, the ideal shape of the injected pulse is described by a Dirac delta function. In practice, the tracer should be injected in as short an elapsed time as is experimentally possible to achieve.

The tracer's concentration in the effluent is then measured as a function time, and the density function can be evaluated using the following analysis. The fraction of tracer molecules that leave the system over some time interval dt is

$$\frac{dN}{N_0} = E(t) dt \quad (3.23)$$

where dN represents the number of tracer molecules that leaves the system over the time interval dt , and N_0 is the total number of tracer molecules injected.

The number of molecules can be expressed in terms of the concentration and the volumetric flow rate,

$$dN = v c(t) dt \quad (3.24)$$

where $C(t)$ is the concentration of tracer in the effluent streams as a function of time.

Thus, the total number of molecules initially injected can also be calculated from the effluent profile by integration over a long time:

$$N_0 = \int_0^\infty v C(t) dt \equiv \frac{N_0}{v} = \int_0^\infty C(t) dt \quad (3.25)$$

Combining Eqs (3.24) and (3.25) into Eq. (3.23) for a constant-density system,

$$\mathbf{E}(t) = \frac{c(t)}{\int_0^\infty c(t) dt} \approx \frac{c_i(t)}{\sum_i c_i(t) \Delta t_i} \quad (3.26)$$

Once $\mathbf{E}(t)$ is determined, the mean residence time, \bar{t} , and the variance of distribution, σ_t^2 , may be calculated based on Eqs. (3.9) and (3.21)

$$\begin{aligned} \bar{t} &= \int_0^\infty t \mathbf{E}(t) dt \approx \sum_i t_i E_i(t) \Delta t_i \\ \sigma_t^2 &= \left(\int_0^\infty t^2 \mathbf{E}(t) dt \right) - \bar{t}^2 \approx \left[\sum_i t_i^2 E_i(t) \Delta t_i \right] - \bar{t}^2 \end{aligned}$$

Advantages of using a pulse input include:

1. requiring only a small amount of tracer.
2. involving usually only a tiny impact on process operation.

Disadvantages include:

1. difficulty in achieving a perfect pulse.
2. difficulty in achieving accurate material balance on traces using equation (3.25)

Obtaining $\mathbf{E}(t)$, \bar{t} and σ_t^2 from experimental tracer data involves determining areas under curves defined continuously or by discrete data. Two simple ways in which discrete data may be treated to obtain the required areas:

1. use of data in histogram form, and
2. use of the trapezoid rule.

In the histogram method, Figure 3.9, the area under the response curve is

$$\begin{aligned} \text{area} &= \sum_{i=1}^{n_C} c_i(t) \Delta t_i \\ \Delta t_i &= \frac{t_{i+1} - t_{i-1}}{2} \end{aligned}$$

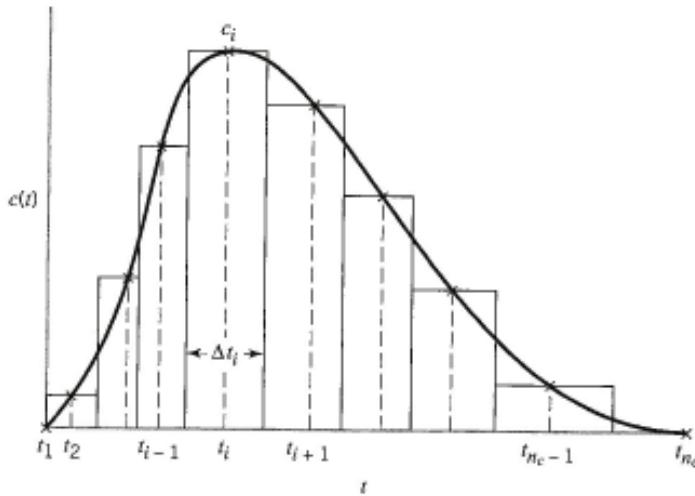


Figure 3.9: Basis for histogram method of area determination. [@missen1999]

In the use of the trapezoid rule, Figure 3.10, the area under the response curve is given by

$$\text{area} = \sum_{i=1}^{n_c-1} c_i(t)_{\text{av}} \Delta t_i = \sum_{i=1}^{n_c-1} \left(\frac{c_i + c_{i+1}}{2} \right) (t_{i+1} - t_i)$$

The only way to determine which numerical method provides the best answer is to predict the experimental concentrations using the calculated parameters in an appropriate mixing model.

Exercise 3.1 (Calculations of RTD and distribution functions curves from pulse impulse method). Consider a vessel through which a fluid is flowing. The RTD function is determined utilizing a pulse injection of the tracer in the inlet stream, and its outlet concentration is monitored as a function of time. The output concentration in mol/L measured as a function of time in seconds is

| t (s) | C (mol/L) |
|-------|-----------|-------|-----------|-------|-----------|-------|-----------|
| 0.0 | 0 | 225 | 7.4 | 275 | 8.2 | 375 | 0.5 |
| 150 | 0 | 240 | 9.4 | 300 | 5.0 | 400 | 0.2 |
| 175 | 1 | 250 | 9.7 | 325 | 2.5 | 450 | 0.0 |
| 200 | 3 | 260 | 9.4 | 350 | 1.2 | 500 | 0.0 |

Determine:

1. Plot of tracer concentration vs time.
2. RTD curve, $E(t)$.
3. Cumulative distribution function plot, $F(t)$.

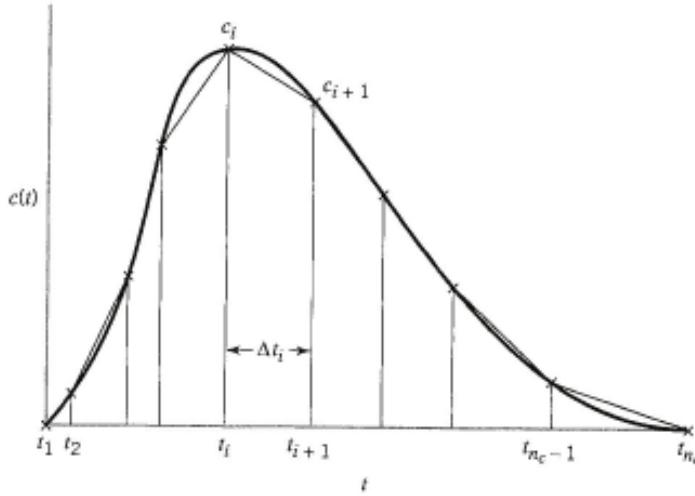


Figure 3.10: Basis for histogram method of area determination. [©missen1999]

4. Washout function plot, $\mathbf{W}(t)$.
5. Mean residence time.
6. Fraction of material leaving the reactor that has spent between 230 and 270 seconds.

Solution

The solution in a Python script is available at link.

- (a) By plotting C as a function of time, the curve shown in Figure 3.11 is obtained. From the $C(t)$ curve is possible to calculate the RTD, according to Eq. (3.26), for a pulse impulse test.

We just need to divide each point of $c(t)$ by the integral

$$\int_0^\infty c(t) dt$$

which is just the area under the $C(t)$ curve.

Figure 3.12 shows the obtained RTD curve

- (b) The cumulative distribution curve, $F(t)$, and washout curve, $W(t)$, were obtained from $E(t)$ curve, and Figure 3.13 shows the results obtained.
- (c) The mean residence time is obtained from (3.9), thus $\bar{t} = 261.615$ seconds.
- (d) To calculate the fraction of material leaving the reactor that has resided in the reactor between 230 and 270 seconds, it is necessary to solve

$$\int_{230}^{270} \mathbf{E}(t) dt$$

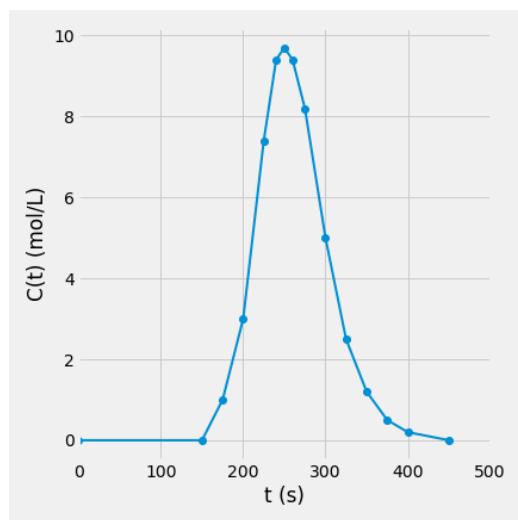


Figure 3.11: Trace concentration curve

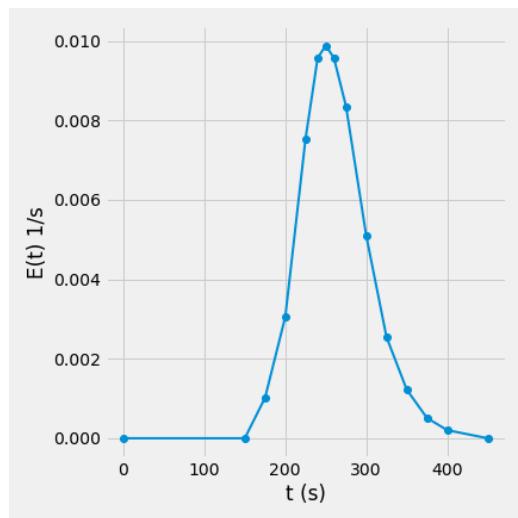
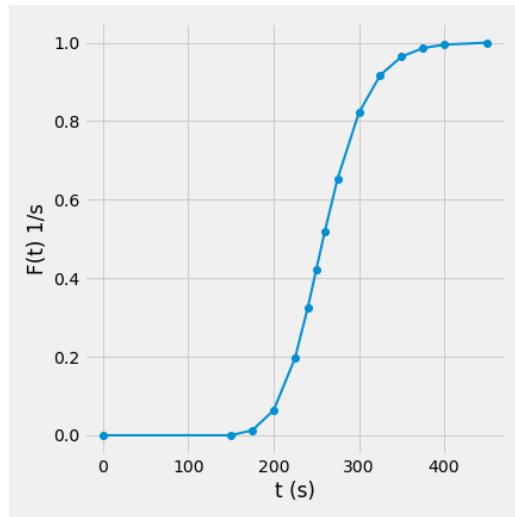
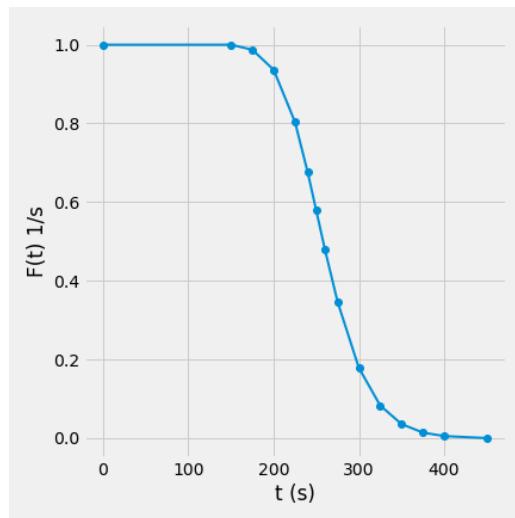


Figure 3.12: RTD curve

Figure 3.13: Cumulative curve, $F(t)$ Figure 3.14: Washout curve, $W(t)$

However, times 230 and 270 seconds are not presented in the original data. It is necessary to append our data by interpolating $E(t)$ points to correspond times 230 and 270 seconds. Then, the data obtained are plotted in Figure 3.15. The shaded area represents the fraction of material leaving the reactor that resided in the reactor between 230 and 270 seconds.

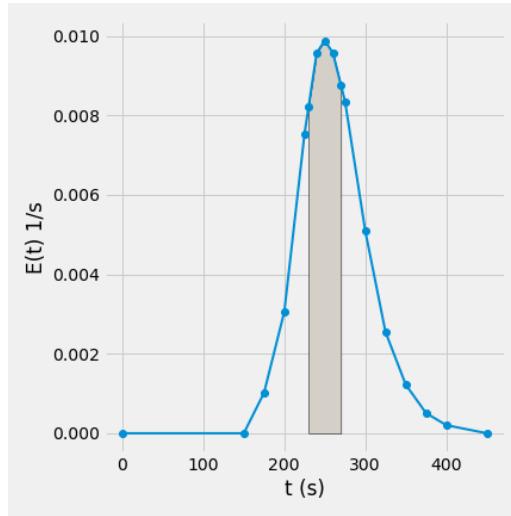


Figure 3.15: Analysis of curve $E(t)$

Then, we learned between 230 and 270 seconds, the 37.53% of the material left into the reactor.

3.6 Determination of $E(t)$ from Step Change

In this case, a step input tracer is a step increase from one steady-state value to another. Usually, as illustrated in Figure 3.16, the step increase is from a zero value, and for a $t \rightarrow \infty$, the final concentration of the tracer will be equal to its inlet concentration. (Hayes and Mmbaga 2013)

For a step change, a material-balance criterion is that the steady-state inlet and outlet tracer concentrations must be equal, both before and after the step change. Then, it may be concluded that the system's response, as shown in Fig. 3.16, is linear to the tracer, and there is no loss of tracer because of reaction or adsorption. (Missen, Mims, and Bradley 1999)

In comparison with pulse input, which is related to $\mathbf{E}(t)$, the response to a step change is related to $\mathbf{F}(t)$. The advantages of this experimental method are:

1. A step change is usually easier to achieve.
2. A material balance is usually easier to achieve.

While disadvantages include:

1. Continuous delivery requires a greater amount of tracer.
2. It may have a significant impact on process operation.

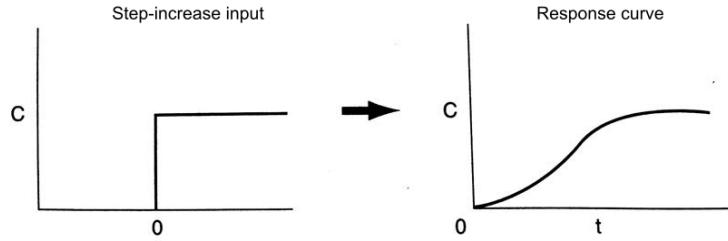


Figure 3.16: Typical step change curves for RTD measurement. [@fogler2008]

Now, considering a constant rate of tracer addition to a feed that is initiated at time $t = 0$, the tracer concentration for a system with a constant volumetric flow rate must achieve following conditions:

$$C_0(t) = \begin{cases} 0 & t < 0 \\ (C_0) \text{ constant} & t \geq 0 \end{cases}$$

Thus, in the case of a step increase from an initial value, $C(0)$, to some final value, $c(\infty)$, the outlet concentration as function of time gives the cumulative distribution function, $\mathbf{F}(t)$, directly from the following equation:

$$\mathbf{F}(t) = \frac{c(t) - c(0)}{C(\infty) - c(0)} \quad (3.27)$$

If the inlet tracer concentration has a step decrease from initial value, $C(0)$, to a final value, $C(\infty)$, then the effluent concentration can be used to calculate the washout function, $\mathbf{W}(t)$:

$$\mathbf{W}(t) = \frac{c(t) - c(\infty)}{c(0) - c(\infty)} \quad (3.28)$$

A tracer study may use a step increase followed later by a step decrease; the transient responses in the two cases are the checked consistency. When considered separately, the washout technique has advantages: less tracer is required, and it avoids having to maintain a steady-state value of C_o for a lengthy period. (Missen, Mims, and Bradley 1999)

The normalized response data may be converted to $\mathbf{E}(t)$, since

$$\mathbf{E}(t) = \frac{d\mathbf{F}(t)}{dt}$$

Or could be estimated depending on the differencing technique used. From backward differencing:

$$\mathbf{E}(t) = \frac{d\mathbf{F}(t)}{dt} \approx \frac{F_{i+1} - F_i}{t_{i+1} - t_i}; \quad i = 1, 2, \dots n-1$$

and central differencing:

$$\mathbf{E}(t) = \frac{d\mathbf{F}(t)}{dt} \approx \frac{F_{i+1} - F_{i-1}}{t_{i+1} - t_{i-1}}; \quad i = 2, 3, \dots n-2$$

Finally, based on the normalized condition of \mathbf{E} curve. The mean residence time could be approximated to:

$$\bar{t} \approx \sum t_i \mathbf{E}_i \Delta t$$

and the variance σ^2

$$\sigma_t^2 \approx \sum t_i^2 \mathbf{E}_i \Delta t - \bar{t}^2$$

Exercise 3.2 (Calculations of RTD and distribution functions curves from step change method). The inlet concentration of helium (tracer A) was step-increased from 1.0 to 2.0 mmol/L to determine the mixing pattern in a fluidized-bed reactor. The response data were as follows:

| t (min) | C (mmol/L) | t (min) | C (mmol/L) |
|---------|------------|---------|------------|
| 0.0 | 1.000 | 30.0 | 1.410 |
| 5.0 | 1.005 | 45.0 | 1.610 |
| 10.0 | 1.020 | 60.0 | 1.770 |
| 15.0 | 1.060 | 90.0 | 1.920 |
| 20.0 | 1.200 | 120.0 | 1.960 |

Determine $F(t)$, $E(t)$, σ^2 for flow through the vessel, and calculating \bar{t}

Solution

The solution in a Python script is available at link.

The figure 3.17 shows results obtained for $F(t)$

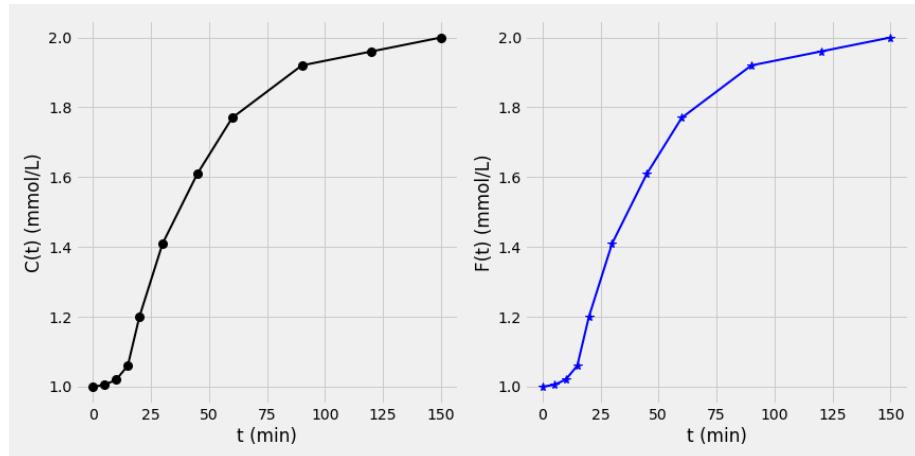
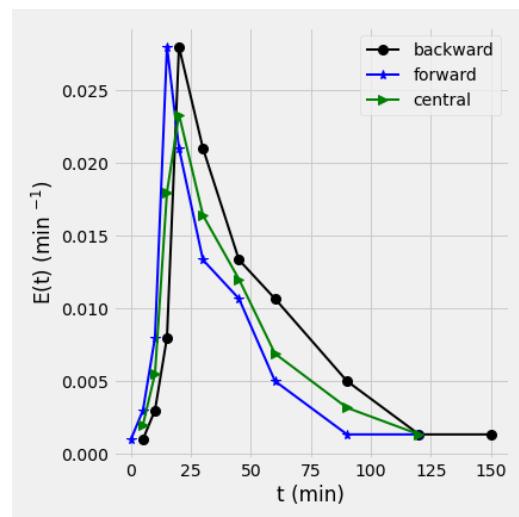
The RTD was calculated by

$$\mathbf{E}(t) = \frac{d\mathbf{F}(t)}{dt}$$

Which was estimated using backward differencing for $F(t)$. The figure 3.18 shows results obtained for $E(t)$

The mean residence time was estimated by trapezoid rule.

$$\bar{t} = \sum_{i=1}^{n_c-1} [t_i E_i(t)]_{av} \Delta t_i$$

Figure 3.17: Left: Trace concentration curve. Right: $F(t)$ curveFigure 3.18: $E(t)$ curve

From this,

$$\bar{t} = 57.537 \text{ min}$$

Finally, the variance was obtained by,

$$\sigma^2 = \left\{ \sum_{i=1}^{n_c-1} [t_i^2 E_i(t)]_{av} \Delta t_i \right\} - \bar{t}^2$$

From this,

$$\sigma^2 = 530.249 \text{ min}^2$$

Chapter 4

Applications for RTD functions

As it was said before, RTD provides a measure of macroscopic mixing; therefore, it could be helpful as a tool for:

1. detecting and characterizing flow behavior.
2. estimating of values of parameters for nonideal flow models.
3. assessment of the performance of a vessel as a reactor.

4.1 RTD functions for ideal reactors

$\mathbf{F}(t)$ fits the behavior either when N particles are injected individually at different times to a steady-state reactor or if they are entered all at once to the reactor as $\mathbf{F}(t)$ represents the volume fraction of the fluid leaving the reactor, which resided in the system over a time of t or less.

Plug Flow Reactor (PFR)

In this reactor, there is not back mixing. Hence, every fluid element has the same mean residence time \bar{t} (or τ). This corresponding to a pulse tracer entering the reactor at time $t = 0$ during an infinitesimally short time and does not mix with fluid elements running ahead or behind it within the reactor.

The flow pattern in PFR could be represented in terms of the Dirac delta function ($\delta(t - \bar{t})$). The Dirac delta function is a generalized function, on the real number line that is zero everywhere except at zero, where it is infinite:

$$\delta(t - \bar{t}) = \begin{cases} \infty & t = \bar{t} \\ 0 & t \neq \bar{t} \end{cases}$$

Therefore, the normalized RTD function is written down in terms of Dirac “delta-function”

$$\mathbf{E}(t) = \delta(t - \bar{t}) = \begin{cases} \infty & \text{when } t = \bar{t} \\ 0 & \text{when } t \neq \bar{t} \end{cases} \quad (4.1)$$

The integral of Dirac δ -function is given as:

$$\int_a^b \delta(t - \bar{t}) f(t) dt = \begin{cases} f(\bar{t}) & \text{when } a < \bar{t} < b \\ 0 & \text{when } a > \bar{t} > b \end{cases}$$

where a and b are any constant.

Therefore,

$$\mathbf{F}(t) = \begin{cases} 0 & \text{when } 0 < t < \bar{t} \\ 1 & \text{when } t \geq \bar{t} \end{cases}$$

 information The moments of the normalized distribution all equal one, while the central moments equal zero.

Continuous Stirred Tank Reactor (CSTR)

An ideal CSTR implies that as soon as a fluid element (or pulse of tracer) is injected into the reactor, it distributes itself uniformly throughout the reaction zone. In “ideal” CSTRs, the exit stream is assumed to have the same composition as the reaction mixture within the reaction zone.

It follows that the exit stream will have the highest possible concentration of material from the tagged fluid element (or pulse tracer) at the outset of the experiment (i.e., $t = 0$). After that, the tracer concentration in the main reactor would be diluted with the inlet stream, and the concentration of tracer in the exit stream would be expected to decay to zero gradually.

The RTD for a CSTR can be easily analyzed using a pulse injection. Assume, in the first instance, that the inlet stream to the vessel contains a concentration of the tracer equals to $C_{TR,0}$, given by

$$C_{TR,0} = \frac{N_{TR}}{V_R} \quad (4.2)$$

The decay of tracer concentration in the reactor is an unsteady state process given by,

$$-v C_{TR} = V_R \frac{dC_{TR}}{dt} \quad (4.3)$$

For a constant-density fluid, Eq. (4.3) could be rewritten as

$$-\frac{v}{V_R} dt = -\frac{dt}{\bar{t}} = \frac{dC_{TR}}{C_{TR}} \quad (4.4)$$

Integrating Eq. (4.4) yields to:

$$C_{TR}(t) = C_{TR,0} \exp\left(-\frac{t}{\bar{t}}\right) \quad (4.5)$$

Now, substituting Eq. (4.5) into Eq. (3.28)

$$\mathbf{W}(t) = \frac{C_{TR}(t) - C_{TR}(\infty)}{C_{TR,0} - C_{TR}(\infty)} = \frac{C_{TR,0} \exp\left(-\frac{t}{\bar{t}}\right)}{C_{TR,0}} = \exp\left(-\frac{t}{\bar{t}}\right) \quad (4.6)$$

And, the RTD function is obtained by differentiation:

$$\mathbf{E}(t) = -\frac{d \mathbf{W}(t)}{dt} = \frac{1}{\bar{t}} \exp\left(-\frac{t}{\bar{t}}\right) \equiv \frac{C(t)}{\int_0^\infty C(t) dt} \quad (4.7)$$

The RTD decays exponentially with time. However, the area under the curve is always equal to unity because of the normalization. The typical residence time distribution for a CSTR is presented in Figure 4.1

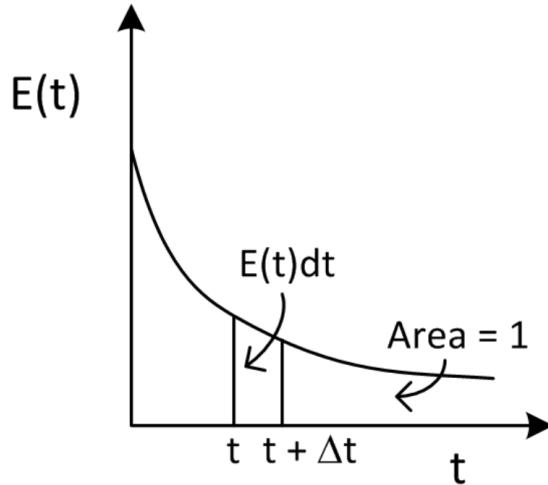


Figure 4.1: The residence time distribution $E(t)$ in a CSTR and the time interval from t to $t+dt$

Other tracer experiments can be used to characterize flow patterns for non-ideal reactors. However, the input of a pulse or a step-change is commonly used in practice. Figures 4.2 and 4.3 summarize the exit concentration curves and the shapes of the $\mathbf{E}(t)$ curves for a step change and input pulse of tracer, respectively.

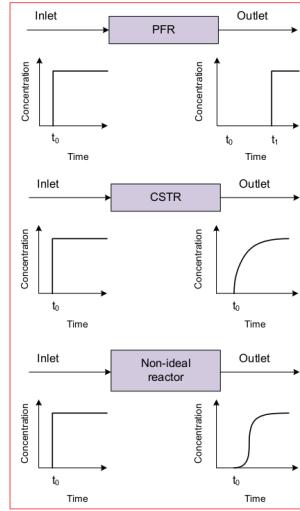


Figure 4.2: Response of tracer species during a step change experiment

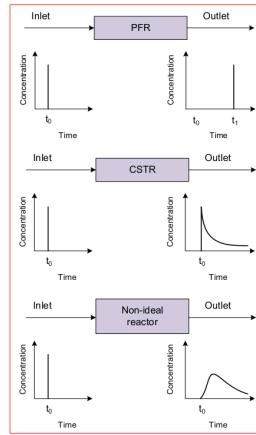


Figure 4.3: Response of tracer species during an input impulse experiment

4.2 RTD as diagnostic tool for characterizing flow behavior

The RTD curve can be used as a diagnostic method to determine the characteristics of reactor flow patterns. The methods of interpretation fall into two main categories:

1. processes with a relatively small degree of mixing, and
2. processes with significant deviations from ideal flow patterns, namely, dead space, bypassing, and general nonuniform regions.

Since these maldistributions can cause unpredictable conversion in reactors, they are usually detrimental to reactor operation.

Relatively Small Degree of Mixing

The age-distribution functions for flow patterns with a relatively small degree of mixing will have the general shapes shown in Figure 4.4

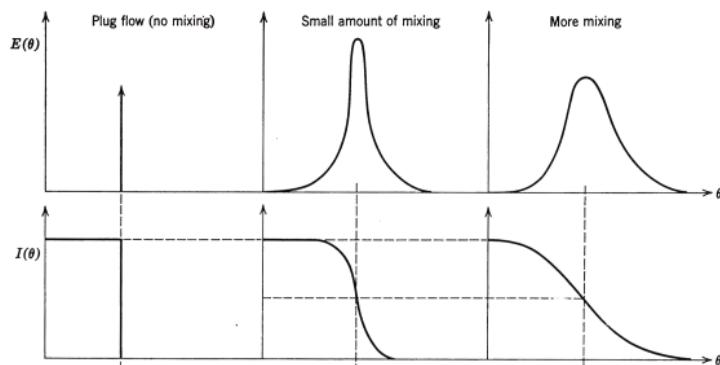


Figure 4.4: Effect of some features of nonideal flow on RTD. [@himmelblau1968]

As is shown, the peak of the $\mathbf{E}(\theta)$ curve will almost be at the mean holding time $\theta = \bar{\theta}/\bar{t} = 1$, and $\mathbf{I}(\theta)$ curve will have a value of about 0.5 at $\theta = 1$. None of the curves will have excessively long tails and, in particular, the $\mathbf{E}(\theta)$ will be almost symmetrical.

These features lead to the use of the type of description based on Gaussian curves, namely, the mean and the variance.

$$\text{mean} = \mu_1 = \int_0^{\infty} \theta \mathbf{E}(\theta) d\theta = 1$$

$$\text{variance} = \sigma^2 = \int_0^{\infty} (\theta - \mu_1)^2 \mathbf{E}(\theta) d\theta$$

Detection of Dead Space

A process vessel may exhibit a region where fluid elements are retained for times of an order of magnitudes more significant than the mean residence time of the total fluid, what is called **dead space**. The existence of dead space is most easily verified from the characteristics of the $E(\theta)$ curve as shown in Figure 4.5. The $E(\theta)$ will have a very long tail indicating that fluid is held in the dead space.

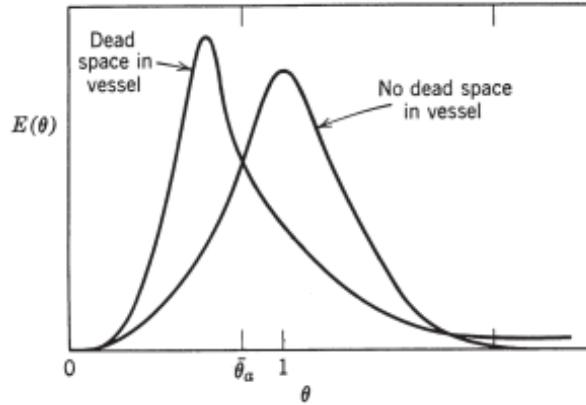


Figure 4.5: Identification of the existence of dead space in a process vessel. [@himmelblau1968]

The *true* mean residence time will be equal to the vessel volume divided by the flow rate $\bar{t} = V/v$. However, the experimental data for times longer than θ equal to 2 or 3 times mean residence time are seldom of sufficient accuracy to use in calculations. Thus, the calculated apparent mean residence time would be

$$\bar{\theta}_a = \int_0^\theta \theta' E(\theta') d\theta', \quad \theta \approx 2 \text{ or } 3$$

whereas the true mean would be

$$\begin{aligned} \theta &= \int_0^\infty \theta E(\theta) d\theta = \int_0^\theta \theta' E(\theta') d\theta' + \int_\theta^\infty \theta' E(\theta') d\theta' = 1 \\ &= \bar{\theta}_a + \int_\theta^\infty \theta' E(\theta') d\theta' = 1 \end{aligned}$$

In presence of dead space, $\bar{\theta}_a < 1$ or $\bar{t}_a < \bar{t}$. The apparent mean gives a measure of the dead volumen of the vessel:

$$\bar{t}_a = \frac{V_{\text{active}}}{v_{\text{active}}} = \frac{V - V_{\text{dead}}}{v_{\text{active}}} = \bar{t} \bar{\theta}_a$$

This equation can be rewritten as

$$\begin{aligned}\frac{V_{\text{dead}}}{V} &= \frac{v_{\text{active}}}{V} \left(\frac{V}{v_{\text{active}}} - \bar{\theta}_a \right) \\ \frac{V_{\text{dead}}}{V} &= 1 - \bar{\theta}_a \bar{t} \frac{v_{\text{active}}}{V} \\ \frac{V_{\text{dead}}}{V} &= 1 - \bar{\theta}_a \left(\frac{v_{\text{active}}}{v} \right) \approx 1 - \bar{\theta}_a\end{aligned}$$

One problem with using these relations is that they assume the true mean holding time, \bar{t} , is known. Since it cannot be found from the trace curve (due to the inaccurate tail), it must be known independently and challenging to obtain.

Detection of Bypassing

If a portion of fluid spends one-tenth of the overall fluid's mean residence time, this fluid can be said to bypass the vessel for all practical purposes. The $E(\theta)$ curve would then appear as in Figure 4.6.

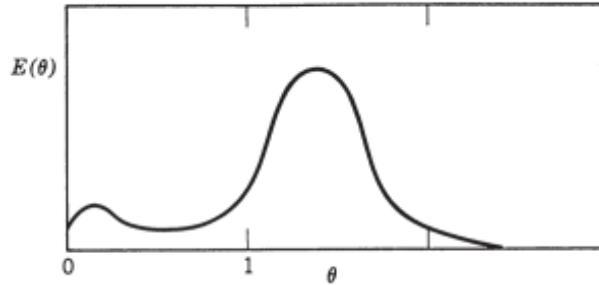


Figure 4.6: Identification of the existence of bypassing in a process vessel. [©himmelblau1968]

If there is a large amount of dead space or bypassing, the distinction between the two is not clear-cut but depends on which part of the fluid is considered the “major” part, a somewhat arbitrary assignment.

However, $E(\theta)$ can be used to detect dead space or bypassing (as discussed above). If the true mean holding time is not known, this curve cannot be used to determine dead space. Instead, the $I(\theta)$ curve must be used because it always has the same shape as regards the existence of maxima no matter what the time scale. Therefore, the most significant utility of the intensity function is to determine dead space from experimental data, especially if the true mean holding time is unknown.

Figure 4.7 summarizes the typical shapes of the $E(\theta)$ curve of (a) stagnation, (b) dispersion and (c) channeling or excessive bypassing.

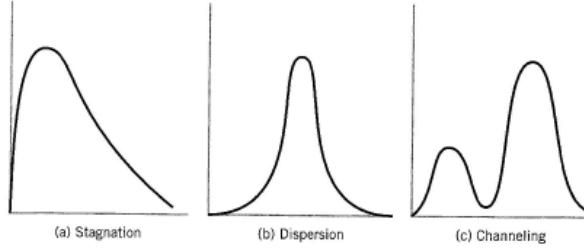


Figure 4.7: Effect of some features of nonideal flow on RTD. [@missen1999]

If large amounts of dead space of bypassing exist, it may not be worthwhile to try to construct a detailed mathematical model because the unit is sure to give poor performance. Thus, some modifications might be called for to eliminate the severe mixing problems.

In order to provide a better picture of the behavior of the distribution functions, a simple mathematical model will be considered that includes the possibility of having well-defined dead space and bypassing. The model consists of two parallel streams, each with a given number of perfectly mixed tanks in series as shown in Figure 4.8

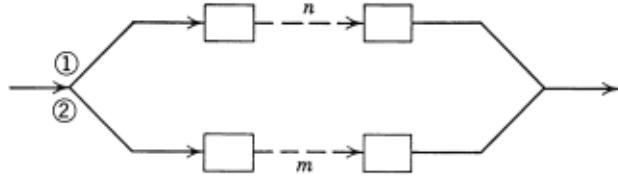


Figure 4.8: Scheme of the mathematical representation. [@himmelblau1968]

The RTD for this model with j stirred tanks in series is

$$\mathbf{E}(t) = \frac{j^j}{(j-1)!} \frac{t^{j-1}}{\bar{t}} \exp\left(-\frac{jt}{\bar{t}}\right)$$

where \bar{t} is the mean residence time. If the equation is used for each branch of the model and weighted with respect to the amount of flow in the branch, the RTD for the entire model is:

$$E(t) = f \left(\frac{n^n}{(n-1)!} \frac{t^{n-1}}{\bar{t}_1} \exp\left(-\frac{n t}{\bar{t}_1}\right) \right) + (1-f) \left(\frac{m^m}{(m-1)!} \frac{t^{m-1}}{\bar{t}_2} \exp\left(-\frac{m t}{\bar{t}_2}\right) \right)$$

where f represents the fraction of flow to branch 1. The mean residence time is

$$\bar{t} = f \bar{t}_1 + (1-f) \bar{t}_2$$

Dimensionless variables based on the total mean residence time, \bar{t} can now be defined:

$$\theta = \frac{t}{\bar{t}} \quad \alpha = \frac{\bar{t}_2}{\bar{t}_1} \quad \beta = f + (1-f)\alpha$$

Three situations were considered:

1. Fifteen tanks in each branch correspond to a relatively small amount of mixing in the branch.
2. Two tanks in each branch correspond to a large amount of mixing in the branch.
3. Four tanks in each branch correspond to a moderate amount of mixing in the branch.

Scenario 1. is shown in Figure 4.9. The rest of scenarios is available clicking on the next link

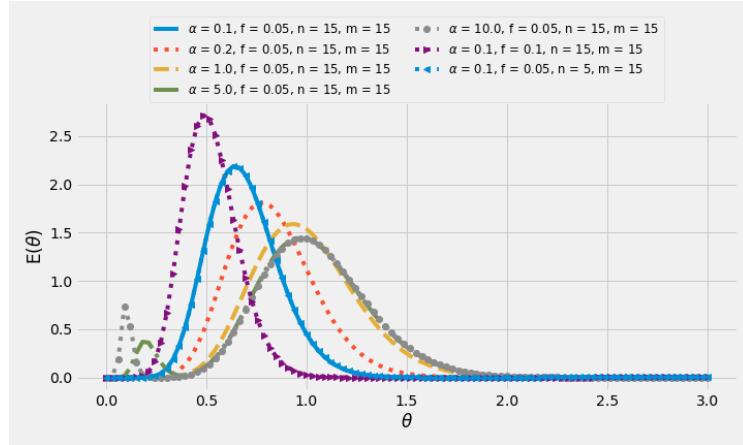


Figure 4.9: RTD curves for parallel stirred-tanks models.

Chapter 5

Models for nonideal flow

The information provided by RTD functions is essential to know if a reactor has dead zones or bypassing. These situations affect the reactor performance. Thus, the main target is answering the question “How much bypassing or dead volume is acceptable?”.

For answering, the chemical engineer needs to calculate the performance of the reactor. Furthermore, to do so, two types of information are required: the flow patterns and the kinetic model.

$$\left\{ \begin{array}{l} \text{Flow pattern} \\ \text{information} \end{array} \right\} + \left\{ \begin{array}{l} \text{Rate} \\ \text{information} \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} \text{Performance} \\ \text{of reactor} \end{array} \right\}$$

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The RTD curves found from tracer studies are only partial information on the details of the flow

patterns because all that is known is the length of time-specific fractions of the fluid stay in the vessel (macromixing), but neither what of these fractions do while in the vessel nor in what geometric locations they reside, that is, information on micromixing.

As a result, several mathematical models of reactor performance have been developed to estimate the conversion levels in a nonideal reactor. (C. Jr. Hill 1977)

The micromixing behavior has two extremes views:

1. Complete segregation: any fluid element is isolated from all other fluid elements and retains its identity throughout the entire vessel. No micromixing occurs, but macromixing may occur.
2. Complete dispersion: fluid elements interact and mix thoroughly at the microscopic level.

Besides the degree of segregation of fluid elements, another aspect of mixing is the relative time in passage through a vessel at which fluid element mix ("earliness" of mixing). (Missen, Mims, and Bradley 1999)

In general, a mathematical model for nonideal flow in a vessel provides a characterization of mixing and flow behavior. Although it may appear to be an independent alternative to the experimental measurement of RTD, the latter may be required to determine the parameter(s) of the model.

For that reason, these mathematical models can be classified in function of the number of adjustable parameters. (Fogler 2008)

1. Zero adjustable parameters
 - segregation model
 - maximum mixedness model
2. One parameter model
 - tanks-in-series model
 - dispersion model
3. Two adjustable parameters
 - actual reactor modeled as combinations of ideal reactors

These parameters are correlated as functions of fluid and flow properties, reactor configurations, along with other vital features, and can be used in design calculations.

Generally speaking, the more adjustable parameters used in a model, the better the correlation between predicted and observed RTD would be. These adjustable parameters are often related to RTD moments and are usually expressed in terms of dimensionless moments about the mean.

The usual approach is developing a model flow system with the same RTD as the existing system. Provided that the conservation equations can be written for this model system, the performance of the actual vessel can be predicted.

5.1 Zero adjustable parameters

Segregational or macrofluid model

This model represents the micromixing condition of complete segregation (no mixing) of fluid elements, which means that fluid flows through a vessel with no mixing between adjacent fluid elements. The feed enters the reactor as little *packets* of fluid. Each packet retains its identity as they pass

through the vessel; there is no mass exchange between individual packets. However, packets can mix each other in the reactor. Thus those that enter at some time, t , will not all leave at the same time.

Each packet can be treated as a small ideal batch reactor. A reaction (or reactions) takes place as the tiny packets move through the vessel. The composition of each packet changes while it is flowing through the vessel. However, its final conversion will depend on how long the packet has spent in the vessel. (Roberts 2009).

After leaving the reactor, all fluid packets are mixed on a molecular level, and the average composition is measured. This situation is represented in Figure 5.1. (Roberts 2009)

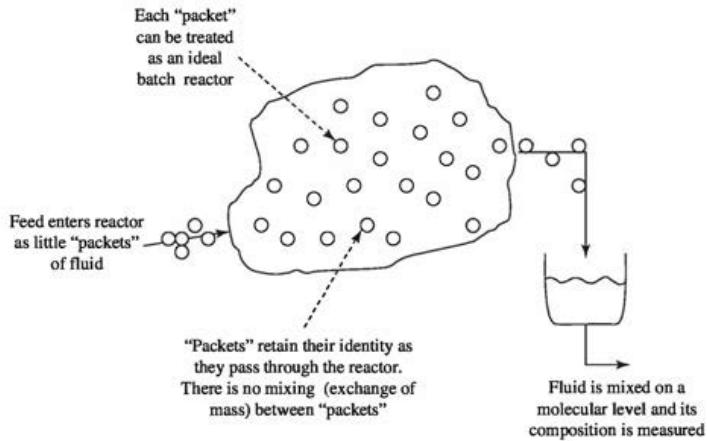


Figure 5.1: Segregational model scheme. [@roberts2009]

When the packets are admitted to a CSTR, we can envisage two scenarios that involve perfect mixing: one with perfect mixing at the macroscale and the other with perfect mixing at the microscale, as is shown in Figure 5.2

The conversion in a segregated tank reactor can be calculated using the ideal batch reactor equation design and the RTD curve. Each batch reactor has its conversion, which depends on its time in the tank. While the RTD gives information about the mean residence time.

The initial concentration of reactants in the packet is the same as the inlet concentration of the reactor. While each fluid element (assuming constant density) behaves as a batch reactor, the total reactor conversion is the average conversion of all the fluid elements at the outlet conditions. That is:

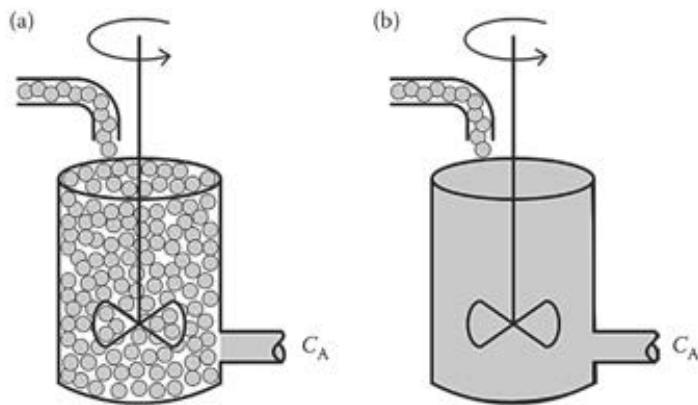


Figure 5.2: Different levels of mixing in a CSTR: (a) Segregational model, (b) Ideal CSTR model.
[@hayes2013]

$$\left[\begin{array}{l} \text{mean concentration} \\ \text{of reactant in} \\ \text{reactor outlet} \end{array} \right] = \sum_{\text{all elements} \\ \text{of exit stream}} \left[\begin{array}{l} \text{concentration of} \\ \text{reactant remaining in} \\ \text{a fluid elements} \\ \text{between } t \text{ and } t + dt \end{array} \right] \left[\begin{array}{l} \text{fraction of exit stream} \\ \text{that consists of fluid} \\ \text{elements of age} \\ \text{between } t \text{ and } t + dt \end{array} \right]$$

where the summation is over all fluid elements in the reactor exit stream. This equation can be written analytically as:

$$\bar{C}_A = \int_0^\infty C_A(\bar{t}) \mathbf{E}(t) d\bar{t} \quad (5.1)$$

Where $C_A(t)$ depends on the residence time of the element.

$$\frac{d C_A(t)}{dt} = -r_A = k C_A(t)$$

The equation (5.1) is rewritten as

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A(\bar{t})}{C_{A0}} \right) \mathbf{E}(t) dt \approx \sum_{\text{all age intervals}} \left(\frac{C_A}{C_{A0}} \right) \mathbf{E}(t) \Delta t \quad (5.2)$$

or in terms of conversions

$$\bar{X}_A = \int_0^\infty (X_A(t))_{\text{element}} \mathbf{E}(t) dt \quad (5.3)$$

Introducing the $\mathbf{E}(t)$ curve for CSTR, Equation (5.1) becomes,

$$\frac{\bar{C}_A}{C_{A0}} = \frac{1}{\bar{t}} \int_0^\infty e^{-kt} e^{-t/\bar{t}} dt = \frac{1}{1+k\bar{t}}$$

Now, introducing the $\mathbf{E}(t)$ curve for a PFR,

$$\frac{\bar{C}_A}{C_{A0}} = \frac{1}{\bar{t}} \int_0^\infty e^{-kt} \delta(t - \bar{t}) dt = e^{-k\bar{t}}$$

The methodology described above can be used without any flow pattern models at all, in that experimental concentration as a function of residence time and the measured RTD can be directly numerically integrated to predict the conversion in the flow reactor.



information The segregational or macrofluid model is essential because it permits reactor behavior to be estimated directly from RTD, $\mathbf{E}(t)$, and the reaction kinetics. No other information is necessary.

However, it is only strictly applicable to isothermal, single-phase systems. Extensions to more complicated behaviors are not straightforward. Therefore, other techniques are required for more general predictive and design purposes.

When we dealt with ideal reactors in series, we learned that:

1. If the order of the reaction is greater than 1 ($n > 1$), we must keep the reactant concentration as high as possible for as long as possible to maximize fractional conversion. In other words, we must avoid mixing as long as possible. For example, the optimum arrangement will be a PFR first, then a small CSTR, and a large CSTR.
2. If the order of the reaction is less than 1 ($n < 1$), we must drop the reactant concentration as low as possible, which means mix as soon as possible.
3. Finally, if the order of the reaction is equal to 1, the order of reactors will not affect the final conversion.

The macrofluid model represents the latest possible mixing for a given RTD because there is no mixing between fluid elements until the reaction is over. For a reaction with an effective order greater than 1, the macrofluid model represents the *best* possible situation. It provides an upper bound on conversion. (Roberts 2009)

Conversely, for a reaction with a practical order of less than 1, the macrofluid model represents the *worst* possible situation. It provides a lower bound on conversion. In summary,

| Reaction order | Segregational model provide |
|----------------|-----------------------------|
| > 1 | Upper bound of conversion |
| $= 1$ | Exact result |
| < 1 | Lower bound of conversion |

Exercise 5.1 (Calculation of conversion based on RTD). Calculate conversion for a reaction



for a given RTD and segregation model.

| t (min) | c (g/m ³) | t (min) | c (g/m ³) |
|---------|-----------------------|---------|-----------------------|
| 1 | 1 | 7 | 4 |
| 2 | 3 | 8 | 3 |
| 3 | 8 | 9 | 2.2 |
| 4 | 10 | 10 | 1.5 |
| 5 | 8 | 12 | 0.6 |
| 6 | 6 | 14 | 0 |

$$r_A = -k C_A; \quad k = 0.1 \text{ min}^{-1}$$

Solution

The solution in a Python script is available at link.

From data problem, the RTD is shown on the left side of Figure 5.3

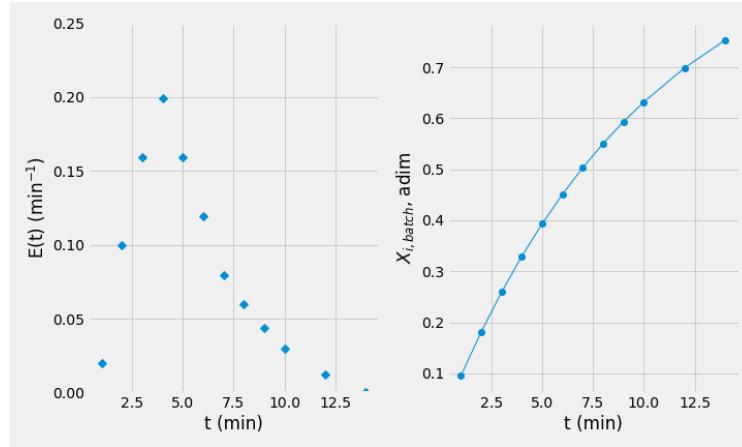


Figure 5.3: Graphical solution for the problem. Left: $E(t)$ curve, Right: Fractional conversion curve.

From kinetic data, the fractional conversion for each batch reactor is

$$X_{i,\text{batch}}(t) = 1 - \exp(-k t)$$

The profile of conversion is plotted right size of Figure 5.3

Finally, the mean conversion is estimated by Eq. (5.3)

$$\bar{X}_i = \int_0^{\infty} [1 - \exp(-k t)] E(t) dt = 0.3871$$

Maximum Mixedness Model (MMM)

The MMM for a reactor represents the micromixing condition of complete dispersion, where fluid elements are entirely mixed at the molecular level, which is the opposite extreme of the segregational model.

The MMM considers that the fluid packages of different residence times are mixed as early as possible in the flow system consistent with the observed RTD. For this reason, this model is also called ***Early mixing model***.

This behavior can be modeled using a PFR with inlet side streams, as shown in Figure 5.4. The feed flow rate is distributed among the side streams in such a way as to match the required RTD function. It can be seen that in this arrangement, fluid entering the reactor in a given side stream, which has a residence time of zero, will mix radially with the fluid already present in the reactor completely.

The conversion in a MM model can be calculated by performing a mole balance that considers all side streams. First, it is necessary to define an alternative variable, λ , defined as the residence time

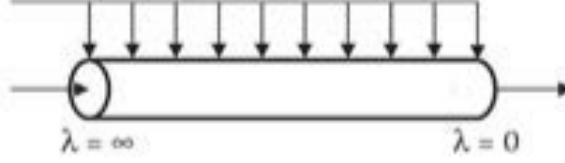


Figure 5.4: Scheme for modeling of maximum mixedness model. [@hayes2013]

remaining for an entering particle. All particles at a given λ have the same time left in the reactor but may have different ages.

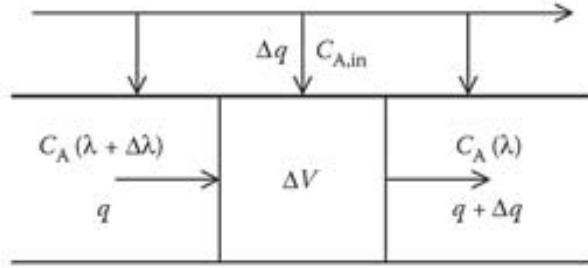


Figure 5.5: Control volume used to develop the mole balance for the maximum mixedness. [@hayes2013]

The concentration at the reactor outlet can be derived from mole balance equation. Take a small control volume of the reactor, as show in Figure 5.5. The mole balance over the discrete volumen element is

$$q C_A(\lambda + \Delta\lambda) + \Delta q C_{A0} + \Delta V r_A = (q + \Delta q) C_A(\lambda) \quad (5.4)$$

The volumetric flow rate at λ is the inlet volumetric flow, q , plus the inlet side streams, Δq , thus

$$\Delta q = v_0 \mathbf{E}(\lambda) \Delta\lambda$$

$$q(\lambda) = q(\lambda + \Delta\lambda) + v_0 \mathbf{E}(\lambda) \Delta\lambda$$

where v_0 is the total inlet volumetric flow rate fed to the reactor.

Rewriting

$$\frac{d q(\lambda)}{d \lambda} = -v_0 \mathbf{E}(\lambda) \quad (5.5)$$

The inlet volumetric flow rate, v_0 at the inlet of the reactor ($X_A = 0$) is equal to zero because the fluid is fed only for side streams. Thus, integrating equation (5.5) considering that $q(\lambda) = 0$ at $\lambda = \infty$ and $q(\lambda) = q(\lambda)$ at $\lambda = \lambda$,

$$q(\lambda) = v_0 \int_{\lambda}^{\infty} \mathbf{E}(\lambda) d\lambda = v_0 [1 - \mathbf{F}(\lambda)] \quad (5.6)$$

where $q(\lambda)$ refers to volumetric flow rate inside the reactor at λ

The volume of fluid with a life expectancy between λ and $\lambda + \Delta\lambda$ is

$$\Delta V(\lambda) = v_0 [1 - \mathbf{F}(\lambda)] \Delta\lambda \quad (5.7)$$

The rate of generation of A in this volume is

$$r_A \Delta V(\lambda) = r_A v_0 [1 - \mathbf{F}(\lambda)] \Delta\lambda \quad (5.8)$$

Now substituting Eqs. (5.6), (5.7) and (5.8) into (5.4)

$$v_0 [1 - \mathbf{F}(\lambda)] C_A (\lambda + \Delta\lambda) + v_0 \mathbf{E}(\lambda) \Delta\lambda C_{A0} + r_A v_0 [1 - \mathbf{F}(\lambda)] \Delta\lambda = \dots \quad (5.9)$$

$$\dots (v_0 [1 - \mathbf{F}(\lambda)] + v_0 \mathbf{E}(\lambda) \Delta\lambda) C_A(\lambda) \quad (5.10)$$

Dividing by $v_0 \Delta\lambda$,

$$\frac{\mathbf{W}(\lambda) C_A (\lambda + \Delta\lambda)}{\Delta\lambda} + \mathbf{E}(\lambda) (C_{A0} - C_A) + r_A \mathbf{W}(\lambda) = \frac{\mathbf{W}(\lambda) C_A(\lambda)}{\Delta\lambda} \quad (5.11)$$

Now, taking the limit as $\Delta\lambda \rightarrow 0$ gives

$$-\frac{\mathbf{W}(\lambda) d C_A}{d \lambda} + \mathbf{E}(\lambda) (C_{A0} - C_A) + r_A \mathbf{W}(\lambda) = 0 \quad (5.12)$$

or

$$\frac{d C_A}{d \lambda} = \frac{\mathbf{E}(\lambda)}{\mathbf{W}(\lambda)} (C_{A0} - C_A) + r_A \quad (5.13)$$

Equation (5.13) can be written in terms of conversion as

$$-C_{A0} \frac{d X}{d \lambda} = \frac{\mathbf{E}(\lambda)}{\mathbf{W}(\lambda)} C_{A0} X + r_A \quad (5.14)$$

or

$$\frac{d X}{d \lambda} = -\frac{\mathbf{E}(\lambda)}{\mathbf{W}(\lambda)} X - \frac{r_A}{C_{A0}} \quad (5.15)$$

Equation (5.14) is solved to determine the concentration at the reactor outlet. The equation usually requires a numerical solution. An initial condition is also required. In this case, the boundary condition is as $\lambda \rightarrow \infty$, then $C_A = C_{A0}$.

Despite this model, it may be impossible to determine the amount of mixing in a reactor and hence obtain an exact prediction of conversion, but it could be helpful to determine the bounds on the expected conversion. This bounding may be represented by the diagram shown in Figure 5.6.

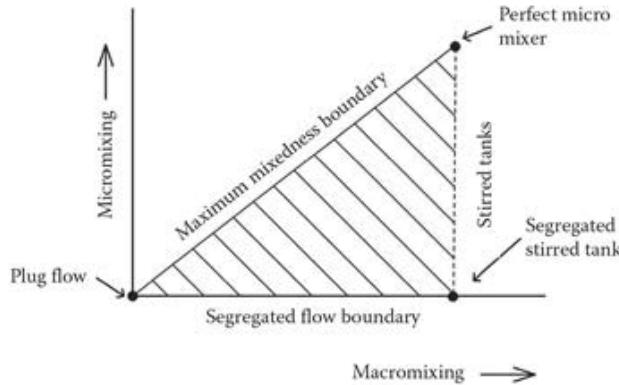


Figure 5.6: The bounding of the micro- and macromixing regions. [@hayes2013]

The horizontal axis represents the extent of macromixing as defined by the RTD. The vertical axis represents the amount of micromixing, which may vary from zero to perfect mixing. A PFR is always a segregated flow reactor, while a CSTR can vary between perfect mixing and segregated flow.

5.2 One adjustable parameter

For a first-order reaction or the flow-pattern fluid can be modeled as complete segregation or maximum mixedness, the zero-adjustable parameter models are enough to predict the conversion. However, for non-first-order reactions over fluids with good micromixing, more than just the RTD is needed.

A model of reactor flow patterns is necessary to predict the conversions and product distribution for such systems. We use combinations or modifications of ideal reactors to represent actual reactors to model these patterns.

However, in this course, we are dealing with two of them that are most common, each of which has one adjustable parameter: The first one is *the tanks-in-series model* and the second is *the dispersion model* which are widely used.

In principle, both models can represent the flow pattern in a single vessel between the two extreme ideal models: CSTR and PFR. Additionally, they are roughly equivalent and could be applied to turbulent flow in pipes, laminar flow in very long tubes, flow in a packed bed, etc. However, the dispersion model is mainly used in catalytic reactions carried out within tubular reactors.

The Tanks-in-Series Model

The tank-in-series (TIS) model for arbitrary flow through a vessel assumes that it can be represented by flow through a series of N equal-sized ideal CSTRs, where N is the adjustable parameter of the model and describes the degree of mixing in the vessel.

The value of N is tailored to match an observed or expected RTD. As N increases from 1 to ∞ , the flow represented in the vessel varies from back mix flow to plug flow. For practical purposes, a plug flow is virtually achieved for $N > 30$.

The volume of the vessel modeled, V , is equal to the sum of the volumes of the N tanks. (Missen, Mims, and Bradley 1999)

$$V = \sum N V_i$$

Consider, as an illustration, 5.7, three equally sized tanks in series through which a constant-density fluid flows, giving an equal space-time (a mean residence time) for each reactor.

A pulse tracer is injected into the first tank at time zero and, instantaneously, becomes uniformly distributed in the first tank, giving an initial concentration of C_0 . The outlet concentration from the first vessel is given by:

$$V_1 \frac{dC_1}{dt} = -v C_1 \quad (5.16)$$

$$C_1(t) = C_0 \exp\left(-\frac{t}{\bar{t}_1}\right) \quad (5.17)$$

where \bar{t}_1 is the mean residence time in a single tank.

The mole balance equation for the second tank is obtained from the perfectly mixed mole balance, without reaction:

$$V \frac{dC_2}{dt} = v (C_1 - C_2) \quad (5.18)$$

Substituting Eq. (5.17) and solving Eq. (5.18) using an integration factor $\exp(t/\bar{t}_2)$ along with the initial condition $C_2(0) = 0$:

$$C_2(t) = C_0 \frac{t}{\bar{t}_2} \exp\left(-\frac{t}{\bar{t}_2}\right) \quad (5.19)$$

Performing the mole balance on the third vessel and solving in a similar way give the outlet concentration with time from the third reactor.

$$C_3(t) = \frac{C_0}{2} \left(\frac{t}{\bar{t}_3}\right)^2 \exp\left(-\frac{t}{\bar{t}_3}\right) \quad (5.20)$$

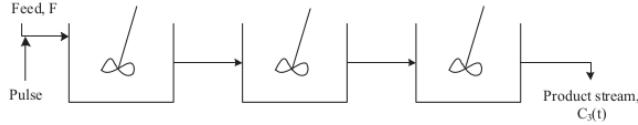


Figure 5.7: The tanks-in-series model uses a number of equally sized CSTRs placed in series

Therefore, generalizing this method to a series of N CSTRs gives the RTD for N CSTRs in series:

$$\frac{C(t)}{C(t_0)} = \frac{t^{N-1}}{(N-1)! \bar{t}^N} \exp\left(-\frac{t}{\bar{t}}\right) \quad (5.21)$$

taking into account that $\bar{t} = N \bar{t}_i$ then

$$\frac{C(t)}{C(t_0)} = \mathbf{C}(t) = \frac{t^N}{(N-1)!} \left(\frac{t}{\bar{t}}\right)^{N-1} \exp\left(-N \frac{t}{\bar{t}}\right) \quad (5.22)$$

Equation (5.22) could be expressed with normalized time using $\mathbf{C}(t) = \bar{t} \mathbf{E}(t)$, leading to the normalized distribution function is:

$$\mathbf{E}_N(\theta) = \frac{N^N}{(N-1)!} \theta^{N-1} \exp(-N\theta) \quad (5.23)$$

where, again, $\theta = t/\bar{t}$.

Figure 5.8 illustrates the RTDs of various numbers of CSTRs in series. As N increases from 1, the spread of distribution decreases. Furthermore, when $N > 2$, the peak would be an infinitive height (behavior of a PFR).

The mathematical illustration is available on the following link

The cumulative RTD function $\mathbf{F}(\theta)$ could be calculated from equation (5.23), for integral values of N

$$\mathbf{F}_N(\theta) = \int_0^\theta \mathbf{E}(\theta) d\theta \quad (5.24)$$

The integral in equation (5.24) can be evaluated analytically:

$$\mathbf{F}_N(\theta) = 1 - \exp(-N\theta) \sum_{i=0}^{N-1} \frac{(N\theta)^i}{i!} \quad (5.25)$$

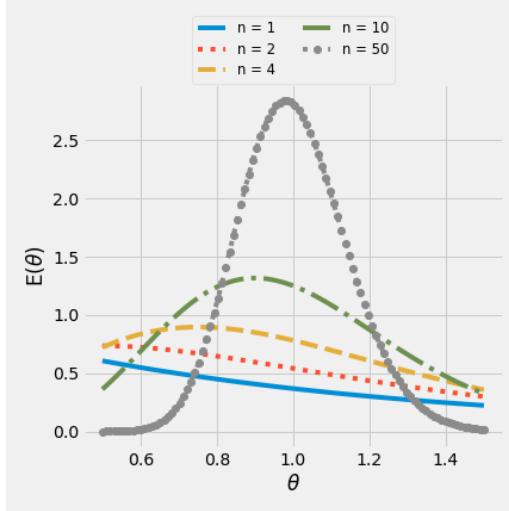


Figure 5.8: $E(\theta)$ curve using the tanks-in-series model

The result for equation (5.24) is shown in Figure 5.9 for several values of N . For $N = 1$, the result is that for a single CSTR, as N increases, the shape becomes more like a step function, corresponding to a plug-flow.

Finally, the washout function, $\mathbf{W}(\theta)$, can be obtained from $\mathbf{F}(\theta)$

$$\mathbf{W}(\theta) = 1 - \mathbf{F}(\theta)$$

To utilize the tanks-in-series model, we need to determine the number of tanks that will give the same RTD as for the real system. This number may be obtained from the variance of RTD, which is given by the second moment about the mean:

$$\sigma_{\theta}^2 = \int_0^{\infty} (\theta - 1)^2 \frac{\theta^{N-1} N^N}{(N-1)!} \exp(-N\theta) d\theta = \int_0^{\infty} \theta^2 \mathbf{E}(\theta) d\theta - 1$$

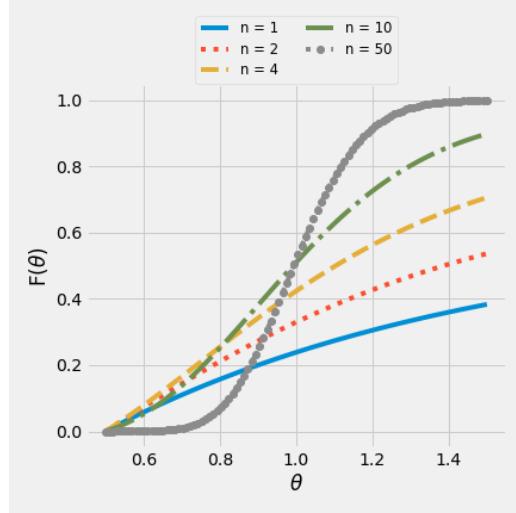
Solution of the integral equation gives the result

$$\sigma_{\theta}^2 = \frac{(N+2-1)!}{N \cdot N!} - 1 = \frac{(N+1)!}{N \cdot N!} - 1 = \frac{1}{N}$$

The variance of the RTD is seen to be equal to the inverse of the number of tanks used. Therefore, if the RTD curve is known, the appropriated number of tanks in series to use may be calculated, so

$$N = \frac{1}{\sigma_{\theta}^2} = \frac{\bar{t}^2}{\sigma^2}$$

Exercise 5.2 (Estimate number of tanks based in Tanks-in-serie model). A step increase in the inlet trace A concentration, from 1.0 to 2.0 mmol/L, was used to determine the mixing pattern inside the fluidized-bed reactor. The response data were as follows:

Figure 5.9: $F(\theta)$ curve using the tanks-in-series model

| t (min) | C (mmol/L) | t (min) | C (mmol/L) |
|---------|------------|---------|------------|
| 0.0 | 1.000 | 30.0 | 1.410 |
| 5.0 | 1.005 | 45.0 | 1.610 |
| 10.0 | 1.020 | 60.0 | 1.770 |
| 15.0 | 1.060 | 90.0 | 1.920 |
| 20.0 | 1.200 | 120.0 | 1.960 |

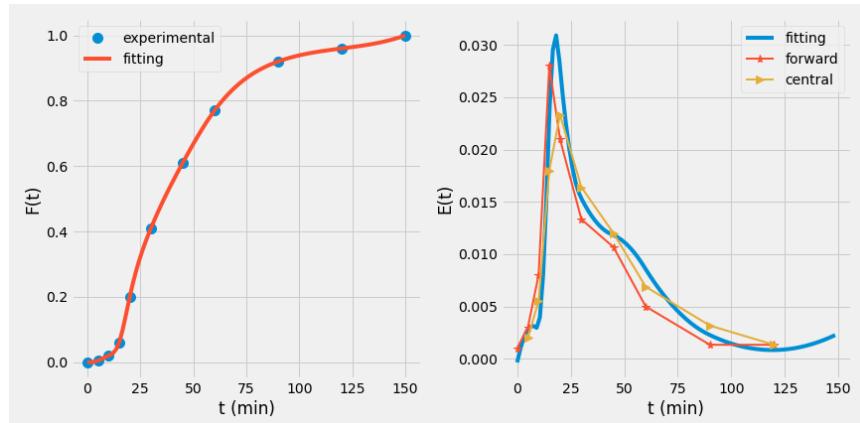
Estimate values of N based on both central and backward differencing and determine which technique best describes the tracer outflow concentrations.

Solution

The solution is available on the next link

For each scenario, the equation (5.25) was applied to calculate the estimated $\mathbf{F}(t)$, then based on Eq. (3.27), the output tracer concentration, $C_{out}(t)$, may be calculated from $\mathbf{F}(t)$.

Figure 5.10 shows the results of $E(t)$ curve based on several numerical techniques. On the other hand, Figure 5.11 shows the values of $C_{out}(t)$ predicted using forward and central differencing technique, and based on a curve fitting approach. The last one provides a superior representation of the experimental data.



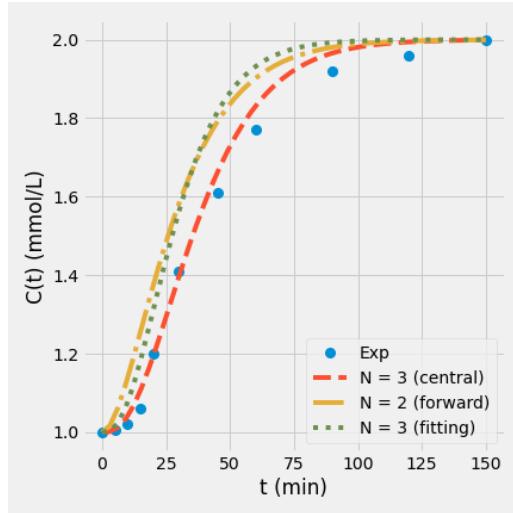


Figure 5.11: Selection of the best technique for the tanks-in-series model

The Dispersion Model

The dispersion model describes nonideal tubular reactors based on the assumption that exists an axial dispersion of the material, governed by Fick's law diffusion-like, superimposed on the flow.

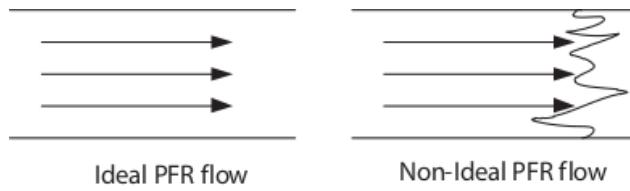


Figure 5.12: The dispersion model

Figure 5.12 shows a sketch of differences between velocity profiles between ideal PFR and actual flow. Fluctuations could be due to different flow and molecular velocities and turbulent diffusion. Although radial dispersion may also be significant, we consider only axial dispersion.

In considering axial dispersion as diffusive flow, it is assumed that Fick's first law applies, with the effective diffusion coefficient replaced by an axial dispersion coefficient, D_L . Thus, for unsteady-

state behavior concerning a species T (tracer), the molar flux (N_T) of T at an axial position x is

$$N_T = -D_L \frac{\partial C_T(x, t)}{\partial x}$$

where $C_T(x, t)$ is the concentration of T .

Consider a material balance for T around the differential control volume shown in Figure 5.13.

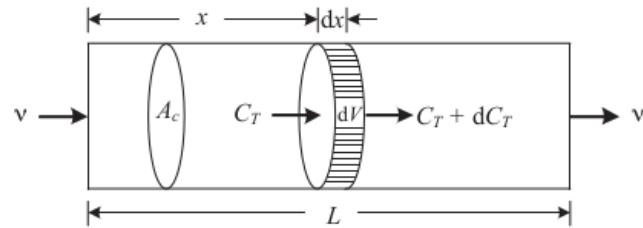


Figure 5.13: Control volume for continuity equation for axial dispersion

We assume steady flow overall, but not for tracer (T); there is no place.

$$\begin{aligned} \left(\begin{array}{l} \text{rate of input} \\ \text{of } T \text{ by} \\ \text{convective flow} \end{array} \right) + \left(\begin{array}{l} \text{rate of input} \\ \text{or } T \text{ by} \\ \text{dispersion} \end{array} \right) - \left(\begin{array}{l} \text{rate of output} \\ \text{of } T \text{ by} \\ \text{convective flow} \end{array} \right) - \dots \\ \dots \left(\begin{array}{l} \text{rate of output} \\ \text{of } T \text{ by} \\ \text{dispersion} \end{array} \right) = \left(\begin{array}{l} \text{rate of accumulation} \\ \text{of } T \text{ in volume} \\ dV = A_c dx \end{array} \right) \end{aligned}$$

Under those assumptions, with $C_T \equiv C_T(x, t)$, A_c and D_L constant, for the transient flow of a non-reacting tracer, the mole balance equation is

$$A_c \nu C_T - D_L A_c \frac{\partial C_T}{\partial x} - A_c \left[\nu C_T + \frac{\partial (\nu C_T)}{\partial x} \right] + D_L A_c \left[\frac{\partial C_T}{\partial x} + \frac{\partial}{\partial x} \left(\frac{\partial C_T}{\partial x} \right) dx \right] = A_c \frac{\partial C_T}{\partial t} dx \quad (5.26)$$

where ν is the average axial velocity (m/s), D_L is the axial dispersion coefficient, (m^2/s).

If system is density-constant and ν is constant, the equation (5.26) becomes to

$$-D_L \frac{\partial^2 C_T}{\partial x^2} + \nu \frac{\partial C_T}{\partial x} = \frac{\partial C_T}{\partial t} \quad (5.27)$$

If we know the boundary conditions of the problem, solving this equation, we get the profile of tracer concentration vs. time.

Equation (5.27) can be made dimensionless by defining the following scaling factors:

$$z = \frac{x}{L}; \quad \theta = \frac{t}{\bar{t}} = t \frac{\nu}{L} \quad C^* = \frac{C_T}{C_0}$$

Here C_0 is usually taken as the maximum concentration in the system.

$$\frac{\partial C^*}{\partial \theta} = \left(\frac{D_L}{\nu L} \right) \frac{\partial^2 C^*}{\partial z^2} - \frac{\partial C^*}{\partial z} \quad (5.28)$$

and $D_L/(\nu L)$ is named the dispersion number, when

$$\begin{aligned} \frac{D_L}{\nu L} \rightarrow 0 & \rightarrow \text{large dispersion, hence well-mixed flow} \\ \frac{D_L}{\nu L} \rightarrow \infty & \rightarrow \text{negligible dispersion, hence plug flow} \end{aligned}$$

We also have a dimensionless group, denoted Pe , which is called **Peclet number** based on vessel length. The physical interpretation is that it represents the ratio of convective flux to diffusive flux:

$$Pe = \frac{\nu L}{D_L} \equiv \frac{\nu C_T}{D_L(C_T/L)} = \frac{\text{rate of transport by convection}}{\text{rate of transport by diffusion or dispersion}}$$

So, we see that

$$\frac{\partial C^*}{\partial \theta} = \frac{1}{Pe} \frac{\partial^2 C^*}{\partial z^2} - \frac{\partial C^*}{\partial z} \quad (5.29)$$

Now, the results of solutions of Eq. (5.29) will depend on the choice of boundary conditions at inlet ($z = 0$) and outlet ($z = 1$). There are several possibilities concerning “closed” and “open” vessels, which do not necessarily satisfy actual positions.

When the flow is undisturbed as it passes the entrance and exit boundaries, we will call this the **open boundary condition**. While, when we have plug flow outside the vessel up to the boundaries,

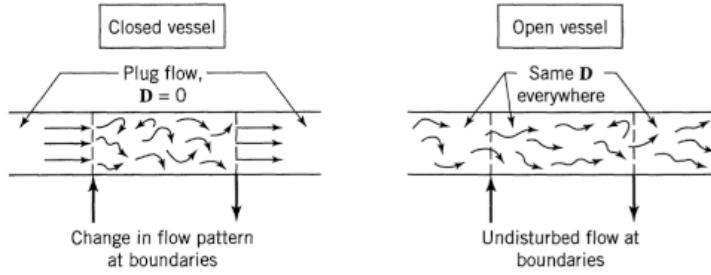


Figure 5.14: Boundary conditions used with dispersion model

we call this the **closed boundary condition**. There are up to four combinations of boundaries, closed-closed, open-open, or mixed, based on previous conditions. Figure 5.14 illustrates the closed and open extremes.

For closed vessels, the flow conditions are illustrated schematically in Figure 5.15. $D_L = 0$, or $Pe = \infty$ characterizes a plug-flow upstream of the vessel inlet. Since flow inside the vessel is dispersed, and the pulse injection is at inlet ($z = 0$), will have a C_T discontinuity across the inlet. In contrast, a continuity on CT across the outlet ($z = 1$) is usually assumed, even though downstream flow ($z > 1$) is plug-flow.

In this course, we only deal with a closed-closed case which is illustrated in Figure 5.15. Danckwerts formulated the closed configuration, and it means that there is no dispersion before $z = 0$ and after $z = 1$.

The equation (5.29) is a second-order boundary value problem requires two boundary conditions. If the system is taken as a closed system, the dimensionless boundary conditions are:

$$C_{\text{in}}^* = C^* - \frac{1}{Pe} \frac{\partial C^*}{\partial z} \quad \text{at } z = 0 \quad (5.30)$$

$$\frac{\partial C^*}{\partial z} = 0 \quad \text{at } z = 1 \quad (5.31)$$

Additionally, the system requires an initial condition:

$$C^* = 1 \quad \text{at } \theta = 0, \text{ and } z = 0 \quad (5.32)$$

$$C^* = 0 \quad \text{at } \theta = 0, \text{ and } 0 < z \leq 1 \quad (5.33)$$

An analytical solution to equation (5.29) with these boundary conditions is given by Otake and Kunigita (1598), but is rather complex, and it was omitted it here. However, moments and relatively

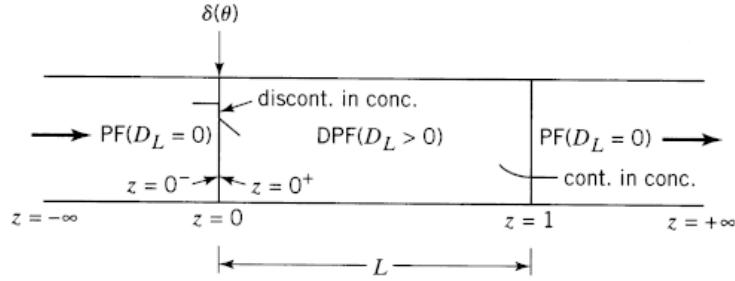


Figure 5.15: Flow conditions for closed-closed vessel

simple an are given by:

$$\bar{\theta} = 1 \quad (5.34)$$

$$\sigma_{\theta}^2 = \frac{2}{Pe^2} (Pe - 1 + \exp(-Pe)) \quad (5.35)$$

An approximate closed form solutions for $Pe > 50$:

$$\begin{aligned} \mathbf{F}(\theta) &= \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{1-\theta}{\sqrt{\theta}} \sqrt{\frac{Pe}{4}} \right) \right] \\ \mathbf{E}(\theta) &= \frac{\exp(-Pe(1-\theta^2)/4)}{\sqrt{4\pi/Pe}} \end{aligned}$$

where erf is the error function.

As a practical matter, these mathematical complexities should probably not be taken too literally since the precise conditions at the boundaries of actual equipment cannot usually be precisely defined in any event.

Where to get the dispersion coefficient?

- (1) **Experimental determination by analyzing pulse response.** The Peclet number can be found experimentally using a pulse injection into the tube inlet and finding the RTD function. The Peclet number depends on the variance of the normalized RTD function:

$$\sigma_{\theta}^2 = \frac{2}{Pe} - \frac{2}{Pe^2} [1 - \exp(-Pe)] \quad (5.36)$$

(2) Calculation from correlations.

$$\frac{1}{Pe_R} = \frac{1}{Re \cdot Sc} + \frac{Re \cdot Sc}{192} \quad \text{For } 1 < Re < 2000 \text{ and } 0.23 < Sc < 1000$$

$$\frac{1}{Pe_R} = \frac{3 \cdot 10^7}{Re^{2.1}} + \frac{1.35}{Re^{1/8}} \quad \text{For } Re > 2000$$

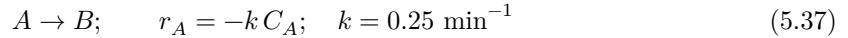
where

$$Pe_R = \frac{wd}{D} \quad \text{: Peclet number in tube}$$

$$Re = \frac{wd}{\nu} \quad \text{: Reynolds number}$$

$$Sc = \frac{\nu}{D_m} \quad \text{: Schmidt number}$$

Exercise 5.3 (Comparison in conversion calculation for a non-ideal flow reactor). For a reaction



Compare final conversions based on:

1. axial dispersion model with closed vessel approximations.
2. tanks in series model, and
3. ideal PFR model.

| t (min) | C (g/m3) | t (min) | C (g/m3) |
|---------|----------|---------|----------|
| 1.00 | 1.000 | 7.00 | 4.000 |
| 5.00 | 2.000 | 8.00 | 4.000 |
| 3.00 | 8.000 | 9.00 | 2.200 |
| 4.00 | 10.00 | 10.0 | 1.500 |
| 5.00 | 8.000 | 12.0 | 0.600 |
| 6.00 | 6.000 | 14.0 | 0.000 |

Solution

The solution is available on the next link

Based on the axial dispersion model. We need to find the Pe number that is following RTD data.

In this case, we calculated from experimental data, the RTD curve, mean time and its variance. Then, the Eq. (5.36) was solved:

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{2}{Pe} - \frac{2}{Pe^2} [1 - \exp(-Pe)] \Rightarrow Pe = 8.007$$

When a chemical reaction is included in the dispersion model, a numerical solution is usually required for the resulting differential equation. so, based on the reactions and considering a simple power-law rate expression, the mole balance of A is written as

$$D_L \frac{\partial^2 C_A}{\partial x^2} - \nu \frac{\partial C_A}{\partial x} - (k C_A^n) = 0$$

Which it could be written in dimensionless variables as:

$$\frac{1}{Pe} \frac{\partial^2 C_A}{\partial z^2} - \nu \frac{\partial C_A}{\partial z} - (k \bar{t} C_A^n) = 0$$

And, in terms of the fractional conversion

$$\frac{1}{Pe} \frac{\partial^2 X_A}{\partial z^2} - \frac{\partial X_A}{\partial z} - k \bar{t} C_{A0}^{n-1} (1 - X_A)^n = 0$$

The fractional conversion is therefore governed by the magnitude of three dimensionless groups, Pe, n , and $k \bar{t} C_{A0}^{n-1}$. There is an analytical solution to this equation only for a first-order reaction:

$$\frac{C_A}{C_{A0}} = 1 - X_A = \frac{4a \exp(Pe/2)}{(1+a)^2 \exp(aPe/2) - (1-a)^2 \exp(-aPe/2)}$$

where

$$a = \left(1 + \frac{4k\bar{t}}{Pe} \right)^{0.5}$$

Solving this equation $X_A = 0.6826$

For calculating the fractional conversion based in TIS model, it is necessary to find de number of reactor that is in accordance with given RTD data.

$$\text{number of reactors} = \frac{\bar{t}}{\sigma^2} = 4.4$$

Then the conversion is

$$X_A = 1 - \frac{C_{AN}}{C_{A0}} = 1 - \frac{1}{(1 + k\bar{t}/N)^N} = 0.6736$$

For an ideal PFR. The fractional conversion is:

$$X_A = 1 - \exp(-k\bar{t}) = 0.7253$$



information In summary, **why is it relevant to perform an analysis of RTDs?**

This approach can ease the following tasks: 1. Diagnostics of problems in reactor operations. 2. Design of unit operations. 3. Predictions of conversion and effluent concentrations.

We have studied models of several simple, partially mixed reactors. These are shown in Figure 5.16 for increasing back mixing.

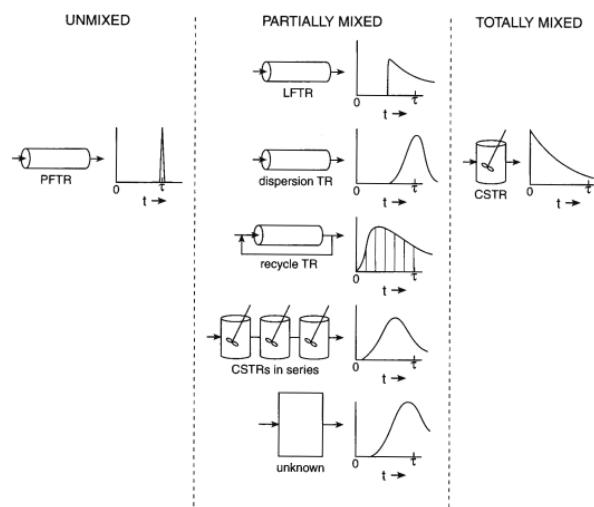


Figure 5.16: Residence time distributions for the nonideal reactors. [©schmidt1998]

Chapter 6

Final Words

I reached the end of this notes compilation for one of my courses as a Chemical Engineering professor at the Central University of Venezuela. I am genuinely thankful for those 15 years dedicated to lecture (to) and learning from my students.

Being an academic advisor was one of the scariest things I had ever done. Every meeting, talk, demonstration, video lecture, code presentation was challenging, but in the end, an enriching task.

Thank you to all my students, professors, teammates for your support and encouragement to be a better human being.

Now, I will be a life learner and keep my dear Alma Mater as one of the priceless life experiences I have had.

| Exercises | Name | Solution (Python) |
|-----------|---|----------------------|
| 2.1 | Operation of a cooled exothermic CSTR | link |
| 2.2 | Non-rigorous coil design for a CSTR | link |
| 2.3 | Heat transfer requirement for multiple CSTRs | |
| 2.4 | Effect of the rate laws over PFR performance | link |
| 2.5 | Heat transfer requirement for a PFR | link |
| 2.6 | Parallel Reactions in a PFR with Heat Effects | link |
| 2.7 | Autocatalytic reaction | link |
| 2.8 | Comparing PFRs performance | link |
| 2.9 | The locus of maximum reaction rates | link |

| Exercises | Name | Solution (Python) |
|-----------|---|-------------------|
| 2.10 | Calculation of the optimal temperature | link |
| 2.11 | Reversible exothermic reaction | link |
| 2.12 | Non-isothermal reactors with interstage cooling | link |
| 2.13 | Heat requirement for a Batch reactor | link |
| 2.14 | Dynamic simulation of a non-isothermal batch reactor | link |
| 3.1 | Calculations of RTD and distribution functions curves from pulse impulse method | link |
| 3.2 | Calculations of RTD and distribution functions curves from step change method | link |
| - | Using RTDs as diagnostic tools | link |
| 5.1 | Calculation of conversion based on RTD | link |
| - | Response of in-serie-tanks model | link |
| 5.2 | Estimate the number of tanks based in Tanks-in-serie model | link |
| 5.3 | Comparison in conversion calculation for a non-ideal flow reactor | link |

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