

Non-Isothermal, Non-Adiabatic Reactor Design

Review of Adiabatic Reactors – Algebraic Energy Balance

From last week, we had obtained the energy balance, which relates temperature and conversion (dependent variables) to space-time (independent variable) as follows:

$$\frac{dE}{dt} = Q - W + F_{AO}(T_O - T(t, z)) \cdot \sum_{i=1}^N \theta_i C_{p_i} + F_{AO} X(t, z) \cdot \left[(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T(t, z) - T_{ref}) \right]$$

If we assume steady-state operation, then we can drop all time-dependencies, and our energy balance reduces to a relationship between temperature and conversion:

$$0 = Q - W + F_{AO}(T_O - T(t, z)) \cdot \sum_{i=1}^N \theta_i C_{p_i} + F_{AO} X(t, z) \cdot \left[(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T(t, z) - T_{ref}) \right]$$

We often neglect work (via isochoric and/or isobaric assumptions). If we also assume adiabatic operation, i.e. $Q = 0$, we obtain a purely algebraic relationship between temperature and conversion, independent of position or time.

$$0 = (T_O - T(z)) \cdot \sum_{i=1}^N \theta_i C_{p_i} + X(z) \cdot \left[(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T(z) - T_{ref}) \right]$$

Note that if we had an Adiabatic Plug Flow Reactor, this energy balance would still be applicable! Remember, that the Mass Balance is still a differential equation relating conversion and temperature (dependent variables) to space-time or position (independent variable).

What if $Q \neq 0$? Then we must consider some possibilities.

If the reactor is not perfectly insulated, then we can assume that there is heat loss to the surrounding fluid; the rate of heat loss is proportional to the temperature gradient, the surface area through which the heat exits, and a heat-transfer coefficient.

$$Q = UA(T - T_c)$$

Where T is our temperature, and in general may be a function of position and time, and T_c is our coolant fluid temperature, which may also be a function of position and time.

Non-Adiabatic CSTR: Another Algebraic Energy Balance

If we have a CSTR, then via well-mixed assumption (no spatial variations in temperature, conversion) and steady-state operation (no temporal variations in temperature or conversion), we also obtain an algebraic relationship from the Energy balance.

$$0 = Q + F_{AO}(T_O - T) \cdot \sum_{i=1}^N \theta_i C_{p_i} + F_{AO} X \cdot [(-\Delta H_{rxn}^O) + \Delta C_p \cdot (T - T_{ref})]$$

Sustituting in our expression for a heating or cooling jacket or coil,

$$0 = -UA(T - T_C) + F_{AO}(T_O - T) \cdot \sum_{i=1}^N \theta_i C_{p_i} + F_{AO} X \cdot [(-\Delta H_{rxn}^O) + \Delta C_p \cdot (T - T_{ref})]$$

$$UAT + F_{AO}T \sum_{i=1}^N \theta_i C_{p_i} - F_{AO}X\Delta C_p T = UAT_C + F_{AO}T_O \sum_{i=1}^N \theta_i C_{p_i} + F_{AO}X \cdot (-\Delta H_{rxn}^O) - F_{AO}X\Delta C_p T_{ref}$$

Solving for the exit temperature as a function of exit conversion, reaction thermodynamics, inlet conditions and the cooling/heating jacket parameters, we get:

$$T = \frac{\frac{UAT_C}{F_{AO}} + T_O \sum_{i=1}^N \theta_i C_{p_i} + X \cdot (-\Delta H_{rxn}^O) - X\Delta C_p T_{ref}}{\frac{UA}{F_{AO}} + \sum_{i=1}^N \theta_i C_{p_i} - X\Delta C_p}, \text{ or}$$

$$X = \frac{\frac{UA}{F_{AO}}(T - T_C) + (T - T_O) \cdot \sum_{i=1}^N \theta_i C_{p_i}}{[(-\Delta H_{rxn}^O) + \Delta C_p \cdot (T - T_{ref})]}$$

$$X = -\frac{\frac{UAT_C}{F_{AO}} + T_O \cdot \sum_{i=1}^N \theta_i C_{p_i}}{[(-\Delta H_{rxn}^O) + \Delta C_p \cdot (T - T_{ref})]} + \left(\frac{\frac{UA}{F_{AO}} + \sum_{i=1}^N \theta_i C_{p_i}}{[(-\Delta H_{rxn}^O) + \Delta C_p \cdot (T - T_{ref})]} \right) T$$

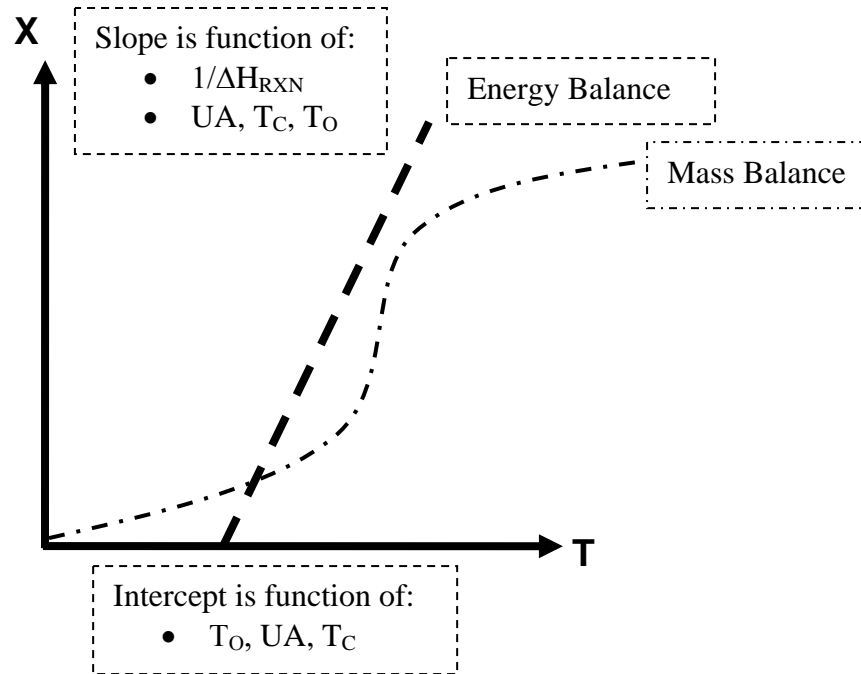
And our Mass Balance is:

$$V = \frac{F_{AO}}{-r_A(T, X)} X$$

If we have a first-order, irreversible, mole-neutral (or liquid-phase) reaction, then mass balance is:

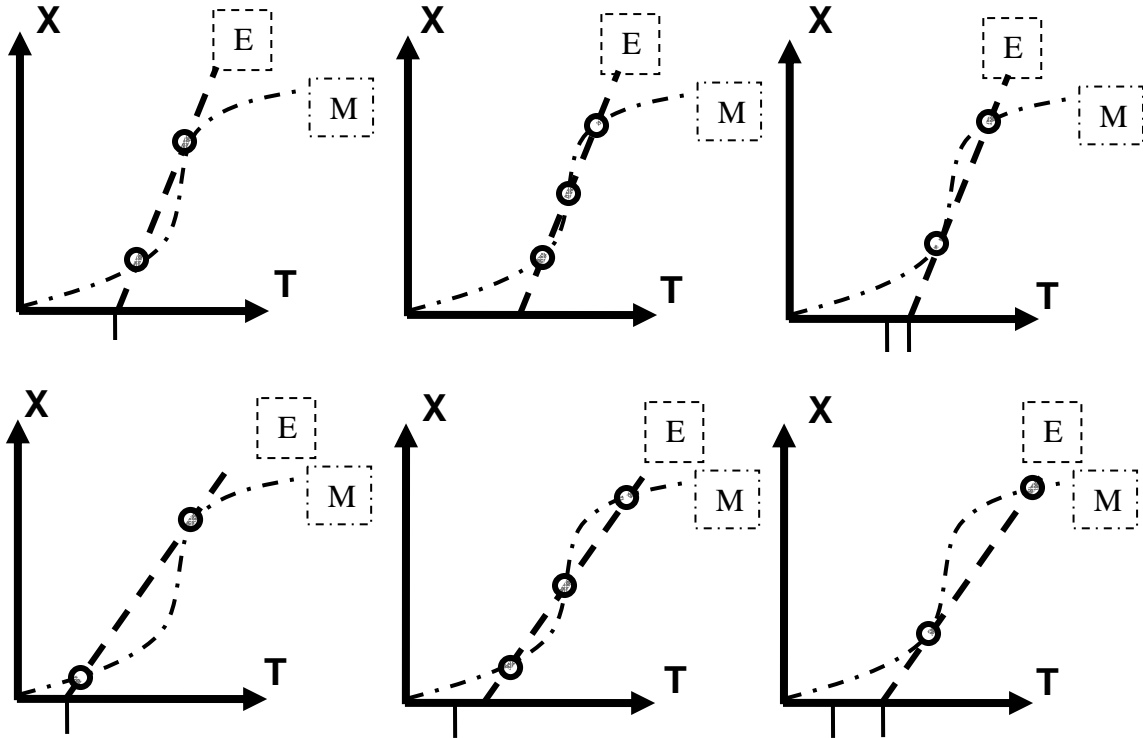
$$V = \frac{F_{AO}}{-k_o \exp\left[\frac{-E_A}{RT}\right] \left(\frac{P}{RT}\right)(1-X)} X$$

These two equations can be solved simultaneously, as before. Showing this solution graphically, we plot both the energy balance and the mass balance equations on a conversion vs. temperature plot:



We can see that the analysis for predicting steady-state multiplicity and for graphically obtaining solutions for CSTR performance is identical to that for adiabatic CSTR analysis. The only changes are that now we have two more “knobs” to adjust the intercept of the energy balance equation.

From this graphical analysis, we can see that as the slope of the energy balance equation increases, the range of inlet temperatures that result in multiplicity shrinks; likewise, as the slope of the energy balance decreases, the range of inlet temperatures that result in multiplicity increases. We can see this with a few sketches, below:



The top row illustrates a narrow range of inlet temperatures that result in multiple steady-states; the bottom row represents the same reactor (mass balance), with identical kinetics, mixing and residence time, only now with a higher heat of reaction. We can see that the range of inlet temperatures that result in multiplicity expands; also, the inlet temperature at which multiplicity onsets has reduced.

But enough of this fun – the important bit is that we see that for a CSTR, the Energy balance is always an algebraic relationship between outlet temperature and conversion.

So, when does the energy balance become a differential equation under steady-state conditions? When we have spatial variations in temperature AND a heat removal/addition function that is a function of temperature (i.e., Q is a function of position as well).

Non-Adiabatic PFR: Differential Energy Balances

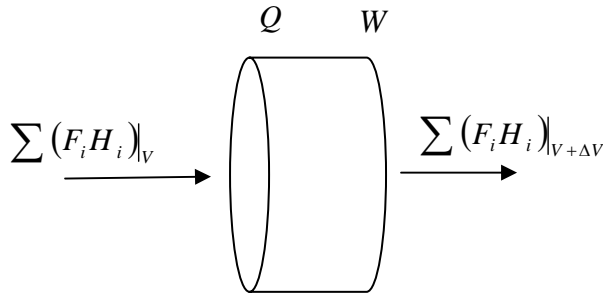
Lets start with the original energy balance, only now we apply it to a differential “Shell” in a plug-flow reactor. Lets re-derive the energy balance over a differential volume:

$$\frac{dE}{dt} = \delta Q - \delta W + \sum (F_i H_i)_{|_V} - \sum (F_i H_i)_{|_{V+\Delta V}}$$

where

$$\sum (F_i H_i)|_V = F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_V + F_{AO} X|_V \cdot [(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_V - T_{ref})]$$

$$\sum (F_i H_i)|_{V+\Delta V} = F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_{V+\Delta V} + F_{AO} X|_{V+\Delta V} \cdot [(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_{V+\Delta V} - T_{ref})]$$



This sets up the steady-state derivation of the energy balance; from here, there are two routes to obtaining Equation 8-35. First, let's look at the elegant method of Fogler, wherein we employ some trickery to circumnavigate the bulk of the derivation.

Derivation One: Fogler's Route

$$\frac{dE}{dt} = Q - W + \sum (F_i H_i)|_V - \sum (F_i H_i)|_{V+\Delta V}$$

First, we neglect the work term, and also assume steady-state.

$$0 = Q + \sum (F_i H_i)|_V - \sum (F_i H_i)|_{V+\Delta V}$$

We then take the limit as $\Delta V \rightarrow 0$, and get:

$$0 = \delta Q - \frac{d \sum (F_i H_i)}{dV} = \delta Q - \sum H_i \frac{dF_i}{dV} - \sum F_i \frac{dH_i}{dV}$$

We recognize that the first derivative term is our mass balance, which for a PFR is:

$$\frac{dF_i}{dV} = \delta_i (-r_A)$$

And we also recognize that the change in enthalpy with volume can be rewritten in terms of a constant heat capacity; Substituting in, we get:

$$0 = \delta Q - \sum H_i \delta_i (-r_A) - \sum F_i C_{p_i} \frac{dT}{dV}, \text{ or}$$

$$0 = \delta Q - (-r_A)\Delta H_{rxn} - \frac{dT}{dV} \sum F_i C_{p_i}, \text{ or}$$

$$\frac{dT}{dV} = \frac{\delta Q + (r_A)\Delta H_{rxn}}{F_{AO} \sum \theta_i C_{p_i}}$$

Assuming the general form for the rate of heat removal,

$$\delta Q = Ua(T - T_c)$$

We get Equation 8-35, which relates temperature to the reaction rate (conversion and temperature) to position via a first-order, non-linear differential equation:

$$\frac{dT}{dV} = \frac{Ua(T_c - T) + (r_A)\Delta H_{rxn}}{F_{AO} \sum \theta_i C_{p_i}}$$

Note that the above equation is still written in terms of the heat of reaction at temperature T; we'll return to this in a minute or two...

Derivation Two: General Shell Balance

As a contrast to Fogler's derivation, we can draw a more detailed shell balance, explicitly writing out the total enthalpy flow in and out of volume ΔV :

$$\frac{dE}{dt} = Q - W + \sum (F_i H_i)|_V - \sum (F_i H_i)|_{V+\Delta V}, \text{ where:}$$

$$\sum (F_i H_i)|_V = F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_V + F_{AO} X|_V \cdot [(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_V - T_{ref})]$$

$$\sum (F_i H_i)|_{V+\Delta V} = F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_{V+\Delta V} + F_{AO} X|_{V+\Delta V} \cdot [(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_{V+\Delta V} - T_{ref})]$$

Substituting in, we get:

$$\begin{aligned} \frac{dE}{dt} = & Q - W + F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_V + F_{AO} X|_V \cdot [(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_V - T_{ref})] \\ & - F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_{V+\Delta V} + F_{AO} X|_{V+\Delta V} \cdot [(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_{V+\Delta V} - T_{ref})] \end{aligned}$$

If we assume steady-state and neglect any work terms, then we get:

$$0 = Q + F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_V + F_{AO} X|_V \cdot \left[(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_V - T_{ref}) \right] \\ - F_{AO} \sum_{i=1}^N \theta_i C_{p_i} T|_{V+\Delta V} - F_{AO} X|_{V+\Delta V} \cdot \left[(-\Delta H_{rxn}^o) + \Delta C_p \cdot (T|_{V+\Delta V} - T_{ref}) \right]$$

Lets re-write in preparation for taking the limit as differential volume, $DV \rightarrow 0$.

$$0 = Q + F_{AO} \sum_{i=1}^N \theta_i C_{p_i} (T|_V - T|_{V+\Delta V}) + F_{AO} (-\Delta H_{rxn}^o) (X|_V - X|_{V+\Delta V}) \\ + F_{AO} \Delta C_p (T|_V X|_V - T|_{V+\Delta V} X|_{V+\Delta V}) - F_{AO} \Delta C_p T_{ref} (X|_V + X|_{V+\Delta V})$$

Now, we see that we can get the following differential equation:

$$0 = Q - F_{AO} \sum_{i=1}^N \theta_i C_{p_i} \frac{dT}{dV} - F_{AO} (-\Delta H_{rxn}^o) \frac{dX}{dV} - F_{AO} \Delta C_p \frac{d(T \cdot X)}{dV} + F_{AO} \Delta C_p T_{ref} \frac{dX}{dV}$$

Lets expand the fourth term via chain rule,

$$0 = Q - F_{AO} \sum_{i=1}^N \theta_i C_{p_i} \frac{dT}{dV} - F_{AO} (-\Delta H_{rxn}^o) \frac{dX}{dV} - F_{AO} \Delta C_p \left(X \frac{dT}{dV} + T \frac{dX}{dV} \right) + F_{AO} \Delta C_p T_{ref} \frac{dX}{dV}$$

We again recognize the mass balance, which is:

$$\frac{dX}{dV} = \frac{-r_A}{F_{AO}}, \text{ and upon substitution the above equation yields:}$$

$$0 = Q - F_{AO} \sum_{i=1}^N \theta_i C_{p_i} \frac{dT}{dV} - (-\Delta H_{rxn}^o) (-r_A) - \Delta C_p \left(F_{AO} X \frac{dT}{dV} + T (-r_A) \right) + \Delta C_p T_{ref} (-r_A)$$

Expanding,

$$0 = Q - F_{AO} \sum_{i=1}^N \theta_i C_{p_i} \frac{dT}{dV} - (\Delta H_{rxn}^o) (r_A) - \Delta C_p T (-r_A) - \Delta C_p F_{AO} X \frac{dT}{dV} - \Delta C_p T_{ref} (r_A)$$

Lumping terms containing the temperature derivation on the left-hand side,

$$F_{AO} \sum_{i=1}^N \theta_i C_{p_i} \frac{dT}{dV} + \Delta C_p F_{AO} X \frac{dT}{dV} = -(\Delta H_{rxn}^o) (r_A) - \Delta C_p T (-r_A) - \Delta C_p T_{ref} (r_A) + Q$$

And finally solving for the temperature derivation,

$$\frac{dT}{dV} = \frac{Q + r_A (\Delta H_{rxn}^o + \Delta Cp(T - T_{ref}))}{F_{AO} \left(\sum_{i=1}^N \theta_i Cp_i + \Delta Cp \cdot X \right)}$$

Lastly, if we substitute in the general function for the rate of heat addition/removal,

$$\frac{dT}{dV} = \frac{Ua(T_c - T) + r_A (\Delta H_{rxn}^o + \Delta Cp(T - T_{ref}))}{F_{AO} \left(\sum_{i=1}^N \theta_i Cp_i + \Delta Cp \cdot X \right)}$$

Note that if we neglect the change in heat capacity with reaction, both derivations yield the same solution. Fogler's textbook begins to neglect change in heat capacity from this point onward.

This gives the exact same solution as before – again, you can choose which one you find more educational. The latter is more exact, and does not appear to employ trickery; this makes it much more rigorous and in-elegant compared to Fogler's derivation.

What About T_C ?

Lets look at the energy balance over the coolant phase, in order to complete the problem. The coolant is either removing or adding heat to the reactor; thus the coolant temperature must be changing some finite amount; from thermodynamics, we can easily determine that:

$$Q_C = m_c Cp_c \Delta T_c$$

The above equation tells us that if we want a significant amount of heat removal/addition via the coolant phase, there must be either (i) significant temperature drop at low mass flows, or (ii) significant mass flow with small temperature drops. The latter limiting case makes life the easiest.

Easiest Model: $T_C = \text{constant}$.

What if T_C changes? For a CSTR, the energy balance does not account for any spatial variations in temperature, either of the reactor or the coolant. We can simply employ either an average or log-mean average coolant temperature, following methods outlined in Geankopolis.

What if T_C changes? For a PFR, the energy balance accounts for axial variations in temperature and conversion on the reacting fluid side – a separate plug-flow derivation can be applied to the coolant side, as follows:

$$\frac{dE}{dt} = Q - W + \sum (F_i H_i)|_V - \sum (F_i H_i)|_{V+\Delta V}$$

We again assume that work is negligible; additionally, because the coolant fluid is not reacting, we can assume the fluid has constant mass, density and physical properties. Thus,

$$0 = Q + m_c C_{p_c} T|_V - m_c C_{p_c} T|_{V+\Delta V}, \text{ and}$$

$$m_c C_{p_c} \frac{dT_c}{dV} = Ua(T - T_c)$$

This differential equation relates the coolant temperature to the reactor temperature and independent variable, volume (axial position). Lets see how we can piece all these parts together.

Solving a Jacketed, Non-Isothermal PFR:

Lets re-visit the exothermic reaction from last week – partial oxidation of methanol to carbon dioxide and hydrogen. We'll try to keep things as similar as possible, so we'll assume the same kinetics as before, the same feed conditions as before, and the same reactor volume as before. Only now, we have to account for the cooling jacket.

What if we have one large, well-mixed volume? i.e., CSTR?

$$\frac{dT}{dV} = \frac{Q + (\Delta H_{rxn}^o)(r_A) + \Delta C_p T(r_A) - \Delta C_p T_{ref}(r_A)}{F_{AO} \left(\sum_{i=1}^N \theta_i C_{p_i} + \Delta C_p \cdot X \right)} = \frac{Q + r_A (\Delta H_{rxn}^o + \Delta C_p (T - T_{ref}))}{F_{AO} \left(\sum_{i=1}^N \theta_i C_{p_i} + \Delta C_p \cdot X \right)}$$

$$T - T_o = \frac{UAT_c - UAT + r_A (\Delta H_{rxn}^o + \Delta C_p (T - T_{ref}))}{F_{AO} \left(\sum_{i=1}^N \theta_i C_{p_i} + \Delta C_p \cdot X \right)}, \text{ or re-writing, we get}$$

$$T = T_o + \frac{UAT_c + r_A (\Delta H_{rxn}^o + \Delta C_p (T - T_{ref}))}{UA + F_{AO} \left(\sum_{i=1}^N \theta_i C_{p_i} + \Delta C_p \cdot X \right)}$$

Compared with what we had obtained before,

$$T = \frac{\frac{UA T_c}{F_{AO}} + T_o \sum_{i=1}^N \theta_i C p_i + X \cdot (-\Delta H_{rxn}^o) - X \Delta C p T_{ref}}{\frac{UA}{F_{AO}} + \sum_{i=1}^N \theta_i C p_i - X \Delta C p}$$

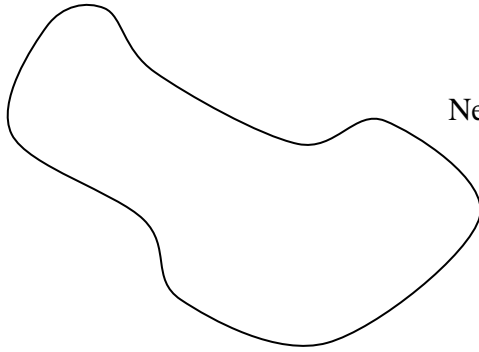
LAST CHAPTER: REAL REACTION ENGINEERING

Challenging Mixing Models: Axial Dispersion; Recycle Reactors; CSTRs in Series

Fundamental, Microscopic Mass Balance

Fundamental, Microscopic Energy Balance

While we are deriving energy balances, we can ask ourselves, how would we derive an energy balance without any assumptions, or limitations to a single spatial dimension? We can draw an arbitrary control volume:



$$\text{Accumulation} = \frac{\partial E}{\partial t} = \int_V \frac{\partial}{\partial t} \left(T \sum_{i=1}^N n_i C p_i \right) dV$$

$$\text{Net Convection Out} := \int_{\delta A} \left(\vec{n} \cdot \left(\vec{v} \sum_{i=1}^N C_i C p_i T \right) \right) \cdot dA$$

$$\text{Net Diffusion Out} := \int_{\delta A} \left(\vec{n} \cdot (k \vec{\nabla} T) \right) \cdot dA$$

$$\text{Generation} := \int_V r_A \cdot \Delta H_{rxn} dV$$

$$\int_V \frac{\partial}{\partial t} \left(T \sum_{i=1}^N n_i C p_i \right) dV = \int_V r_A \cdot \Delta H_{rxn} dV + \int_{\delta A} \delta Q \cdot dA - \int_{\delta A} \delta W \cdot dA$$

$$+ \int_{\delta A} \left(\vec{n} \cdot \left(\vec{v} \sum_{i=1}^N C_i C p_i T \right) \right) \cdot dA + \int_{\delta A} \left(\vec{n} \cdot (\hat{k} \vec{\nabla} T) \right) \cdot dA$$

We can incur the divergence theorem to convert the surface integrals to volume integrals,

$$\int (\vec{n} \cdot \vec{f}) dA = \int \nabla \cdot \vec{f} dV, \text{ and}$$

$$\int_V \frac{\partial}{\partial t} \left(T \sum_{i=1}^N n_i C p_i \right) dV = \int_V r_A \cdot \Delta H_{rxn} dV + \int_V \nabla(\delta Q) \cdot dV - \int_V \nabla(\delta W) dV$$

$$+ \int_V \nabla \left(\bar{v} \sum_{i=1}^N C_i C p_i T \right) \cdot dV + \int_V \nabla(\hat{k} \bar{\nabla} T) \cdot dV$$

Now that all of our terms are written as volume integrals, we assume a differential volume, and do away with all those integrals, i.e. obtain a differential form of the energy balance:

$$\frac{\partial}{\partial t} \left(T \sum_{i=1}^N n_i C p_i \right) = r_A \cdot \Delta H_{rxn} + \nabla(\delta Q) - \nabla(\delta W) + \nabla \left(\bar{v} \sum_{i=1}^N C_i C p_i T \right) + \nabla(\hat{k} \bar{\nabla} T)$$

The above vector-notation equation can be written out in terms of three spatial dimensions and a temporal dimension, recognizing the definition of the gradient function,

$$\nabla T = \begin{pmatrix} \frac{\partial T}{\partial x} & \frac{\partial T}{\partial y} & \frac{\partial T}{\partial z} \end{pmatrix}, \text{ and } \nabla \bar{v} = \begin{pmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{pmatrix}$$

Obviously, this can get somewhat out of hand for the undergraduate level; however the textbook does look at one simple case, the steady-state laminar-flow reactor. Of course, that derivation is obtained via shell-balances, which loses some elegance.

If steady state, the time derivative vanishes; if laminar flow in a perfect tube, then we can incur a lot of symmetry after transforming to cylindrical coordinates. The solution to Navier-Stokes equation, assuming perfectly unidirectional laminar flow results in the classic parabolic velocity solution, such that our velocity vector is purely a function of radial position (not axial position b/c its fully developed, i.e. steady-state).

$$v_z = v_{\max} \left(1 - \left(\frac{r}{R} \right)^2 \right), \text{ and } v_r = v_\theta = 0$$

$$\nabla \bar{v} = \begin{pmatrix} \frac{\partial v_z}{\partial z} & \frac{\partial v_z}{\partial r} & \frac{\partial v_z}{\partial \theta} \\ \frac{\partial v_r}{\partial z} & \frac{\partial v_r}{\partial r} & \frac{\partial v_r}{\partial \theta} \\ \frac{\partial v_\theta}{\partial z} & \frac{\partial v_\theta}{\partial r} & \frac{\partial v_\theta}{\partial \theta} \end{pmatrix}, \text{ or } \nabla \bar{v} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \frac{\partial v_r}{\partial r} & 0 \end{pmatrix}$$

(insert velocity equation)

We can assume symmetry in the theta dimension, if perfectly round tube. This means we have a two-dimensional partial differential equation for the energy balance.

The mass balance is likewise a two-dimensional blah blah blah