Example 3: Single Reaction Equilibrium

This example demonstrates the exploration of staged adiabatic beds with intercoolers and with quench fluid, and estimation of the optimum isothermal temperature for a cooled, tubular reactor.

Benzene hydrogenation to cyclohexane

C6H6 + 3 H2 <---> C6H12

miscellaneous parameters

$Rg := 1.987 \cdot \frac{cal}{mol \cdot K}$ gas law constant

atomic weights

$Aw := \begin{pmatrix} 12 \\ 1 \end{pmatrix} \cdot \frac{gm}{mol}$ C H

molecular formulas

$Atom := \begin{pmatrix} 6 & 6 \\ 0 & 2 \\ 6 & 12 \end{pmatrix}$ benzene, H2, cyclohexane

$NC := rows(Atom)$ number of components

$i := 0 .. NC - 1$ component indexes

Thermophysical properties

molecular weights

$$Mw := Atom \cdot Aw = \begin{pmatrix} 0.078 \\ 2 \times 10^{-3} \\ 0.084 \end{pmatrix} \frac{kg}{mol}$$

heats of formation

$$\Delta Hf := \begin{pmatrix} 19.82 \\ 0 \\ -29.43 \end{pmatrix} \cdot 10^3 \cdot \frac{cal}{mol}$$

free energies

$$\Delta Ff := \begin{pmatrix} 30.99 \\ 0 \\ 7.59 \end{pmatrix} \cdot 10^3 \cdot \frac{cal}{mol}$$

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Fluid composition and conditions

mole fractions in feed

$$molf := \begin{pmatrix} .25 \\ .75 \\ 0 \end{pmatrix}$$

benzene
H2
cyclohexane

$$M_f := molf \cdot Mw = 0.021 \frac{kg}{mol}$$

molecular weight of feed mixture

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

convert mole fractions to weight fractions

$$T_0 := 500 \cdot K$$

inlet temperature

$$Ptot := 10 \cdot atm$$

pressure

Gas heat capacity

Molar heat capacities by Reid et al (1977) are provided below. The heat capacity expression is a cubic polynomial in absolute temperature, in Kelvin. The parameters for the expression for each component are given in the cp matrix. The temperature functions are in the vector $CpTf(T)$. Including the unit, K, in the definition will allow the use of temperatures given in any unit.

each row of cp contains the parameters for one component

$$cp := \begin{pmatrix} -8.101 & .1133 & -7.206 \cdot 10^{-5} & 1.703 \cdot 10^{-8} \\ 6.483 & .00215 & -3.298 \cdot 10^{-6} & 1.826 \cdot 10^{-9} \\ -13.03 & .1460 & -6.027 \cdot 10^{-5} & 3.156 \cdot 10^{-9} \end{pmatrix} \cdot \frac{cal}{mol \cdot K}$$

benzene
H2
cyclohexane

$$CpTf(T) := \begin{bmatrix} 1 & \frac{T}{K} & \left(\frac{T}{K}\right)^2 & \left(\frac{T}{K}\right)^3 \end{bmatrix}^T$$

heat capacity temperature functions

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Reactions

Stoichiometry

rows are reactions, columns are components

$\nu := \begin{pmatrix} -1 & -3 & 1 \end{pmatrix}$ $NR := rows(\nu) = 1$ number of reactions

check stoichiometry and Mw

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

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

The formulas for heat of reaction and Keq were given in Example 1. They are present in the collapsed area below.

Equilibrium coefficient as a function of temperature

Figure E3.1: Equilibrium Coefficients

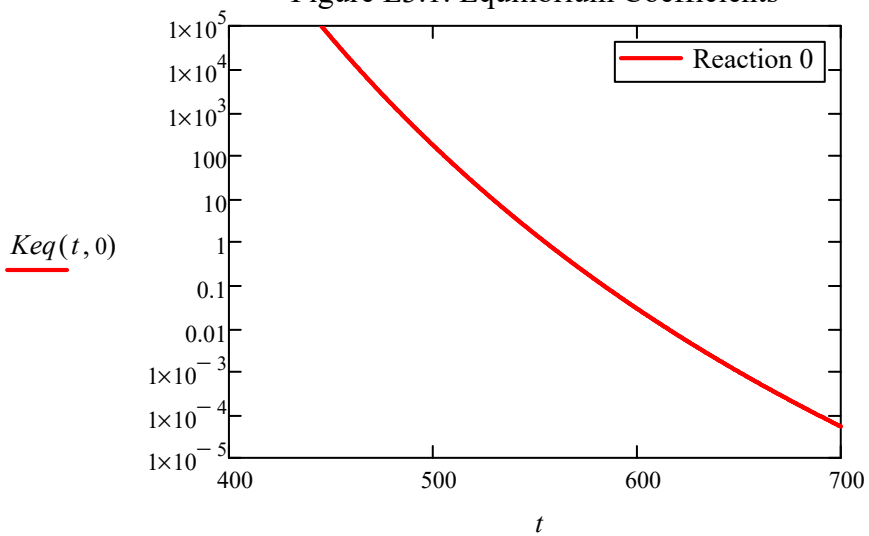

Figure E3.1 may be used to determine a reasonable temperature range. A starting range might be 500 - 700 K.

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Equilibrium extent of reaction as a function of temperature

The equilibrium extent of reaction is to be plotted as a function of temperature. The procedure will involve finding the extent of reaction that equates the thermodynamic equilibrium coefficient with the gas mole fraction coefficient (assume ideal gas and ideal solutions).

$lr := 0$ — lr is the designated component number of the limiting reactant

$nf := molf \cdot mol$ — moles fed

$$nf = \begin{pmatrix} 0.25 \\ 0.75 \\ 0 \end{pmatrix} mol$$

$$K = K_y \cdot \left(\frac{P}{atm}\right)^{\sum \nu} = \mathrm{KY}$$ — from eq (5.29) in main text

$$lnKY(\xi) := ln\left[\left(\frac{Ptot}{atm}\right)^{\sum \left(\nu^T\right)^{\langle 0 \rangle}} \cdot \frac{\prod_{i=0}^{NC-1} \left(\frac{nf_i - \frac{\nu_{0,i}}{\nu_{0,lr}} \cdot \xi \cdot nf_{lr}}{mol}\right)^{\nu_{0,i}}}{\left[\sum \left(\frac{nf - \nu^T \cdot \xi \cdot \frac{nf_{lr}}{\nu_{0,lr}}}{mol}\right)\right]^{\sum \left(\nu^T\right)^{\langle 0 \rangle}}}\right] \quad \text{(E3.3)}$$

$\xi := 0.999$ — starting guess (a value near 1 appears to work best for exothermic reaction)

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$fK(x,t) := lnK(t,0) - lnKY(x)$

the root operation below will make $lnK = lnKX$ at extent x and temperature t (E3.4)

$\xi e(t) := root(fK(\xi,t),\xi)$

equilibrium extent of reaction as a function of temperature (E3.5)

create the equilibrium plot

$Tmin := 400 \cdot K \qquad Tmax := 675 \cdot K$

$nj := 50$

$j := 0..nj$

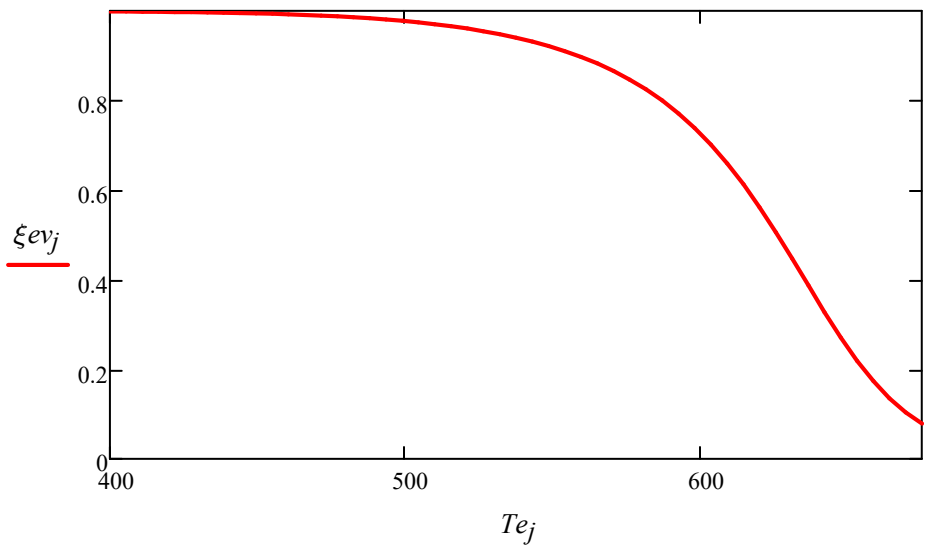
$Te_j := Tmin + \frac{Tmax - Tmin}{nj} \cdot j$

$Tmin$ and $Tmax$ are the end points for the horizontal axis in Fig E3.2. The temperature range end points need to be found by trial and error in order to obtain the roots throughout the temperature range. If Fig E3.2 has an error, choose a smaller temperature range.

$\xi ev_j := \xi e(Te_j)$

Using a vector of values, ξev, instead of the continuous function, ξe(t) speeds up the plot computations.

Figure E3.2: Equilibrium Extent of Reaction vs Temperature



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Adiabatic curves for staged beds with intercoolers

Equilibrium controlled reactions may be conducted in staged beds with intercooling. This allows the reaction to reach a higher conversion than is possible in a single bed. The inlet and outlet temperatures and extents of reaction can be determined in an interactive manner using Mathcad. First, the general enthalpy balance for a bed needs to be defined, Eq (E3.7)

$$fad\left(\xi_{in}, t_{out}, t_{in}\right) := H\left(t_{out}\right) \cdot \left(nf - \nu^{T} \cdot \xi e\left(t_{out}\right) \cdot \frac{nf_{lr}}{\nu_{0,lr}}\right) - H\left(t_{in}\right) \cdot \left(nf - \nu^{T} \cdot \xi_{in} \cdot \frac{nf_{lr}}{\nu_{0,lr}}\right) \quad \text{(E3.6)}$$

$t_{out} := 650 \cdot K$ initial guess of outlet temperature (E3.7)

$Teq\left(\xi_{in}, t_{in}\right) := root\left(fad\left(\xi_{in}, t_{out}, t_{in}\right), t_{out}\right)$ outlet temperature as a function of inlet fractional extent of reaction and temperature (E3.8)

The ξad function will be used to plot the adiabatic curves for each stage. The reaction rates decline rapidly as the fluid approaches the equilibrium. Thus, the amount of catalyst needed to increase conversion increases as the equilibrium condition is approached. In order to determine the number of stages needed, an approach temperature, 25 C, is assumed. Later, simulations of each bed can be used to determine more optimal end point temperatures.

The approach temperature is handled by adding the approach temperature to the desired inlet temperature. Then the intersection of the adiabatic curve and the equilibrium curve determines the equilibrium temperature for the outlet. Once all of the beds and cooling curves have been determined, the approach amount is subtracted from the stage lines.

$approach := 25 \cdot K$ approach temperature is positive for exothermic reactions and negative for endothermic reactions

$Tin := 450 \cdot K + approach$

$Tstg_0 := Tin$

$\xi stg_0 := 0$

$Tstg_1 := Teq\left(\xi stg_0, Tin\right) = 655.783\,K$ first bed

$\xi stg_1 := \xi e\left(Tstg_1\right) = 0.196$

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$Tstg_2 := Tin$

$\xi stg_2 := \xi stg_1$

first intercooling

$Tstg_3 := Teq(\xi stg_2, Tin)$

$\xi stg_3 := \xi e(Tstg_3)$

second bed

$Tstg_4 := Tin$

$\xi stg_4 := \xi stg_3$

second intercooling

$Tstg_5 := Teq(\xi stg_4, Tin)$

$\xi stg_5 := \xi e(Tstg_5)$

third bed

$Tstg_6 := Tin$

$\xi stg_6 := \xi stg_5$

third intercooling

$Tstg_7 := Teq(\xi stg_6, Tin)$

$\xi stg_7 := \xi e(Tstg_7)$

fourth bed

$Tstg := Tstg - approach$

adjustment of $Tstg$ for the approach temperature

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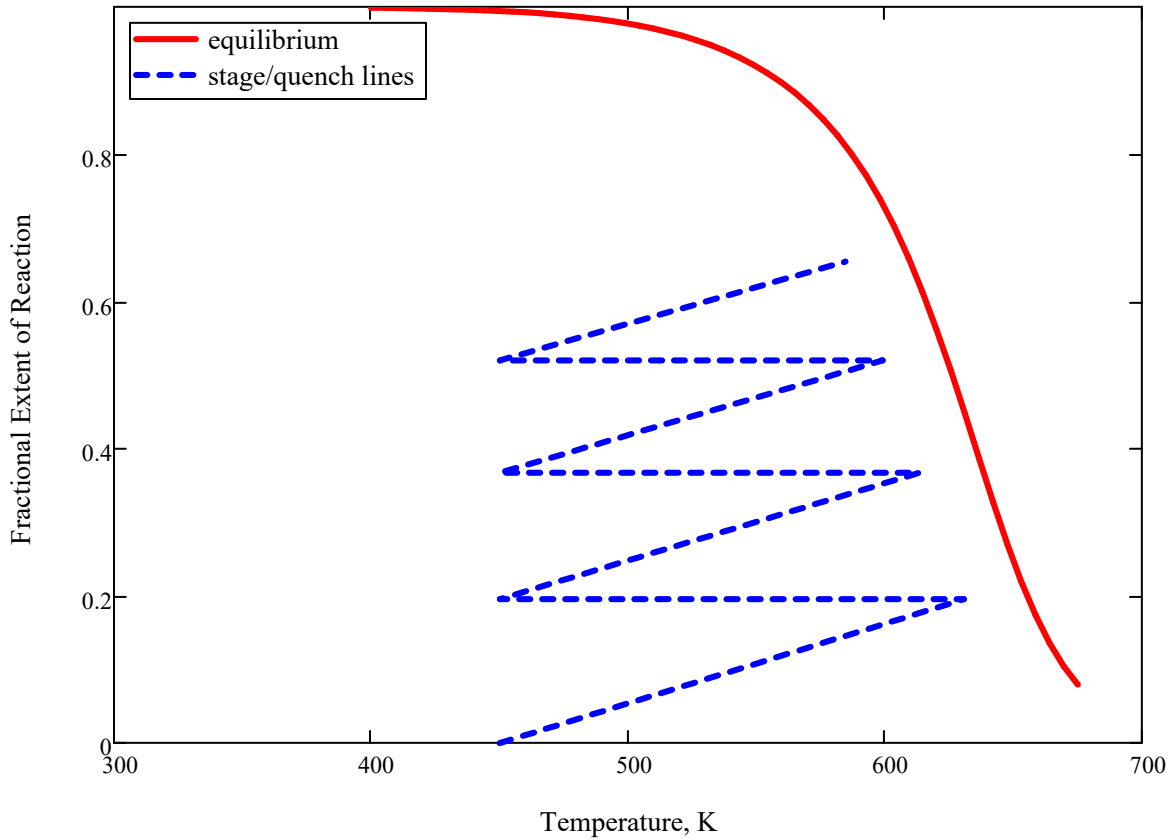
Figure E3.3: Staged Adiabatic Reactors



With intercoolers, $\xi stg_7 = 0.654$ extent of reaction was achieved with four beds.

Adiabatic beds using quench fluid instead of intercoolers

Intercoolers can be expensive. In some systems, injecting a portion of the feed steam between beds can provide the cooling needed. The graphical procedure below may be used to examine the feasibility of the quench method of cooling.

Assume the quench fluid composition (extent of reaction) and temperature have been determined by loop calculations (see example CS-106 in Rase (1977) **Vol 2**) and Example 7 in Rase (1990).

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$\xi_q := 0.$ $\quad T_q := 50\ °C$ $\quad T_q = 323.15\,K$ quench fluid composition and temperature (E3.9)

$T_{cool} := 450 \cdot K$ desired feed temperature for each bed

$$\frac{\xi_m - \xi_q}{t - T_q} = \frac{\xi_{out} - \xi_q}{t_{out} - T_q}$$

The mixing line uses the outlet extent of reaction and temperature from the previous bed, ξ_{out} , t_{out} , and the quench conditions in E3.9 to determine the line between the two conditions. (E3.10)

$$\xi_m(t, \xi_{out}, t_{out}) := \frac{\xi_q \cdot t + T_q \cdot \xi_{out} - \xi_q \cdot t_{out} - t \cdot \xi_{out}}{T_q - t_{out}}$$

E3.10 may be solved for the mixing extent, ξ_m (E3.11)

$\xi_{in}(T_{cool}, \xi_{out}, t_{out}) := \xi_m(T_{cool}, \xi_{out}, t_{out})$ mixing extent at desired feed temperature

Stage 0

$Tstg_q_0 := T_{cool}$ $\quad \xi stg_q_0 := 0$ inlet conditions for the bed

$Temp := Teq(\xi stg_q_0, Tstg_q_0 + approach)$ outlet temperature for the bed (equilibrium temp when inlet is adjusted for the approach temp.

$\xi stg_q_1 := \xi e(Temp)$ outlet extent of reaction

$Tstg_q_1 := Temp - approach$ apply the approach temp to the outlet temp

Quench 0

$Tstg_q_2 := T_{cool}$ the inlet temperature for the next stage

$\xi stg_q_2 := \xi_{in}(T_{cool}, \xi stg_q_1, Tstg_q_1)$ inlet extent of reaction for the next stage (using mixing rule from eq (E3.11))

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Stage 1 repeat procedure

$$Temp := Teq\left(\xi stg_q_2, Tstg_q_2 + approach\right)$$

$$\xi stg_q_3 := \xi e(Temp)$$

$$Tstg_q_3 := Temp - approach$$

Quench 1

$$Tstg_q_4 := T_{cool}$$

$$\xi stg_q_4 := \xi_{in}\left(T_{cool}, \xi stg_q_3, Tstg_q_3\right)$$

max conversion with infinite number of beds using quench cooling

With an infinite number of beds, the last bed would be on the adiabatic line from the quench point. This line determines the limit of the quench cooling method.

$$Tmax_0 := T_q \qquad \xi max_0 := \xi_q$$

$$Temp := Teq\left(\xi_q, T_q + approach\right)$$

$$\xi max_1 := \xi e(Temp)$$

$$Tmax_1 := Temp - approach$$

$$\xi max = \begin{pmatrix} 0 \\ 0.3 \end{pmatrix} \qquad Tmax = \begin{pmatrix} 323.15 \\ 619.701 \end{pmatrix} K$$

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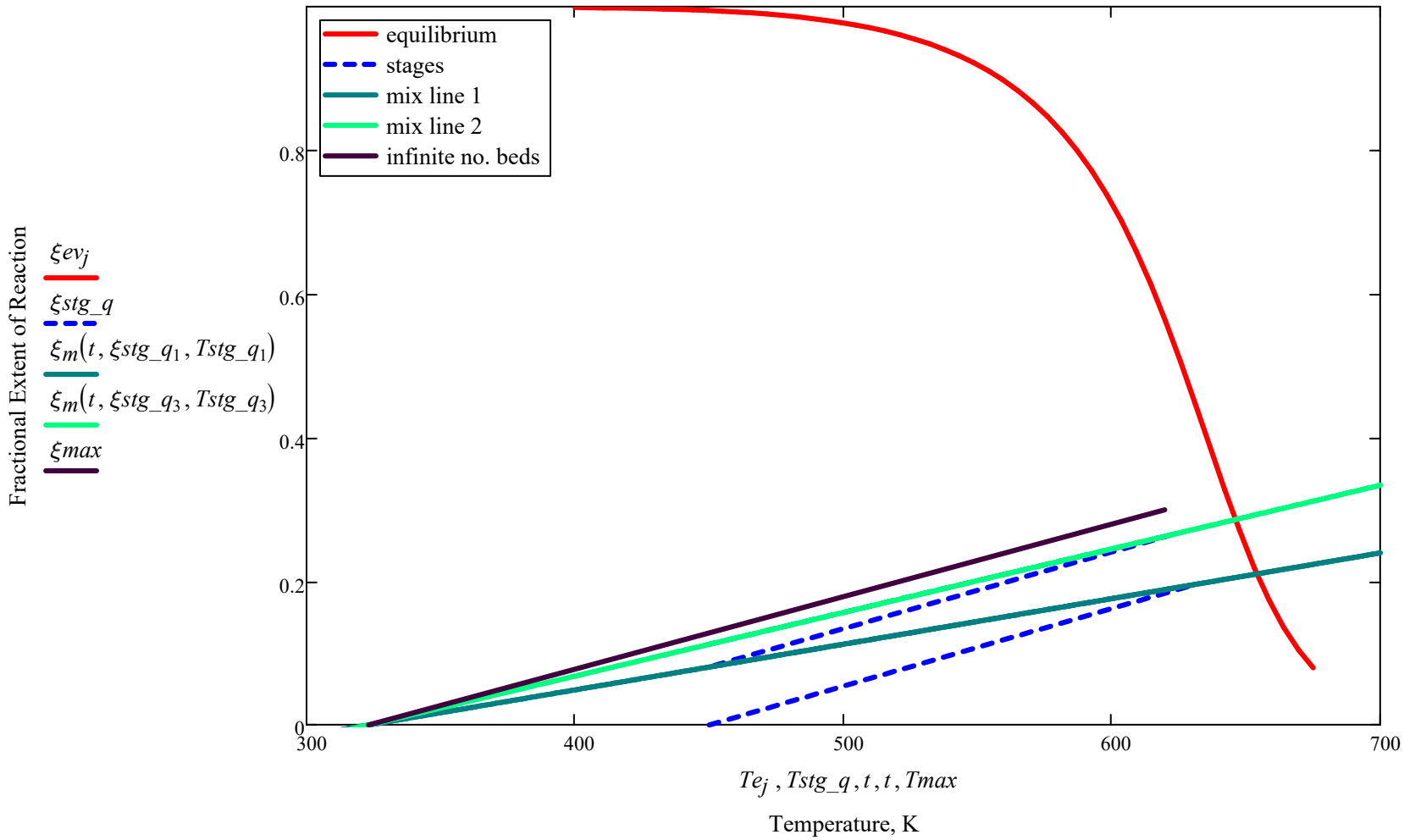
Figure 3.4: Staged Reactors with Quench Fluid



The green lines in Fig E3.4 are the mixing lines and the dotted blue lines are the adiabatic curves for the reactor beds.

This example shows that quench cooling doesn't work well unless the reactor temperatures are much higher than the quench temperature and the conversion per bed is high. Note how the second mixing curve is nearly a reversal of the second reactor bed adiabatic curve. Thus, the third bed will achieve very little in the way of higher conversion.

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Reaction rate contours

As an alternative to staged adiabatic reactors, tubular reactors with either heating or cooling at the tube wall may be used to achieve higher conversions in a single bed. The following procedure provides the designer a means of estimating the optimal isothermal bed temperature without a full reactor simulation. The example is for a single reaction. However, the method may also be useful if a single reaction in a reaction network dominates the reaction rate due to its equilibrium.

The rate expression and parameters below were given by Rase (1990), Example 7.

pre-exponential rate constants

$$A_0 := exp\left(\frac{33.5 \cdot \frac{cal}{mol \cdot K}}{Rg}\right)\frac{mol}{gm \cdot hr}$$

activation temperatures

$$B_0 := \frac{13.3 \cdot 10^3 \frac{cal}{mol}}{Rg}$$

adsorption temperatures

$$Bad := \frac{1}{Rg} \cdot \begin{pmatrix} -11.2 \\ -15.5 \\ -8.9 \end{pmatrix} \cdot 10^3 \cdot \frac{cal}{mol}$$

adsorption constants

$$Kad := \begin{pmatrix} exp\left(\frac{-23.1 \cdot \frac{cal}{mol \cdot K}}{Rg}\right) \\ exp\left(\frac{-31.9 \cdot \frac{cal}{mol \cdot K}}{Rg}\right) \\ exp\left(\frac{-19.4 \cdot \frac{cal}{mol \cdot K}}{Rg}\right) \end{pmatrix} \cdot \frac{1}{bar}$$

adsorption coefficient functions

$$K_{ad}(T) := \begin{pmatrix} Kad_0 \cdot exp\left(\frac{-Bad_0}{T}\right) \\ Kad_1 \cdot exp\left(\frac{-Bad_1}{T}\right) \\ Kad_2 \cdot exp\left(\frac{-Bad_2}{T}\right) \end{pmatrix}$$

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Reaction rate as a function of temperature and extent of reaction

The rate expression has been divided into parts in order to fit the functions on the page.

$$forward(t,\xi) := \prod_{i=0}^{NC-1} \left[\frac{\left(nf_i - \frac{\nu_{0,i}}{\nu_{0,lr}} \cdot \xi \cdot nf_{lr} \right) \cdot \frac{Ptot}{atm}}{\sum \left(nf - \nu^T \cdot \xi \cdot \frac{nf_{lr}}{\nu_{0,lr}} \right)} \right]^{if\left(\nu_{0,i}<0,\,-\nu_{0,i},\,0\right)}$$

forward equilibrium driving force

$$K_y(t) := Keq(t \cdot K, 0) \cdot \left(\frac{atm}{Ptot} \right)^{\sum \left(\nu^T\right)^{\langle 0 \rangle}}$$

gas mole fraction equilibrium coefficient

$$reverse(t,\xi) := \frac{1}{K_y(t)} \cdot \prod_{i=0}^{NC-1} \left[\frac{\left(nf_i - \frac{\nu_{0,i}}{\nu_{0,lr}} \cdot \xi \cdot nf_{lr} \right) \cdot \frac{Ptot}{atm}}{\sum \left(nf - \nu^T \cdot \xi \cdot \frac{nf_{lr}}{\nu_{0,lr}} \right)} \right]^{if\left(\nu_{0,i}\geq 0,\,\nu_{0,i},\,0\right)}$$

reverse equilibrium driving force

$$\rho_s := 1.2820 \cdot \frac{gm}{cm^3}$$

catalyst bulk density

$$rate_k(t,\xi) := \frac{atm^4 \cdot \rho_s \frac{A_0}{\frac{mol}{m^3 \cdot s}} \cdot exp\left(\frac{-B_0}{t \cdot K} \right) \cdot \left(K_{ad}(t \cdot K)_1 \right)^3 \cdot K_{ad}(t \cdot K)_0}{\left[1 + \left[\sum_{i=0}^{NC-1} \left[K_{ad}(t \cdot K)_i \cdot \left(nf_i - \frac{\nu_{0,i}}{\nu_{0,lr}} \cdot \xi \cdot nf_{lr} \right) \right] \right] \cdot \frac{Ptot}{\sum \left(nf - \nu^T \cdot \xi \cdot \frac{nf_{lr}}{\nu_{0,lr}} \right)} \right]^4}$$

kinetic rate / adsorption

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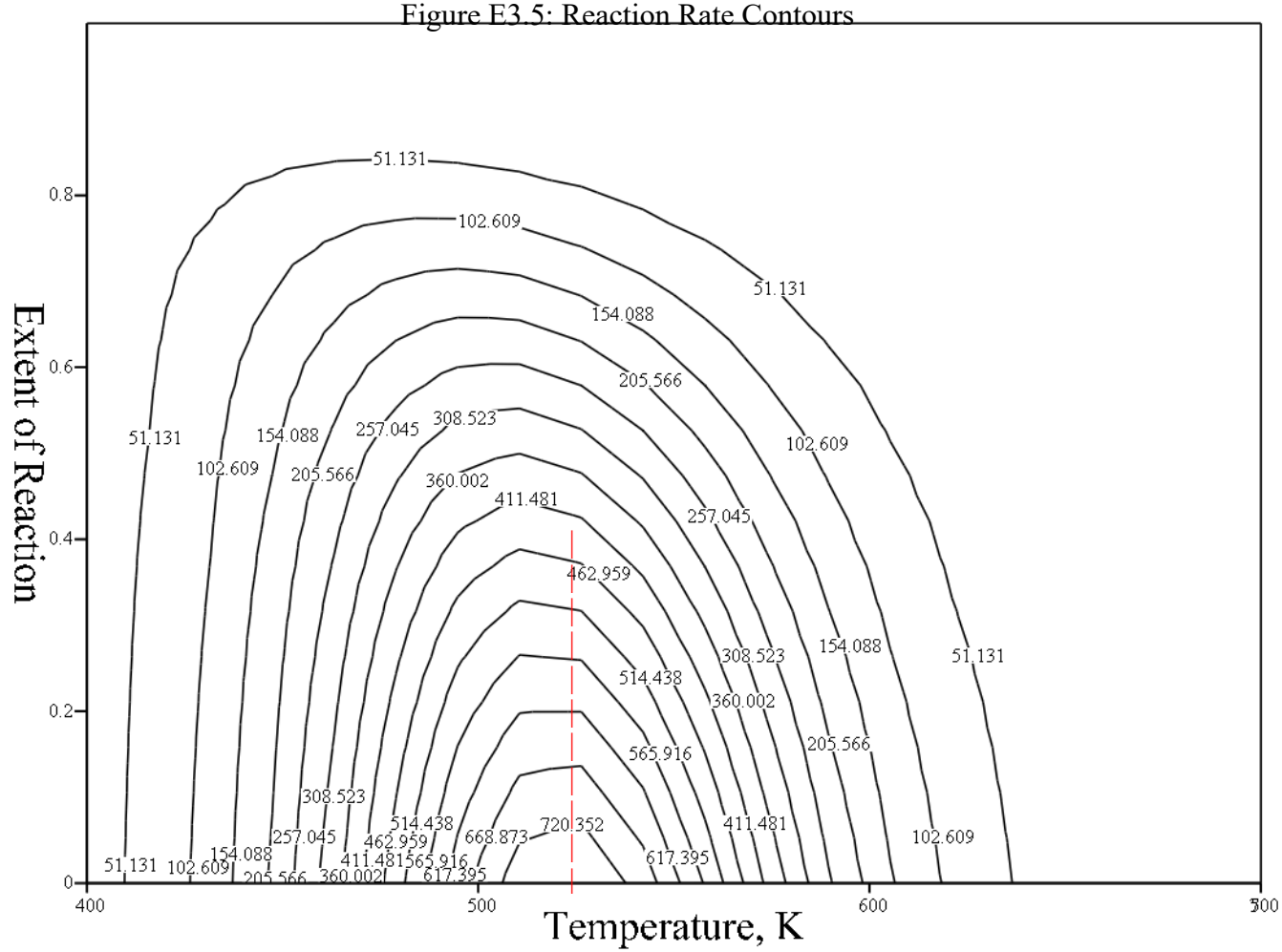
$r(t,\xi) := rate_k(t,\xi) \cdot (forward\,(t,\xi) - reverse(t,\xi))$ full rate expression

$Rx := CreateMesh(r, 400, 700, 0, 1)$ Create the matrix of reaction rates with temperatures between 400 K and 700 K and extents of reaction between 0 and 1.

Figure E3.5: Reaction Rate Contours



Rx

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The optimum isothermal temperature is near 525 K, as shown by the dashed red line. This temperature can be used by the design engineer to determine the cooling fluid and it's pressure. In the Example 7 in Rase (1990), 525 K was given as the maximum allowed temperature due to unwanted decomposition reactions. The procedures demonstrated above did not consider that constraint. .

Summary

The staged beds with quench fluid have been eliminated, leaving staged beds with intercoolers and cooled tubular reactors as options. The number of staged beds needed to reach a desired extent of reaction has been determined, but not their size. Further analysis would require the kinetic models for fixed beds developed in Chapter 7. However, in order to demonstrate the models with multiple reactions, another reaction system will be used in those examples.

References

Rase, H.F., "Fixed-Bed Reactor Design and Diagnostics: Gas Phase Reactions", Butterworths 1990

Rase, H.F., "Chemical Reactor Design for Process Plants", **vol 1 and 2,** Wiley-Interscience 1977

Reid, R.C., J.M. Prausnitz, and T.K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill, 1977

Exercises

1. Repeat this example with 4:1 hydrogen/benzene in the feed.
2. Add nitrogen to the system and explore its effect. Which of the five graphs is most affected by the addition of nitrogen?
3. In order to achieve higher conversion in Fig. E3.3, should the pressure be decreased or increased?
4. In the intercooler case, lowering the inlet temperature would allow a greater change in extent of reaction per bed. How would that have a negative impact on the design?

Answers To see answers in Mathcad, open the collapsed area below. To see them in pdf file, open in Adobe and click on the redacted area. Then click on the trash bin to remove the black highlight. The answers will then be visible.

[redacted]

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