

Example 8: CSTR with Multiple Solutions

This model studies the multiple steady-states of exothermic reactions. The example is from Parulekar (2007) which in turn was modified from one by Fogler (1999).

The species and reactions do not represent a real system. Therefore, the physical properties have been specified to match the conditions given by Parulekar. Some conditions have been changed to give more realistic results, but the basic results regarding the multiple steady states have been retained. For this example, the intermediate compound, B, will be assumed the desired product.

A Simple Reaction System



$$R_g := 1.987 \cdot \frac{\text{cal}}{\text{mol} \cdot \text{K}} \quad \text{gas law constant}$$

$$T_0 := 300 \cdot \text{K} \quad \text{reference temperature for dimensionless temperature (not the inlet temperature)}$$

Thermophysical properties

species	molecular weights	heats of formation	C, H, O atoms in each species
A B C Inert	$M_w := \begin{pmatrix} 33 \\ 33 \\ 33 \\ 33 \end{pmatrix} \cdot \frac{\text{gm}}{\text{mol}}$	$\Delta H_f := \begin{pmatrix} 0 \\ -55 \\ -126.5 \\ 0 \end{pmatrix} \cdot 10^3 \cdot \frac{\text{J}}{\text{mol}}$	$\text{Atom} := \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 1 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$

These were selected based on given ΔH_{rxn} , Parulekar (2007)

The product of the molecular weight of A and the molar density, c , must equal the liquid density, which is assumed below to be that of water. The initial concentration of A was given as 0.3 mol/L by Parulekar. That would result in molecular weights of 3333. To be more realistic, the above molecular weights have been assumed, which makes the molar concentration 30 mol/L. These changes do not affect the solution because the two parameters, M_w and c , are always multiplied by each other, and the result is thus constant.

$NC := rows(Mw)$

number of components

$n := 0..NC - 1$

component index

Inlet conditions

mole fractions

$$mfin := \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

A
B
C
Inert

$$\sum mfin = 1 \quad \text{check sum}$$

$$M_f := mfin \cdot Mw$$

molecular weight of feed mixture

$$M_f = 0.033 \frac{kg}{mol}$$

$$\omega_0 := \frac{\overrightarrow{(mfin \cdot Mw)}}{M_f}$$

convert mole fractions to weight fractions

Fluid properties

$$\rho := 1 \cdot \frac{gm}{cm^3}$$

density of fluid

$$c := \frac{\rho}{M_f} = 30.303 \cdot \frac{mol}{L}$$

molar density of feed

$$cp := \begin{pmatrix} 300 \\ 300 \\ 300 \\ 300 \end{pmatrix} \cdot \frac{J}{mol \cdot K}$$

heat capacities, molar basis

$$CpTf(T) := 1$$

temperature function when cp is not a function of temperature

$$Cp(\omega, \theta) := cp \cdot CpTf(\theta \cdot T_0) \cdot \frac{\omega}{Mw} \longrightarrow$$

Stoichiometry

$$\nu := \begin{pmatrix} -1 & 1 & 0 & 0 \\ 0 & -1 & 1 & 0 \end{pmatrix}$$

rows are reactions, columns are components

check stoichiometry and Mw

$$\frac{\nu \cdot Mw}{\frac{kg}{mol}} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This vector should be null if Mw and ν are correct.

Heat of reaction

$$\Delta H_o := \nu \cdot \Delta H_f$$

standard state, at 298 K

$$\Delta Cp := \nu \cdot cp = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \cdot \frac{J}{mol \cdot K}$$

difference in heat capacities of products and reactants

$$DHT(T) := T$$

This function provides the dependence of enthalpy on temperature. For cp constant with temperature, the function is simply the absolute temperature, T .

$$\Delta H(T) := \Delta H_o + \Delta Cp \cdot (DHT(T) - DHT(298 \cdot K))$$

heat of reaction is constant for this example because $\Delta Cp = 0$

Reaction Rate Expressions

activation energies

$$E := \left(\frac{9900}{27000} \right) \cdot \frac{\text{cal}}{\text{mol}}$$

pre-exponential rate constants

$$A_0 := 3.3 \cdot \exp\left(\frac{E_0}{Rg \cdot 300 \cdot K}\right) \cdot \frac{1}{\text{min}}$$

$$A_1 := 4.58 \cdot \exp\left(\frac{E_1}{Rg \cdot 500 \cdot K}\right) \cdot \frac{1}{\text{min}}$$

The above rate constants result in a nominal space time of 0.01 min [Parulekar (2007)]. To make the problem more typical for industry, the rate constants will be divided by 1000. This will correspondingly increase the space times to the order of 10 min. These changes do not affect the multiple temperature solutions.

$$A := \frac{A}{1000}$$

The rate expressions in terms of the state variables

$$act := 1$$

$$rxn(\omega, \theta, p, act) := c \cdot \begin{bmatrix} A_0 \cdot \exp\left(\frac{-E_0}{\theta \cdot T_0 \cdot Rg}\right) \cdot \frac{\frac{\omega_0}{Mw_0}}{\sum\left(\frac{\omega}{Mw}\right)} \\ A_1 \cdot \exp\left(\frac{-E_1}{\theta \cdot T_0 \cdot Rg}\right) \cdot \frac{\frac{\omega_1}{Mw_1}}{\sum\left(\frac{\omega}{Mw}\right)} \end{bmatrix}$$

The concentrations used in the rate expressions are in terms of mol/cu m. The concentrations have been written using the weight fractions, converting to mole fractions, and multiplying by the molar density, c .

The catalyst activity, act , has been assumed to be 1.

Net production rates

$$Rxn(\omega, \theta, p, act) := \nu^T \cdot rxn(\omega, \theta, p, act) \quad \text{mol/vol/time}$$

The energy balance will use the difference in enthalpy of feed and effluent streams instead of a heat production term.

CSTR with reactor temperature and space time as a parameters

This is a design model for a non-adiabatic reactor. The adiabatic version will be solved in the next section. Each expression below is set equal to zero in the solve block that follows.

$$\text{resid}(\omega, \tau, Tr) := \left[\begin{array}{c} \omega_{0_0} - \omega_0 + \frac{Mw_0 \cdot Rxn\left(\omega, \frac{Tr}{T_0}, 1, act\right)_0 \cdot \tau}{\rho} \\ \omega_{0_1} - \omega_1 + \frac{Mw_1 \cdot Rxn\left(\omega, \frac{Tr}{T_0}, 1, act\right)_1 \cdot \tau}{\rho} \\ \omega_{0_2} - \omega_2 + \frac{Mw_2 \cdot Rxn\left(\omega, \frac{Tr}{T_0}, 1, act\right)_2 \cdot \tau}{\rho} \\ \omega_{0_3} - \omega_3 + \frac{Mw_3 \cdot Rxn\left(\omega, \frac{Tr}{T_0}, 1, act\right)_3 \cdot \tau}{\rho} \\ 1 - \sum \omega \\ \left[Atom^T \cdot \left(\frac{\omega_0 - \omega}{Mw} \right) \right]_0 \cdot \frac{gm}{mol} \\ \left[Atom^T \cdot \left(\frac{\omega_0 - \omega}{Mw} \right) \right]_1 \cdot \frac{gm}{mol} \end{array} \right]$$

4 mass balances with mass fractions

these are NOT molar balances

wt fractions must sum to 1

These last two constraints are C, H balances. Since the method used to solve the reactor balances is an optimization routine, there is danger that the results may not be realistic. These atom balances provide an additional constraint on the solution.

Because of the dummy species, these constraints are not actually needed for this example.

Solve block

used to solve a system of equations

$$\omega := \omega_0$$

initial guesses for outlet weight fractions and temperature

$$Tr := 500 \cdot K$$

Given

$$resid(\omega, \tau, Tr) = 0$$

$$CSTR(\tau, Tr) := Find(\omega)$$

use Levenberg-Marquardt method (right click on Find to check or change method)

The result, *CSTR*, is the outlet weight fraction vector as a function of τ and Tr .

End of solve block

Define space time and temperature cases

$$t := 0..8$$

time index

$$\tau_{c_t} := 1000 \cdot (.1 \cdot t + .2) \cdot s$$

space times

$$i := 0..40$$

reactor temperature index

$$Tout_0 := 200 \cdot K$$

$$Tout_{i+1} := Tout_i + 20 \cdot K$$

outlet temperatures

solve for each case

$$\omega_{out_{t,i}} := CSTR(\tau_{c_t}, Tout_i)$$

outlet mass fractions for each case

examine a case to check for errors

$$tc := 4 \quad ic := 15$$

select the space time and outlet temperature indexes of the case

$$\tau_{c_{tc}} = 10 \cdot \text{min}$$

$$T_{out_{ic}} = 500 \text{ K}$$

the case values for the independent variables

$$mf_{out_{t,i}} := \frac{\overrightarrow{(\omega_{out_{t,i}})}}{Mw} \cdot \frac{Mw}{\sum \left(\frac{\omega_{out_{t,i}}}{Mw} \right)}$$

outlet mole fractions, converted from outlet mass fractions

inlet weight fractions

outlet weight fractions

inlet mole fractions

outlet mole fractions

$$\omega_0 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\omega_{out_{tc,ic}} = \begin{pmatrix} 0.038 \\ 0.92 \\ 0.042 \\ 0 \end{pmatrix}$$

$$mf_{in} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$mf_{out_{tc,ic}} = \begin{pmatrix} 0.038 \\ 0.92 \\ 0.042 \\ 0 \end{pmatrix}$$

$$\sum \omega_0 = 1$$

$$\sum \omega_{out_{tc,ic}} = 1$$

$$\sum mf_{in} = 1$$

$$\sum mf_{out_{tc,ic}} = 1$$

check mass balances of elements

$$Atom^T \cdot \frac{\overrightarrow{(\omega_0 - \omega_{out_{tc,ic}})}}{Mw} \cdot \frac{gm}{mol} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

This result should be a null vector.

Determine desired operating condition from plots

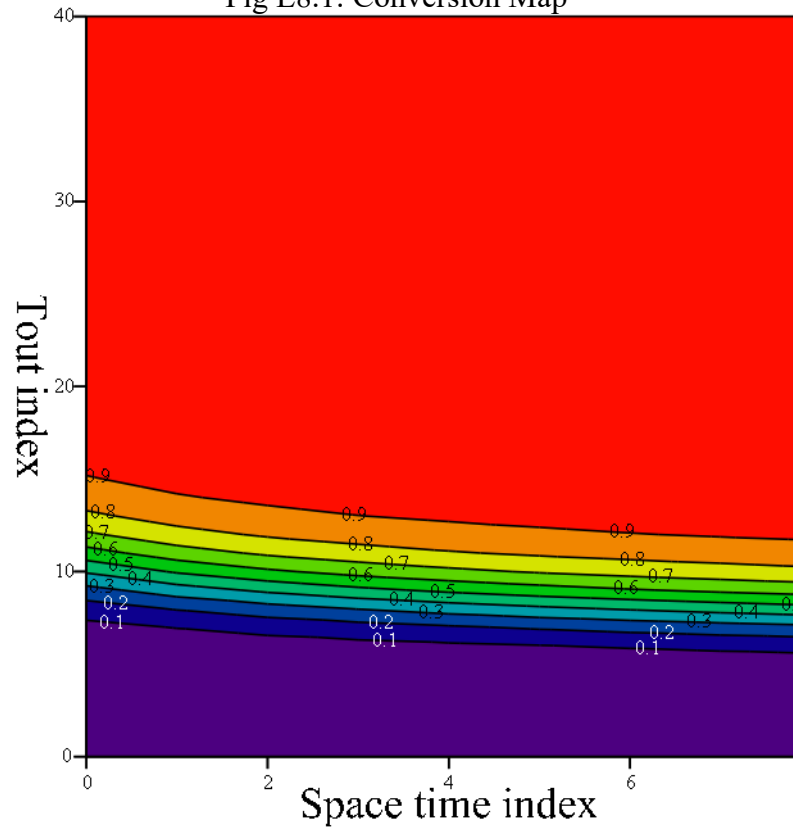
conversion for each case

$$conv_{t,i} := 1 - \frac{(\omega_{out_{t,i}})_0}{\omega_0}$$

intermediate B outlet mass fraction

$$B_{out_{t,i}} := (\omega_{out_{t,i}})_1$$

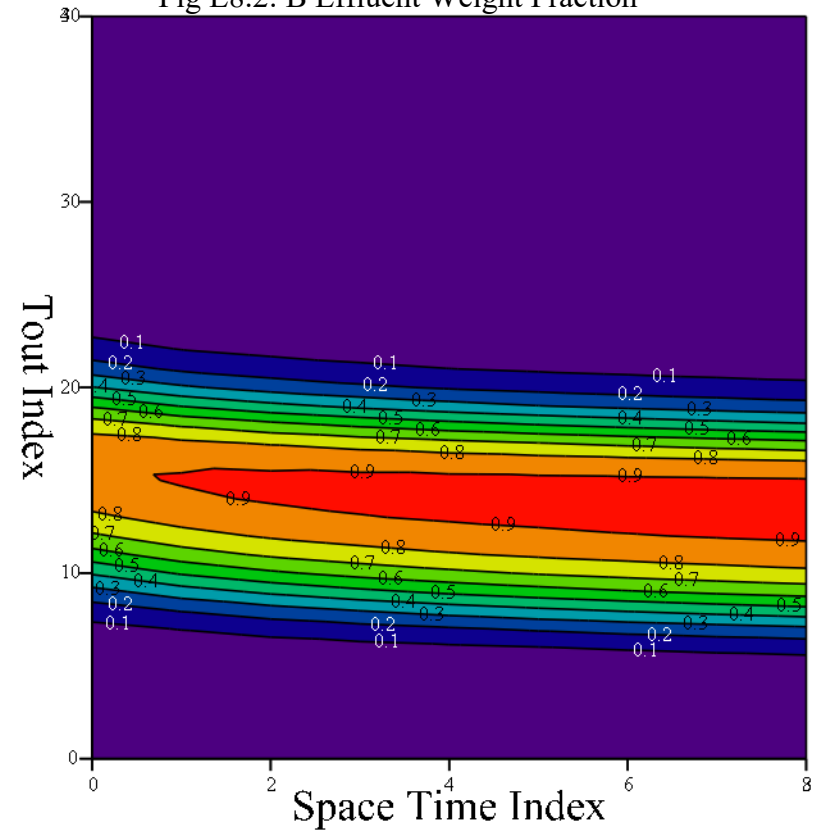
Fig E8.1: Conversion Map



conv

Conversion is sensitive to temperature but not space velocity for the ranges selected.

Fig E8.2: B Effluent Weight Fraction



Bout

There is a narrow window of reactor temperature that yields a high selectivity to the intermediate product.

Select optimum (high conversion and selectivity to desired product) space time index and *Tout* index using above plots.

$$\tau_{opt} := 4$$

$$\tau_{opt} := \tau_{c\tau_{opt}} = 10 \cdot \text{min}$$

$$tout := 15$$

$$T_{opt} := Tout_{tout} = 500 \text{ K}$$

Now that the desired reactor space time and temperature have been set, include the heat balance to see if operation at those conditions is feasible.

Energy balance

Thus far, the results have not been dependent on the inlet temperature. For an energy balance, the inlet temperature, T_{in} , is needed.

Enthalpy out - Enthalpy in

$$Del_H(T_{in}, Tr, \omega_0, \omega_l) := \left[\begin{array}{l} \left[\Delta H_f \cdot \frac{\omega_l}{M_w} + cp \cdot (DHT(Tr) - DHT(298 \cdot K)) \cdot \frac{\omega_l}{M_w} \right] \dots \\ + \left[\Delta H_f \cdot \frac{\omega_0}{M_w} + cp \cdot (DHT(T_{in}) - DHT(298 \cdot K)) \cdot \frac{\omega_0}{M_w} \right] \end{array} \right]$$

The wrap feature always includes a plus at the break, but a minus can be added with the desired effect, i.e. plus a minus is a negative.

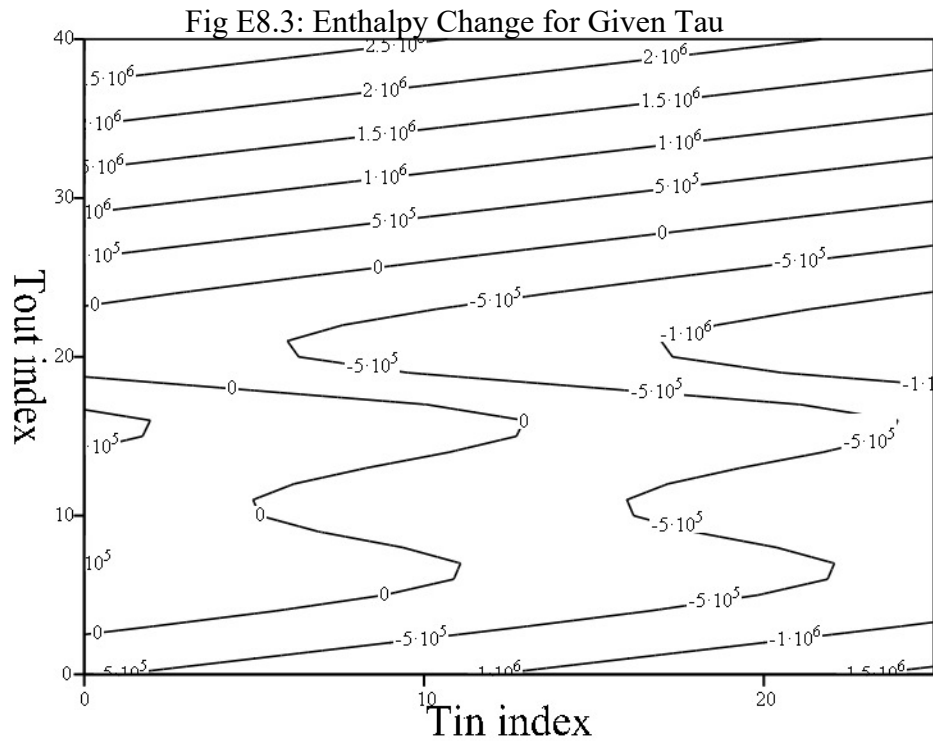
Heat balance for a given (optimal) space time $\tau_{opt} = 10 \cdot min$

$j := 0..25$ inlet temperature index

$T_{in_0} := 250 \cdot K$

$T_{in_{j+1}} := T_{in_j} + 5 \cdot K$ inlet temperature vector

$DH_{j,i} := \frac{Del_H(T_{in_j}, T_{out_i}, \omega_0, \omega_{out\tau_{opt},i})}{\left(\frac{J}{kg}\right)}$ matrix of enthalpy difference for the given space time, which is given implicitly via $\omega_{out\tau_{out}}$



	0		0
1	255		200
2	260		220
3	265		240
4	270		260
5	275		280
6	280		300
7	285	K	320
8	290		340
9	295		360
10	300		380
11	305		400
12	310		420
13	315		440
14

DH

$tin := 10$ index for Tin chosen from above plot

Figure E8.3 can be used to explore the possibility of operating at the desired outlet temperature in order to achieve the conversion and selectivity of the optimum. The chosen $Tout$ index, $tout = 15$, may be found on the vertical axis, and then the heat exchange required at different inlet temperatures are examined by moving at constant $Tout$ across the plot. The contours are constant heat exchanged, negative for cooling, positive for heating.

For the current example, it appears that multiple solutions will exist regardless of the chosen Tin . Even for a single reaction, there may be three solutions at some conditions.

A horizontal line at $Tout$ index of 15 in Fig E8.3 intersects the adiabatic curve at Tin index of about $tin = 10$. This is $Tin_{tin} = 300K$ as shown to the

right of the graph. The slope of the heat exchange curve is positive at this intersection, indicating the operating point is stable. The T_{in} and heat exchange chosen will be used for initial guesses for Fig E8.4.

$$Q_m := 0 \cdot 10^5 \cdot \frac{J}{kg}$$

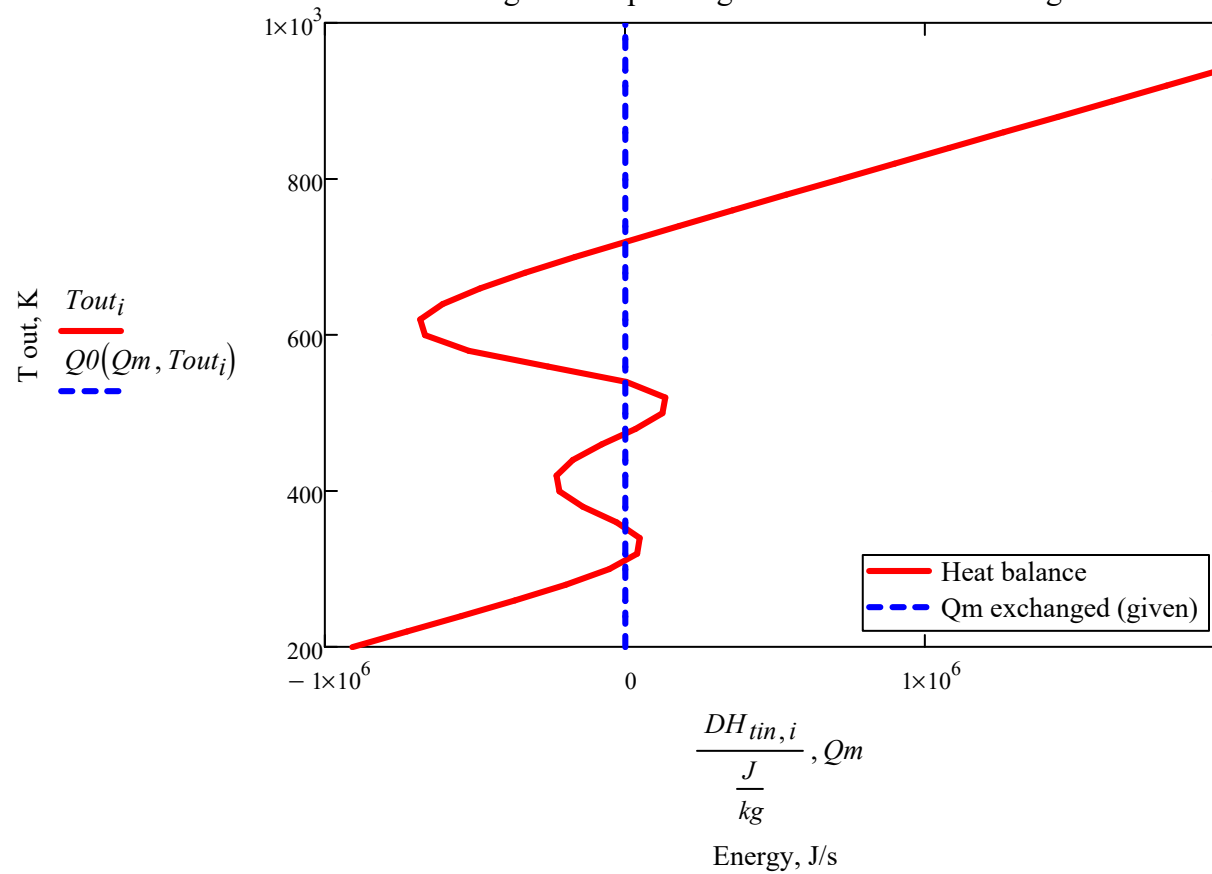
select a heat exchange rate for Fig E8.4 (the DH contours in Fig E8.3 are equal to Q_m)

$$Q0(x,y) := y$$

heat exchange curve (to plot the vertical line below at Q_m)

$$T_{in_{tin}} = 300 K$$

Fig E8.4: Operating Curve and Heat Exchange



The red curve in Fig E8.4 is the heat produced at T_{out} , including the sensible heat of the inlet and outlet streams, but excluding any heat exchanged. The blue curve, Q_m , is the amount of heat exchanged per kg of feed, a value chosen by the user. The solutions are where the heat exchanged equals the heat produced. Traditionally, as shown by Parulekar, the red curve would exclude the sensible heat and the second curve would be a sloping line representing the heat removed by the sensible heat difference. The intersections of the curves in the traditional plot are difficult to detect due to the nearly equal slopes of the two curves. Parulekar therefore used an iterative calculation to find the roots. With the above plot, the intersections are readily determined using the Trace feature in the Mathcad plot.

The vertical line in the above graph is moved to the left for cooling...to the right for heating (change Q_m prior to the plot). Also, the red line can be moved to left or right by selecting a higher or lower inlet temperature (i.e. value of t_{in}), respectively. With experimentation, the plot shows that the middle solution area can be reached with $T_{in} = 300 \text{ K}$ and $Q_m = 0$ (as shown).

The possibility of multiple solutions is a red flag for unstable operation even if the point is "stable". The dynamic CSTR model in Example 9 will be used to simulate the startup to the desired intermediate solution. A better option may be to include an inert in the feed.

Operation at desired conditions

The desired conditions have been selected from the simulations and plots E8.1-4, but the actual design condition has not yet been fully simulated with accuracy. The heat balance is now included in the model so that the reactor temperature becomes a dependent variable. The inlet temperature and space time are specified. Using this model, the conditions selected with the above procedure can be simulated to find the complete composition and outlet temperature at the given space time and inlet temperature.

$$T_0 := 300 \cdot K$$

$$\tau := \tau_{opt}$$

$$Q_m := 0 \cdot 10^5 \cdot \frac{J}{kg}$$

$$\text{resid2}(\omega I, \theta) := \left[\begin{array}{c} \frac{-Del_H(T0, \theta \cdot T0, \omega_0, \omega I) + Qm}{\frac{J}{kg}} \\ \omega_{0_0} - \omega I_0 + \frac{Mw_0 \cdot Rxn(\omega I, \theta, 1, act)_0 \cdot \tau}{\rho} \\ \omega_{0_1} - \omega I_1 + \frac{Mw_1 \cdot Rxn(\omega I, \theta, 1, act)_1 \cdot \tau}{\rho} \\ \omega_{0_2} - \omega I_2 + \frac{Mw_2 \cdot Rxn(\omega I, \theta, 1, act)_2 \cdot \tau}{\rho} \\ \omega_{0_3} - \omega I_3 + \frac{Mw_3 \cdot Rxn(\omega I, \theta, 1, act)_3 \cdot \tau}{\rho} \\ 1 - \sum \omega I \\ \left[Atom^T \cdot \left(\frac{\omega_0 - \omega I}{Mw} \right) \right]_0 \frac{gm}{mol} \\ \left[Atom^T \cdot \left(\frac{\omega_0 - \omega I}{Mw} \right) \right]_1 \frac{gm}{mol} \end{array} \right]$$

This constraint has been added.

Solve block

Initial guesses obtained from the automated cases studied above allow the optimization routine to find the desired stable solution. Without the case studies above, finding that solution may have been difficult.

$T_{out} := 480 \cdot K$ From Fig 8.4 with intersection of red and blue curves

$$\theta 1 := \frac{T_{out}}{T_0}$$

$$\omega 1 := \omega_{out\tau_{opt}, tout}$$

Given

$$resid2(\omega 1, \theta 1) = 0$$

$$(x_{design} \ \theta_{design}) := Find(\omega 1, \theta 1) \quad \text{finding the output composition and temperature}$$

End of solve block

results

$$x_{design} = \begin{pmatrix} 0.064 \\ 0.926 \\ 9.469 \times 10^{-3} \\ 0 \end{pmatrix}$$

$$Tr := \theta_{design} \cdot T_0 = 473.849 K$$

$$conv_{ad} := 1 - \frac{x_{design_0}}{\omega_{0_0}} = 0.936$$

conversion of A

$$selectivity := \frac{x_{design_1}}{\omega_{0_0} - x_{design_0}} = 0.99$$

selectivity to B

Summary

Both a CSTR model and a design procedure were demonstrated. The procedure shown arrives at a desired design without trial and error. By first mapping the conversion and selectivity without the heat balance, multiple steady states are not an issue. After finding the desirable inlet and outlet temperatures and the heat exchange needed, those conditions and an outlet composition from a nearby mapped case provide the initial guesses needed to obtain the desired steady state solution.

When compared to the combined analytical/numerical method used by Parulekar, the fully numerical method used above appears quite complicated. Parulekar's method achieves the goal of demonstrating the multiple steady state problem that can arise in CSTRs in a simple manner. The goal for the model presented above is a generic model that is easily changed for other systems.

In **Example 9**, the startup procedure needed to reach the desired operating point will be explored.

References

Fogler, H.S., "Elements of Chemical Reaction Engineering", 3rd Ed., Prentice-Hall (1999).

Parulekar, S.J., Illinois Inst. of Technology, Chemical Engineering Education, Winter (2007)

Exercise

Explore the addition of inerts to obtain a system with a single stable operating point at high conversion and selectivity. An inert compound has already been supplied.