REB, The Course
Class 20 Learning Activity Solution

The desired product, D, can be synthesized from reagents A and B as shown in equation (1), but reagent B also reacts according to equation (2) to form an undesired product, D. Use of an adiabatic SBSTR has been suggested as a means to improve selectivity. Specifically the SBSTR, operating at 1 atm, will be charged with 550 gal of a 100 °F solution containing the catalyst and reagent A at a concentration of 0.015 lbmol gal^{-1}. Two thousand gallons of a 100 °F solution containing only B at a concentration of 0.004 lbmol gal^{-1} will be fed to the reactor at a constant rate. At least 90% of the added B must be converted in the process, so if necessary, the reaction will continue in batch mode until that conversion is attained. What volumetric feed rate will maximize the net rate of production of D if the turnaround time for the reactor is 30 min?

Reaction (1) is first order in each reactant. The rate coefficient pre–exponential factor is 2.193 x 10^{12} gal lbmol^{-1} h^{-1} and the activation energy is 32,400 BTU lbmol^{-1}. The heat of reaction is –16,190 BTU lbmol^{-1}. Reaction (2) is second order in reagent B, the pre–exponential factor is 6.087 x 10^{14} gal lbmol^{-1} h^{-1} and the activation energy is 36,900 BTU lbmol^{-1}. The heat of reaction is –14,030 BTU lbmol^{-1}. Solutions containing the reagents have a heat capacity that is essentially equal to that of the solvent, 7.2 BTU gal^{-1} °R^{-1}.

$$A + B \rightarrow D \tag{1}$$

$$2B \rightarrow U \tag{2}$$

Assignment Summary

<u>Reactions</u>

$$A + B \rightarrow D \tag{1}$$

$$2B \rightarrow U \tag{2}$$

Rate Expressions

$$r_1 = k_1 C_A C_B \tag{3}$$

$$r_2 = k_2 C_B^2 \tag{4}$$

Reactor: Adiabatic, liquid-phase SBSTR

Given Constants: P = 1 atm, V_0 = 550 gal, T_0 = 100 °F, $C_{A,0}$ = 0.015 lbmol gal^{-1}, T_{in} = 100 °F, V_B = 2000 gal, $C_{B,in}$ = 0.004 lbmol gal^{-1}, $f_{B,min}$ = 0.9, t_{turn} = 30 min, $k_{0,1}$ = 2.193 x 10^{12} gal lbmol^{-1} h^{-1}, E_1 = 32,400 BTU lbmol^{-1}, ΔH_1 = –16,190 BTU lbmol^{-1}, $k_{0,2}$ = 6.087 x 10^{14} gal lbmol^{-1} h^{-1}, E_2, = 36,900 BTU lbmol^{-1}, ΔH_2 = –14,030 BTU lbmol^{-1}, and $\breve{C}_p$ = 7.2 BTU gal^{-1} °R^{-1}.

Deliverables: $\dot{V}_{in,opt} = \underset{\dot{V}_{in}}{\arg\max} \left(r_{D,net}\right)$

Formulation of the Equations

Reactor Model Equations:

$$\frac{dn_A}{dt} = -\, r_1 V \tag{5}$$

$$\frac{dn_B}{dt} = \dot{n}_{B,in} - \left(r_1 + 2r_2\right) V \tag{6}$$

$$\frac{dn_D}{dt} = r_1 V \tag{7}$$

$$\frac{dn_U}{dt} = r_2 V \tag{8}$$

$$\frac{dT}{dt} = \frac{-\dot{V}_{in}\breve{C}_p\left(T - T_{in}\right) - r_1 V\Delta H_1 - r_2 V\Delta H_2 + P\dot{V}_{in}}{V\breve{C}_p} \tag{9}$$

$$\frac{dV}{dt} = \dot{V}_{in} \tag{10}$$

Reactor Model Variables: $\underline{t}$, $\underline{n}_A$, $\underline{n}_B$, $\underline{n}_D$, $\underline{n}_U$, $\underline{T}$, and $\underline{V}$

Additional Computable Unknowns: r_1, r_2, k_1, k_2, C_A, C_B, and $\dot{n}_{B,in}$

$$k_i = k_{0,i}\exp\left(\frac{-E_i}{RT}\right) \qquad i = 1 \text{ and } 2 \tag{11}$$

$$C_i = \frac{n_i}{V} \qquad i = A \text{ and } B \tag{12}$$

$$\dot{n}_{B,in} = C_{B,in}\dot{V}_{in} \tag{13}$$

Additional Uncomputable Unknowns: $\dot{V}_{in}$

$$\underline{\dot{V}}_{in} = \left[20,\cdots,40\right] \text{ gal h}^{-1} \tag{14}$$

IVODE Solver Inputs:

1. Stage 1
    a. Initial values of the reactor model variables shown in Table 1.
    b. Stopping criterion that V equals the final value shown in Table 1.
    c. Residuals/Derivatives function that
        i. receives the reactor model variables at the start of an integration step
        ii. calculates the additional unknowns, equations (11) - (14)
        iii. evaluates and returns the design equation derivatives, equations (5) - (10)

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

Variable	Initial Value	Final Value
t	0	
n_A	$C_{A,0}V_0$	
n_B	0	
n_D	0	
n_U	0	
T	T_0	
V	V_0	$V_0 + V_B$

1. Stage 2, only if $\dfrac{C_{B,in}V - n_{B,f,1}}{C_{B,in}V} < f_{B,min}$
   a. Initial values of the reactor model variables shown in Table 2.
   b. Stopping criterion that n_B equals the final value shown in Table 2.
   c. Residuals/Derivatives function that
      i. receives the reactor model variables at the start of an integration step
      ii. calculates the additional unknowns, equations (11) - (14)
      iii. evaluates and returns the design equation derivatives, equations (5) - (10)

Table 2. Initial and final values of the design equation variables for stage 2.

Variable	Initial Value	Final Value
t	$t_{f,1}$	
n_A	$n_{A,f,1}$	
n_B	$n_{B,f,1}$	$C_{B,in}V_B\left(1-f_{B,min}\right)$
n_D	$n_{D,f,1}$	
n_U	$n_{U,f,1}$	
T	$T_{f,1}$	
V	V_0+V_B	

Deliverables Equations:

$$\forall \dot{V}_{in,n} \in \underline{\dot{V}}_{in} \qquad r_{D,net,n} = \left.\frac{n_{D,f,2}}{t_{f,2}+t_{turn}}\right|_{\dot{V}_{in,n}} \tag{15}$$

$$\dot{V}_{in,opt} = \underset{\dot{V}_{in}}{\arg\max}\left(\underline{r}_{D,net}\right) \tag{16}$$

Implementation of the Calculations

The Python script, activity_20.py, that was written to perform the calculations accompanies this solution. It defines an SBSTR model function and a derivatives function that solve the design equations for both stages (if the second stage is needed) for a given inlet volumetric feed rate. The calculations begin by selecting a range of values for the volumetric feed rate. The design equations are solved for each feed rate and the corresponding net rate of production of D is calculated and stored. The maximum net rate and corresponding volumetric feed rate are then identified.

The maximum net rate did fall within the initial range of values chosen for the inlet volumetric flow rate. To improve the accuracy, the range about that maximum was narrowed and the calculations were repeated. The optimum volumetric feed rate did not change significantly with the narrower range of values.

Results and Discussion

The calculations were performed as described. Figure 1 shows the net rate of production of reagent D as a function of the volumetric feed rate. It shows that the net rate of production of D is maximized at a volumetric feed rate of 26.8 gal h^{-1}. At that feed rate the net rate of production of D is 3.84 x 10^{-3} lbmol h^{-1}.

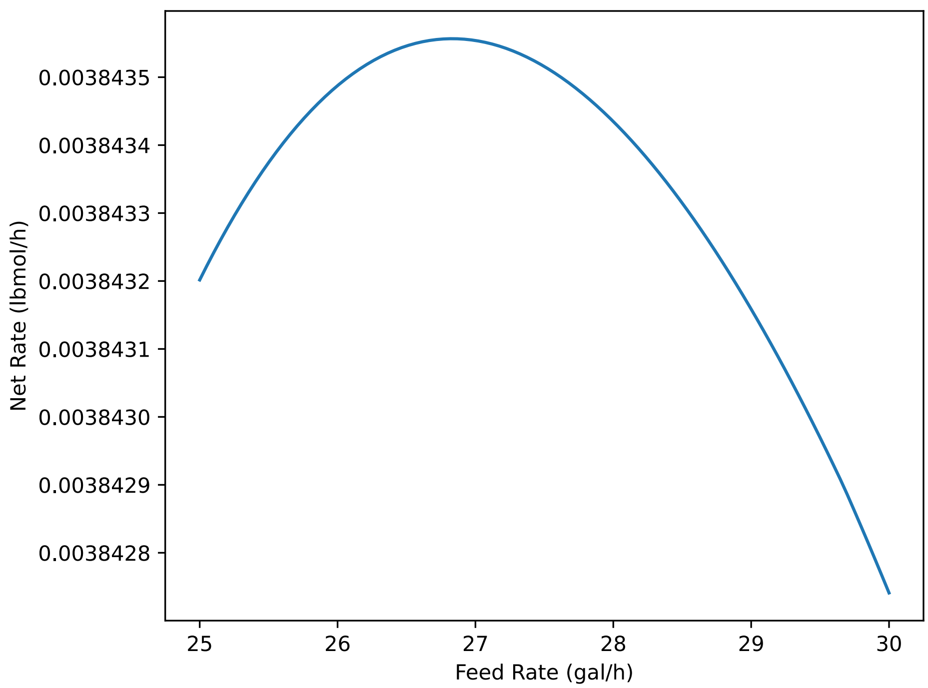

Figure 1. Net rate of production of reagent D as a function of the volumetric feed rate.

The instantaneous selectivity is the rate of production of the desired product to that of the undesired product. For this system, the selectivity for D over U is given in equation (17). It clearly shows that high concentration of A and low concentration of B give the highest instantaneous selectivity. That is why the reactor is initially filled with A (to keep its concentration as high as possible) and B is added to it slowly (so it reacts nearly as fast as it is added and its concentration stays small).

$$S_{D/U,inst} = \frac{k_1}{k_2}\frac{C_A}{C_B} \tag{17}$$

Operating in that way introduces a trade-off between reaction rate and selectivity. A low concentration of B offers high selectivity, but it also results in both reaction rates being small. At the two ends of the spectrum, the rate at which D is produced is low. At low concentration of B it is produced very selectively, but at a very low rate. At high concentration of B, the rate is very high, but a large amount of U is being produced instead of D.

This can be seen by examination of the expression for the net rate of production of D, equation (18). Operation at low concentration of B produces a large amount of D, but requires a long processing time to do so. Operating at high concentration of B requires a short processing time, but also reduces the amount of D that is generated. Put differently, increasing the feed rate decreases both the numerator and the denominator in equation (18). At low feed rates the decrease in the denominator predominates and the net rate increases. At high feed rates, the numerator predominates and the rate decreases. The maximum net rate of production occurs at the feed rate where the change in the numerator and denominator are equal.

$$r_{D,net} = \frac{n_{D,f}}{t_f + t_{turn}} \tag{18}$$

Deliverables

The maximum net rate of production of reagent D is 3.84×10^{-3} lbmol h^{-1}, and it occurs when the volumetric feed rate is 26.8 gal h^{-1}.