

Introduction to Chemical Reactors

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4. Design of Nonisothermal Reactors

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Objectives

- Determine the operation models for **nonisothermal operation of CSTR and PFR** reactors
- Calculate the **adiabatic operation** temperature and conversion of CSTR and PFR reactors
- Analyse and determine **multiple steady states for CSTR**

Sources for the section

- Schmidt: chapters 5 and 6

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Motivation

Real reactors are almost always operated nonisothermally because:

- reactions naturally generate/absorb heat
- reaction rates vary strongly with temperature (increased rate)

We usually want to operate exothermic reactors nonisothermally to make use of the heat released.

At the same time, **nonisothermal behaviour is the major cause of accidents** in chemical plants (re: thermal runaway and pressure buildup).

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Solution of nonisothermal reactor models

To obtain the operation temperature (profile) in the reactor we have to solve simultaneously

(a) Mass balance(s) (MB), i.e. the Design Equations

(b) Energy balance (EB)

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In the next two sections an Energy Balance in terms of Enthalpy (H) is set out for the cases of CSTR and PFR reactors.

Nonisothermal reactors are designed by solving this Energy Balance *simultaneously* with the reactor design equation (a Material Balance).

4.1 Nonisothermal CSTRs

In the case of a CSTR, and similar to its design equation, the Energy Balance can be dynamic or steady state.

Surprisingly, its solution may result in more than one steady state ...

Energy balance in a CSTR

+ve terms: energy added
-ve terms: energy removed

$$\left[\begin{array}{c} \text{accumulation} \\ \text{of heat} \end{array} \right] = \left[\begin{array}{c} \text{heat} \\ \text{flow in} \end{array} \right] - \left[\begin{array}{c} \text{heat} \\ \text{flow out} \end{array} \right] + \left[\begin{array}{c} \text{heat generation} \\ \text{by reaction} \end{array} \right] + \left[\begin{array}{c} \text{heat removal} \\ \text{to surroundings} \end{array} \right]$$

$$\frac{dH}{dt} = \rho C_p V \frac{dT}{dt} = v \rho C_p (T_0 - T) + V \sum_{i=1}^R (-\Delta H_{R_i}) r_i - U A_c (T - T_c) + \dot{W}_s \quad \left[\frac{\text{J}}{\text{s}} \right]$$

U: heat transfer coefficient [J/s/m²/K]

A_c: cooling area

[heat of
reaction]

\dot{Q}

[shaft
work]

Assumptions:

- constant density
- omit gravity and kinetic terms
- fluid thermal properties (ΔH_R , ρC_p , U) are constant

$\dot{Q} > 0$ heat removed from system
 $\dot{W}_s > 0$ work done by system

Energy balance in a CSTR - Steady State (SS)

$$(T - T_0) = \tau \sum_{i=1}^R \frac{-\Delta H_{R_i}}{\rho C_p} r_i - \frac{UA_c}{v\rho C_p} (T - T_c) \quad [\text{K}]$$

Solution of a nonisothermal CSTR (single reaction)

For limiting reactant A

Design equation (MB): $C_{A0} - C_A = \tau r(C_A, T)$

Energy Balance (EB): $(T - T_0) = \tau \frac{-\Delta H_R}{\rho C_p} r(C_A, T) - \frac{UA_c}{v\rho C_p} (T - T_c)$

We have two coupled algebraic equations, sometimes with multiple roots (i.e. multiple steady states).

For multiple reactions we get $(R+1)$ algebraic equations, where R is the number of reactions.

4.2 Nonisothermal PFRs

It is convenient to pose the Energy Balance of a PFR in terms of the variation of *temperature* with respect to *distance* (length of the reactor).

Its solution always results in a single steady state.

Energy balance in a PFR

From a differential balance
between z and $z + dz$:

+ve terms: energy added
-ve terms: energy removed

$$\left[\begin{array}{c} \text{accumulation} \\ \text{of heat} \end{array} \right] = \left[\begin{array}{c} \text{heat generation} \\ \text{by reaction} \end{array} \right] + \left[\begin{array}{c} \text{heat removal} \\ \text{to surroundings} \end{array} \right]$$

$$u \frac{dT}{dz} = \sum_{i=1}^R \frac{-\Delta H_{R_i}}{\rho C_p} r_i - \frac{U p_w}{\rho C_p A_t} (T - T_c) \quad \left[\frac{K}{s} \right]$$

A_t : cross sectional area of the tube ($\pi D^2/4$)
 p_w : tube wall perimeter (πD)

Solution of a nonisothermal PFR (single reaction)

For limiting reactant A

Design equation (MB): $u \frac{dC_A}{dz} = -r(C_A, T)$

Energy Balance (EB): $u \frac{dT}{dz} = \frac{-\Delta H_R}{\rho C_p} r(C_A, T) - \frac{U p_w}{\rho C_p A_t} (T - T_c)$

BCs: $C_A = C_{A0}$; $T = T_0$ @ $z = 0$

Two coupled first-order differential equations (highly non-linear),
always with a single solution (i.e. single steady state).

For multiple reactions we get $(R + 1)$ simultaneous differential
equations with $(R + 1)$ boundary conditions $\{R: \# \text{ of reactions}\}$.

Energy balance in a Batch reactor

The model and solutions for the batch reactor can be obtained
from the PFR Energy Balance by

- transforming dz/u into dt , and
- replacing p_w/A_t by A_c/V

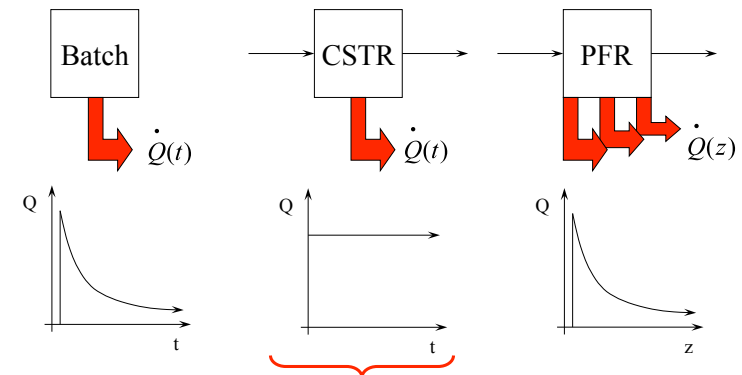
+ve terms: energy added
-ve terms: energy removed

$$\left[\begin{array}{c} \text{accumulation} \\ \text{of heat} \end{array} \right] = \left[\begin{array}{c} \text{heat generation} \\ \text{by reaction} \end{array} \right] + \left[\begin{array}{c} \text{heat removal} \\ \text{to surroundings} \end{array} \right]$$

$$\frac{dT}{dt} = \sum_{i=1}^R \frac{-\Delta H_{R_i}}{\rho C_p} r_i - \frac{U A_c}{V \rho C_p} (T - T_c) \quad \left[\frac{K}{s} \right]$$

A_c : coolant area

Heat removal / addition to maintain a reactor isothermal $\dot{Q} = U A_c (T - T_c)$



- easier to maintain a constant temperature
- higher U because of convective heat transfer

The generation/consumption of energy in a CSTR

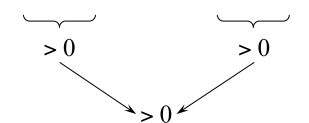
- does not depend on time as in the case of Batch reactors,
- nor it depends on length as in the case of PFRs.

The analysis of heat removal/addition results in a new situation:

for the first time we see that a CSTR has advantages over a PFR, in this case in terms of ease of operation (and, thus, potentially a safer operation).

Some words about ΔH_R

- For an exothermic reaction $\Delta H_R < 0$, e.g. $\Delta H_R = -25 \text{ kJ mole}^{-1}$

$$(T - T_0) = \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A)$$


In reality $\Delta H_R = f(T)$, i.e. it is not constant:

$$\Delta H_R = \Delta H_{R,298}^0 + \int_{298}^T \sum_j \nu_j C_{p,j} dT$$

4.3 Adiabatic reactors

Sometimes we want to operate reactors adiabatically (as in the case of a furnace).

At other times reactors will operate adiabatically even though they were designed to be isothermal: think of the case where the reactor cooling system breaks down (because of a ruptured or blocked pipe, a broken pump, or lack of electricity to run the coolant pump).

The analysis of adiabatic operation is done by setting to zero the heat removal term from the Energy Balance equation.

Adiabatic reactors

An **isothermal** reactor is the limiting case with perfect heat removal.

An **adiabatic** reactor is the limiting case with no heat removal.

$$\dot{Q} = 0$$

- heat generation is proportional to V.
 - heat removal is proportional to A_c , i.e. it is proportional to $V^{1/2}$ for a tube or $V^{2/3}$ for a spherical reactor.
- ➡ hence, cooling becomes more difficult as the reactor becomes larger!

Understanding adiabatic operation is important for safety reasons

Adiabatic CSTR (single reaction)

Design equation (MB): $C_{A0} - C_A = \tau r(C_A, T)$

Energy Balance (EB): $(T - T_0) = \tau \frac{-\Delta H_R}{\rho C_p} r(C_A, T)$

Eliminate $r(C_A, T)$ and rearrange:

$$(T - T_0) = \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A)$$

Define J (> 0 if the reaction is exothermic):

$$J \equiv \frac{-\Delta H_R C_{A0}}{\rho C_p} \quad [\text{K}] \quad \rightarrow \quad T - T_0 = JX$$

Adiabatic PFR (single reaction)

Design equation (MB): $u \frac{dC_A}{dz} = -r(C_A, T)$

Energy Balance (EB): $u \frac{dT}{dz} = \frac{-\Delta H_R}{\rho C_p} r(C_A, T)$

BCs: $C_A = C_{A0} \quad ; \quad T = T_0 \quad @ \quad z = 0$

Eliminate $r(C_A, T)$ and integrate: $(T - T_0) = \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A)$

$$J \equiv \frac{-\Delta H_R C_{A0}}{\rho C_p} \quad [\text{K}]$$

$$T - T_0 = JX$$

*same as
adiabatic
CSTR !*

It turns out that this expression is valid for any adiabatic reactor with a single reaction (i.e. **independent of kinetics or type of reactor**)

The Adiabatic Balance Equation (AEB)

$$T - T_0 = JX$$

tells us how the temperature in an adiabatic reactor varies with respect to conversion, X.

We can also obtain expressions for the

- concentration, C_A
- residence time, τ

for the case of adiabatic operation in

- CSTRs (algebraic expressions) and
- PFRs (differential/integral expressions).

Solution of adiabatic CSTR (single reaction, 1st order)

Design equation (MB): $C_{A0} - C_A = \tau k(T) C_A$ $k(T) = k_0 e^{-E/RT}$

Adiabatic Energy Balance (AEB): $T = T_0 + \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A)$

Substitute T from AEB into $k(T)$, and then $k(T)$ into design equation:

$$C_{A0} - C_A = \tau k_0 \exp \left[\frac{-E}{R \left(T_0 + \left(\frac{-\Delta H_R}{\rho C_p} \right) (C_{A0} - C_A) \right)} \right] \cdot C_A$$

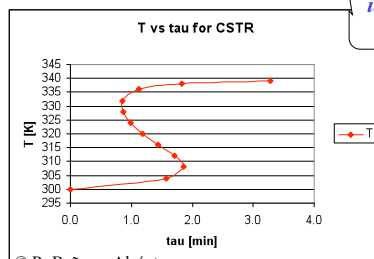
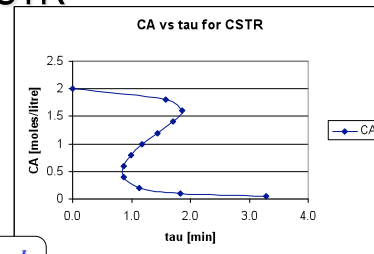
Solution of adiabatic CSTR (single reaction, 1st order)

Solving for τ :

$$\tau = \frac{C_{A0} - C_A}{k_0 \exp \left[\frac{-E}{R \left(T_0 + \left(\frac{-\Delta H_R}{\rho C_p} \right) (C_{A0} - C_A) \right)} \right]} \cdot C_A$$

τ and T in an adiabatic CSTR

- for a set of values of C_A , substitute into expression for $\tau(C_A)$
- note multiple steady states in a range of values of $\tau(C_A)$



identical shapes

- for a set of values of C_A , substitute into AEB expression, $T(C_A)$
- note multiple steady states in a range of values of $\tau(C_A)$ (from τ 0.8 to 1.9)

Note the peculiar behaviour of an adiabatic CSTR:
for a certain range of residence times it exhibits **multiple operation states**, i.e. there are up to three Composition-Temperature pairs for a given residence time.

The two extreme states are stable and the one in the centre is unstable.

More details in Section 4.4: Multiple steady states in a CSTR ...

Solution of adiabatic PFR (single reaction, 1st order)

Design equation (MB): $u \frac{dC_A}{dz} = \frac{dC_A}{d\tau} = -k(T)C_A$ $k(T) = k_0 e^{-E/RT}$

Adiabatic Energy Balance (AEB): $T = T_0 + \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A)$

Substitute T from AEB into $k(T)$, and then $k(T)$ into design equation:

$$\frac{dC_A}{d\tau} = -k_0 \exp \left[\frac{-E}{R \left(T_0 + \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A) \right)} \right] \cdot C_A$$

BC: $C_A = C_{A0}$ @ $z = 0$

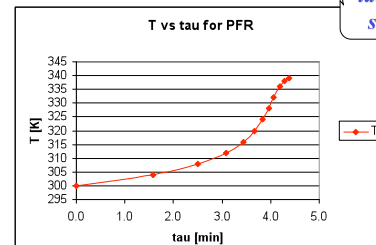
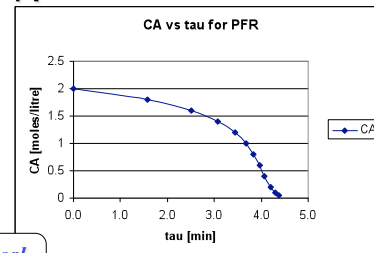
Solution of adiabatic PFR (single reaction, 1st order)(2)

Solve for τ (separable):

$$\tau = - \int_{C_{A0}}^{C_A} \frac{dC_A}{k_0 \exp \left[\frac{-E}{R \left(T_0 + \frac{-\Delta H_R}{\rho C_p} (C_{A0} - C_A) \right)} \right] \cdot C_A}$$

τ and T in an adiabatic PFR

- solve design eqns. numerically, e.g. using Euler's method; tabulate:
 C_A , T , k , $1/kC_A$, $\Delta C_A/kC_A$, $\Sigma(\Delta C_A/kC_A)$
- note that there is a single steady state for the whole range of values of $\tau(C_A)$



identical shapes

- for a set of values of C_A , substitute into AEB expression, $T(C_A)$
- note that there is a single steady state for the whole range of values of $\tau(C_A)$
- CSTR requires shorter τ than PFR**

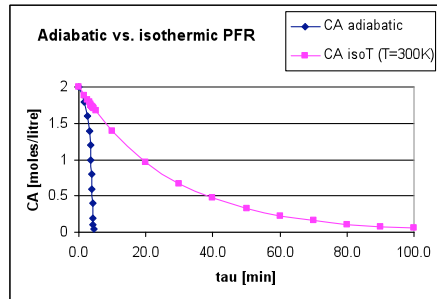
Both, in the case of isothermal and adiabatic operation in a PFR, the conversion increases as the length of the PFR increases.

Or, in terms of other variables, the concentration of the reactant decreases as the residence time increases.

But while their behaviour is qualitatively similar, the change is at least one order of magnitude faster in the case of an adiabatic PFR.

Isothermal vs. Nonisothermal PFR

- isothermal PFR: exponential decay $\frac{dC_A}{d\tau} = -kC_A \Rightarrow C_A = C_{A0}e^{-k\tau}$
- adiabatic PFR: rate acceleration (due to temperature increase)



- Adiabatic PFR attains complete conversion in a much shorter τ

4.4 Multiple steady states in a CSTR

To simplify the analysis of multiple steady states in a CSTR, the two equations that model the reactor:

- the design equation (a Mass Balance)
- the Energy Balance

are expressed in terms of two functions:

- Energy Removal, $R(T)$
- Energy Generation, $G(T)$

The steady states are the intersection of $R(T)$ and $G(T)$.

Multiple Steady States in a CSTR revisited

Design equation (MB): $C_{A0} - C_A = \tau r(C_A, T)$ (1 reac, 1st order) $A \rightarrow B$

Energy Balance (EB): $T - T_0 = \tau \frac{-\Delta H_R}{\rho C_p} r(C_A, T) - \frac{UA_c}{v\rho C_p} (T - T_c)$

Define J and κ :

$$J \equiv \frac{-\Delta H_R C_{A0}}{\rho C_p} \quad [\text{K}]$$

$$\kappa \equiv \frac{UA_c}{v\rho C_p}$$

[dimensionless]

EB becomes:

$$T - T_0 = \frac{J\tau r(C_A, T)}{C_{A0}} - \kappa(T - T_c)$$

Multiple SSs in a CSTR revisited (2) (1 reac, 1st order)



MB in terms of $X(T)$: $(C_{A0} - C_A) = C_{A0}X = \tau r(C_A, T) = \tau k(T)C_{A0}(1 - X)$

proportional to
heat generated
by the reaction

$$C_{A0}X = \tau k(T)C_{A0}(1 - X)$$

$$X(T) = \frac{\tau k(T)}{1 + \tau k(T)}$$

subst. into EB: $T - T_0 = \frac{J\tau r(C_A, T)}{C_{A0}} - \kappa(T - T_c)$

$$X = \frac{\tau r(C_A, T)}{C_{A0}}$$

$$T - T_0 = JX(T) - \kappa(T - T_c)$$

$$X(T) = \frac{(T - T_0) + \kappa(T - T_c)}{J}$$

heat flow due
to I/O streams

heat transfer
through walls

Multiple SSs in a CSTR revisited (3) (1 reac, 1st order)

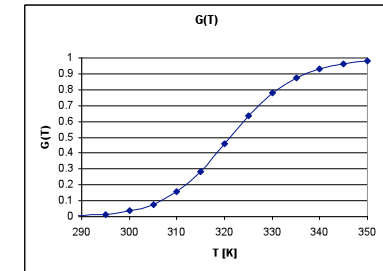
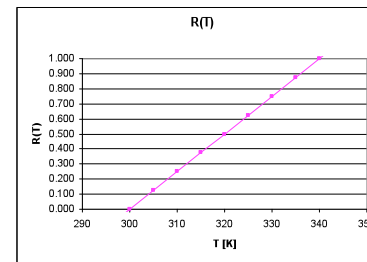


$$\frac{(T - T_0) + \kappa(T - T_c)}{J} = \frac{\tau k(T)}{1 + \tau k(T)}$$

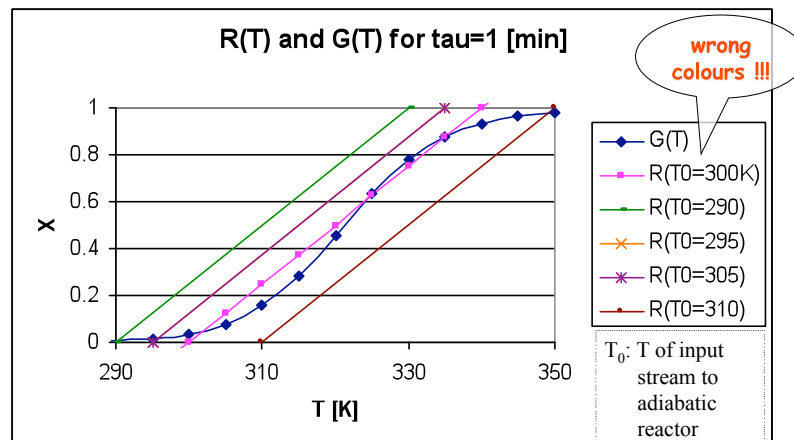
dimensionless
rate of
Energy Removal
(always linear)

$$R(T) = G(T)$$

dimensionless
rate of
Energy Generation
(highly nonlinear)



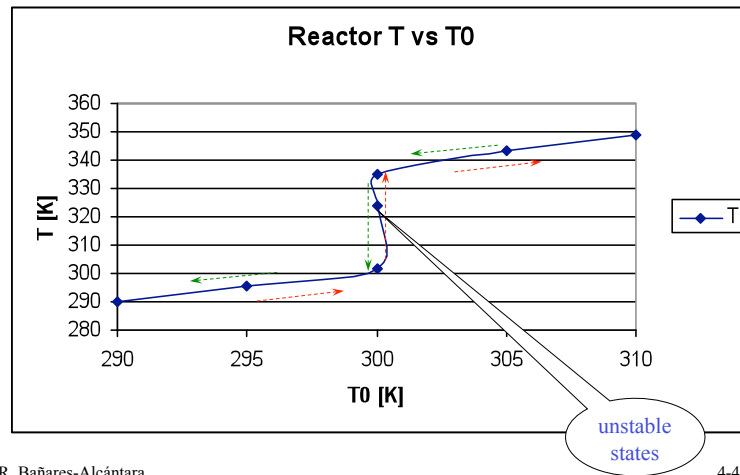
Multiple SSs in a CSTR revisited (1 reac, 1st order) (4)



Runaway, or ignition, occurs when the operating point move from the lower SS to the upper SS, i.e. at the point where the heat removal curve ($R(T)$) and the heat generation curve ($G(T)$) are tangential.

$$\frac{dR(T)}{dT} = \frac{dG(T)}{dT}$$

Multiple SSs in a CSTR revisited (1 reac, 1st order) (5)



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A steady state is **stable** when the reactor returns to its original state following a small perturbation away from it.

When there are three steady states, the first and the third are stable, and the middle is always unstable.

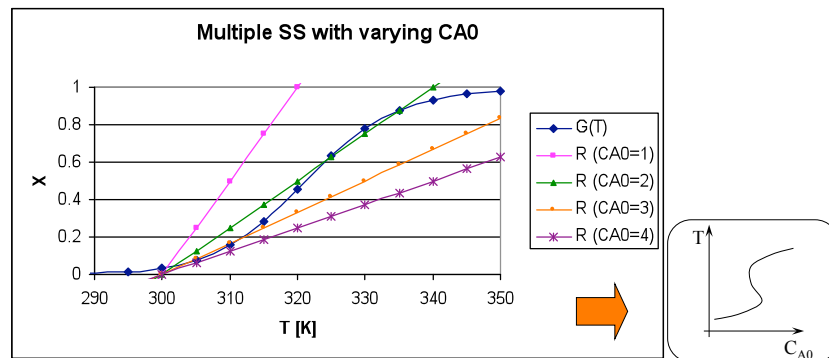
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Multiple SSs in a CSTR revisited (1 reac, 1st order) (6)



Of course, multiple steady states can be attained by varying other variables such as v , C_{A0} , U and A_c (not only T_0):



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4.5 Design of nonisothermal reactors

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Design of nonisothermal reactors

Non-isothermal operation can lead to much smaller V_{reactor} than isoT operation; however, it can lead to multiple SSs (in CSTR).

- *Isothermal reactors*: used in slow processes (e.g. fermentation).
- *Adiabatic reactors*:
 - endothermic reactions: reactor shuts itself off as it cools
 - exothermic reactions: used when heat release is fast, e.g. combustion
- *Interstage heating/cooling*:
sequence of adiabatic reactors with interstage heat transfer.
- *Heated/Cooled reactors*:
external jacket (PFR or CSTR) or cooling/heating coil (CSTR).

Summary

- CSTR Energy Balance: $(T - T_0) = \tau \frac{-\Delta H_R}{\rho C_p} r(C_A, T) - \frac{UA_c}{v\rho C_p} (T - T_c)$
- PFR Energy Balance: $u \frac{dT}{dz} = \frac{-\Delta H_R}{\rho C_p} r(C_A, T) - \frac{Up_w}{\rho CpA_t} (T - T_c)$
BCs: $C_A = C_{A0}$; $T = T_0$ @ $z = 0$
- Adiabatic operation ($Q = 0$)
is important for safety reasons $T - T_0 = JX$ $J = \frac{-\Delta H_R C_{A0}}{\rho C_p}$
- Adiabatic operation of CSTR can result in multiple steady states
- Adiabatic PFR requires much shorter τ than isothermal PFR
- Adiabatic CSTR requires shorter τ than PFR