REB, The Course
Class 16 Practice Assignment Solution

In the Class 16 Learning Activity a BSTR operating protocol with a heating stage and a cooling stage was analyzed, The reaction was endothermic, and the conversion was found to depend mostly on the duration of the heating stage. The net rate was also calculated.

It can be useful to plot the net rate as a function of the conversion for systems like this. On the same graph, plot the net rate of production for the system from the Class 16 Learning activity as a function of conversion for turnaround times of 0.25, 0.5, and 0.75. Discuss the shape of the graphs and the trends associated with turnaround time.

Assignment Summary

<u>Reaction</u>

$$A \rightarrow Z \tag{1}$$

<u>Rate Expression</u>

$$r_1 = k_1 C_A \tag{2}$$

<u>Reactor</u>: Non-isothermal BSTR with a 2 stage operational protocol

<u>Given Constants</u>: V = 10 L, U_1 = 76 cal h^{-1} cm^{-2} K^{-1}, A_1 = 600 cm^2, $T_{ex,1}$ = 110 °C, U_2 = 91 cal h^{-1} cm^{-2} K^{-1}, A_2 = 375 cm^2, $T_{ex,2}$ = 30 °C, $k_{0,1}$ = 2.85 x 10^{15} h^{-1},E_1 =25 kcal mol^{-1}, ΔH_1 = 20 kcal mol^{-1}, $\breve{C}_p$ = 1000 cal L^{-1} K^{-1}, $C_{A,0}$ = 5 M, T_0 = 25 °C, and T_f = 35 °C.

<u>Parameters</u>: t_1 and $\underline{t}_{turn}$ = [0.25, 0.5, 0.75] h.

<u>Deliverables</u>: $\underline{r}_{Z,net}$ vs. $\underline{f}_A$ as graphs for three values of t_{turn}

Formulation of the Equations

Reactor Model Equations for stage i:

$$\frac{dn_A}{dt} = - r_1 V \tag{3}$$

$$\frac{dn_Z}{dt} = r_1 V \tag{4}$$

$$\frac{dT}{dt} = \frac{\dot{Q}_i - r_1 V \Delta H_1}{\breve{C}_p V} \tag{5}$$

Reactor Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_Z$, and $\underline{T}$

Additional Computable Unknowns: r_1, k_1, C_A, and $\dot{Q}$

$$k_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \tag{6}$$

$$C_A = \frac{n_A}{V} \tag{7}$$

$$\dot{Q}_i = U_i A_i \left(T_{ex,i} - T\right) \qquad i = 1 \text{ and } 2 \tag{8}$$

IVODE Solver Inputs:

1. Stage 1
   a. Initial values of the reactor model variables shown in Table 1
   b. Stopping criterion that t equals the final value shown in Table 1
   c. Derivatives function that
      i. receives the reactor model variables at the start of an integration step
      ii. calculates the additional unknowns
      iii. evaluates and returns the BSTR design equation derivatives

Table 1. Initial and final values of the design equation variables for the first stage of the operating protocol.

Variable	Initial Value	Final Value
t	0	t_1
n_A	$n_{A,0} = C_{A,0}V$	
n_Z	0	
T	T_0	

2. Stage 2
   a. Initial values of the reactor model variables shown in Table 2
   b. Stopping criterion that T equals the final value shown in Table 2
   c. Derivatives function that
      i. receives the reactor model variables at the start of an integration step
      ii. calculates the additional unknowns
      iii. evaluates and returns the BSTR design equation derivatives

Table 2. Initial and final values of the design equation variables for the first stage of the operating protocol.-1

Variable	Initial Value	Final Value
t	$t\big\|_{t_1}$	
n_A	$n_A\big\|_{t_1}$	
n_Z	$n_Z\big\|_{t_1}$	
T	$T\big\|_{t_1}$	T_f

<u>Deliverables Equations</u>: (for each t_{turn})

$$\underline{t}_1 = \left[0.05,\cdots,1.5\right] \text{ h} \tag{9}$$

$$\forall t_{1,n} \in \underline{t}_1 \qquad \begin{pmatrix} r_{Z,net,n} = \dfrac{\underline{n}_Z\Big|_{T=T_f}}{\underline{t}\Big|_{T=T_f} + t_{turn}} \\ f_{A,n} = \dfrac{n_{A,0} - \underline{n}_A\Big|_{T=T_f}}{n_{A,0}} \end{pmatrix} \tag{10}$$

Implementation of the Calculations

The Python script, practice_16.py, that was written to perform the calculations accompanies this solution. It defines a BSTR function and a derivatives function that solve the design equations for both stages of the protocol, given the heating time. A global flag, set by the BSTR function, is used in the derivatives function to determine which stage of the protocol is being analyzed. The calculations loop through the turnaround times, then within that loop they loop through the heating times, performing the calculations as indicated above.

Results and Discussion

Originally the range of t_1 values chosen in equation (9) began at 0.01. The calculations ran for a very long time and were killed before they completed. The range was modified as shown in equation (9) and execution was completed in a reasonable amount of time.

The net rate as a function of the conversion is shown in Figure 1 for three different turnaround times. Three features are apparent. For any turnaround time, the net rate passes through a maximum as the conversion increases. The net rate decreases as the turnaround time increases. Finally, the maximum net rate occurs at higher conversions as the turnaround time increases.

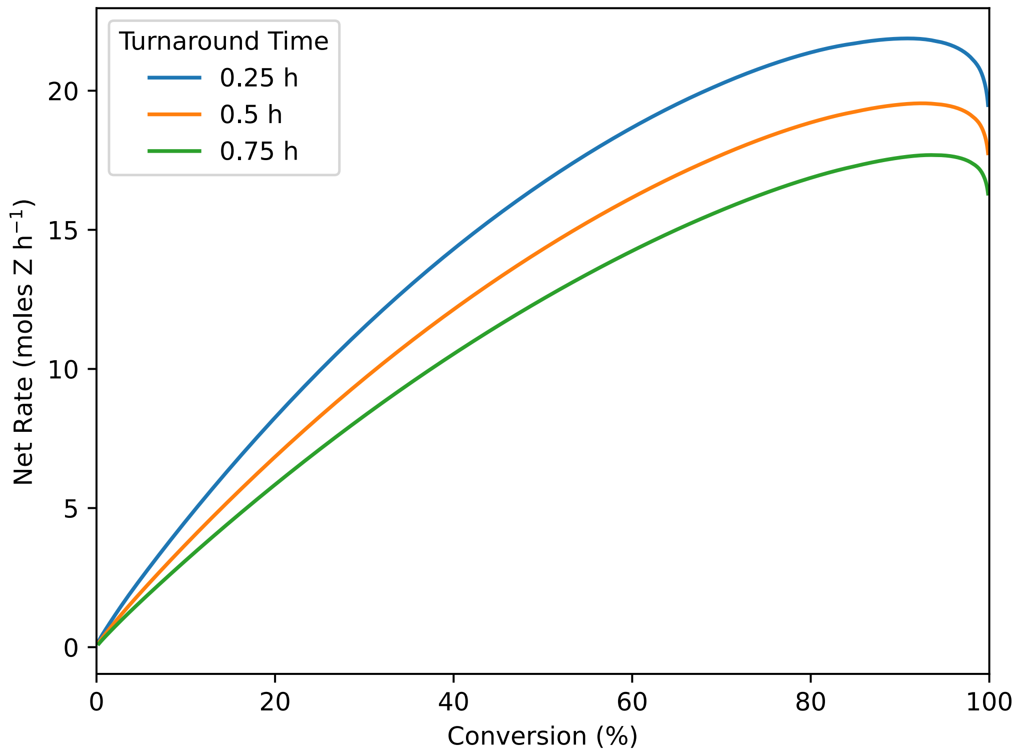

Figure 1. Net rate of production of Z as a function of conversion of A for three turnaround times.

The maximum in the net rate as the conversion increases can be understood by examination of the definition of net rate shown for this example in equation (11). At low conversions, the duration of the operational protocol, t_{op}, is small compared to the turnaround time. Hence, the denominator is nearly constant and equal to t_{turn}. In contrast, the molar amount of Z in the numerator starts at zero and increases. Thus at low conversions the net rate is expected to increase with conversion because the numerator in equation (11) is increasing while the denominator is nearly constant.

$$r_{Z,net} = \frac{n_{Z,f}}{t_{op} + t_{turn}} \tag{11}$$

The opposite is true at high conversions. The total molar amount of Z is approaching its stoichiometric limit. It is nearly constant, changing only in the second or third significant figure. Meanwhile, the duration of the operational protocol is now a significant term in the denominator. It is still increasing steadily as the conversion increases. Hence at high conversions the net rate decreases with increasing conversion because the numerator in equation (11) is nearly constant at its stoichiometric limit while the denominator is still increasing steadily.

So at low conversions the net rate is increasing with increasing conversion and at high conversions it is decreasing. That can only happen if at some intermediate conversion is passes through a maximum and changes from increasing to decreasing.

As noted, Figure 1 also shows two trends associated with the turnaround time. The net rate decreases as the turnaround time increases, and the maximum net rate occurs at higher conversions as the turnaround time increases. The first trend is easy to understand, increasing the turnaround time increases the denominator in the expression for the net rate and has no effect upon the numerator. Hence increasing the turnaround time decreases the net rate.

The maxima in Figure 1 are not sharp, so they are summarized in Table 1 where it is clearly seen that as the turnaround time increases, the maximum net rate appears at increasing conversions. While a bit more subtle, this trend can be understood by again referring to equation (11). When the turnaround time is larger, the duration of the operational protocol must be larger when it becomes comparable to the turnaround time and starts causing the denominator to increase. In other words, since the conversion increases with the duration of the operational protocol, the net rate starts decreasing at larger conversions, and hence the maximum rate occurs at larger conversion as the turnaround time increases.

Table 1. The maximum rate occurs at higher conversions as the turnaround time increases.

Turnaround Time (h)	**Maximum Net Rate (moles Z per h)**	**Conversion at Maximum Net Rate (%)**
0.25	21.9	90.8
0.5	19.5	92.2
0.75	17.7	93.5

Deliverables

Figure 1 shows the net rate as a function of conversion for the three specified turnaround times.